On the Electron Correlation Problem in Quantum Chemistry

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Outline

- Traditional and “New” Wave-Function based Correlation Methods for Strongly-Correlated Molecular Systems
- Insights from Applications in Quantum Chemistry
- Conclusions

Electronic structure theory – the Hamiltonian

- Non-relativistic many-electron Hamiltonian in position space (Hartree atomic units):

$$H_{el} = \sum_i^N \left(-\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}} \right) + \sum_{i<j}^N \frac{1}{r_{ij}}$$

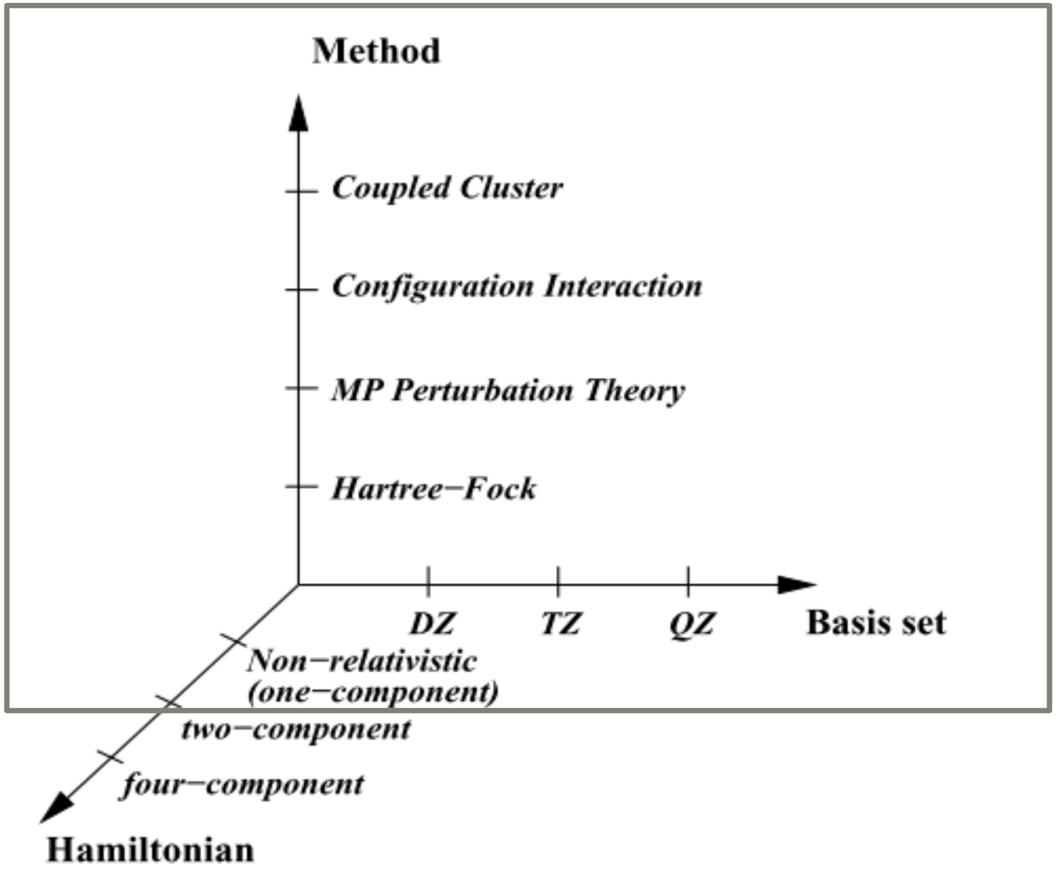
with $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and N being the number of electrons.

- Eigenvalue equation: electronic Schrödinger equation:

$$H_{el}\Psi_{el}^{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\}) = E_{el}(\{\mathbf{R}_I\})\Psi_{el}^{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\})$$

- Central problem: How to approximate Ψ_{el} ?

Electronic structure theory – the two-dimensional view



How to approximate Ψ_{el}?

