Chemistry, Quantum Mechanics, Applied Mathematics, Computer Programing, and Electronic Structure Theory

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1 Chemical Problem

Identification of the
chemal property to be calculated

2 Translation into Quantum Mechanics

Development of a QM Method

- Many Body Perturbation Theory
- Coupled Cluster Theory
- Relativistic theory: Dirac
- Normalized Elimination of the Small Component

3 Mathematical formulation of the QM method

- Multidimensional integrals
- Linear Algebra
- Nonlinear optimizations
- Tensor algebra
- Statistics

7 Solution of the Chemical Problem

6 Translation of data into chemical language

Utilizing electronic structure theory

5 Calculation of relevant data

- Solving the Schrodinger or Dirac equation
- Geometry optimization
- Calculation of the environmental effects
- Dynamics calculations
- Property calculations

4 Programming of the QM method

always within a Master Program
developed in the last 4 decades

Removing Heavy Metals

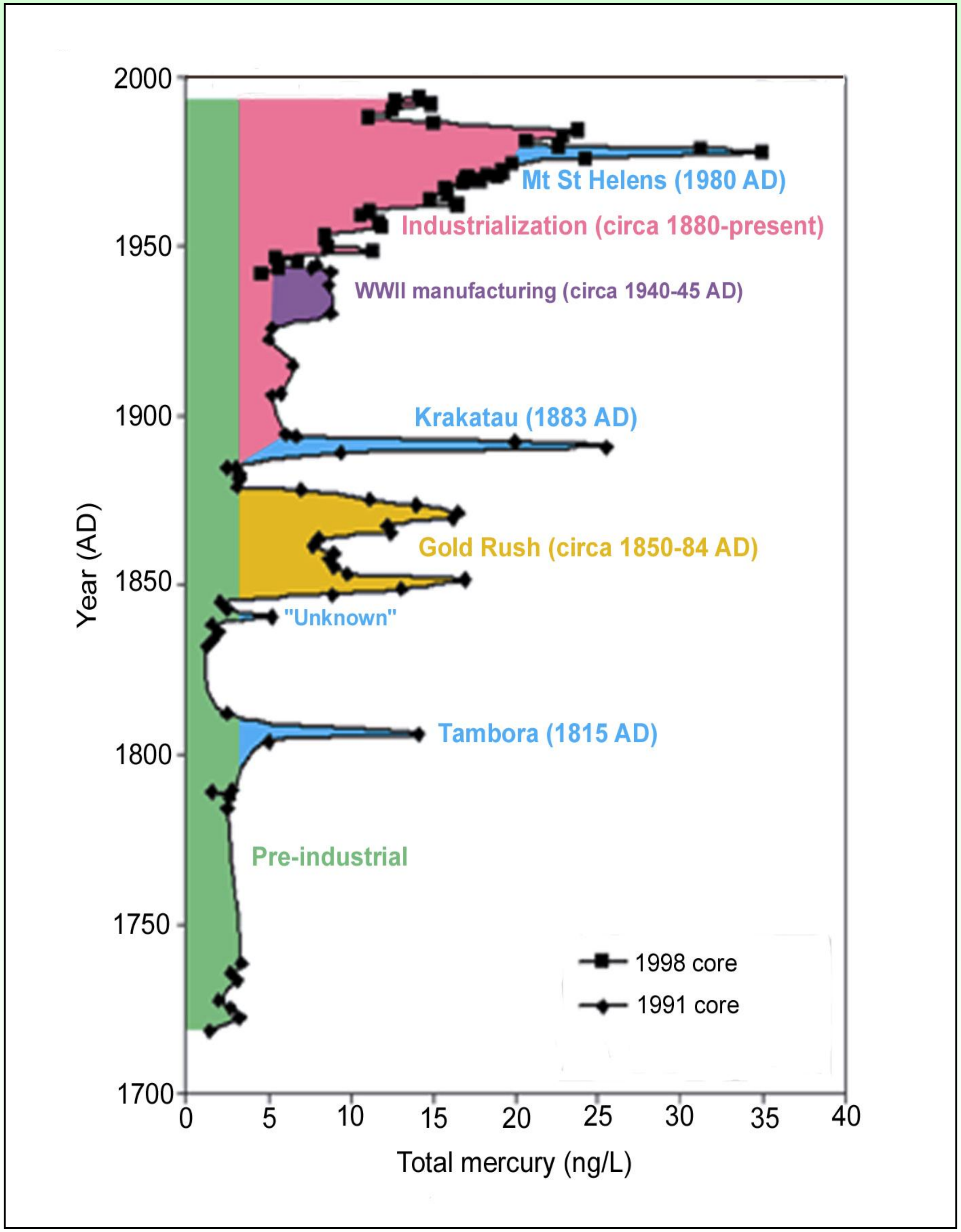
Permanently

From the Environment

Environmental Sources of Mercury

- Natural: corrosion of rocks
- volcano eruptions
- Anthropogenic: combustion of fossil fuels
- gold mining
- industrial discharges and was
- incineration & crematories
- fungicides, pesticides,
- vaccines, dental amalgams

$$Hg^0 \longrightarrow Hg^{2+} \longrightarrow \text{methyl-Hg}$$



A 270-year history of atmospheric Hg

Major atmospheric releases

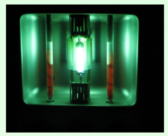
- Natural
  - Background (42%)
  - Volcanic (6%)
- Anthropogenic (52%)
  - Gold rush
  - WWII
  - Industrialization

Significantly

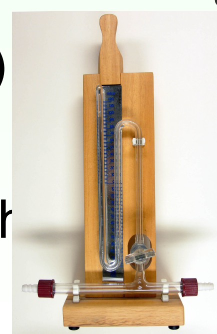
The last 100 years
anthropogenic: 70%

The last 10-15 years
an apparent decline

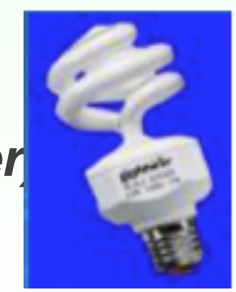
Mercury is a Common, Everyday Material



- Pesticides
- Paint pigments and solvents
- Fertilizers
- Cinnabar (used in jewelry)
- **Amalgam** (silver fillings)
- Laxatives
- **Drinking water** (tap and well)
- **Cosmetics** (mascara)
- **Auto exhaust**
- Floor waxes and polish
- **Thermometers**



- ***Felt***
- ***Wood preservatives***
- ***Plumbing (piping)***
- ***Adhesives***
- ***Bleached flour***
- ***Batteries***
- ***Processed foods***
- ***Air conditioner filters***
- ***Fabric Softeners***
- ***Fish***
- ***Calomel (talc, body powder)***
- ***Fluorescent bulbs***



