

An introduction to Relativistic Quantum Chemistry

Lucas Visscher
VU University Amsterdam

© L. Visscher (2011)

Basic Theory

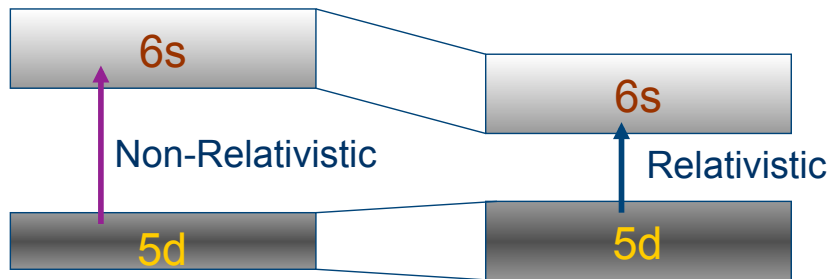


Dirac (1929)

- 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 which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei.
- The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and **the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.**

Visible Relativistic Effects

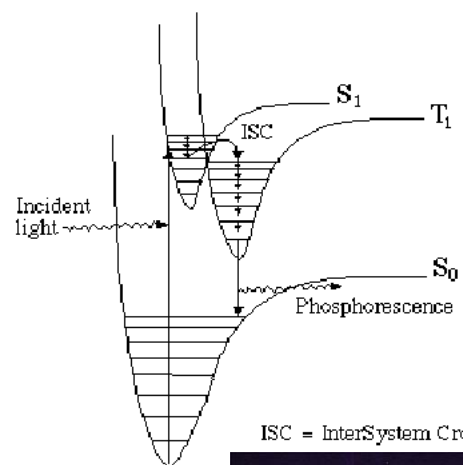
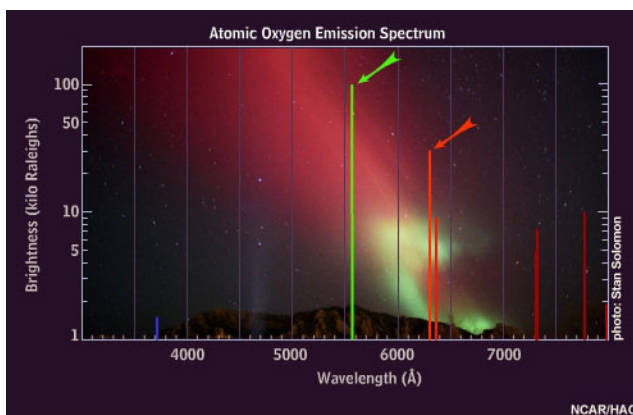
- Non-relativistic gold is silver
 - The 5d-6s transition is shifted from the UV to the visible part of the spectrum by relativistic effects



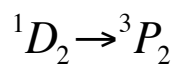
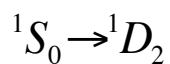
3

Visible Relativistic Effects

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



ISC = InterSystem Crossing



Lifetime 0.75 s

Lifetime 110 s



The hydrogenic atom

- The exact non-relativistic energy

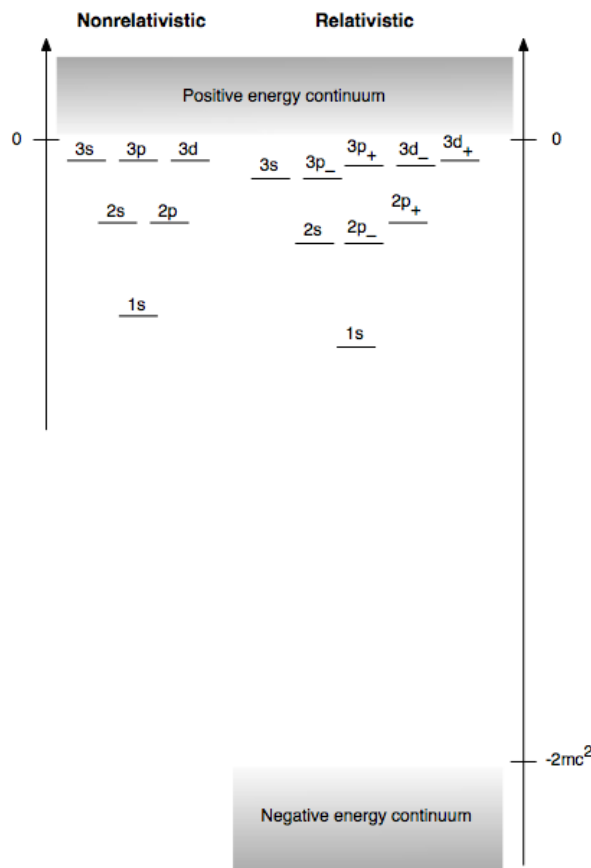
$$E^{NR} = -\frac{Z^2}{2n^2}$$

- The exact relativistic energy

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

- Spin-orbit coupling : $j = l \pm s$

5



6

Day 1: Basic theory, qualitative discussion

- Basic Theory
 - Special relativity
 - The Dirac equation
 - Relation to quantum electrodynamics
 - Treatment of the electron-electron interaction
- Relativistic Effects in Chemistry
 - Orbital radii and energies
 - Reaction energies
 - Molecular structure
- Day 2: Approximate Hamiltonians
- Day 3: Frozen cores and Effective Core Potentials
Relativistic effects on molecular properties

7

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

$$\begin{aligned}x &= x' + vt & r_{12} &= \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \\y &= y' & r'_{12} &= \sqrt{(x'_1 - x'_2)^2 + (y'_1 - y'_2)^2 + (z'_1 - z'_2)^2} \\z &= z' & r_{12} &= r'_{12}\end{aligned}$$

