

Relativistic quantum chemistry



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The Dirac village







Trond Saue (LCPQ, Toulouse)

Our playground: the periodic table



	Tabelle II.										
Reihen	Grappe I.	Grappe II. RO	Gruppe III. R*03	Gruppe IV. RH ⁴ RO ²	Gruppo V. RH ^s R*0 ⁵	Gruppe VL RH ² RO ³	Gruppo VII. RH R ² 0 ⁷	Gruppe VIII.			
1	H=1 Li=7	Bc=9,4	B=11	C=12	N=14	0=16	F=19				
\$	Na=23	Mg=24	A1=27,3	Si=28	P=31	S=32	Cl== 35,5				
4	X=39	Ca=40	-=44	Ti=48	V=51	Cr=52	Mn== 55	Fe=56, Co=59, Ni=59, Cu=63.			
5	(Cu=63)	Zn=65	-=68	-=72	As=75	Se=78	Br = 80				
6	Rb=85	Sr=87	?Yt=88	Zr = 90	Nb = 94	Mo=96	-=100	Ru=104, Rh=104, Pd=106, Ag=108.			
1	(Ag=108)	Cd=112	In=113	Sn == 118	Sb=122	Te=125	J=127				
8	Cs== 133	Ba=137	?Di==138	?Ce=140		-					
9	()	. –	-	-	-	-	_				
10	-	-	?Er == 178	?La=180	Ta == 182	W=184	-	Os=195, Ir=197, Pt=198, Au=199.			
11	(Au=199)	Hg=200	Ti=204	Pb=207	Bi=208	-	-				
12	-	-	-	Th = 231	-	U=240	-				

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	N=05	03-10	-=11	11=40	V=51	Cr=02	Mil = 00	Ni=59, Cu=63.			
5	(Cu = 63) Eb=85	Zn=65 Sr=87	-=68 ?Yt=88	-=72 Zr=90	As=75 Nb=94	Se=78 Mo=96	Br=80 -=100	Ru=104, Rh=104,			
1	(Åg=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127				
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eka-aluminium: gallium (1875)



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eka-aluminium: gallium (1875)



eka-silicon: germanium (1886)



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Relativistic Quantum Chemistry

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eka-aluminium: gallium (1875)



eka-silicon: germanium (1886)



eka-boron: scandium (1879)



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Relativistic Quantum Chemistry

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Broken trends



Goldschmidt and Einstein in Norway 1920

Relativistic effects

- scalar effects
- spin-orbit interaction

Lorentz factor:



Broken trends



Goldschmidt and Einstein in Norway 1920

Relativistic effects

- scalar effects
- spin-orbit interaction

Lorentz factor:



Lanthanide contraction

V.M. Goldschmidt, T. Barth, G. Lunde: Norske Vidensk. Selsk. Skrifter I Mat. Naturv. Kl. 7, 1 (1925) D. R. Lloyd, J. Chem. Ed. 63 (1986) 503

- La^{3+} Lu^{3+} (117.2 100.1 pm)
- Ca²⁺ Zn²⁺ (114 88 pm)
- Cu (138 pm) < Au (144 pm) < Ag (153 pm)



lonization energy of gold

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355



Electron affinity of gold

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355



Electron affinity of gold

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• Gold and caesium are extremes on the electron affinity scale — 2.309 eV vs. 0.472 eV

Electron affinity of gold

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355



- Gold and caesium are extremes on the electron affinity scale 2.309 eV vs. 0.472 eV
- CsAu is a semi-conductor with a CsCl crystal structure in the solid state; it forms an ionic melt. The oxidation state of gold is -I.

Spectroscopic constants of CsAu and homologues

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355

	Method		<i>r</i> e (pm)	$\omega_e \ (\mathrm{cm}^{-1})$	$\omega_e x_e \ (\mathrm{cm}^{-1})$	$D_e^{cov}(eV)$	μ (D)
CsAu	CCSD(T)	rel	326.3	89.4	0.21	2.52	11.73
		nrel	357.1	67.9	0.08	1.34	11.05
		nrel-ps	376.3	59.9	0.13	1.17	9.47
	Exp.[1]a		(320)	(125)		$2.58 {\pm} 0.03$	
	Exp.[1]b		-	-	-	$2.53 {\pm} 0.03$	-
CsAg	CCSD(T)	rel	331.6	88.0	0.17	1.51	10.69
		nrel	345.9	78.5	0.02	1.26	10.89
CsCu	CCSD(T)	rel	319.8	101.6	0.09	1.36	10.34
		nrel	327.7	97.1	0.18	1.31	10.88

1) B. Busse and K. G. Weil, Ber. Bunsenges. Phys. Chem. 85(1981) 309



Without relativity



.. gold would have the same color as silver

Without relativity



.. gold would have the same color as silver

...mercury would not be liquid at room temperature

Without relativity



.. gold would have the same color as silver

...mercury would not be liquid at room temperature

.. your car would not start

Einstein's special theory of relativity

Einstein's special theory of relativity





Reference frames





The theory of *special* relativity is restricted to **inertial** frames : reference frames related by constant velocity



The theory of *special* relativity is restricted to **inertial** frames : reference frames related by constant velocity

It is based on two postulates:

The principle of relativity



The principle of relativity



1. The laws of motion are the same in all inertial frames

The principle of relativity



1. The laws of motion are the same in all inertial frames



Galileo Galilei (1632)





• Speed of boat with respect to the river bank: 3 km/h



- Speed of boat with respect to the river bank: 3 km/h
- Speed of water with respect to the river bank: 7 km/h



- Speed of boat with respect to the river bank: 3 km/h
- Speed of water with respect to the river bank: 7 km/h
- Hint: you do not need this information....

Einsteins contribution (1905)

2. The speed c of light is the same in all inertial frames

speed =
$$\frac{\text{distance}}{\text{time}}$$

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2. The speed c of light is the same in all inertial frames



 $\mathsf{speed} = \tfrac{\mathsf{distance}}{\mathsf{time}}$

Relativistic Quantum Chemistry

Simultaneity: a relative concept



Observer in the train:

$$t_b = t_a$$

Simultaneity: a relative concept



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Simultaneity: a relative concept



Observer in the train:

$$t_b = t_a$$

Observer on the ground:

 $t_b < t_a$
Simultaneity: a relative concept



Observer in the train:

$$t_b = t_a$$

Observer on the ground:

 $t_b < t_a$

Two events that are simultaneous in one inertial frame are generally not so in another inertial frame.

Picture credit: Griffiths: Introduction to Electrodynamics (1999)





Observer in the train:

 $c\Delta \overline{t} = h$



Observer in the train:

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Observer in the train:

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Observer on the ground: $c\Delta t = \sqrt{h^2 + \left(v\Delta t\right)^2}$



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Observer on the ground: $c\Delta t = \sqrt{h^2 + \left(v\Delta t\right)^2}$

 $\Delta t = \gamma \Delta \overline{t} > \Delta \overline{t};$ Lorentz factor: $\gamma = rac{1}{\sqrt{1-v^2/c^2}}$



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Clocks in movement go slower.