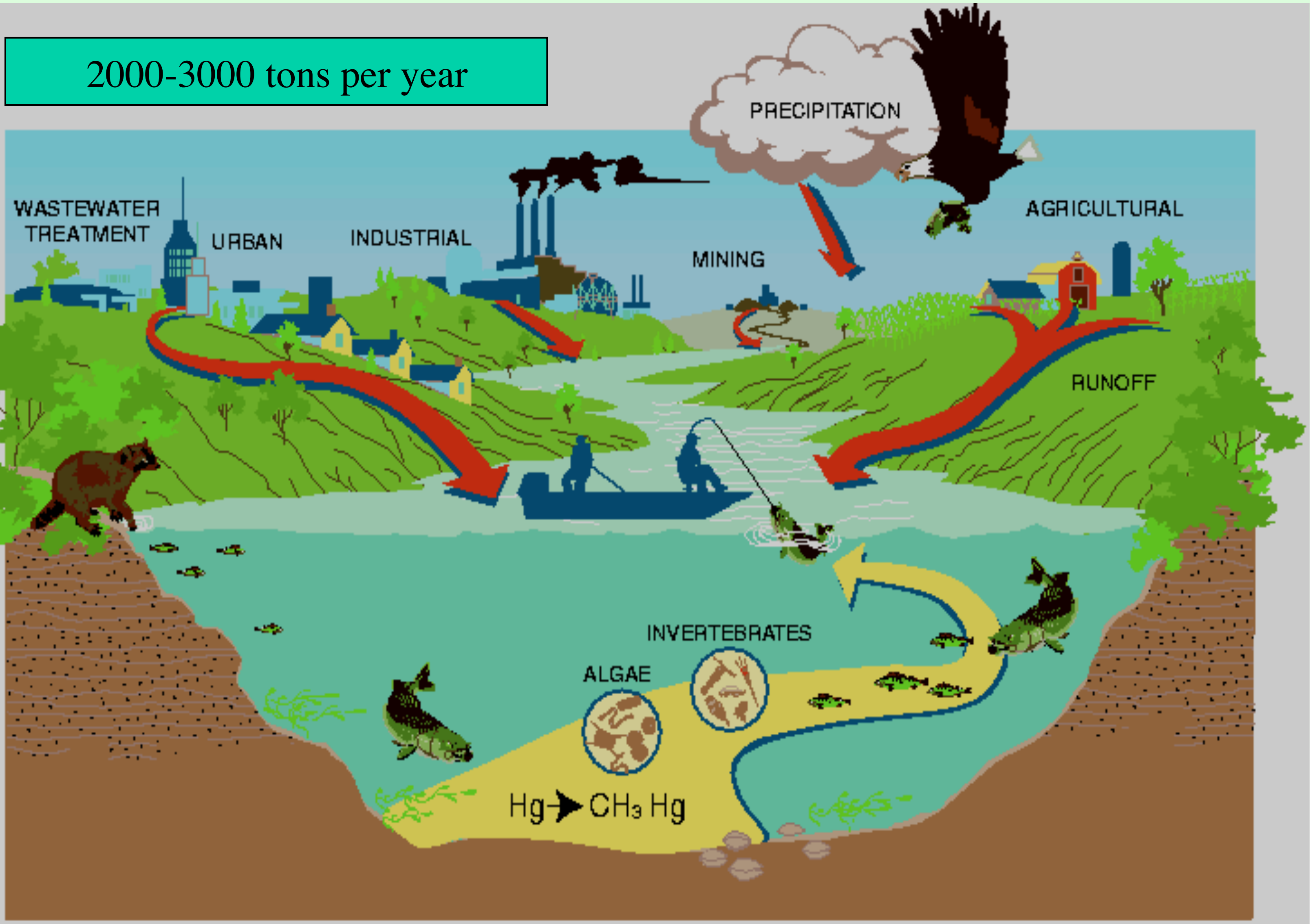
Four “Bad” Properties of Mercury

- Biomethylation of Hg
- High toxicity of mercury
- Bioaccumulation of Hg in the food chain
- Global transport and distribution of Hg

The Mercury Cycle

elemental mercury (Hg^0), reactive gaseous mercury RGM), particulate mercury (PHg)

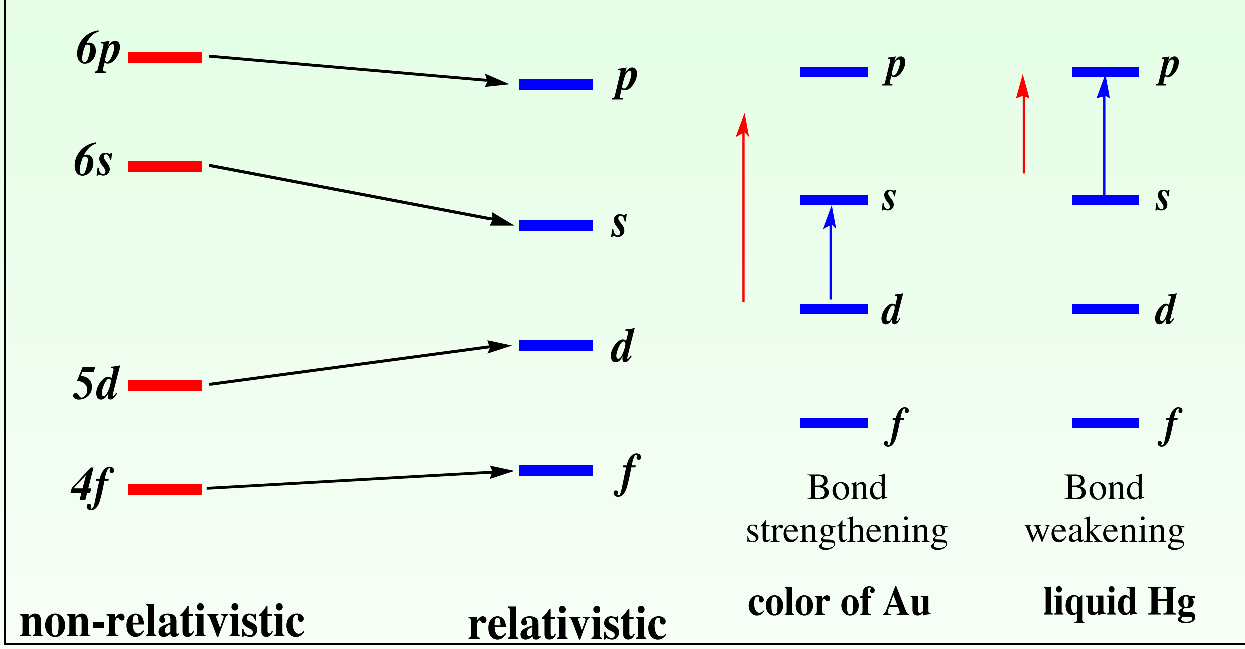
2000-3000 tons per year



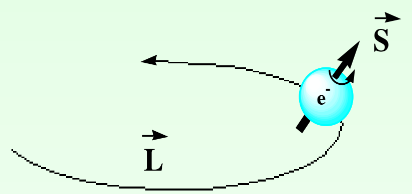
(Illustration by Connie J. Dean, U.S. Geological Survey)