- Construct many-electron (determinantal) basis set $\{\Phi_I\}$ from a given (finite) one-electron (orbital) basis set ϕ_i
- From the solution of the Roothaan–Hall equations, one obtains as *n* orbitals from *n* one-electron basis functions:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$

- From the *N* orbitals with the lowest energy, the Hartree–Fock (HF) Slater determinant Φ_0 is constructed
- The other determinants (configurations) are obtained by subsequent substitution of orbitals in the HF Slater determinant Φ_{0}:

$$\{\Phi_I\} \to \Phi_i^a, \Phi_j^b, \ldots \to \Phi_{ij}^{ab}, \Phi_{ik}^{ac}, \ldots \to \Phi_{ijk}^{abc}, \Phi_{ijl}^{abd}, \ldots$$

Electron Correlation

- Correlation energy in a given basis set as difference between the exact and the Hartree-Fock energy:

$$E_{corr} = E_{exact} - E_{HF}$$

- Dynamical correlation:
  - related to the movements of the individual electrons
  - short-range
- Non-dynamical or static correlation:
  - Electronic ground state as a function of many (nearly)-degenerate Slater determinants
  - Requires multi-determinantal reference wave function

Full Configuration Interaction (FCI)

- The number of possible determinants is determined by the number of virtual orbitals $n-N$
- Including all possible excited Slater determinants for a finite or infinite one-electron basis set leads to the so-called **full CI** approach
- Number of Slater determinants n_{SD} for *N* spin orbitals chosen from a set of *n* spin orbitals:

$$\mathrm{n}_{\mathrm{SD}} = \frac{n!}{N!(n-N)!}$$

Example: There are ≈ 10^{12} different possibilities to distribute 21 electrons in 43 spin orbitals

- FCI only feasible for small basis sets!

Approximate Correlation Methods I

- Truncated CI:
  - **Assumption**: Substitution hierarchy is a useful measure to generate a systematically improvable many-electron basis set
  - For example CISD:

$$\Psi_{el}^{CISD} = C_0\Phi_0 + \sum_{(ai)} C_{(ai)}\Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)}\Phi_{ij}^{ab}$$

- Truncated Coupled Cluster:
  - Exponential ansatz

$$\Psi_{el}^{CC} = \exp(T)\ \Phi_0$$

  - excitation operator T = $T_1 + T_2 + T_3 + \ldots$
  - Truncation of T defines the level of hierarchy: CCSD: T = T_1+T_2
  - Improves on truncated CI because of inclusion of disconnected terms, CC is size-consistent → $\exp(T) = 1 + T + \frac{1}{2!}T^2 + \ldots$

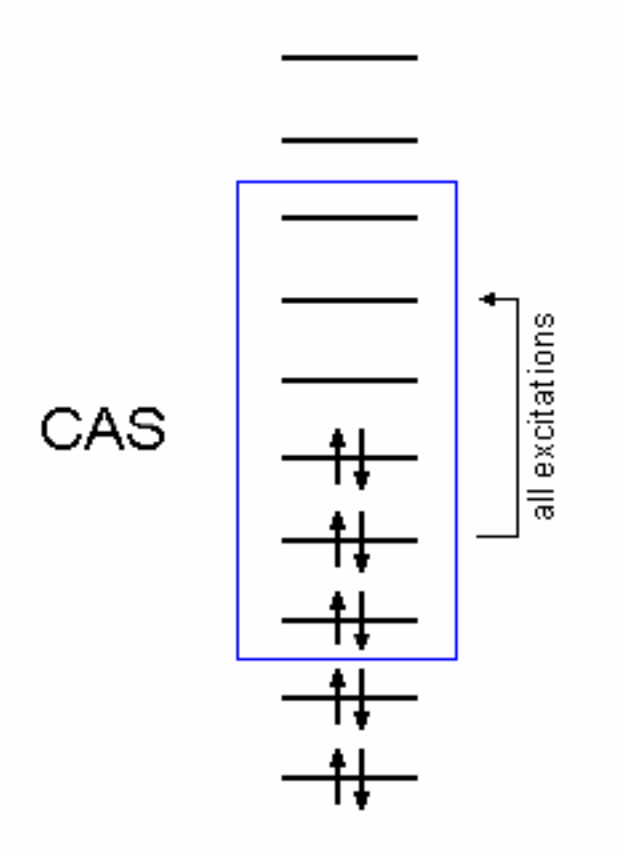
Approximate Correlation Methods II

- Multi-configuration Self-Consistent-Field method (MCSCF):

$$\Psi_{el}^{MCSCF} = \exp(\hat{\kappa}) \left(\sum_{\nu} C_{\nu} \Phi_{\nu} \right)$$