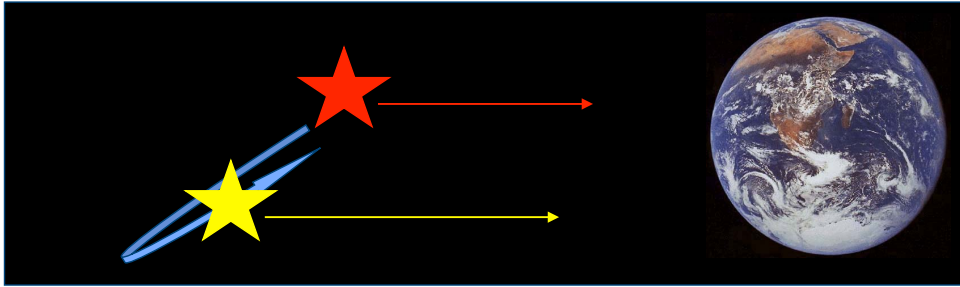
- Simple addition of velocities, no speed limit

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

8

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

9

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

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

← Scaling factor

$$y = y'$$

$$z = z'$$

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

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

← General expression for t

10

Lorentz transformation

- Substitute this ansatz in the unprimed equations and solve

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

- Lorentz transformation

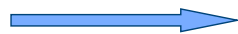
$$x = \gamma(x' + vt')$$

$$y = y'$$

$$z = z'$$

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

Generalize to 3d



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

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

- Time and spatial coordinates transform into each other
- 4-dimensional space-time coordinate system
- Nonrelativistic limit ($c \rightarrow \infty$) gives Galileo transformation

11

Special relativity

Postulate 1: All inertial frames are equivalent

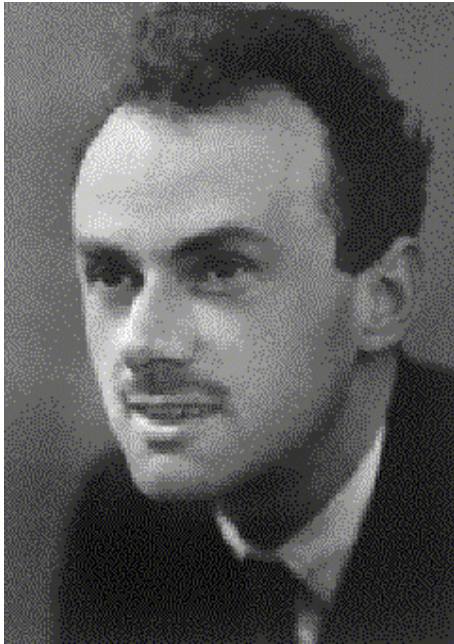
Postulate 2: The laws of physics have the same form in all inertial frames

Postulates **hold for electromagnetism** (Maxwells relations)

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

12

Relativistic Quantum Mechanics



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

13

Non-relativistic quantization 1

The nonrelativistic Hamilton function

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

Quantization

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

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

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

14

Non-relativistic quantization 2

The nonrelativistic Hamilton function

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

$$\pi = \mathbf{p} - q\mathbf{A} \quad \leftarrow \text{Mechanical } (\pi) \text{ and canonical momentum } (\mathbf{p})$$

Principle of minimal electromagnetic coupling

Quantization

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

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

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

15

Spin and non-relativistic quantization 1

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

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

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

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

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

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

Quantization

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

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

16

Spin and non-relativistic quantization 2

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

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

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

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

Spin in NR quantum mechanics

The Pauli Hamiltonian in two-component form

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

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

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

Quantization recipe gives

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

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.

19

Relativistic quantization 2

Eliminate the square root before quantization

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

Quantization

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

Klein-Gordon Equation

☺ Lorentz invariant

☹ No spin

☹ $\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = f(t)$ \leftarrow Charge is conserved, particle number is not

The KG-equation is used for spinless particles (e.g mesons)

20

Relativistic quantization 3

Define a new type of “square root”

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

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

Quantization

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

The Dirac equation

Suitable for relativistic description of electrons

21

The Dirac equation

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

- ☺ First derivatives with respect to time and position
- ☺ Linear in scalar and vector potentials
- ☺ Lorentz invariant (should be proved !)

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

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

22

Densities

- Charge density

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

- Current density

$$\mathbf{j}(\mathbf{r}, t) = q\psi^\dagger(\mathbf{r}, t) c\boldsymbol{\alpha} \psi(\mathbf{r}, t) \quad \leftarrow \text{ } \boldsymbol{\alpha} \text{ is the relativistic velocity operator}$$

- Continuity relation

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

23

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

$$\hat{H}\psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad \leftarrow \text{Time dependent Dirac equation}$$

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

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad \leftarrow \text{Time independent Dirac equation}$$

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

24

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: $E < -mc^2$

25

Free particle Dirac equation

- Take simplest case : $\phi = 0$ and $\mathbf{A} = 0$
- 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

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

← After insertion into time-independent Dirac equation

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

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

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

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

26

Free particle Dirac equation

- Two doubly degenerate solutions

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

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

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

- Compare to classical energy expression

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

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

27

Free particle Dirac equation

- Wave function for $E = E_+$

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

$$\boxed{\hbar |k| \equiv p \ll mc} \quad \leftarrow \text{For particles moving with "nonrelativistic" velocities}$$

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

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

- Upper components are the "Large components"
- Lower components are the "Small components"