Effects of relativity

Scalar-relativistic effects



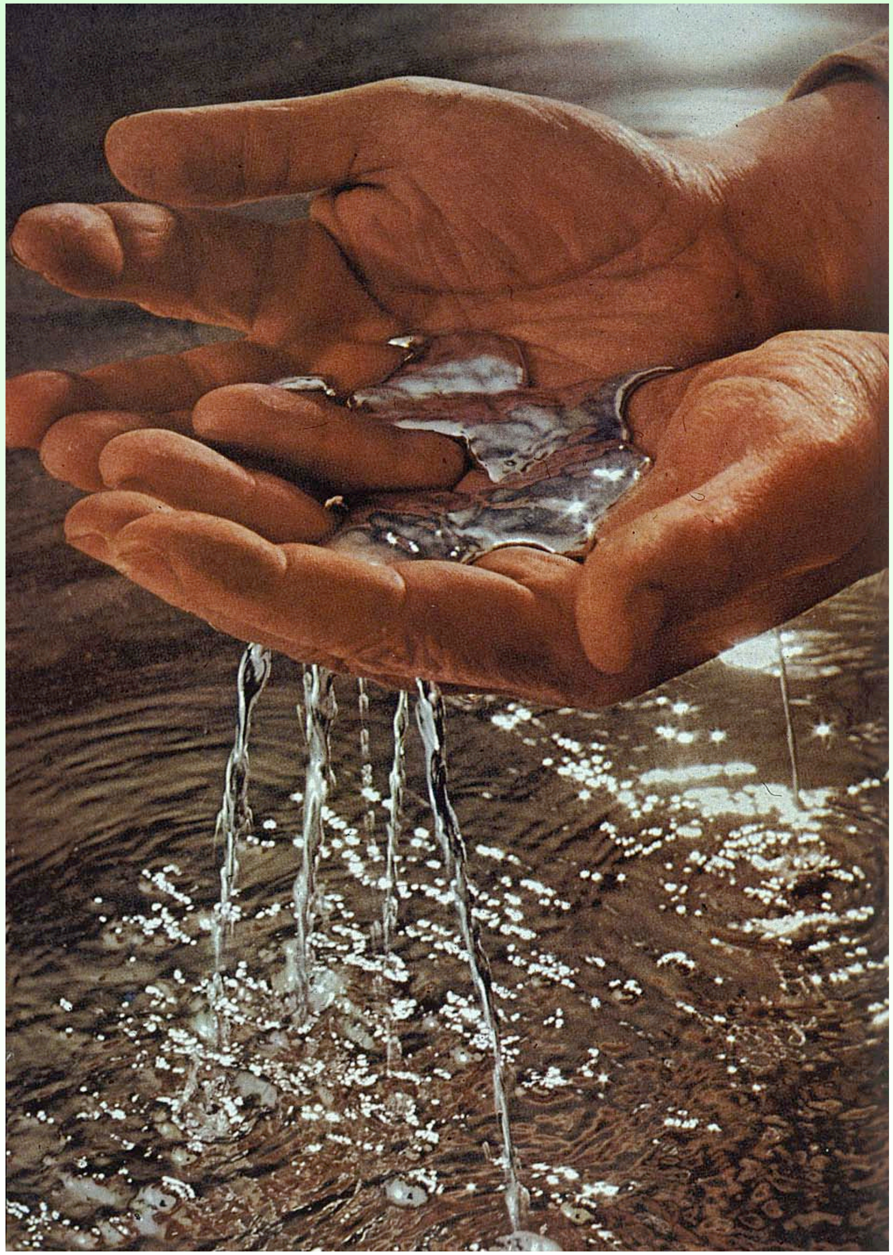
spin-orbit coupling



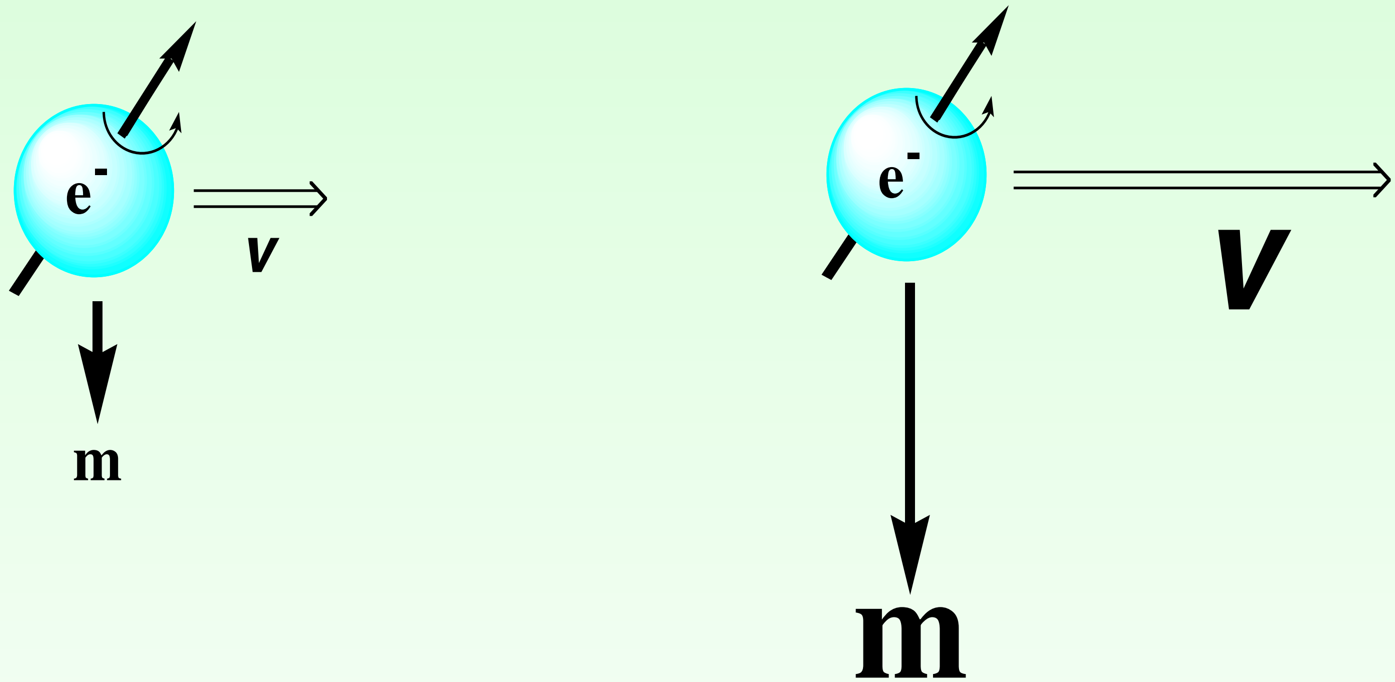
forbidden transitions become allowed

gold: Au [Xe] $4f^{14}5d^{10}6s^{1}$ mercury: Hg [Xe] $4f^{14}5d^{10}6s^{2}$

Elemental Mercury (Hg) – Like Water



Relativistic increase of mass



$$m(v) = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} = \gamma \, m_0$$

m_0 : rest mass of the electron

c : speed of light

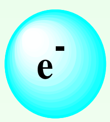
v : velocity of the electron

non-relativistic QM

Schrödinger Equation

$$H\Psi = E\Psi$$

Ψ – *scalar*



Ψ

$c \rightarrow \infty$

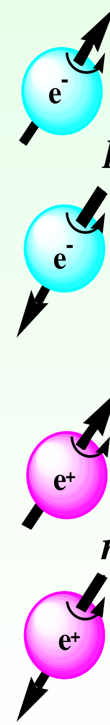
relativistic QM

Dirac Equation

$$H_D\Psi_D = E\Psi_D$$

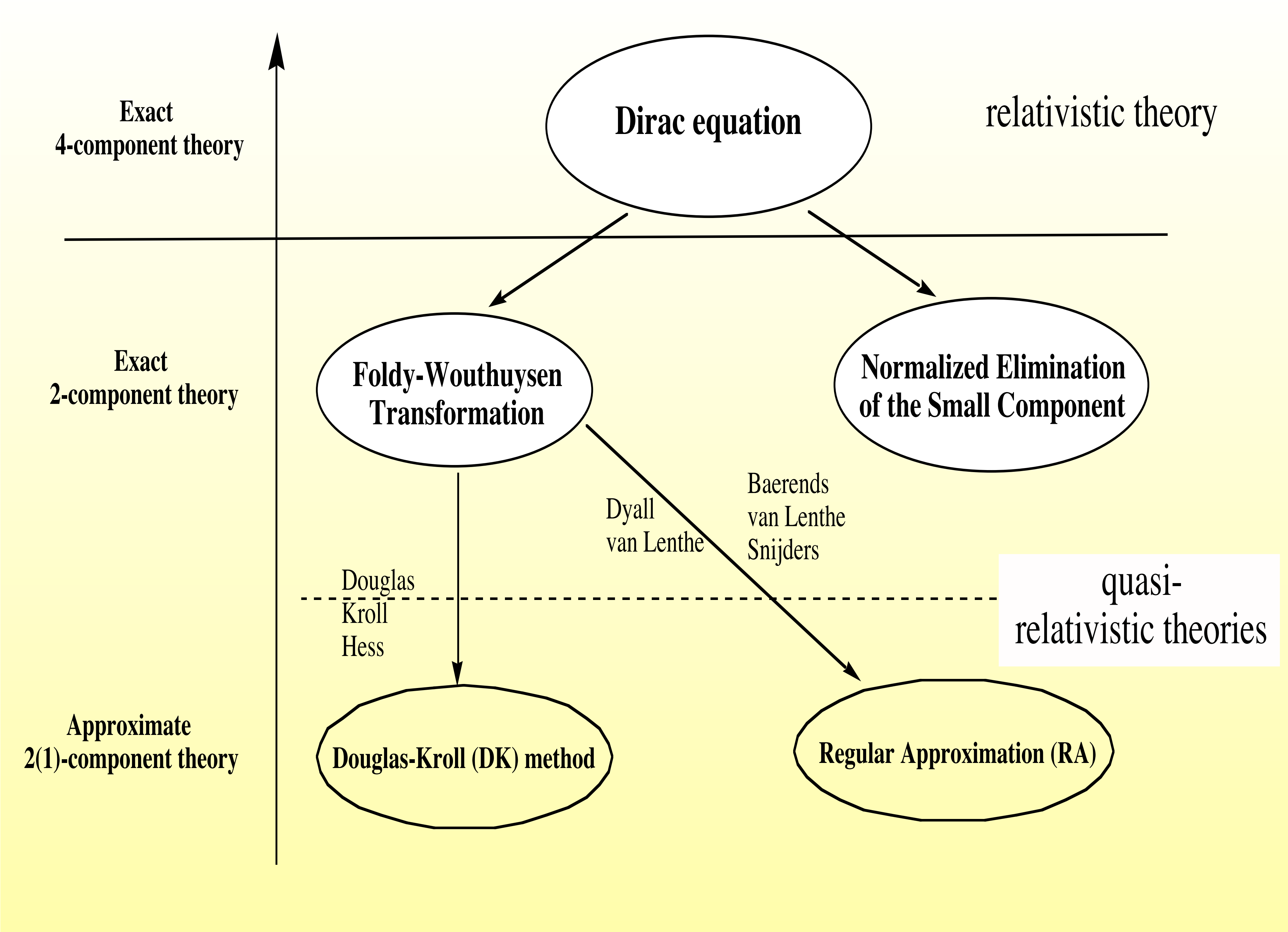
Ψ_D – *4-component quantity*

$$\Psi_D = \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix}$$



positive-energy states

negative-energy states


Exact
4-component theory
Dirac equation
relativistic theory
Exact
2-component theory
Foldy-Wouthuysen
Transformation
Normalized Elimination
of the Small Component
Baerends
van Lenthe
Snijders
Dyall
van Lenthe
Douglas
Kroll
Hess
quasi-
relativistic theories
Approximate
2(1)-component theory
Douglas-Kroll (DK) method
Regular Approximation (RA)

NESC Equation

$$\tilde{\mathbf{L}}\mathbf{A} = \tilde{\mathbf{S}}\mathbf{A}\boldsymbol{\varepsilon} \quad (1)$$

$$\tilde{\mathbf{L}} = \mathbf{T}\mathbf{U} + \mathbf{U}^{\dagger}\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T} - \mathbf{W})\mathbf{U} + \mathbf{V}$$

$$\mathbf{U} = \mathbf{T}^{-1}(\mathbf{S}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} - \mathbf{V}) \quad (2)$$