  - Simultaneous optimization of CI coefficients and orbital rotation parameters
  - used to generate qualitatively correct reference states for systems with quasi-degenerate electronic ground states (static correlation!)
  - Most popular approach: Complete Active Space SCF (CASSCF):
    - Perform Full CI for *n* electrons within a set of chosen, active orbitals *m*
    - CAS(*n*,*m*)

The CASSCF model



Approximate Correlation Methods III

- Truncated Multi-reference CI:
  - Same assumptions made as in the single-reference case
  - Φ_0 is replaced by a sum of reference configurations from for example a CASSCF wave function optimization
- Multi-reference CC:
  - Multi-reference analog of single-reference CC
  - No ultimate approach exists (yet)
  - Further reading: D. Lyakh *et al.*, Chem. Rev., 112, 182-243 (2012)
- Multi-reference Perturbation Theory (to 2nd order):
  - For example: MP2 theory for a CAS wave function
  - Different choices of 0th-order Hamiltonian: CASPT2 or NEVPT2

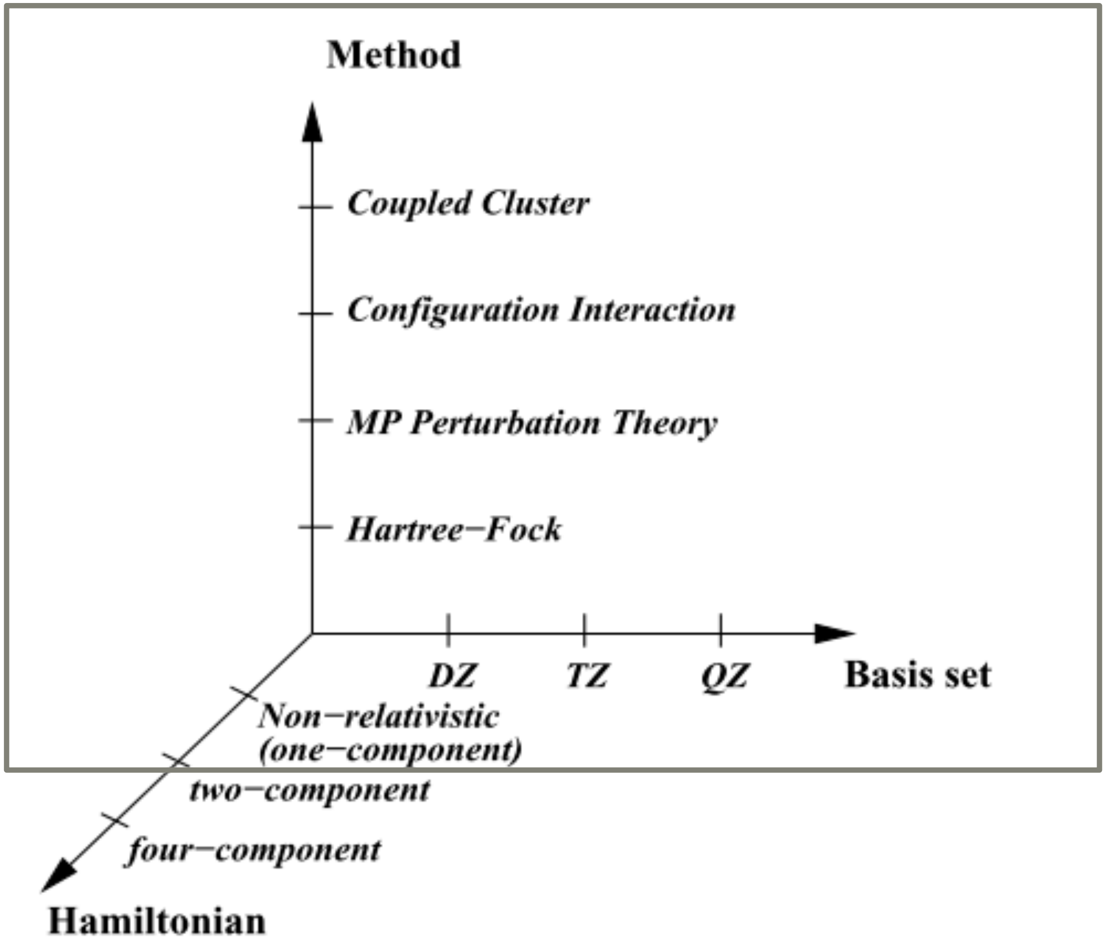
Approximate Correlation Methods IV

- Density Matrix Renormalization Group (DMRG):
  - Is a CAS approach
  - DMRG state is a superposition of FCI-type basis states
  - A FCI/CAS solution can be converged; but the basis cannot be completely known if DMRG shall be efficient
  - Can be extended by orbital optimization → DMRG-SCF
  - DMRG exploits a “linear” optimization algorithm