Picture credit: Griffiths: Introduction to Electrodynamics (1999)





Observer in the train:

$$c\Delta \overline{t} = 2\Delta \overline{x}$$



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Observer in the train:

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Observer on the ground:

$$c\Delta t_1 = \Delta x + v\Delta t_1$$

$$c\Delta t_2 = \Delta x - v\Delta t_2$$



 Δt

$$=\Delta t_1 + \Delta t_2 = rac{\Delta x}{c-v} + rac{\Delta x}{c+v}$$



$$c\Delta \overline{t} = 2\Delta \overline{x}$$

Observer on the ground:

$$c\Delta t_1 = \Delta x + v\Delta t_1$$
$$c\Delta t_2 = \Delta x - v\Delta t_2$$

$$\Delta t = \Delta t_1 + \Delta t_2 = \frac{\Delta x}{c - v} + \frac{\Delta x}{c + v}$$
$$\Delta t = 2\frac{\Delta x}{c}\gamma^2 = \gamma\Delta\overline{t} = \gamma\frac{2\Delta\overline{x}}{c}$$



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 $\Delta \overline{x} = \gamma \Delta x$

An object in movement is contracted in the direction of movement

Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Paradox of the barn and the ladder



Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Lorentz transformation



$$x = d + vt$$

$$d = \begin{cases} \overline{x}; & \text{(Galilei)} \\ \gamma^{-1}\overline{x}; & \text{(Lorentz)} \end{cases}$$

$$\overline{x} = \gamma (x - vt)$$

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$$d = \begin{cases} \overline{x}; & \text{(Galilei)} \\ \gamma^{-1}\overline{x}; & \text{(Lorentz)} \end{cases}$$

$$\overline{x} = \gamma (x - vt)$$



 $\begin{aligned} x &= \gamma \left(\overline{x} + v \overline{t} \right) \\ \overline{t} &= \gamma \left(t - \frac{v}{c^2} x \right) \end{aligned}$

Let us look at a relativistic theory ...

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Electrodynamics

Maxwell's equations (SI-based atomic units: $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$)

• The homogeneous pair:

$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}$$

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 The inhomogeneous pair includes sources: the charge density ρ and current density j (c is the speed of light)

$$\nabla \cdot \mathbf{E} = 4\pi\rho$$
$$\nabla \times \mathbf{B} - \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c^2} \mathbf{j}$$

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 The inhomogeneous pair includes sources: the charge density ρ and current density j (c is the speed of light)

 Are the electric field E and the magnetic field B uniquely determined by their divergence (∇ · . . .) and curl (∇ × . . .) ?

• The answer is NO !!!!

The two vectors

$$\begin{array}{rcl}
 F_1 &=& (0,0,0) \\
 F_2 &=& (yz,zx,xy)
 \end{array}$$

both have zero divergence and zero curl

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• Boundary conditions must be introduced:

• The answer is NO !!!!

The two vectors

$$F_1 = (0, 0, 0)$$

 $F_2 = (yz, zx, xy)$

both have zero divergence and zero curl

• Boundary conditions must be introduced:

• E and B go to zero at infinity

• The vector relation

$$abla^2 \mathbf{F} = \mathbf{
abla} \left(\mathbf{
abla} \cdot \mathbf{F}
ight) - \mathbf{
abla} imes \left(\mathbf{
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can also be seen as an equation

• The vector relation

$$\nabla^{2}\boldsymbol{\mathsf{F}}=\boldsymbol{\nabla}\left(\boldsymbol{\nabla}\cdot\boldsymbol{\mathsf{F}}\right)-\boldsymbol{\nabla}\times\left(\boldsymbol{\nabla}\times\boldsymbol{\mathsf{F}}\right)$$

can also be seen as an equation

• and has solution

$$\mathsf{F}(\mathsf{r}) = - \nabla s(\mathsf{r}) + \nabla imes \mathsf{v}(\mathsf{r})$$

where

$$s(\mathbf{r}_1) = \frac{1}{4\pi} \int \frac{\boldsymbol{\nabla}_2 \cdot \boldsymbol{\mathsf{F}}(\mathbf{r}_2)}{r_{12}} d^3 \mathbf{r}_2; \quad \mathbf{v}(\mathbf{r}_1) = \frac{1}{4\pi} \int \frac{\boldsymbol{\nabla}_2 \times \boldsymbol{\mathsf{F}}(\mathbf{r}_2)}{r_{12}} d^3 \mathbf{r}_2$$

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• The divergence and curl of **F** must go to zero faster than $\frac{1}{r^2}$; otherwise the above integrals blow up in the limit.

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- The divergence and curl of **F** must go to zero faster than $\frac{1}{r^2}$; otherwise the above integrals blow up in the limit.
- This results show that we can reconstruct a vector function from knowledge of its divergence and curl combined with proper boundary conditions.

• General solutions of Maxwell's equations are

$$\mathbf{E}(\mathbf{r}_{1},t) = \int \left\{ \frac{\rho(\mathbf{r}_{2},t_{r})\mathbf{r}_{12}}{r_{12}^{3}} + \frac{\dot{\rho}(\mathbf{r}_{2},t_{r})\mathbf{r}_{12}}{r_{12}^{2}} - \frac{\dot{j}(\mathbf{r}_{2},t_{r})}{c^{2}r_{12}} \right\} d^{3}\mathbf{r}_{2} \\ \mathbf{B}(\mathbf{r}_{1},t) = \frac{1}{c^{2}} \int \left\{ \frac{\mathbf{j}(\mathbf{r}_{2},t_{r}) \times \mathbf{r}_{12}}{r_{12}^{3}} + \frac{\dot{j}(\mathbf{r}_{2},t_{r}) \times r_{12}}{cr^{2}r_{12}} \right\} d^{3}\mathbf{r}_{2}$$

where $\dot{x} = \frac{dx}{dt}$.

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• Note that we can always add the solutions of the homogeneous (source-free) equations, that is, electromagnetic waves.



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• A nasty fellow:

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where $\dot{x} = \frac{dx}{dt}$.

 Note that we can always add the solutions of the homogeneous (source-free) equations, that is, electromagnetic waves.



- A nasty fellow:
 - Retarded time

$$t_r = t - \frac{r_{12}}{c}$$

Looking into space ...

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Relativistic Quantum Chemistry

@Jeff的星空之旅

Looking into space ...



@Jeff的星空之旅

Helmholtz decomposition

Any vector function **F** (differentiable) who goes to zero faster than $\frac{1}{r}$ when $r \to \infty$ can be expressed as the sum of the gradient of a scalar and the curl of a vector

$$\mathbf{F}(\mathbf{r}) = - \mathbf{\nabla} \mathbf{s}(\mathbf{r}) + \mathbf{\nabla} imes \mathbf{v}(\mathbf{r})$$
Helmholtz decomposition

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Longitudinal component ("parallel"):

$$\mathbf{F}_{\parallel}=-oldsymbol{
abla} \mathbf{s}(\mathbf{r}); \quad oldsymbol{
abla} imes \mathbf{F}_{\parallel}=\mathbf{0}$$



Solenoidal component ("perpendicular"):

$$\mathbf{F}_{\perp} = \mathbf{\nabla} imes \mathbf{v}(\mathbf{r}); \quad \mathbf{\nabla} \cdot \mathbf{F}_{\perp} = 0$$

• $\boldsymbol{\nabla}\cdot \boldsymbol{B}=0$ means that magnetic fields are always solenoidal

$$\mathbf{B} = \mathbf{B}_{\perp} = \mathbf{\nabla} \times \mathbf{A}(\mathbf{r}) \text{ and } \mathbf{B}_{\parallel} = \mathbf{0}$$

 $\bullet~\boldsymbol{\nabla}\cdot\boldsymbol{B}=0$ means that magnetic fields are always solenoidal

$$\mathbf{B} = \mathbf{B}_{\perp} = \mathbf{\nabla} \times \mathbf{A}(\mathbf{r}) \quad \text{and} \quad \mathbf{B}_{\parallel} = \mathbf{0}$$

• $\mathbf{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0$ then becomes $\mathbf{\nabla} \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t}\right) = 0$ and one may write
 $\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\mathbf{\nabla}\phi(\mathbf{r}) \quad \Rightarrow \quad \mathbf{E} = -\mathbf{\nabla}\phi(\mathbf{r}) - \frac{\partial \mathbf{A}}{\partial t}$

 $\bullet~\boldsymbol{\nabla}\cdot\boldsymbol{B}=0$ means that magnetic fields are always solenoidal

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 $\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\mathbf{\nabla}\phi(\mathbf{r}) \quad \Rightarrow \quad \mathbf{E} = -\mathbf{\nabla}\phi(\mathbf{r}) - \frac{\partial \mathbf{A}}{\partial t}$

• The electric field generally has both a longitudinal and solenoidal component

$$\mathbf{E}_{\parallel} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}_{\parallel}}{\partial t}; \quad \mathbf{E}_{\perp} = -\frac{\partial \mathbf{A}_{\perp}}{\partial t}$$

• $\boldsymbol{\nabla}\cdot\boldsymbol{B}=0$ means that magnetic fields are always solenoidal

$$\mathbf{B} = \mathbf{B}_{\perp} = \mathbf{\nabla} \times \mathbf{A}(\mathbf{r}) \quad \text{and} \quad \mathbf{B}_{\parallel} = \mathbf{0}$$
$$\mathbf{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \text{ then becomes } \mathbf{\nabla} \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t}\right) = 0 \text{ and one may write}$$
$$\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\mathbf{\nabla}\phi(\mathbf{r}) \quad \Rightarrow \quad \mathbf{E} = -\mathbf{\nabla}\phi(\mathbf{r}) - \frac{\partial \mathbf{A}}{\partial t}$$

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• With the introduction of the scalar potential ϕ and the vector potential A, the homogeneous pair of Maxwell's equations is automatically satisfied.