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2mc^2}\mathbf{U}^{\dagger}\mathbf{T}\mathbf{U} \quad (3)$$

$$\mathbf{A}^{\dagger}\tilde{\mathbf{S}}\mathbf{A} = \mathbf{I} \quad (4)$$

Matrix of the elimination of the small component operator U

B = U A

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W}-\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{A}_- & \mathbf{A} \\ \mathbf{B}_- & \mathbf{B} \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2mc^2}\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{A}_- & \mathbf{A} \\ \mathbf{B}_- & \mathbf{B} \end{pmatrix} \begin{pmatrix} \mathbf{E}_- & 0 \\ 0 & \mathbf{E} \end{pmatrix}$$

Matrix Dirac Equation

E ; **E**$_-$: matrix of positive and negative eigenvalues

A ; **A**$_-$: matrices of eigenvectors of large components

B ; B$_-$: matrices of eigenvectors of pseudolarge components

One-step Solution

$$\mathbf{U} = \mathbf{U}^{IORA}\left[\mathbf{I} - \frac{1}{2mc^2}\mathbf{U}\mathbf{S}^{-1}\left(\mathbf{T}\mathbf{U} + \mathbf{V}\right)\right]$$

α β γ δ

$$\mathbf{U}\left(\frac{1}{2mc^2}\mathbf{S}^{-1}\mathbf{T}\right)\mathbf{U} + \left(\mathbf{U}^{IORA}\right)^{-1}\mathbf{U} + \mathbf{U}\left(\frac{1}{2mc^2}\mathbf{S}^{-1}\mathbf{V}\right) - \mathbf{I} = \mathbf{0}$$

which corresponds to a non-symmetric algebraic Riccati equation:

$$\mathbf{U}\boldsymbol{\alpha}\mathbf{U} + \boldsymbol{\beta}\mathbf{U} + \mathbf{U}\boldsymbol{\gamma} + \boldsymbol{\delta} = \mathbf{0}$$

where $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, and $\boldsymbol{\delta}$ are known matrices.