  - See talk by Ö. Legeza for details on algorithm and MPS formulation

Approximate Correlation Methods V

- Methods not further mentioned here:
    - Greens function approaches → ADC(X) methods
    - Perturbation Theory
    - Response Theory
    - …
- Further reading:
    - T. Helgaker, P. Jørgensen and, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley (2000).
    - Special Issue in Chem. Rev. Vol. 112, 2012.

Electronic structure theory – the two-dimensional view



Electronic structure theory – the Hamiltonian II

- Relativistic many-electron Hamiltonian:

$$H_{el} = \sum_{i=1}^{N} \left(c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta'_i mc^2 - \left(\sum_{I} \frac{Z_I}{r_i I} \mathbf{I}_{4\times 4} \right) \right) + \sum_{i<j}^{N} \hat{g}_{ij}$$

- 4-component wave function Ψ_{el} (e+p-like solutions!)
- Two-electron interaction:
  - Coulomb: $\hat{g}_{ij} = \frac{\mathbf{I}_{4\times 4} \otimes \mathbf{I}_{4\times 4}}{r_{ij}}$
  - Coulomb-Breit: $\hat{g}_{ij} = \frac{\mathbf{I}_{4\times 4} \otimes \mathbf{I}_{4\times 4}}{r_{ij}} - \frac{1}{2r_{ij}} \left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r_{ij}})(\boldsymbol{\alpha}_\mathbf{j} \cdot \mathbf{r_{ij}})}{r_{ij}^2} \right)$
  - Higher-orders of fine structure constant α (QED)
- Relativity adds new axis to electronic structure problem!

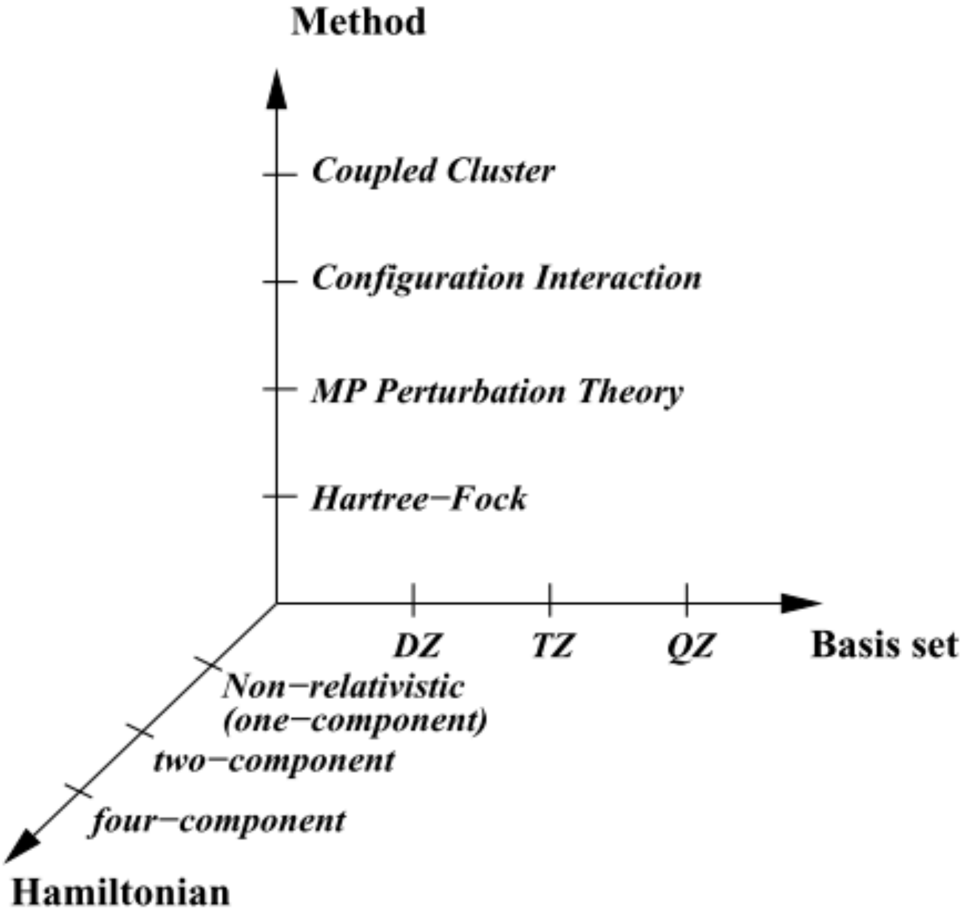
Implications for choosing an appropriate QC Model