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• $\nabla \cdot \mathbf{E} = 4\pi\rho$ becomes

$$\nabla^2 \phi + \frac{\partial}{\partial t} \left(\boldsymbol{\nabla} \cdot \mathbf{A} \right) = -4\pi\rho$$

or $\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \phi + \frac{\partial}{\partial t} \left[\left(\boldsymbol{\nabla} \cdot \mathbf{A} \right) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right] = -4\pi\rho$

• $\nabla \cdot \mathbf{E} = 4\pi\rho$ becomes $\nabla^2 \phi + \frac{\partial}{\partial t} (\nabla \cdot \mathbf{A}) = -4\pi\rho$ or $\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right] \phi + \frac{\partial}{\partial t} \left[(\nabla \cdot \mathbf{A}) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right] = -4\pi\rho$ • $\nabla \times \mathbf{B} - \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c^2} \mathbf{j}$ becomes $\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right] \mathbf{A} - \nabla \left[(\nabla \cdot \mathbf{A}) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right] = -\frac{4\pi}{c^2} \mathbf{j}$

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is the relativistic transformation between inertial frames.

• It involves space and time which can be combined into 4-position: $r_{\mu} = (\mathbf{r}, ict)$ whose norm $(r_{\mu}r_{\mu} = r^2 - c^2t^2)$ is conserved under Lorentz transformations

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 - 4-potential: $A_{\mu} = (\mathbf{A}, (i/c)\phi)$
 - 4-current:: $i_{\mu} = (\mathbf{j}, ic\rho)$
- They all transform in the same way !

Maxwell's equations: 4-vector notation

• We start from:

$$\begin{bmatrix} \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \end{bmatrix} \phi + \frac{\partial}{\partial t} \begin{bmatrix} (\nabla \cdot \mathbf{A}) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \end{bmatrix} = -4\pi\rho$$
$$\begin{bmatrix} \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \end{bmatrix} \mathbf{A} - \nabla \begin{bmatrix} (\nabla \cdot \mathbf{A}) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \end{bmatrix} = -\frac{4\pi}{c^2} \mathbf{j}$$

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• This can be written more compactly as

$$\Box^{2}\phi + \frac{\partial}{\partial t}(\partial_{\mu}A_{\mu}) = -4\pi\rho$$

;
$$\Box^{2} = \partial_{\mu}\partial_{\mu} = \nabla^{2} - \frac{1}{c^{2}}\frac{\partial^{2}}{\partial t^{2}}$$
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• .. and finally squashed into

$$\Box^2 A_{eta} - \partial_{eta} (\partial_{lpha} A_{lpha}) = -rac{4\pi}{c^2} j_{eta}$$

• $B = \nabla \times A$ implies that the longitudinal component A_{\parallel} of the vector potential can be modified without changing B, that is

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \mathbf{\nabla} \chi$$

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• The electric and magnetic fields are gauge invariant.

Lorentz gauge:
$$\partial_{\mu}A_{\mu} = \boldsymbol{\nabla}\cdot\boldsymbol{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t} = 0$$

• Maxwell's equations simplifies to

$$\Box^2 A_\beta = -\frac{4\pi}{c^2} j_\beta$$

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• General solution:

$$A(\mathbf{r}_1,t) = \int \frac{\mathbf{j}(\mathbf{r}_2,t_r)}{r_{12}} d^3 \mathbf{r}_2; \quad \phi(\mathbf{r}_1,t) = \int \frac{\rho(\mathbf{r}_2,t_r)}{r_{12}} d^3 \mathbf{r}_2$$

where appears retarded time

$$t_r = t - \frac{r_{12}}{c}$$

• Maxwell's equations simplifies to:

$$\nabla^2 \phi = -4\pi\rho$$
$$\left(\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}\right) - \boldsymbol{\nabla} \frac{1}{c^2} \frac{\partial \phi}{\partial t} = -\frac{4\pi}{c^2} \mathbf{j}$$

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• The scalar potential is the solution of the Poisson equation

$$\phi(\mathbf{r}_1,t) = \int \frac{\rho(\mathbf{r}_2,t)}{r_{12}} d^3 \mathbf{r}_2$$

and describes the instantaneous Coulomb interaction.

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 - The theory of relativity does not allow instantaneous interactions.

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- Problem (?):
 - The theory of relativity does not allow instantaneous interactions.
- Retardation is hidden in the solution for the purely transversal vector potential

$$\mathbf{A}(\mathbf{r}_1,t) = \mathbf{A}_{\perp}(\mathbf{r}_1,t) = \frac{4\pi}{c^2} \int \frac{\mathbf{j}_{\perp}(\mathbf{r}_2,t_r)}{r_{12}} d^3 \mathbf{r}_2$$

• Complete Hamiltonian

 $\textit{H} = \textit{H}_{\rm particles} + \textit{H}_{\rm interaction} + \textit{H}_{\rm fields}$

• Complete Hamiltonian

$$H = H_{\rm particles} + H_{\rm interaction} + H_{\rm fields}$$

• Fields specified:

Non-relativistic limit

$$(i\gamma_{\mu}\partial_{\mu}-mc)\psi=0$$
 \rightarrow

Dirac equation

$$\left(\frac{p^2}{2m} - i\frac{\partial}{\partial t}\right)\psi = 0$$
Schrödinger equation

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• Particles (sources) specified:

Non-relativistic limit

$$\Box^2 A_{\mu} - \partial_{\mu} (\partial_{\nu} A_{\nu}) = -\frac{4\pi}{c^2} j_{\mu} \quad \to \qquad ???$$

Maxwell's equations

The non-relativistic limit of electrodynamics

T. Saue, Adv. Quantum Chem., 48 (2005) 383

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \cdot \mathbf{B} = 0$$
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$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \qquad c \to \infty \qquad \nabla \times \mathbf{E} = 0$$
$$\nabla \cdot \mathbf{E} = 4\pi\rho \qquad \Rightarrow \qquad \nabla \cdot \mathbf{E} = 4\pi\rho$$
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- The Coulomb gauge bears its name because it singles out the instantaneous Coulomb interaction, which constitutes the proper non-relativistic limit of electrodynamics and which is the most important interaction in chemistry.
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- In the strict non-relativistic limit there are no magnetic fields and no effects of retardation !
- The Coulomb gauge bears its name because it singles out the instantaneous Coulomb interaction, which constitutes the proper non-relativistic limit of electrodynamics and which is the most important interaction in chemistry.
- All retardation effects as well as magnetic interactions are to be considered corrections of a perturbation series of the total interaction (in $1/c^2$).

P. A. M. Dirac, Proc. Roy. Soc. A 123 (1929) 714

Quantum Mechanics of Many-Electron Systems. By P. A. M. DIRAC, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.-Received March 12, 1929.)

§ 1. Introduction.

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity 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 elsetrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. P. A. M. Dirac, Proc. Roy. Soc. A 123 (1929) 714

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theory (1930)

§ 8. THE WAVE CONCEPT FOR MATTER AND RADIATION: CLASSICAL THEORY

The classical wave theory is that of the de Broglie waves for matter and of electromagnetic waves for radiation. This section will treat primarily those waves which are associated with the electron (the proton waves can be treated in an entirely similar manner), though light waves will also be considered briefly. No attempt will be madeto include relativistic effects, and it is then logical to treat only electrostatic forces and to neglect magnetic and retardational benomena.