Comparison of 4c-Dirac-Hartee-Fock with NESC/HF calculations for H-like ions

Z	4c-DHF RKB	NESC/HF	Diff.
20	-201.076522	-201.076522	$< 1\times10^{-8}$
40	-817.807490	-817.807490	$< 1\times10^{-8}$
60	-1895.682307	-1895.682307	$< 1\times10^{-8}$
80	-3532.191201	-3532.191201	4×10^{-8}
100	-5939.164858	-5939.164858	5×10^{-8}
120	-9708.579727	-9708.579727	6×10^{-8}

all values in hartrees

Analytical Derivative of the NESC Hamiltonian $\tilde{\mathbf{L}}$

$$\tilde{\mathbf{L}} = \mathbf{T}\mathbf{U} + \mathbf{U}^{\dagger}\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T}-\mathbf{W})\mathbf{U} + \mathbf{V}$$

$$\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} = \frac{\partial \mathbf{T}}{\partial \lambda}\mathbf{U} + \mathbf{U}^{\dagger}\frac{\partial \mathbf{T}}{\partial \lambda} - \mathbf{U}^{\dagger}\left(\frac{\partial \mathbf{T}}{\partial \lambda} - \frac{\partial \mathbf{W}}{\partial \lambda}\right)\mathbf{U} + \frac{\partial \mathbf{V}}{\partial \lambda} +$$

$$\frac{\partial \mathbf{U}^{\dagger}}{\partial \lambda}\left[\mathbf{T} - (\mathbf{T}-\mathbf{W})\mathbf{U}\right] + \left[\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T}-\mathbf{W})\right]\frac{\partial \mathbf{U}}{\partial \lambda}$$

$$tr\tilde{\mathbf{P}}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} = tr\left[\mathbf{U}\tilde{\mathbf{P}} + \tilde{\mathbf{P}}\mathbf{U}^{\dagger} - \mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^{\dagger}\right]\frac{\partial \mathbf{T}}{\partial \lambda} + tr\tilde{\mathbf{P}}\frac{\partial \mathbf{V}}{\partial \lambda} + tr\left(\mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^{\dagger}\right)\frac{\partial \mathbf{W}}{\partial \lambda} +$$

$$tr\left[\mathbf{T} - (\mathbf{T}-\mathbf{W})\mathbf{U}\right]\tilde{\mathbf{P}}\frac{\partial \mathbf{U}^{\dagger}}{\partial \lambda} + tr\tilde{\mathbf{P}}\left[\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T}-\mathbf{W})\right]\frac{\partial \mathbf{U}}{\partial \lambda}$$

Solution of the Sylvester Equation

$$\mathbf{A}\,\mathbf{X} + \mathbf{X}\,\mathbf{B} = \mathbf{C}$$

$$\mathbf{X} = \frac{\partial \mathbf{U}}{\partial \lambda}$$

$$\mathbf{A} = \mathbf{U}_0^{-1} + \frac{1}{2mc^2}\mathbf{U}\mathbf{S}^{-1}\mathbf{T} \qquad \mathbf{B} = \frac{1}{2mc^2}\mathbf{S}^{-1}(\mathbf{T}\mathbf{U}+\mathbf{V}) \qquad \mathbf{U}_0 = \mathbf{U}^{IORA}$$

$$\mathbf{C} = -\mathbf{T}^{-1}\frac{\partial \mathbf{T}}{\partial \lambda}\mathbf{T}^{-1}\mathbf{W}\mathbf{U} + \mathbf{T}^{-1}\frac{\partial \mathbf{W}}{\partial \lambda}\mathbf{U} - \frac{1}{2mc^2}\left[-\mathbf{U}\mathbf{S}^{-1}\frac{\partial \mathbf{S}}{\partial \lambda}\mathbf{S}^{-1}(\mathbf{T}\mathbf{U}+\mathbf{V}) + \mathbf{U}\mathbf{S}^{-1}\left(\frac{\partial \mathbf{T}}{\partial \lambda}\mathbf{U} + \frac{\partial \mathbf{V}}{\partial \lambda}\right)\right]$$

- One-step solution of Sylvester equation
- Iterative solution of Sylvester equation

$$\mathbf{X}_{n+1} = \mathbf{A}^{-1}\mathbf{C} - \mathbf{A}^{-1}\mathbf{X}_n\,\mathbf{B}$$

NESC: Analytical 2nd Derivatives

$$
\begin{aligned}
\frac{\partial^2 \tilde{L}}{\partial\mu\partial\lambda} = {} & \frac{\partial^2 T}{\partial\mu\partial\lambda}U + \frac{\partial T}{\partial\lambda}\frac{\partial U}{\partial\mu} + \frac{\partial U^+}{\partial\mu}\frac{\partial T}{\partial\lambda} + U^+\frac{\partial^2 T}{\partial\mu\partial\lambda} + \frac{\partial^2 V}{\partial\mu\partial\lambda} \\
& - \frac{\partial U^+}{\partial\mu}\left(\frac{\partial T}{\partial\lambda} - \frac{\partial W}{\partial\lambda}\right)U - U^+\left(\frac{\partial T}{\partial\lambda} - \frac{\partial W}{\partial\lambda}\right)\frac{\partial U}{\partial\mu} - U^+\left(\frac{\partial^2 T}{\partial\mu\partial\lambda} - \frac{\partial^2 W}{\partial\mu\partial\lambda}\right)U \\
& + \frac{\partial^2 U^+}{\partial\mu\partial\lambda}\left[T - (T-W)U\right] + \frac{\partial U^+}{\partial\lambda}\left[\frac{\partial T}{\partial\mu} - (T-W)\frac{\partial U}{\partial\mu} - \left(\frac{\partial T}{\partial\mu} - \frac{\partial W}{\partial\mu}\right)U\right] \\
& + \left[T - U^+(T-W)\right]\frac{\partial^2 U}{\partial\mu\partial\lambda} + \left[\frac{\partial T}{\partial\mu} - \frac{\partial U^+}{\partial\mu}(T-W) - U^+\left(\frac{\partial T}{\partial\mu} - \frac{\partial W}{\partial\mu}\right)\right]\frac{\partial U}{\partial\lambda} \\
= {} & \frac{\partial^2 T}{\partial\mu\partial\lambda}U + U^+\frac{\partial^2 T}{\partial\mu\partial\lambda} - U^+\left(\frac{\partial^2 T}{\partial\mu\partial\lambda} - \underline{\frac{\partial^2 W}{\partial\mu\partial\lambda}}\right)U + \frac{\partial^2 V}{\partial\mu\partial\lambda} \\
& + \frac{\partial T}{\partial\lambda}\frac{\partial U}{\partial\mu} + \frac{\partial T}{\partial\mu}\frac{\partial U}{\partial\lambda} + \frac{\partial U^+}{\partial\lambda}\frac{\partial T}{\partial\mu} + \frac{\partial U^+}{\partial\mu}\frac{\partial T}{\partial\lambda} - U^+\left(\frac{\partial T}{\partial\lambda}\frac{\partial U}{\partial\mu} + \frac{\partial T}{\partial\mu}\frac{\partial U}{\partial\lambda}\right) - \left(\frac{\partial U^+}{\partial\lambda}\frac{\partial T}{\partial\mu} + \frac{\partial U^+}{\partial\mu}\frac{\partial T}{\partial\lambda}\right)U \\
& + U^+\left(\frac{\partial W}{\partial\lambda}\frac{\partial U}{\partial\mu} + \frac{\partial W}{\partial\mu}\frac{\partial U}{\partial\lambda}\right) + \left(\frac{\partial U^+}{\partial\lambda}\frac{\partial W}{\partial\mu} + \frac{\partial U^+}{\partial\mu}\frac{\partial W}{\partial\lambda}\right)U - \frac{\partial U^+}{\partial\lambda}(T-W)\frac{\partial U}{\partial\mu} - \frac{\partial U^+}{\partial\mu}(T-W)\frac{\partial U}{\partial\lambda} \\
& + \underline{\frac{\partial^2 U^+}{\partial\mu\partial\lambda}\left[T - (T-W)U\right] + \left[T - U^+(T-W)\right]\frac{\partial^2 U}{\partial\mu\partial\lambda}}
\end{aligned}
$$