28


Free particle Dirac equation

- Wave function for $E = E_-$

$$a_4 = 0$$

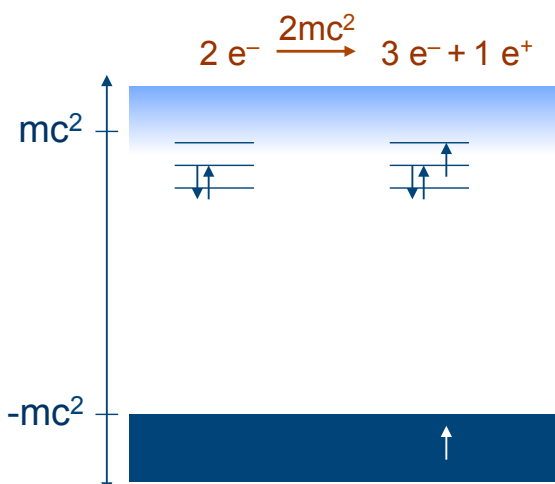
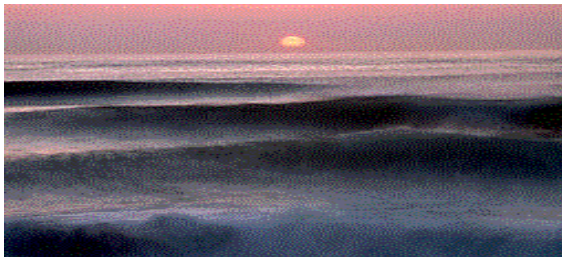
$$a_1 = a_3 \frac{c\hbar k_z}{E_- - mc^2} \approx a_3 \frac{p_z}{-2mc}$$

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

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

29

Dirac sea of electrons



- 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

30

Quantum Electro Dynamics

- Introduce a m -dimensional Fock space $F(m)$
 - States are defined by the occupation number vector \mathbf{n}

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

$$n_i = 0, 1$$

- The vacuum has all $n=0$

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

- We use an orthonormal basis

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

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

31

Second Quantization

- Second quantized operators

- Creation operator

$$a_i^\dagger |n_1, \dots, n_i, \dots, n_m\rangle = 0 \quad (n_i = 1)$$

$$a_i^\dagger |n_1, \dots, n_i, \dots, n_m\rangle = C_i |n_1, \dots, 1, \dots, n_m\rangle \quad (n_i = 0)$$

$$a_i^\dagger |vac\rangle = |0, \dots, 1, \dots, 0\rangle$$

- Annihilation operator

$$a_i |n_1, \dots, n_i, \dots, n_m\rangle = C_i |n_1, \dots, 0, \dots, n_m\rangle \quad (n_i = 1)$$

$$a_i |n_1, \dots, n_i, \dots, n_m\rangle = 0 \quad (n_i = 0)$$

$$a_i |vac\rangle = 0$$

- Define all operators in terms of these elementary operators

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

32

Fock space Hamiltonian

Positive and negative energy solutions define a Fock space Hamiltonian

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

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

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

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

33

Renormalization

1. Subtract energy from the occupied negative energy states

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

2. Re-interpretation

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

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

3. Normal ordered Hamiltonian

Due to the anticommutation relation

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

34

Quantum Electro Dynamics

- Positive energy for positrons

$$\begin{aligned}
 E(1p;0e) &= \langle \dots, 1, \dots; \dots | \hat{H}^{QED} | \dots, 1, \dots; \dots \rangle \\
 &\quad \text{Neg. Pos.} \quad \text{positron states} \quad \text{Neg. Pos.} \\
 &= \langle \dots, 1, \dots; \dots | - \sum_{\alpha, \beta} H_{\alpha\beta} b_{\alpha}^{\dagger} b_{\beta} | \dots, 1, \dots; \dots \rangle = -E_{\gamma} \geq mc^2
 \end{aligned}$$

- Total charge is also redefined

$$\begin{aligned}
 Q_{vac}^{QED} &= -e \langle vac | \hat{N}^{QED} | vac \rangle \\
 &= -e \langle vac | \sum_p^{electron\ states} b_p^{\dagger} b_p - \sum_{\alpha}^{positron\ states} b_{\alpha}^{\dagger} b_{\alpha} | vac \rangle = 0
 \end{aligned}$$

35

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

36

Electron-electron interaction

- Quantize also the EM-field

$$| \rangle = | p - \text{states}; e - \text{states}; \text{photons} \rangle$$

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

- 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})

37

Electron-electron interaction

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

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

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

38

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. Dyll & Faegri, Reiher & Wolf)

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

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

39

Hydrogenic orbitals

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

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

- Solutions to the radial equation

$$P_{n\kappa}(r) = N_{n\kappa}^P e^{-\lambda r} r^\gamma (F_1(r) + F_2(r)) \quad \text{Large component}$$

$$Q_{n\kappa}(r) = N_{n\kappa}^Q e^{-\lambda r} r^\gamma (F_1(r) - F_2(r)) \quad \text{Small component}$$

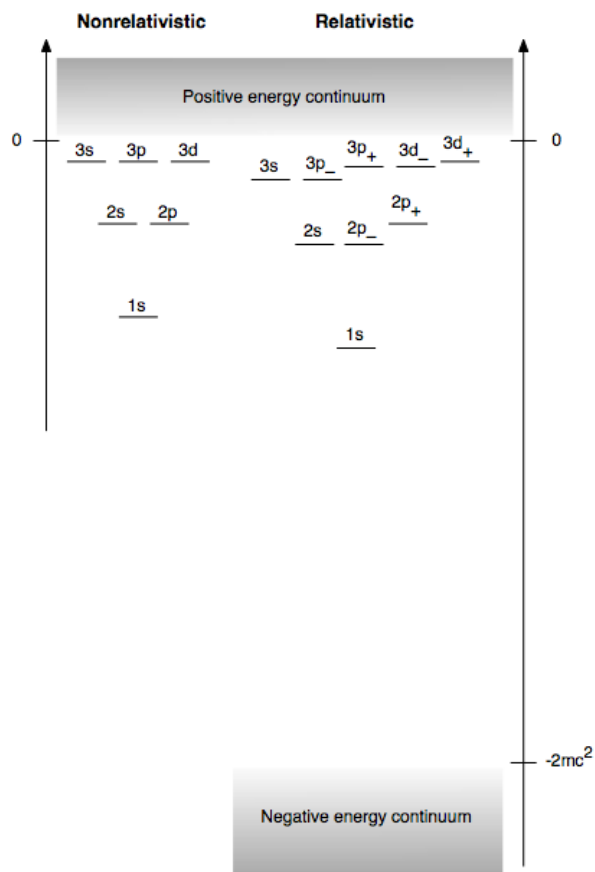
$$R_{nl}(r) = N_{nl}^R e^{-(\sqrt{-2E})r} r^{l+1} F(r) \quad \text{Nonrelativistic}$$