Scalar relativistic effects in chemistry

• The Lorentz factor

$$\gamma = rac{1}{\sqrt{1-v^2/c^2}}; \quad egin{cases} v & - ext{ speed of particle} \ c & - ext{ speed of light} \end{cases}$$

is a diagnostic of relativistic effects.

• The Lorentz factor

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• So what goes fast in an atom or a molecule ?





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Neutral atom: Z electrons



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 - d, f orbitals : expansion

The colour of gold



The colours of silver and gold can be traced back to the energy difference between the (n-1)d and *ns* orbitals in the atom. For silver this transition is in the ultraviolet, giving the metallic luster. For gold it is in the visible, but only when relativistic effects are included.

Metal-water interaction

C. Gourlaouen, J.-P. Piquemal, T. Saue and O. Parisel, J. Comp. Chem. 27 (2006) 142



 $[Ag(H_2O)]^+$: electrostatic interaction

bonding dominated by charge-dipole interaction

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 $[Au(H_2O)]^+$: orbital interaction

relativistic stabilisation of the Au 6s orbital induces charge transfer and covalent bonding

Two contrasting neighbours: gold and mercury L. J. Norrby, J. Chem. Ed. 68 (1991) 110



1064°C 12.5 kJ/mol 9.29 J/Kmol 19.32 g/cm³ 426 kS/m dimer [Xe]4f¹⁴5d¹⁰6s¹ pseudo halogen $\begin{array}{c} \mathsf{Mp.}\\ \Delta \mathcal{H}_{\mathit{fus}}\\ \Delta \mathcal{S}_{\mathit{fus}}\\ \rho\\ \mathsf{Conductivity}\\ \mathsf{Gas \ phase} \end{array}$



-39°C 2.29 kJ/mol 9.81 J/Kmol 13.53 g/cm³ 10.4 kS/m monomer [Xe]4f¹⁴5d¹⁰6s² pseudo noble gas

The low-temperature melting of mercury is a relativistic effect

Florent Calvo, Elke Pahl, Michael Wormit and Peter Schwerdtfeger, Ang. Chemie. Int. Ed. 52 (2013) 7583

Mercury melts at 234.32 K (-38.83 $^{\circ}$ C)

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Cars start due to relativity

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non-relativistic calculation: +0.39 V relativistic calculation: +2.13 V experiment: +2.11 V

Spin-orbit interaction

Spin-orbit interaction

a much misunderstood interaction !

$$h^{\rm so} = \frac{1}{2m^2c^2}\mathbf{s} \cdot \left[(\boldsymbol{\nabla} V) \times \mathbf{p} \right] \quad \stackrel{V = -\frac{Z}{r}}{\to} \quad \frac{Z}{2m^2c^2r^3}\mathbf{s} \cdot \mathbf{I}$$

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- This operator couples the degrees of freedom associated with spin and space and therefore makes it impossible to treat spin and spatial symmetry separately.








• These are DFT calculations using *collinear* magnetization: $s = m_z =
ho^lpha -
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Energy: $\equiv 0 E_h$

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- Spin magnetization : $\mathbf{m} = \sum_{i} \psi_{i}^{\dagger} \boldsymbol{\sigma} \psi_{i}$
- A solution is to use *non-collinear* magnetization: $s = |\mathbf{m}|$

Spin-orbit interaction in atoms

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• Orbitals are accordingly characterized by quantum numbers j and m_j

$$\hat{j}^{2}\left|j,m_{j}
ight
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ight)\left|j,m_{j}
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Term	L	L S Possible J value	
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• The actual energy levels are

Term	J	Level (cm $^{-1}$)
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	1	158.265
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¹ S	0	33792.583

http://physics.nist.gov/PhysRefData/Handbook/Tables/oxygentable1.htm

Term	J	Oxygen	Sulfur	Selenium	Tellurium	Polonium
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• For heavier atoms the interval rule breaks down because of coupling between different LS terms as well as change in the spatial extent of radial parts between spin-orbit components.

Atomic oxygen emissions in northern lights



	Transition	Wavelength(Å)	Туре	Lifetime(s)
Green line	$^{1}S_{0} \rightarrow ^{1}D_{2}$	5577	E2	0.75
Red line	$^{1}D_{2} \rightarrow {}^{3}P_{2}$	6300	M1	110



• In the absence of spin-orbit interaction, molecular states are denoted ${}^{2S+1}\Lambda$, with $\Lambda = |M_L|$.



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$a^1\Delta_g$	7918.1
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http://webbook.nist.gov/chemistry/

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- In the presence of spin-orbit interaction, molecular states are characterized by $\Omega = |M_L + M_S|$.
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 - Singlets are totally symmetric; triplets transform as rotations.
 - We obtain:

$${}^{3}\Sigma_{g}^{-}: \qquad \frac{1}{2} \left(\pi_{+}\pi_{-} - \pi_{-}\pi_{+} \right) \left(\alpha \beta + \beta \alpha \right) \quad \rightarrow \quad 0_{g}^{+}$$
$${}^{1}\Sigma_{g}^{+}: \qquad \frac{1}{2} \left(\pi_{+}\pi_{-} + \pi_{-}\pi_{+} \right) \left(\alpha \beta - \beta \alpha \right) \quad \rightarrow \quad 0_{g}^{+}$$

- The ground state of the oxygen molecule is a triplet.
 - It is split by spin-orbit interaction into 0_g^+ and 1_g (zero-field splitting).
 - A magnetic interaction such as spin-orbit interaction is required for interaction with singlet states.
 - This is crucial for life !

Term	$T_e(\mathrm{cm}^{-1})$
$X^{3}\Sigma_{g}^{-}$	0.0
$a^1\Delta_g$	7918.1
$b^1 \Sigma_g^+$	13195.1

http://webbook.nist.gov/chemistry/

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- Zero-field splitting:
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 - ▶ Se₂ : 510.0 cm⁻¹
• Oxygen dimer:

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 - Se₂ : 510.0 cm^{-1} Te₂ : 1974.9 cm⁻¹

 - ▶ Po₂ : ~ 7000 cm⁻¹

Relativistic effects: valence orbital energies (E_h) of the uranium atom



- Scalar relativistic effects (SR): relativistic mass increase of the electron
- Spin-orbit effects (SO): the interaction of the electron spin with the magnetic field induced by charges (e.g. nuclei and other electrons) in relative motion

• Relativistic effects are important for heavy elements (Z>40). We distinguish between:

Summary so far

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 - scalar relativistic effects are associated with the relativistic mass increase of the electron

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}};$$
 $c = 137.0359998 \ a.u.;$ One-electron atom: $v_{1s} = Z \ a.u.$

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- Since relativistic effects are most pronounced in the core region, a straightforward and widely used way to introduce relativity in quantum chemical calculations is to replace the core orbitals by an effective potential, leading to the **pseudopotential** approach.
- In the following we shall, however, first look at Hamiltonians derived directly from the Dirac equation.

Wolfgang Pauli and 137





Throughout his life, Pauli was preoccupied with the question of why the fine structure constant, a dimensionless fundamental constant, has a value nearly equal to 1/137.

Wolfgang Pauli (1900-1958)

Wolfgang Pauli and 137





In 1958, Pauli fell ill with pancreatic cancer. When his last assistant, Charles Enz, visited him at the Rotkreuz hospital in Zurich, Pauli asked him: "Did you see the room number?" It was number 137. Pauli died in that room on December 15, 1958.