NESC/CCSD Gradient Calculations

NESC/CCSD(T) energies at NESC/CCSD geometries

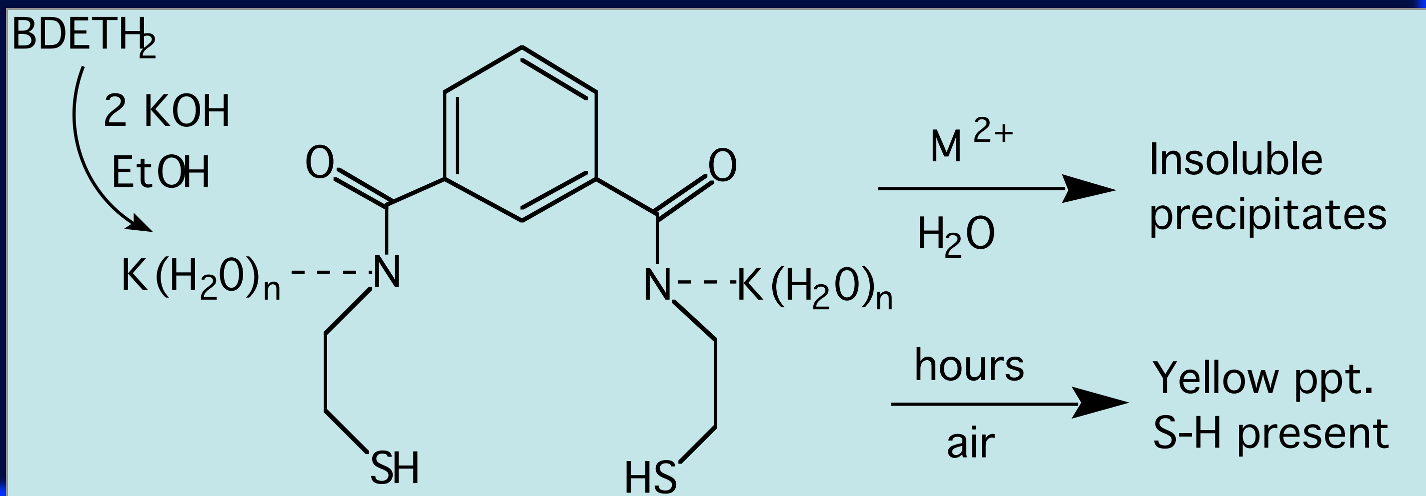
Property \ Molecules	HgF $^2\Sigma^+$	HgCl $^2\Sigma^+$	HgBr $^2\Sigma^+$	HgI $^2\Sigma^+$
Bond length r_e(HgX) [Å]	2.024	2.402	2.546	2.709
Exp. r_e(HgX) [Å]	na	2.395	2.62	2.81
D_0(HgX) [kcal/mol]	32.3	23.4	17.5	7.6
Exp. D_0(HgX) [kcal/mol]	32.9	23.4	17.2	7.8

Convergence criteria: 10^{-5} Hartree/bohr for forces

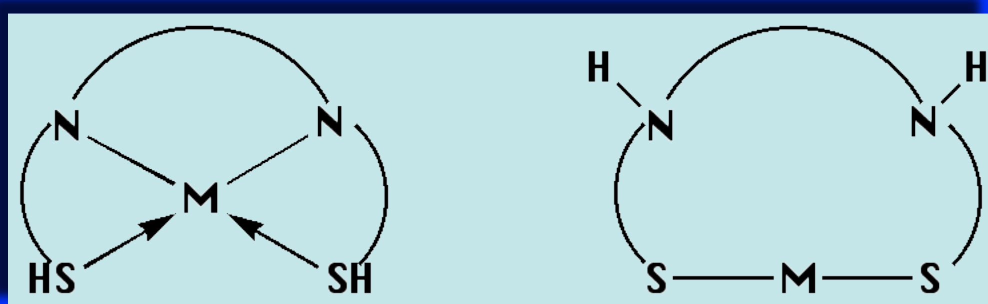
Hg: (22s19p12d9f) [15s13p8d5f]; BSSE corrected; SOC included