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

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

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
	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$

40



41

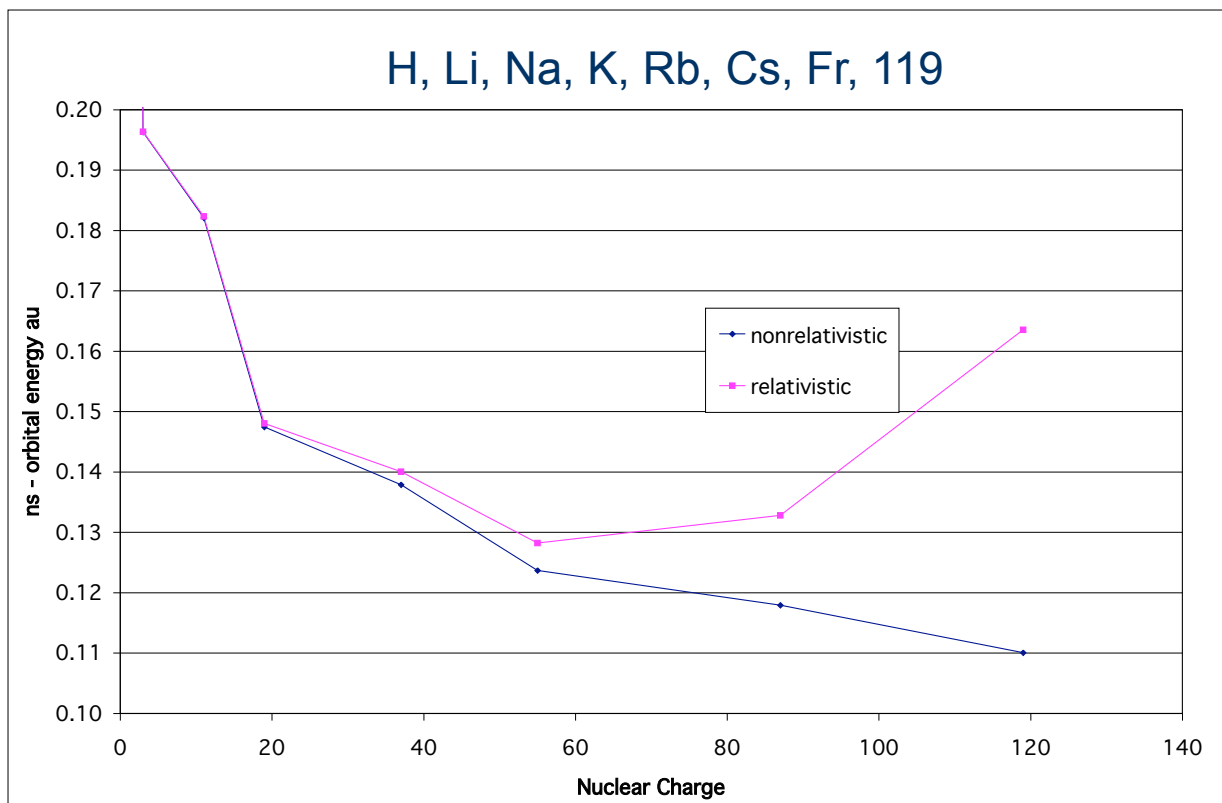
Explore **key information** about the chemical elements through this periodic table

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	*										57 Lu	58 Hf	59 Ta	60 W	61 Re	62 Os	63 Ir	64 Pt	65 Au	66 Hg	67 Tl	68 Pb	69 Bi	70 Po	71 At	72 Rn
7	87 Fr	88 Ra	**										73 Lr	74 Rf	75 Db	76 Sg	77 Bh	78 Hs	79 Mt	80 Ds	81 Rg	82 Cn	83 Uut	84 Uuq	85 Uup	86 Uuh	87 Uus	88 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											

Confirmation of the discoveries of elements 114 and 116

A news reports from IUPAC indicates the confirmation of the discoveries of elements 114 and 116. Proposals for the names of the two elements will follow in due course: [Discovery of the Elements with Atomic Number 114 and 116](#)