Wolfgang Pauli (1900-1958)

The Old and the New Testament

- Handbuch der Physik (1926): The Old Testament
- Handbuch der Physik (1933): The New Testament

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Theoretical model chemistries



Theoretical model chemistries



The electronic Hamiltonian, relativistic or not, has the same generic form

$$\hat{H} = V_{NN} + \sum_{i} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j); \quad V_{NN} = \frac{1}{2} \sum_{K \neq L} \frac{Z_K Z_L}{R_{KL}}$$

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Computational cost: $\times N^{\gamma}$

Constructing the relativistic Hamiltonian





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• Wave equation for non-relativistic free particle:

$$E = rac{1}{2}mv^2 = rac{p^2}{2m}; \quad o irac{\partial}{\partial t}\psi = rac{\hat{p}^2}{2m}\psi = \hat{h}_0\psi$$

• Relativistic free-particle

$$E = \pm \sqrt{m^2 c^4 + c^2 p^2} \in \langle -\infty, -mc^2 | \cup | +mc^2, +\infty \rangle$$





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- Connecting to the non-relativistic expression

$$E = +mc^2\sqrt{1 + \left(\frac{p}{mc}\right)^2} = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$





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• The first term explodes in the non-relativistic limit $(c \to \infty)$, but can be avoided by aligning the relativistic energy scale with the non-relativistic one

$$E \rightarrow E - mc^2$$

(only works for positive-energy branch)



 $+mc^2$

Dirac equation for a relativistic free particle

• Dirac equation

$$\left(h_0 - i\frac{\partial}{\partial t}\right)\psi = 0$$

with relativistic free-particle Hamiltonian

$$\hat{h}_{0} = \beta mc^{2} + c \left(\boldsymbol{\alpha} \cdot \mathbf{p} \right) = \begin{bmatrix} +mc^{2} & c \left(\boldsymbol{\sigma} \cdot \mathbf{p} \right) \\ c \left(\boldsymbol{\sigma} \cdot \mathbf{p} \right) & -mc^{2} \end{bmatrix}$$





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ight]$$



• The solutions are 4-component vector functions

$$\psi = \left[\begin{array}{c} \psi^L \\ \psi^S \end{array} \right] = \left[\begin{array}{c} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{array} \right]$$



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• Why four components ?

 $+mc^2$

 $-mc^2$

(M. Gell-Mann, Nuovo Cimento Suppl. 4 (1956) 848)

• The Hamiltonian of a particle interacting with external fields is obtained from the free-particle Hamiltonian through the substitutions:

$$p_{\mu} \rightarrow p_{\mu} - qA_{\mu} \Rightarrow ext{Electron:} q = -e \Rightarrow E \rightarrow E + e\phi$$

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- The complete Dirac Hamiltonian reads

$$\hat{h}_{D} = eta' \mathit{mc}^{2} + c \left(lpha \cdot \pi
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where appears the mechanical momentum $\pi = \mathbf{p} + e\mathbf{A}$

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where appears the mechanical momentum ${m \pi}={m p}+e{m A}$

• Energy shift: $\beta \rightarrow \beta' - mc^2 \quad \Rightarrow \quad E \rightarrow E' = E - mc^2$



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- In quantum mechanics, these solutions are problematic because there is always a finite transition probability.
 - \blacktriangleright It can be shown that the hydrogen atom would not be stable and would disintegrate in $10^{-9}~{\rm s.}$
 - The electron descending down the negative-energy band would cause an ultraviolet catastrophe.

Electron-positron pair creation



The solution proposed by Dirac


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• All negative-energy solutions are occupied.



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hole=positron

The solution proposed by Dirac

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- The excitation of an electron from the negative-energy band leaves a hole of positive charge, corresponding to the creation of a electron-positron pair.



The theory of Dirac is confirmed in 1932 when the US physicist Carl Anderson discover the positron.



• Introduction of fields require specification of charge.



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- Introduction of fields require specification of charge.
- For q = -e, all solutions, of both positive and negative energy, are *electronic*.
- For q = +e, all solutions are *positronic*.
- Solutions of opposite charge are related by charge conjugation symmetry.

• Heisenberg's equation:

$$rac{d\langle\Psi|\hat{A}|\Psi
angle}{dt}=-i\langle\Psi|[\hat{A},\hat{H}]|\Psi
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• Free particle : conservation of (linear) momentum

$$\begin{bmatrix} \mathbf{p}, \hat{h}_0^{NR} \end{bmatrix} = \mathbf{0} = \begin{bmatrix} \mathbf{p}, \hat{h}_0^R \end{bmatrix}$$

• Non-relativistic free particle:

$$\begin{bmatrix} \boldsymbol{\ell}, \, \hat{h}_0^{NR} \end{bmatrix} = \frac{i}{m} \left(\mathbf{p} \times \mathbf{p} \right) = 0$$
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- The economy of Nature's laws.

Minimal substitution gives

$$h_0^{NR} = \frac{\hat{p}^2}{2m} \quad \rightarrow \quad h^{NR} = \frac{\hat{\pi}^2}{2m} - e\phi = \frac{\hat{p}^2}{2m} + \frac{e}{2m} \left[\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}} \right] + \frac{e^2 A^2}{2m} - e\phi$$

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- no spin interactions
- The Dirac identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B})=\mathbf{A}\cdot\mathbf{B}+i\boldsymbol{\sigma}\cdot(\mathbf{A} imes\mathbf{B})$$

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$$= \frac{\hat{p}^2}{2m} + \frac{e}{2m} \left[\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}} \right] + \frac{e^2 A^2}{2m} + \frac{e}{2m} \left(\boldsymbol{\sigma} \cdot \mathbf{B} \right) - e\phi$$

Minimal substitution gives

$$h_0^{NR} = \frac{\hat{p}^2}{2m} \quad \rightarrow \quad h^{NR} = \frac{\hat{\pi}^2}{2m} - e\phi = \frac{\hat{p}^2}{2m} + \frac{e}{2m} \left[\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}}\right] + \frac{e^2 A^2}{2m} - e\phi$$

- no spin interactions
- The Dirac identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B})=\mathbf{A}\cdot\mathbf{B}+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B})$$

A special case

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})=\hat{p}^2$$

suggests that spin is "hidden" in the non-relativistic operator.

Minimal substitution then gives

$$h_0^{NR} = \frac{(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})^2}{2m} \rightarrow h^{NR} = \frac{(\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}})^2}{2m} - e\phi$$
$$= \frac{\hat{p}^2}{2m} + \frac{e}{2m} [\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}}] + \frac{e^2 A^2}{2m} + \frac{e}{2m} (\boldsymbol{\sigma} \cdot \mathbf{B}) - e\phi$$

• Is spin a relativistic effect ?

• The coupling of particles and fields is relativistic

$$\langle \hat{h}_{int} \rangle = \int \left[\rho(\mathbf{r},t)\phi(\mathbf{r},t) - \mathbf{j}(\mathbf{r},t) \cdot \mathbf{A}(\mathbf{r},t) \right] d^{3}\mathbf{r} = -\int j_{\mu}A_{\mu}d^{3}\mathbf{r}$$

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• .. and allows us to extract charge and current density

$$\rho^{R} = \frac{\delta \langle \hat{h}_{int} \rangle}{\delta \phi} = \psi^{\dagger}(\mathbf{r}) \underbrace{\{-\mathbf{el}_{4}\}}_{\text{density operator}} \psi(\mathbf{r}); \quad \mathbf{j}^{R} = -\frac{\delta \langle \hat{h}_{int} \rangle}{\delta \mathbf{A}} = \psi^{\dagger}(\mathbf{r}) \underbrace{\{-\mathbf{ec}\alpha\}}_{\text{current operator}} \psi(\mathbf{r});$$

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• The corresponding non-relativistic expressions are

$$\begin{split} \rho^{NR} &= -e\psi^{\dagger}(\mathbf{r})\psi(\mathbf{r}) \\ \mathbf{j}^{NR} &= -\frac{e}{2m}\left\{\psi^{\dagger}(\mathbf{r})\hat{\mathbf{p}}\psi(\mathbf{r}) - \psi^{T}(\mathbf{r})\hat{\mathbf{p}}\psi^{*}(\mathbf{r})\right\} - \frac{e^{2}}{2m}\psi^{\dagger}(\mathbf{r})\mathbf{A}\psi(\mathbf{r}) \\ &- \frac{e}{2m}\boldsymbol{\nabla}\times\psi^{\dagger}(\mathbf{r})\boldsymbol{\sigma}\psi(\mathbf{r}) \end{split}$$

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The expression for current density is clearly more complicated.