- Approximations to the “full” relativistic Hamiltonian:
  - From a four-component to a two-component (electrons only) wave function through block-diagonalization of the one-electron Hamiltonian

$$\hat{h}_{bd} = U^{\dagger} \left[\begin{array}{cc} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{array} \right] U = \left[\begin{array}{cc} \hat{h}_{+} & 0 \\ 0 & \hat{h}_{-} \end{array} \right]$$

  - Neglect of spin-orbit effects: scalar-relativistic approach
  - Treat spin-orbit effects *a posteriori* as perturbation to a scalar-relativistic correlation model
- Increase of computational cost → loss of spin symmetry

Electronic structure theory – the three-dimensional view



Further Literature On Relativistic QC

- Book: M. Reiher and A. Wolf, *Relativistic Quantum Chemistry: The Fundamental Theory of Molecular Science* (Wiley, 2009)
- J. Autschbach, *Perspective: Relativistic effects*, J. Chem. Phys. 136, 150902 (2012)
- T. Fleig, *Relativistic wave-function based electron correlation methods*, Chem. Phys. 395, 2 - 15 (2012)
- S. Knecht, O. Legeza, and M. Reiher, *Four-component density matrix renormalization group,* J. Chem. Phys. 140, 041101 (2014)

Applications

The electronic ground state of U_2

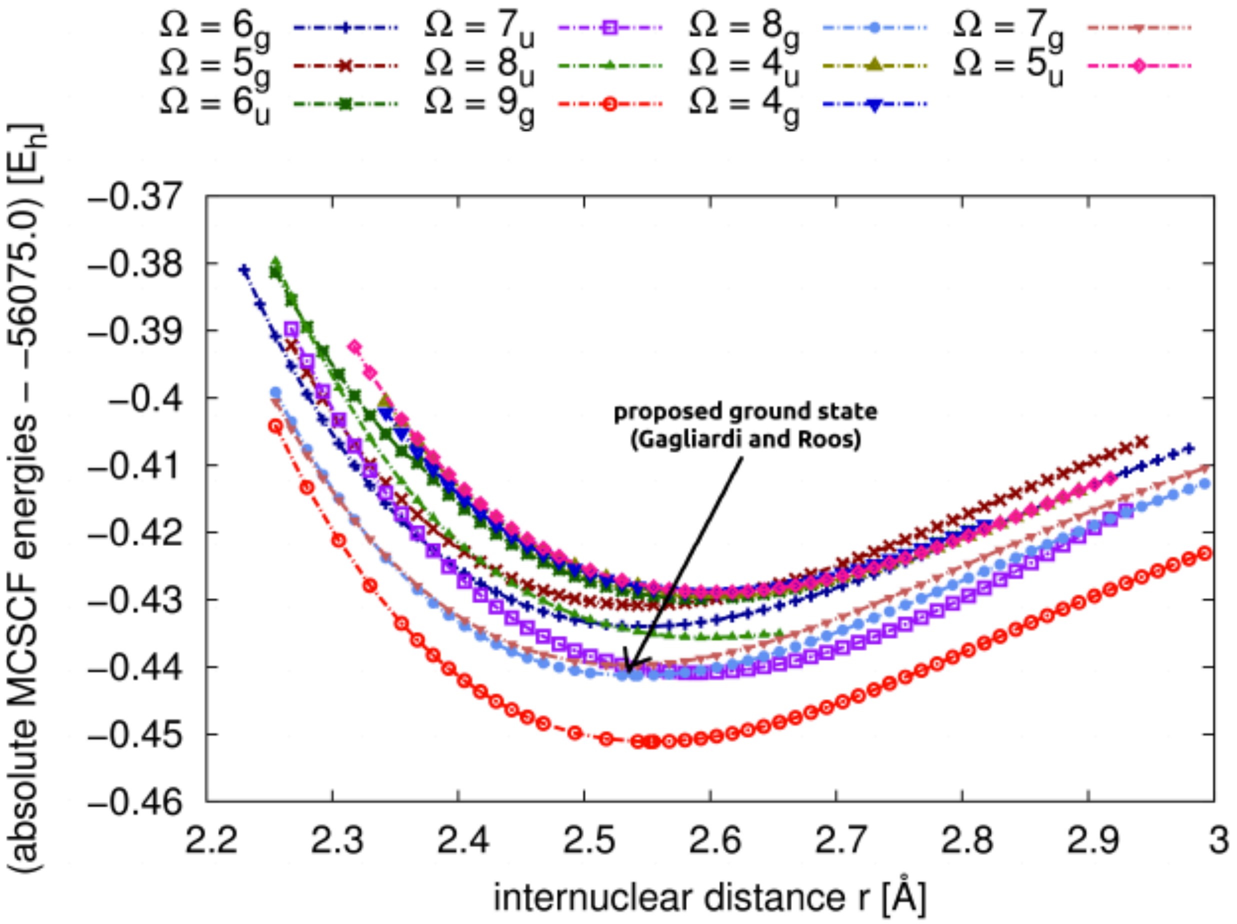