Removing Heavy Metals Permanently From the Environment

Use of Organic Tweezers Molecules

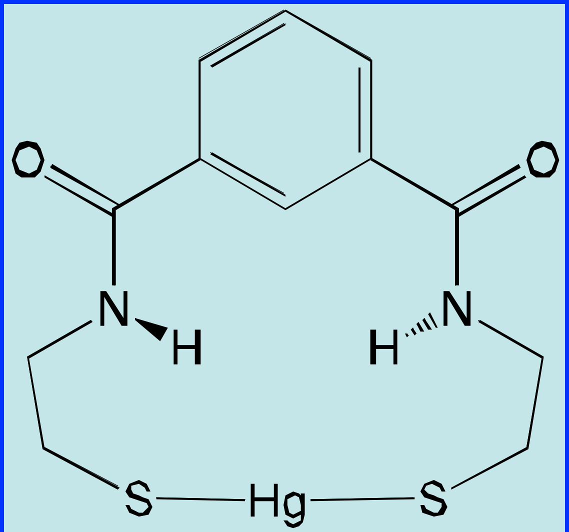


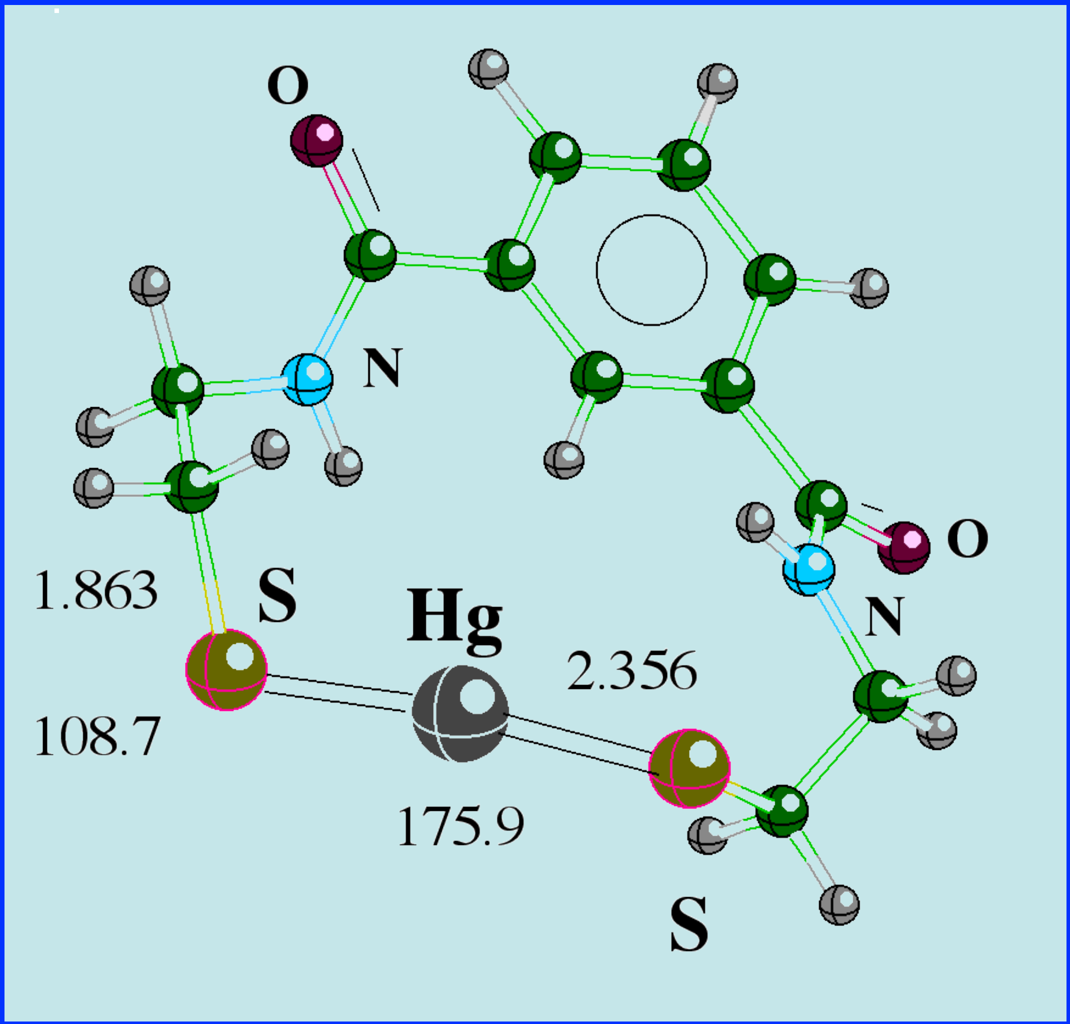
Possibility 1



Possibility 2

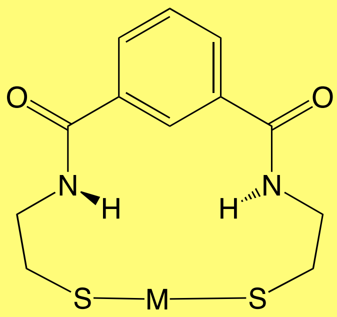
Investigation of Organic Tweezers Molecules for Picking up Mercury from the Environment





NESC/
B3LYP/
SARC

Typical HgS bond lengths from X-ray : 2.35 - 2.42 Å



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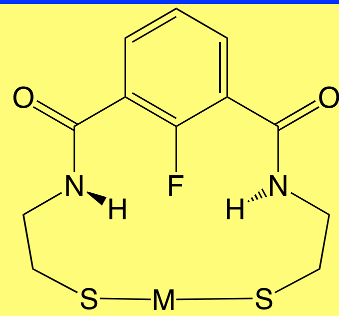
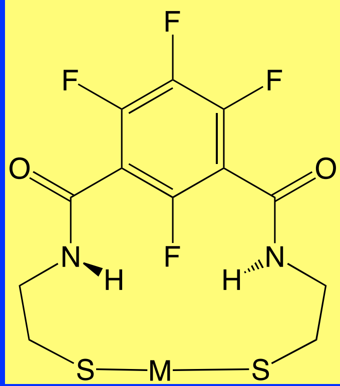
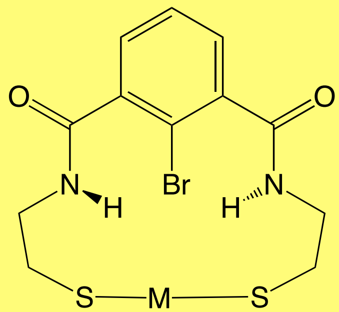


7.1



6.6



-0.1

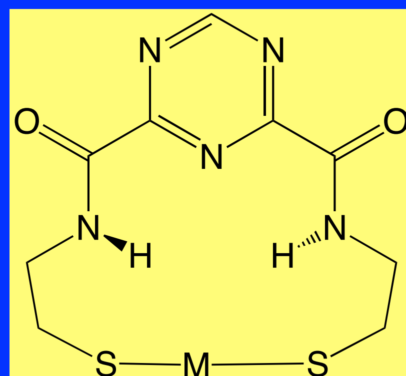
aqueous solution

NESC/

B3LYP/SARC

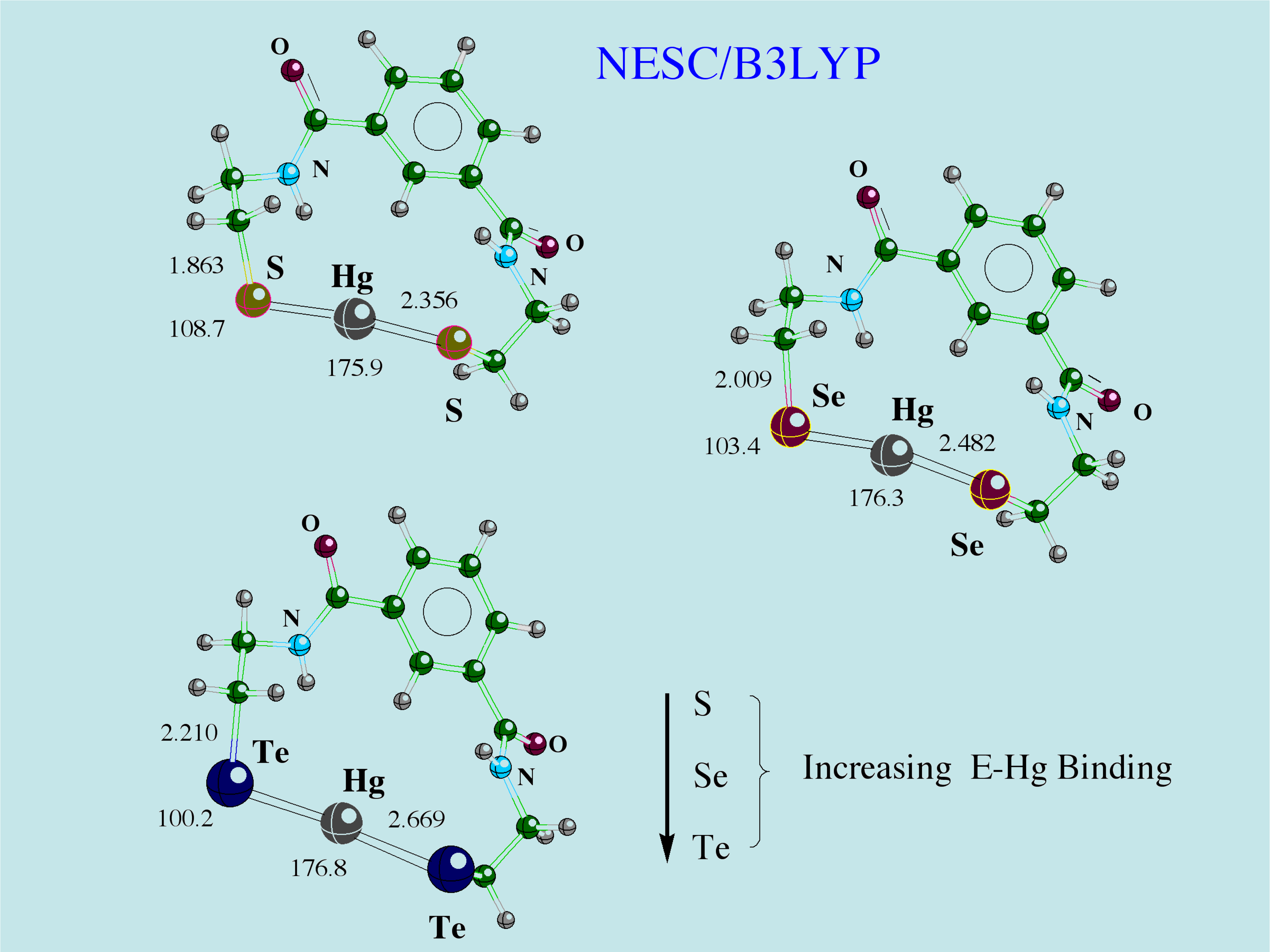
Squeezing the Tweezer

Investigation of Organic Tweezers Molecules
for Picking up Mercury from the Environment