• Consider the non-relativistic and relativistic velocity operators obtained by the Heisenberg equation of motion

$$\frac{d\mathbf{r}}{dt} = -i\left[\mathbf{r}, \hat{h}^{\text{NR}}\right] = -i\left[\mathbf{r}, \frac{\hat{p}^2}{2m}\right] = \frac{\hat{\mathbf{p}}}{m}$$
$$\frac{d\mathbf{r}}{dt} = -i\left[\mathbf{r}, \hat{h}^{\text{R}}\right] = c\boldsymbol{\alpha}$$

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• The curious form of the relativistic velocity operator is due to *Zitterbewegung*, to be explained later.

$$\rho^{\rm R}=\rho^{\rm L}+\rho^{\rm S}$$



(isosurface 0.01)

$$\rho^{\rm R} = \rho^{\rm L} + \rho^{\rm S}$$



(isosurface 0.01)

(isosurface 0.0001)



(molecular plane)



• General form:

$$g(1,2) = q_1\phi_2 - q_1\mathbf{v}_1\cdot\mathbf{A}_2$$

Two-electron interaction

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$$\phi(\mathbf{r}_1,t) = \int \frac{\rho(\mathbf{r}_2,t)}{r_{12}} d^3 \mathbf{r}_2; \quad \mathbf{A}(\mathbf{r}_1,t) = \mathbf{A}_{\perp}(\mathbf{r}_1,t) = \frac{4\pi}{c^2} \int \frac{\mathbf{j}_{\perp}(\mathbf{r}_2,t_r)}{r_{12}} d^3 \mathbf{r}_2$$

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• Quantification and truncation

$$\hat{g}(1,2) = \frac{1}{r_{12}} - \underbrace{\left[\underbrace{\frac{c\boldsymbol{\alpha}_{i} \cdot c\boldsymbol{\alpha}_{j}}{c^{2}r_{12}}}_{Gaunt} + \frac{(c\boldsymbol{\alpha}_{1} \cdot \boldsymbol{\nabla}_{1})(c\boldsymbol{\alpha}_{2} \cdot \boldsymbol{\nabla}_{2})r_{12}}{2c^{2}}\right]}_{\text{Breit}}_{\text{Breit}} + O(c^{-2})$$

4-component relativistic Hamiltonian

• Generic form of electronic Hamiltonian:

$$H = V_{NN} + \sum_{i} h(i) + \frac{1}{2} \sum_{i \neq j} g(i, j); \quad h(i) = h_0 + V_{eN}$$

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- Two-electron operator: (Coulomb gauge)

$$\hat{g}(i,j) = rac{1}{r_{ij}} - rac{c oldsymbol{lpha}_i \cdot c oldsymbol{lpha}_j}{c^2 r_{ij}} - rac{(c oldsymbol{lpha}_i \cdot oldsymbol{
abla}_i) (c oldsymbol{lpha}_j \cdot oldsymbol{
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• Starting from the Dirac equation in a molecular field

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

we would like to generate a 2-component Hamiltonian h_{++} which reproduces the positive-energy spectrum of the parent Hamiltonian.

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• The transformation can be expressed as

J.-L. Heully, I. Lindgren, E. Lindroth, A.-M. Mårtensson-Pendrill, Phys. Rev. A 33 (1986) 4426;
 W. Kutzelnigg in *Relativistic Electronic Structure Theory*. Part 1. Fundamentals, (Ed.: P. Schwerdtfeger), Elsevier, Amsterdam, 2002, p. 66

$$U = W_1 W_2; \quad W_1 = \begin{bmatrix} 1 & -R^{\dagger} \\ R & 1 \end{bmatrix}; \quad W_2 = \begin{bmatrix} \Omega_+ & 0 \\ 0 & \Omega_- \end{bmatrix}; \quad \begin{array}{c} \Omega_+ & = & \left(1 + R^{\dagger}R\right)^{-1/2} \\ \Omega_- & = & \left(1 + RR^{\dagger}\right)^{-1/2} \end{array}$$

• We have seen that the decoupling transformation is given by

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• The 2-component positive-energy solutions take the form

$$\psi_+ = rac{1}{\sqrt{1+R^\dagger R}} \left(\psi^{\scriptscriptstyle L} + R^\dagger \psi^{\scriptscriptstyle S}
ight) = rac{1}{\sqrt{1+R^\dagger R}} \left(\psi^{\scriptscriptstyle L} + R^\dagger R \psi^{\scriptscriptstyle L}
ight) = \sqrt{1+R^\dagger R} \psi^{\scriptscriptstyle L}$$

Approximate 2-component relativistic Hamiltonians in one step

• The exact decoupling requires in principle to solve the Dirac equation

$$R = \left(2mc^2 - V + E\right)^{-1} c \left(\boldsymbol{\sigma} \cdot \mathbf{p}\right)$$

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$$R = \frac{1}{2mc} \left[1 + \frac{E - V}{2mc^2} \right]^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p}) \sim \frac{1}{2mc} (\boldsymbol{\sigma} \cdot \mathbf{p})$$

and retaining terms only to $O(c^{-2})$ gives the Pauli Hamiltonian.

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Using the approximate decoupling (regular approximation)

$$R = \frac{c}{2mc^2 - V} \left[1 + \frac{E}{2mc^2 - V} \right]^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p}) \sim \frac{c}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p})$$

without/with renormalization gives the ZORA/IORA Hamiltonians.

• The Pauli Hamiltonian is based on an approximative decoupling of the large and small components

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$$\hat{h}^{\text{Pauli}} = V + T \underbrace{-\frac{p^4}{8m^3c^2}}_{\text{mass-velocity}} \underbrace{+\frac{1}{8m^2c^2}\left(\nabla^2 V\right)}_{\text{Darwin}} \underbrace{+\frac{1}{4m^2c^2}\sigma \cdot \left[(\nabla V) \times \mathbf{p}\right]}_{\text{spin-orbit}}$$

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• Let us investigate the physics it contains !

• Relativistic mass correction



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• Problem: The mass-velocity term has no lower bound.

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• The Pauli-Hamiltonian can not be used in variational calculations.

$$\hat{h}^{\text{Darwin}} = \frac{1}{8m^2c^2} \left(\nabla^2 V\right) = \frac{-e}{8m^2c^2} \left(\nabla^2 \phi\right)$$

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$$-e\phi({f r})$$
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We perform a Taylor expansion

$$\phi(\mathbf{r}+\boldsymbol{\delta}) = \phi(\mathbf{r}) + (\boldsymbol{\delta}\cdot\boldsymbol{\nabla})\,\phi(\mathbf{r}) + \frac{1}{2}\,(\boldsymbol{\delta}\cdot\boldsymbol{\nabla})^2\,\phi(\mathbf{r}) + \dots$$

• We consider the time average of the interaction

$$\begin{aligned} -e\left\langle\phi(\mathbf{r}+\delta)\right\rangle_{T} &= -e\phi(\mathbf{r}) - e\left\langle(\delta\cdot\boldsymbol{\nabla})\right\rangle_{T}\phi(\mathbf{r}) - \frac{1}{2}e\left\langle(\delta\cdot\boldsymbol{\nabla})^{2}\right\rangle_{T}\phi(\mathbf{r}) + \dots \\ &= -e\phi(\mathbf{r}) - e\frac{\left\langle\delta^{2}\right\rangle_{T}}{6}\nabla^{2}\phi(\mathbf{r}) + \end{aligned}$$

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$$\begin{aligned} -e \langle \phi(\mathbf{r} + \boldsymbol{\delta}) \rangle_{T} &= -e \phi(\mathbf{r}) - e \langle (\boldsymbol{\delta} \cdot \boldsymbol{\nabla}) \rangle_{T} \phi(\mathbf{r}) - \frac{1}{2} e \left\langle (\boldsymbol{\delta} \cdot \boldsymbol{\nabla})^{2} \right\rangle_{T} \phi(\mathbf{r}) + \dots \\ &= -e \phi(\mathbf{r}) - e \frac{\langle \delta^{2} \rangle_{T}}{6} \nabla^{2} \phi(\mathbf{r}) + \end{aligned}$$