- U_2: electronic ground state is proposed to have a quintuple bond between the U atoms

L. Gagliardi and B. O. Roos, Quantum chemical calculations show that the uranium molecule U2 has a quintuple bond, Nature 433, 848-851 (2005).

- Scalar-relativistic CASSCF(6,20) calculations with an *a posteriori* perturbative treatment of spin-orbit coupling
- Our *ansatz*: relativistic two-component CASSCF(6,20) calculations with a variational inclusion of spin-orbit coupling → different electronic ground state and bond order of 4 for the uranium dimer!

S. Knecht et al., in preparation 2014.

The electronic ground state of U_2



The electronic ground state of U_2

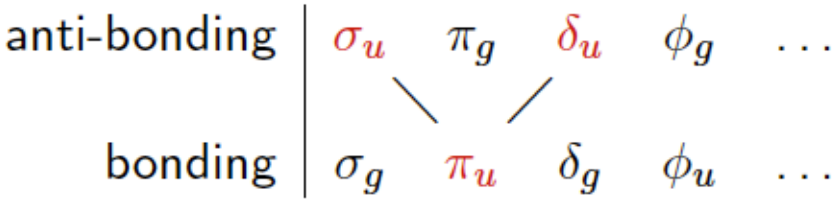
mixing of bonding and anti-bonding

classification of bonding and anti-bonding molecular orbitals:

non- and scalar-relativistic picture

anti-bonding	σ_u	π_g	δ_u	ϕ_g	$\ldots$
bonding	σ_g	π_u	δ_g	ϕ_u	$\ldots$

$\downarrow$ spin-orbit coupling



The electronic ground state of U_2

$\Omega = 8_g$ ground state from Roos and Gagliardi

$$7s\sigma_g^{2.00} \quad 6d\sigma_g^{0.97} \quad 6d\delta_g^{0.98} \quad 5f\pi_g^{0.37} \quad 5f\delta_g^{0.63} \quad 5f\phi_g^{1.00}$$

$$6d\pi_u^{4.00} \quad 5f\pi_u^{0.63} \quad 5f\delta_u^{0.37} \quad 5f\phi_u^{1.00}$$