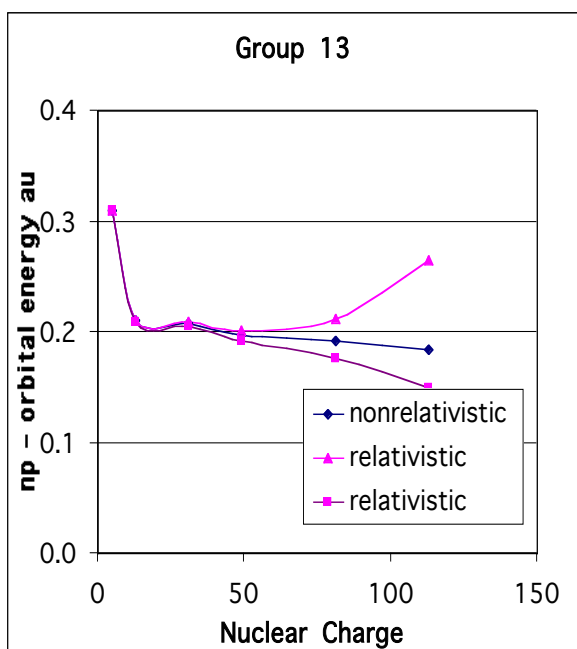
Orbital stabilisation



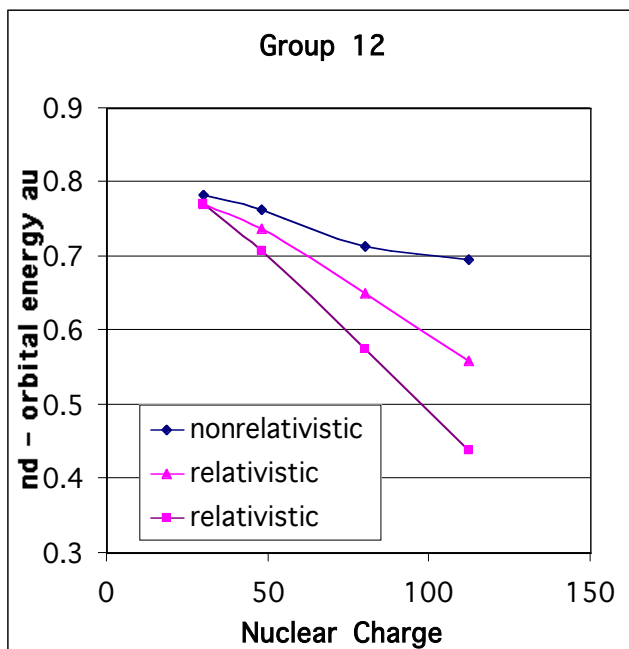
43

Orbital destabilization and spin-orbit splitting

B, Al, Ga, In, Tl, 113



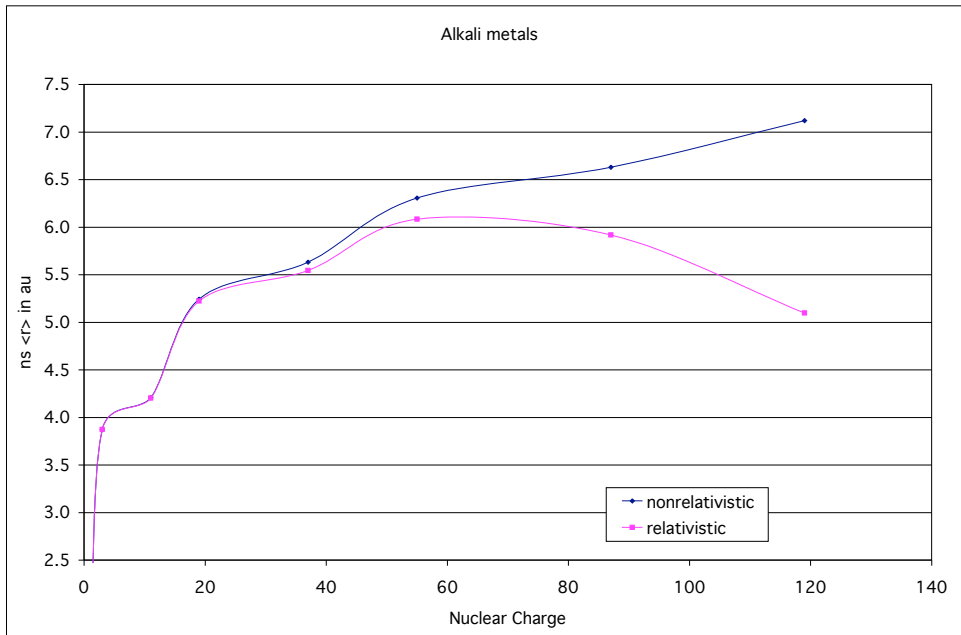
Zn, Cd, Hg, 112



44

Orbital contraction

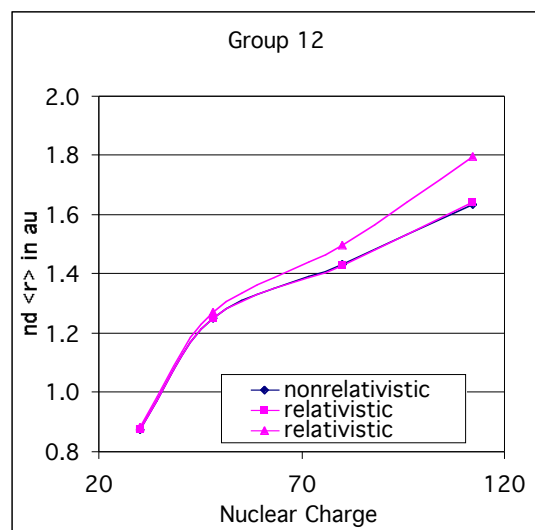
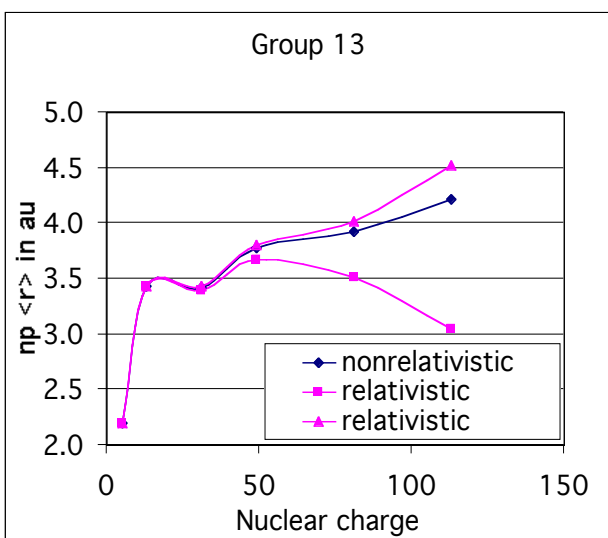
- The outermost s-orbital becomes more compact