• We make the identification

$$\left< \delta^2 \right>_{\tau} = \frac{3}{4m^2c^2}; \quad \Rightarrow \delta_x = \delta_y = \delta_z = \frac{1}{2mc}$$

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which gives the Darwin term

$$\hat{h}^{\rm Darwin} = \frac{-e}{8m^2c^2} \left(\nabla^2\phi\right)$$



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• The creation of an electron-positron pair requires at least $2mc^2$ from which we obtain

$$\Delta t pprox rac{1}{2mc^2}$$



- One interpretation is that in the vicinity of an electron its field is sufficiently strong to allow the creation of a electron-positron pair.
- The positron annihilates the original electron and the "new" electron takes over.
- Consider the energy-time uncertainity relation

$\Delta E \Delta t \geq 1$

• The creation of an electron-positron pair requires at least $2mc^2$ from which we obtain

$$\Delta t pprox rac{1}{2mc^2}$$

• In this time a particle can move a maximum distance of

$$\Delta x \approx \frac{1}{2mc}$$
 !

• Spin-orbit interaction term of the Pauli Hamiltonian

$$h^{\rm so} = \frac{1}{2m^2c^2}\mathbf{s} \cdot \left[(\boldsymbol{\nabla}V) \times \mathbf{p} \right] \qquad \stackrel{V = -\frac{Z}{r}}{\rightarrow} \qquad \frac{Z}{2m^2c^2r^3}\mathbf{s} \cdot \mathbf{I}$$

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 - There is no explicit operator since the electronic Hamiltonian is formulated in the nuclear frame.

Spin-orbit interaction is magnetic induction



Spin-orbit interaction with other electrons



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Relativistic Quantum Chemistry

• The ZORA Hamiltonian is based on an approximative decoupling of the large and small components

$$R = \frac{c}{2mc^2 - V} \left[1 + \frac{E}{2mc^2 - V} \right]^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p}) \sim \frac{c}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p})$$

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• Zeroth-Order Regular Approximation (ZORA) [renormalization terms ignored]:

$$\hat{h}^{\mathrm{ZORA}} = V + rac{1}{2m} \left(\boldsymbol{\sigma} \cdot \mathbf{p} \right) rac{2mc^2}{2mc^2 - V} \left(\boldsymbol{\sigma} \cdot \mathbf{p} \right)$$

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- Electric gauge-dependence: $(V \rightarrow V + \Delta \implies E \rightarrow E + \Delta)$
 - Usually fixed by approximating the potential in the denominator by a superposition of atomic potentials.

Missing renormalization

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▶ For one-electron systems the Dirac eigenvalues are reproduced.

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- 2b) Iterating the coupling equation of the free-particle transformed Hamiltonian to obtain the coupling correct through some odd order 2k 1 in c⁻¹ and then perform a single unitary transformation defines the Barysz, Sadlej and Snijders (BSS) Hamiltonian to order 2k.

M. Iliaš, H. J. Aa. Jensen, V. Kellö, B. O. Roos and M. Urban, Chem. Phys. Lett. 408 (2005) 210; W. Kutzelnigg and W. Liu, J. Chem. Phys. 123 (2005) 241102; M. Iliaš and T. Saue, J. Chem. Phys. 126 (2007) 064102

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Trond Saue (LCPQ, Toulouse)

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- However, many molecular properties probe the electron density near nuclei, providing local information with great sensitivity to the chemical environment,
 - for instance electric field gradients at nuclei, NMR parameters, molecular gradients and Mössbauer isomer shifts.

	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
$1s_{1/2}$	-4262.599	-4281.813	-4272.178	-4253.946	-4568.402	-4890.081	-4267.639
2s _{1/2}	-804.292	-806.637	-804.996	-802.931	-840.315	-829.339	-804.400
2p _{1/2}	-773.067	-777.035	-775.649	-774.270	-791.143	-799.722	-775.573
2p _{3/2}	-633.274	-635.783	-635.010	-635.027	-634.978	-651.542	-634.900
3s _{1/2}	-206.265	-206.730	-206.350	-205.894	-214.216	-208.368	-206.214
3p _{1/2}	-192.463	-193.251	-192.949	-192.624	-196.579	-194.945	-192.940
3p _{3/2}	-159.897	-160.378	-160.206	-160.220	-160.067	-161.622	-160.178
3d _{3/2}	-138.721	-139.070	-138.997	-139.024	-138.568	-140.214	-138.982
3d _{5/2}	-132.183	-132.426	-132.367	-132.393	-131.938	-133.477	-132.350
4s _{1/2}	-54.250	-54.355	-54.259	-54.140	-56.332	-54.425	-54.223
4p _{1/2}	-48.048	-48.232	-48.161	-48.077	-49.085	-48.334	-48.159
4p _{3/2}	-39.454	-39.554	-39.515	-39.522	-39.437	-39.633	-39.508
$4d_{3/2}$	-29.688	-29.744	-29.734	-29.743	-29.590	-29.817	-29.730
$4d_{5/2}$	-28.100	-28.130	-28.123	-28.132	-27.980	-28.197	-28.119
$4f_{5/2}$	-15.207	-15.202	-15.211	-15.220	-15.089	-15.247	-15.210
4f _{7/2}	-14.802	-14.786	-14.795	-14.803	-14.676	-14.828	-14.792

	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
5s _{1/2}	-12.582	-12.603	-12.582	-12.553	-13.081	-12.587	-12.573
5p _{1/2}	-10.098	-10.136	-10.122	-10.103	-10.320	-10.133	-10.122
5p _{3/2}	-8.077	-8.095	-8.088	-8.091	-8.049	-8.094	-8.087
5d _{3/2}	-4.347	-4.352	-4.353	-4.356	-4.305	-4.356	-4.353
5d _{5/2}	-4.040	-4.041	-4.042	-4.045	-3.995	-4.044	-4.041
5f _{5/2}	-0.350	-0.346	-0.349	-0.350	-0.321	-0.349	-0.349
5f _{7/2}	-0.323	-0.318	-0.321	-0.322	-0.294	-0.321	-0.321
6s _{1/2}	-2.135	-2.139	-2.135	-2.130	-2.234	-2.134	-2.133
6p _{1/2}	-1.338	-1.344	-1.342	-1.339	-1.371	-1.343	-1.342
6p _{3/2}	-0.983	-0.985	-0.984	-0.985	-0.968	-0.984	-0.984
6d _{3/2}	-0.193	-0.193	-0.193	-0.194	-0.181	-0.193	-0.193
6d _{5/2}	-0.183	-0.183	-0.184	-0.184	-0.173	-0.184	-0.184
7s _{1/2}	-0.202	-0.202	-0.202	-0.202	-0.211	-0.202	-0.202

SO	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
2р	139.793	141.252	140.638	139.244	156.165	148.179	140.672
Зр	32.565	32.874	32.743	32.404	36.512	33.324	32.762
3d	6.538	6.644	6.630	6.631	6.631	6.737	6.632
4p	8.594	8.678	8.645	8.555	9.648	8.701	8.651
4d	1.588	1.614	1.611	1.611	1.611	1.620	1.612
4f	2.021	2.041	2.034	2.012	2.271	2.038	2.035
5p	0.307	0.312	0.311	0.311	0.310	0.312	0.312
5d	0.307	0.312	0.311	0.311	0.310	0.312	0.312
5f	0.027	0.028	0.028	0.028	0.027	0.028	0.028
бр	0.797	0.795	0.793	0.790	0.862	0.791	0.791
6d	0.009	0.010	0.010	0.010	0.008	0.010	0.010

Basis set considerations



Villa Casale, Sicily

• Hydrogen atom (bound solutions):

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{\ell m}(\theta, \phi); \quad R_{nl}(r) = \mathcal{N}_{n\ell} \rho^{\ell} e^{-\rho/2} L_{n-\ell-1}^{2\ell+1}(\rho); \quad \rho = \frac{2r}{na_0}$$

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• What about relativistic atomic solutions ?