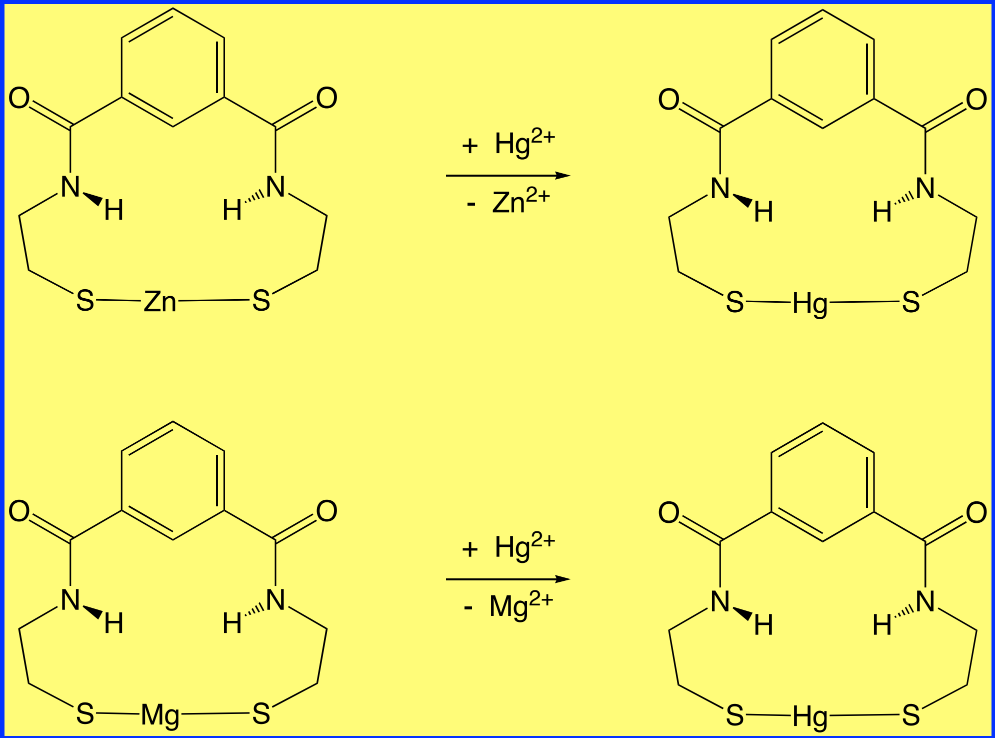


2.1 kcal/mol

M = Mg, Hg


NESC/B3LYP
O
N
O
N
1.863
S
Hg
2.356
108.7
175.9
S
O
N
O
N
2.009
Se
Hg
2.482
103.4
176.3
Se
O
N
O
N
2.210
Te
Hg
2.669
100.2
176.8
Te
S
Se
Te
Increasing E-Hg Binding

Reaction A



Reaction B

NESC/ B3LYP/SARC

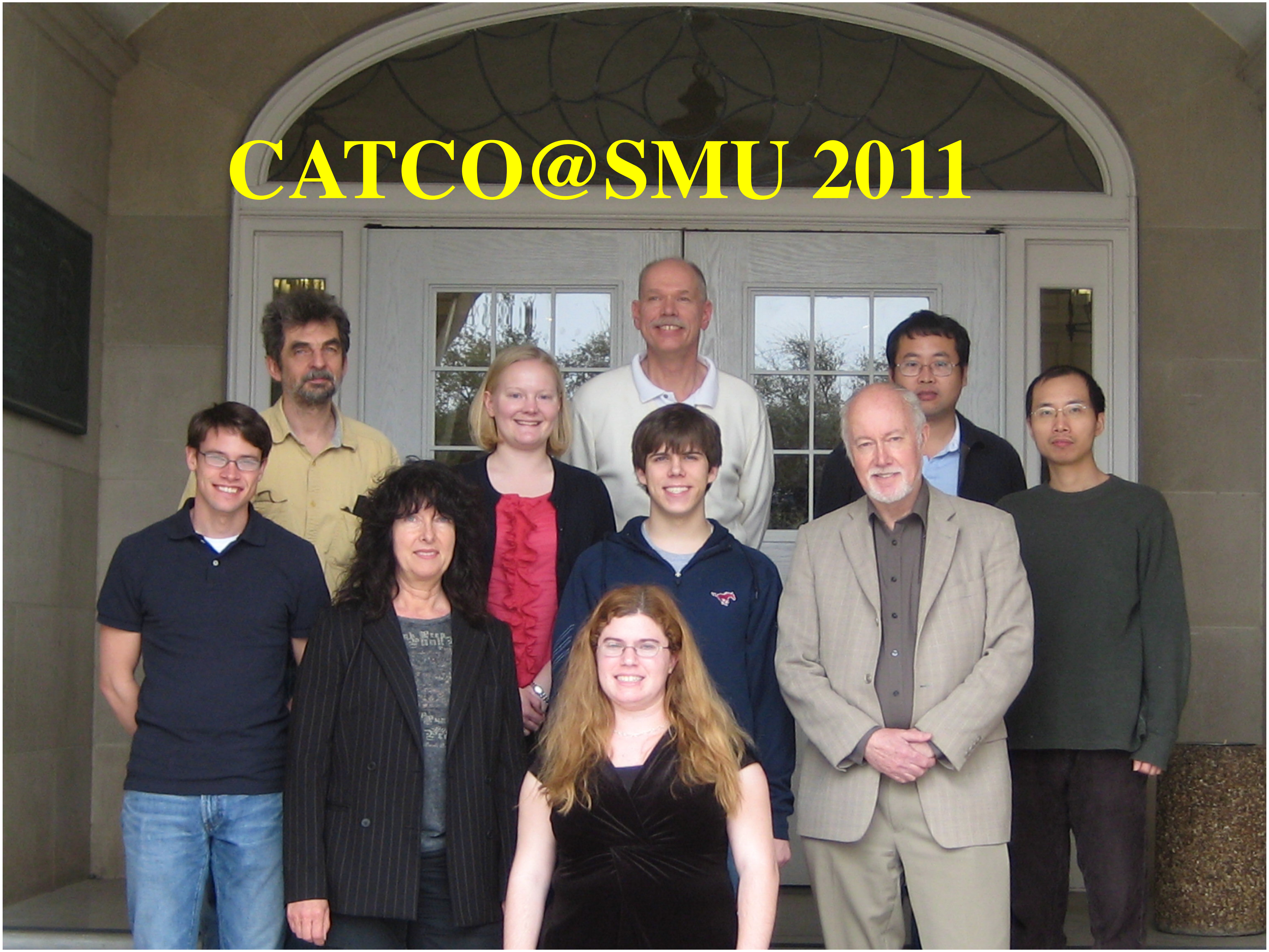
Reaction A   Reaction B

kcal/mol

	Zn	Mg
S	-10.6	-94.5
Se	-14.0	-99.7
Te	-17.6	-106.2

aqueous solution

Investigation of Organic Tweezers Molecules for Picking up Mercury from the Environment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