45

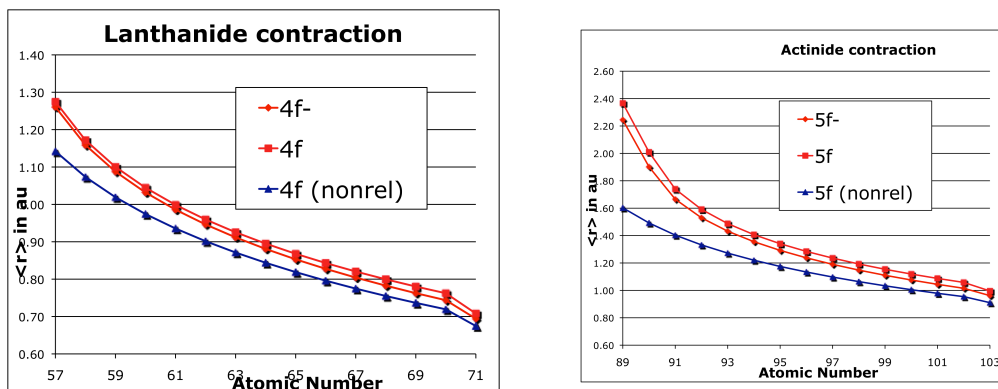
Orbital expansion

- The outermost p- and d-orbitals expand



46

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, LnH₃ and AnH₃ molecules.

47

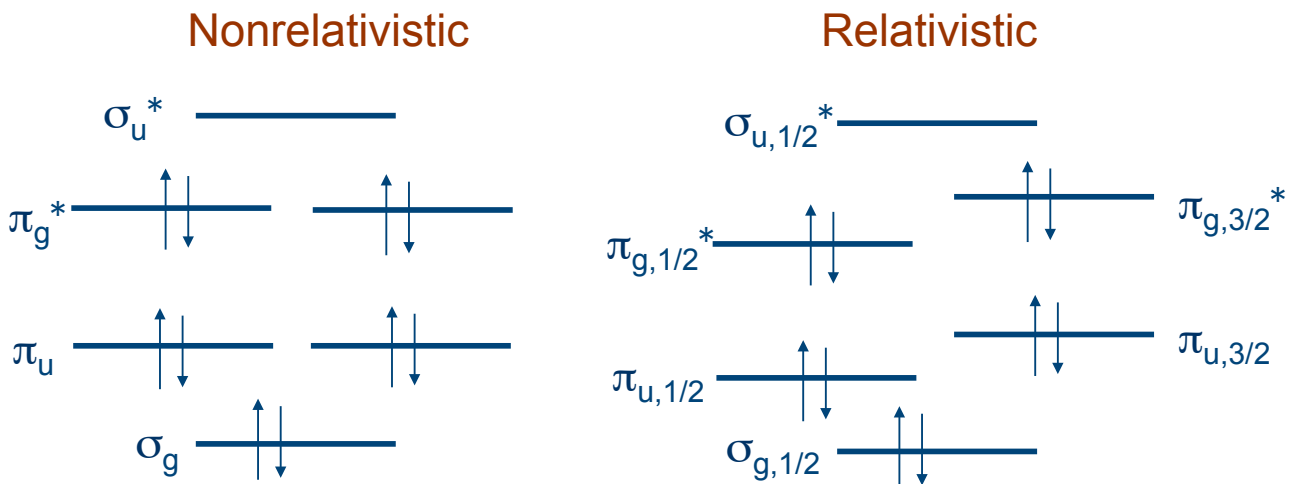
Spin-Orbit coupling

- 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

48

Atomization energies

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

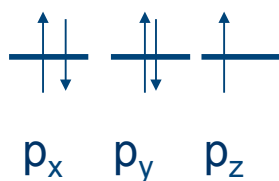


49

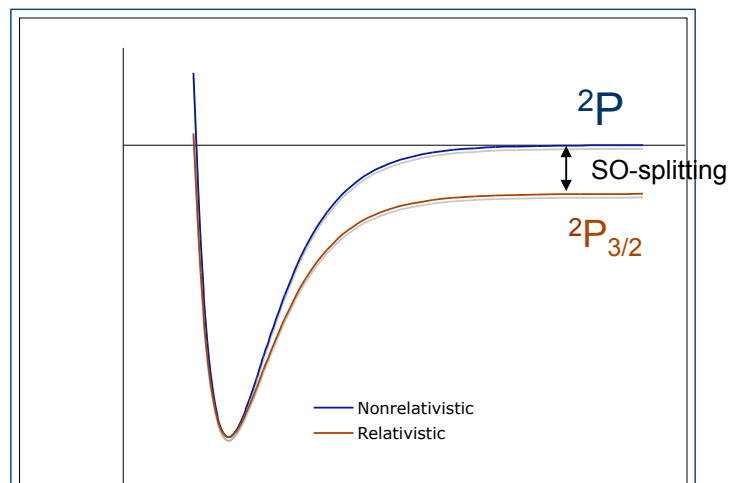
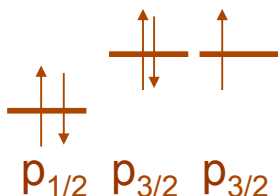
Atomization energies