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$$\psi_{njm_j}(\mathbf{r}) = R_{nj}(\mathbf{r}) \chi_{j,m_j}(\theta,\phi); \quad \begin{cases} \hat{j}^2 \chi_{j,m_j} = j(j+1) \chi_{j,m_j} \\ \hat{j}_z \chi_{j,m_j} = m_j \chi_{j,m_j} \end{cases}$$

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where

$$m_j = m_\ell + m_s \quad \Rightarrow \quad m_\alpha = m_j - \frac{1}{2}; \quad m_\beta = m_j + \frac{1}{2}$$

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Associated densities



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Radial functions

$$\begin{bmatrix} R^{L} \\ R^{S} \end{bmatrix} = \mathcal{N}r^{\gamma-1}e^{-\lambda r} \begin{bmatrix} \mathcal{N}^{L}[F_{1}(r) + F_{2}(r)] \\ \mathcal{N}^{S}[F_{1}(r) - F_{2}(r)] \end{bmatrix}$$

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- Radial functions with $|\kappa| = 1$ have a weak singularity at the origin
 - serves as a "black hole" in basis set optimizations



Basis sets for relativistic calculations

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 - Allows the use of non-relativistic integral codes

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- Assumes $V \ll 2mc^2$
 - non-singular potential; finite nuclei

Relativistic effective core potentials



4-component relativistic Hartree–Fock calculations

• Hg: polarizability (\mathring{A}^{-3})

$$\begin{array}{c|c} 1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^2 & 6.61\\ 5s^25p^65d^{10}6s^2 & 6.61\\ 5d^{10}6s^2 & 6.60\\ 6s^2 & 6.31 \end{array}$$

4-component relativistic Hartree–Fock calculations

• Hg: polarizability
$$(\mathring{A}^{-3})$$

1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰4f¹⁴5s²5p⁶5d¹⁰6s² | 6.61
5s²5p⁶5d¹⁰6s² | 6.61
6.60
6s² | 6.31

• Au: ionization potential/electron affinity (eV)

	IP	EA
1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ⁶ 4d ¹⁰ 4f ¹⁴ 5s ² 5p ⁶ 5d ¹⁰ 6s ¹	7.688	0.581
5s ² 5p ⁶ 5d ¹⁰ 6s ¹	7.689	0.580
5d ¹⁰ 6s ¹	7.693	0.579
6s ¹	7.923	0.505

4-component relativistic Hartree–Fock calculations

• Hg: polarizability
$$(\mathring{A}^{-3})$$

1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰4f¹⁴5s²5p⁶5d¹⁰6s² | 6.61
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• Heavy elements = many electrons !

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Heavy elements = many electrons !



coronene

176 electrons



 Pt_2

Relativistic Quantum Chemistry

Valid for a single valence orbital φ_v outside a closed-shell core $\{\varphi_c\}$

• Hartree–Fock equation

$$\hat{F}|arphi_{v}
angle = |arphi_{v}
angle arepsilon_{v}; \quad \langle arphi_{v}|arphi_{c}
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and set up a new Hartree–Fock equation

$$\hat{F}|\chi_{\nu}\rangle = |\varphi_{\nu}\rangle\varepsilon_{\nu} + \sum_{c}|\varphi_{c}\rangle a_{c\nu}\varepsilon_{c}$$

$$+ \sum_{c}|\varphi_{c}\rangle a_{c\nu}\varepsilon_{\nu} - \sum_{c}|\varphi_{c}\rangle\langle\varphi_{c}|\chi_{\nu}\rangle\varepsilon_{\nu}$$

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• This can be rearranged to

$$\left(\hat{F} + \sum_{c} \left(\varepsilon_{v} - \varepsilon_{c}\right) |\varphi_{c}\rangle\langle\varphi_{c}|\right) |\chi_{v}\rangle = |\chi_{v}\rangle\varepsilon_{v}$$

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• Further manipulation gives

$$\left(\hat{F}_{v}+V_{PP}
ight)|\chi_{v}
angle =|\chi_{v}
angle arepsilon_{v}; \quad V_{PP}=\hat{F}_{c}+\sum_{c}\left(arepsilon_{v}-arepsilon_{c}
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angle\langlearphi_{c}|$$

$$V_{MCP} = \sum_{A} \left\{ \sum_{k} A_{k} r_{iA}^{n_{k}} e^{-\alpha_{k} r_{i}^{2}} + \sum_{b} B_{c} |\varphi_{A;c}\rangle \langle \varphi_{A;c}| \right\}$$

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 - ★ Relativistic effects enter through parametrization
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• Valence-only electronic Hamiltonian

$$H_{\nu} = \sum_{i}^{n_{\nu}} \left[-\frac{1}{2} \nabla_{i}^{2} + \sum_{A} \left(V_{PP;A} \left(\mathbf{r}_{iA} \right) - \frac{Q_{A}}{r_{iA}} \right) \right] + \frac{1}{2} \sum_{i \neq j}^{n_{\nu}} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{A \neq B} \frac{Q_{A} Q_{B}}{R_{AB}}$$

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• How do we determine parameters $\{A_k, \alpha_k, n_k\}$?

• Energy-consistent pseudopotentials:

(Preuss, Stoll, Dolg, Schwerdtfeger.....)
Pseudopotential parametrization

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Semi-empirical vs. ab initio

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$$R_{p}(r) = \begin{cases} R_{v}(r); & r \geq r_{c} \\ f(r); & r < r_{c} \end{cases}$$

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Pseudovalence orbital

$$R_{p}(r) = \begin{cases} R_{v}(r); & r \geq r_{c} \\ f(r); & r < r_{c} \end{cases}$$

• V_{PP} is then found by inversion of radial equation for the pseudovalence orbital

$$\left(\hat{F}_{v}\left(r\right)+V_{PP}\right)R_{p}\left(r\right)=R_{p}\left(r\right)\varepsilon_{v} \quad \Rightarrow \quad V_{PP}\left(r\right)=\frac{\left(\varepsilon_{v}-\hat{F}_{v}\left(r\right)\right)R_{p}\left(r\right)}{R_{p}\left(r\right)}$$

Introducing relativistic effects

• With both scalar relativistic (SR) and spin-orbit (SO) interaction included one would expect the form

$$V_{PP;A}(\mathbf{r}_{iA}) = \sum_{\ell=0}^{\ell_{max}} \sum_{j=|\ell-1/2|}^{\ell+1/2} \tilde{V}_{\ell j}(\mathbf{r}_{iA}) \sum_{m_j=-j}^{j} |\ell j m_j \rangle \langle \ell j m_j |$$

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• In practice the contributions are separated

$$\begin{split} V_{PP;A}^{SR} &= \sum_{\ell=0}^{\ell_{max}} \frac{1}{(2\ell+1)} \left[(\ell+1) \, \tilde{V}_{\ell,\ell+1/2} + \ell \tilde{V}_{\ell,\ell-1/2} \right] \sum_{m_{\ell}=-\ell}^{\ell} |\ell m_{\ell} \rangle \langle \ell m_{\ell}| \\ V_{PP;A}^{SO} &= \sigma \cdot \sum_{\ell=0}^{\ell_{max}} \frac{1}{(2\ell+1)} \left[\tilde{V}_{\ell,\ell+1/2} - \tilde{V}_{\ell,\ell-1/2} \right] \sum_{m_{\ell},m_{\ell}'=-\ell}^{\ell} |\ell m_{\ell} \rangle \langle \ell m_{\ell}| \ell |\ell' m_{\ell}' \rangle \langle \ell' m_{\ell}'| \end{split}$$

Some important points

• Size of core

- Size of core
- Choice of valence basis

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- RECPs have names, just like basis sets !

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- Choice of valence basis
- RECPs have names, just like basis sets !
- Effective core potentials have limited applicability (in principle no core properties), but are an excellent choice for many applications.

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