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

Nonrelativistic

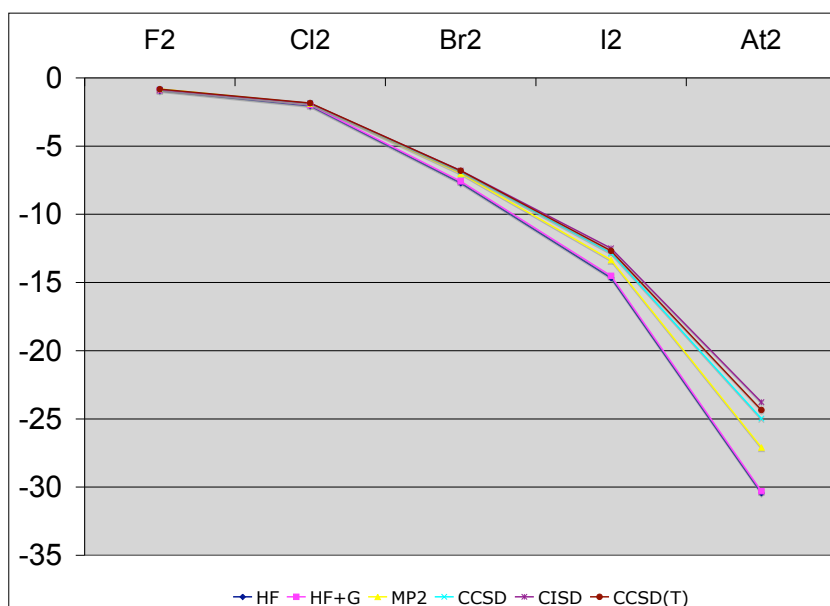


Relativistic



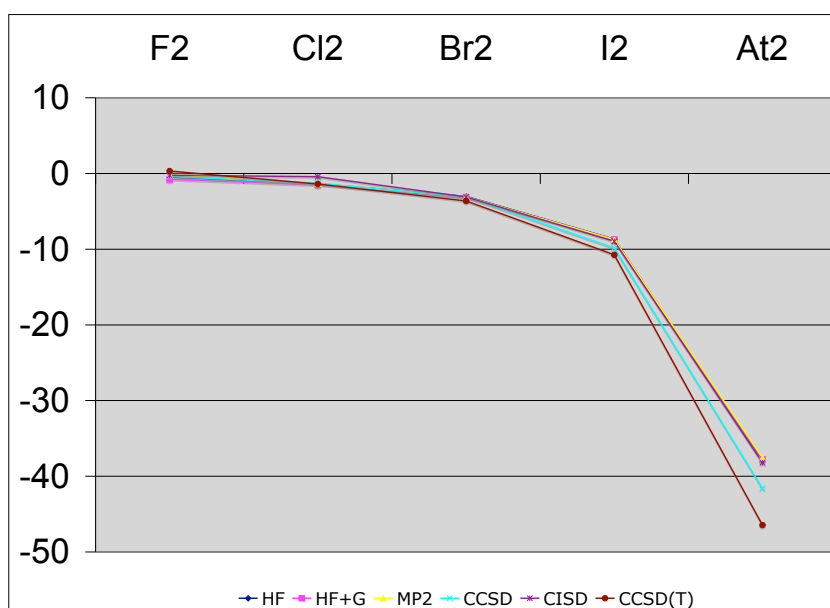
50

Relativistic effect on atomization energies (kcal/mol)



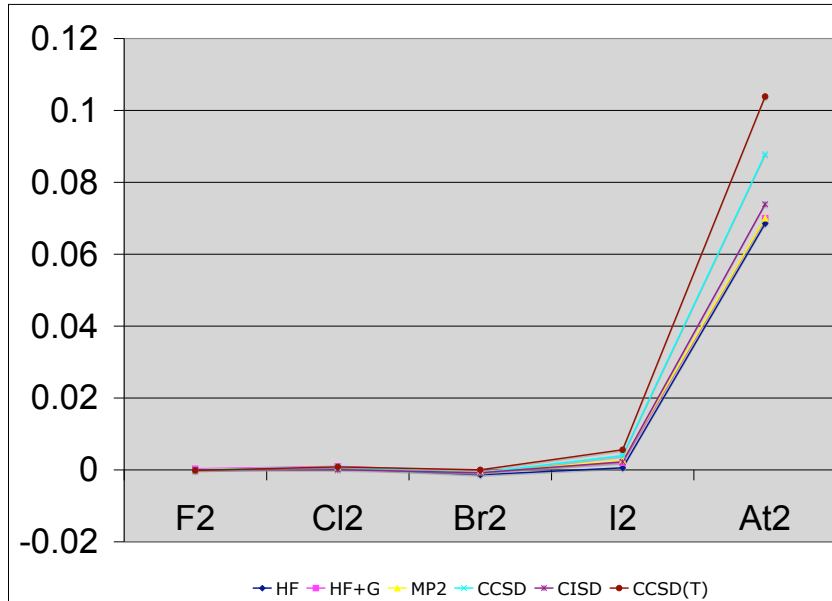
Relativistic effect on atomization energies is well-reproduced by correcting only the asymptote

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)

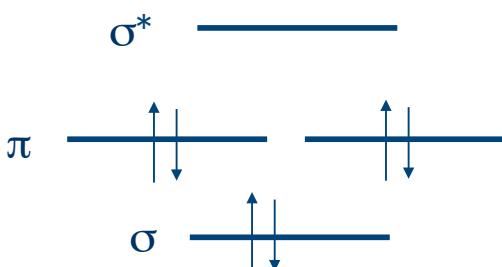


Important and slightly method dependent for 6p elements

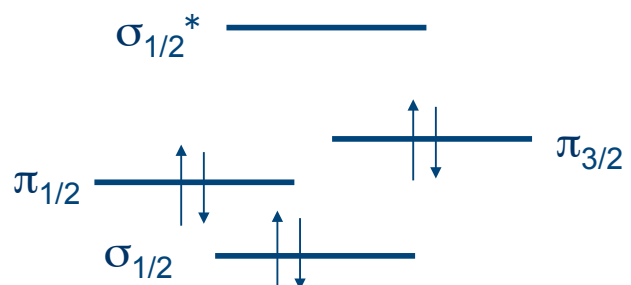
Atomization energies

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

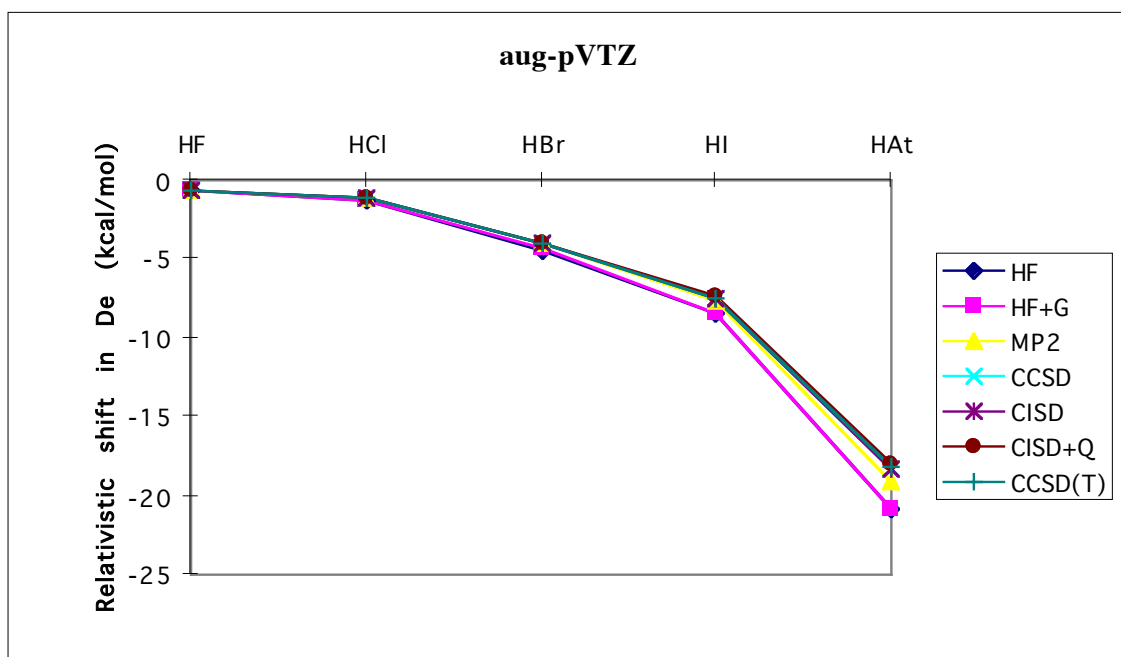
Nonrelativistic



Relativistic

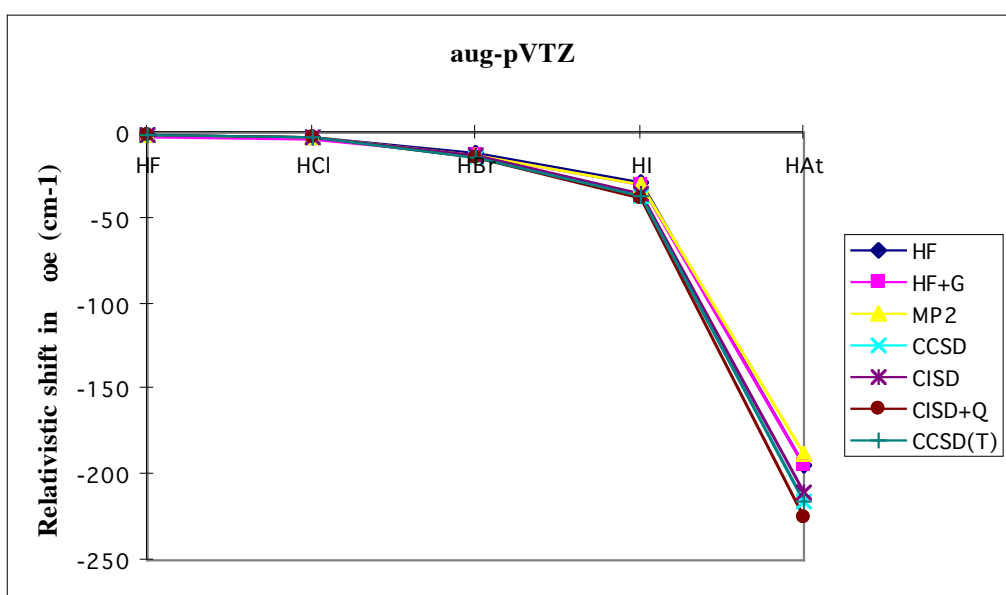


Atomization Energies



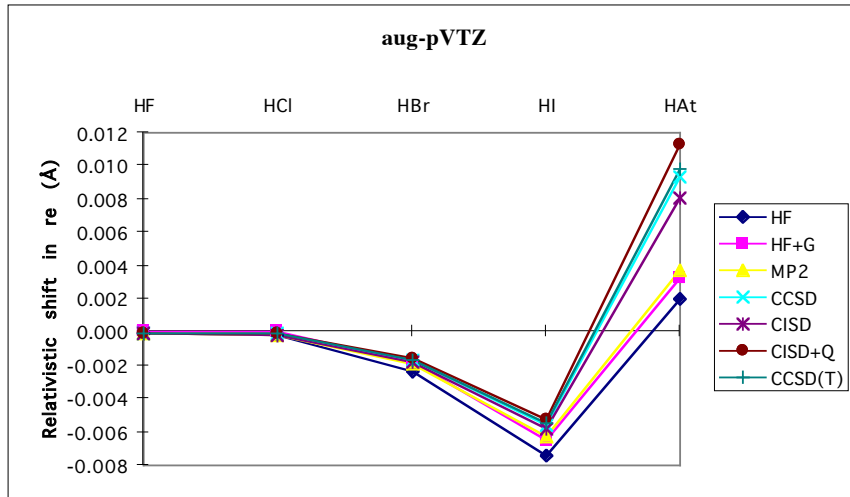
SO-coupling : a good estimate for atomization energies can be obtained by correcting only the asymptote

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 ($< 0.01 \text{ \AA}$) and can be neglected
for most practical cases.