$\Omega = 9_g$ ground state from our relativistic CASSCF calculations:

approximate scalar-relativistic notation

$$7s\sigma_g^{1.92} \quad 6d\sigma_g^{0.97} \quad 6d\delta_g^{0.97} \quad 5f\pi_g^{0.00} \quad 5f\delta_g^{1.00} \quad 5f\phi_g^{0.99}$$

$$6d\pi_u^{3.79} \quad 5f\pi_u^{0.00} \quad 5f\delta_u^{0.99} \quad 5f\phi_u^{1.00}$$

$\Omega = 8_g$ state from our relativistic CASSCF calculations:

approximate scalar-relativistic notation

$$7s\sigma_g^{1.91} \quad 6d\sigma_g^{0.97} \quad 6d\delta_g^{0.97} \quad 5f\pi_g^{0.41} \quad 5f\delta_g^{0.59} \quad 5f\phi_g^{0.99}$$

$$6d\pi_u^{3.80} \quad 5f\pi_u^{0.59} \quad 5f\delta_u^{0.41} \quad 5f\phi_u^{1.00}$$

Mössbauer isomer shifts in Hg complexes

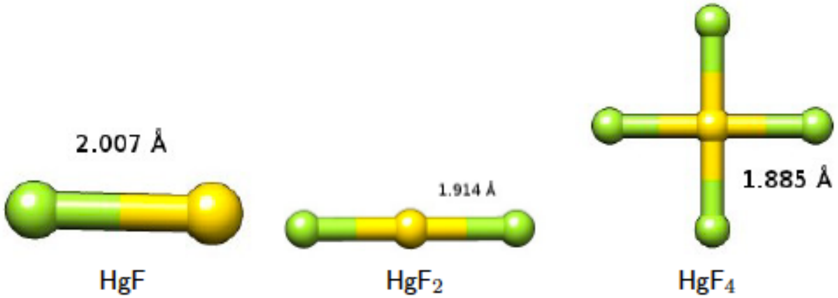
- Mössbauer spectroscopy: Recoil-free, resonant nuclear absorption and emission of gamma rays in solids
- E_γ is modified by the local chemical environment

$$\Delta E_\gamma \propto \Delta\rho(0)$$

with $\rho(0)$ being the density at the nucleus

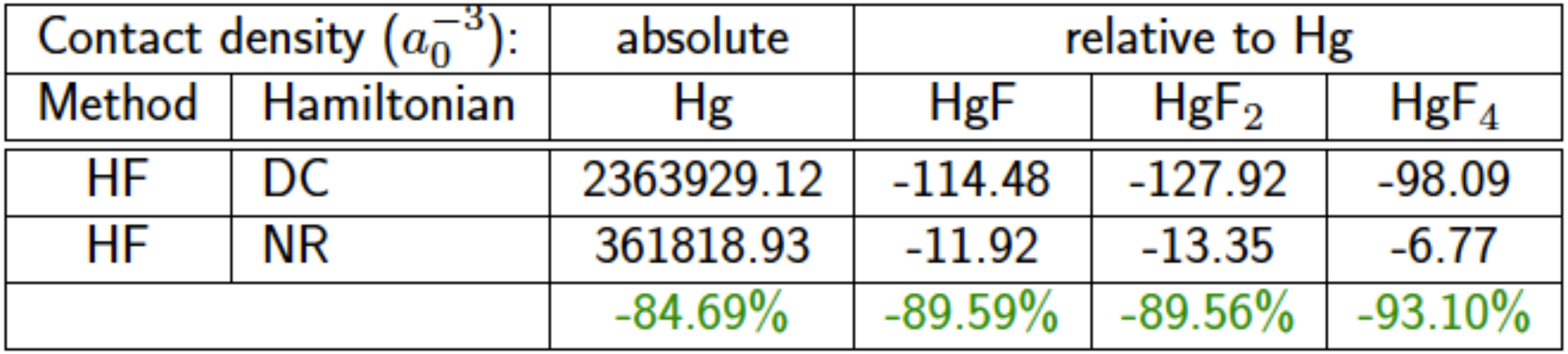
- Relativistic benchmark for the series HgF_n (n=0,1,2,4)

S. Knecht *et al.*, Theor. Chem. Acc., 129, 631 (2011)



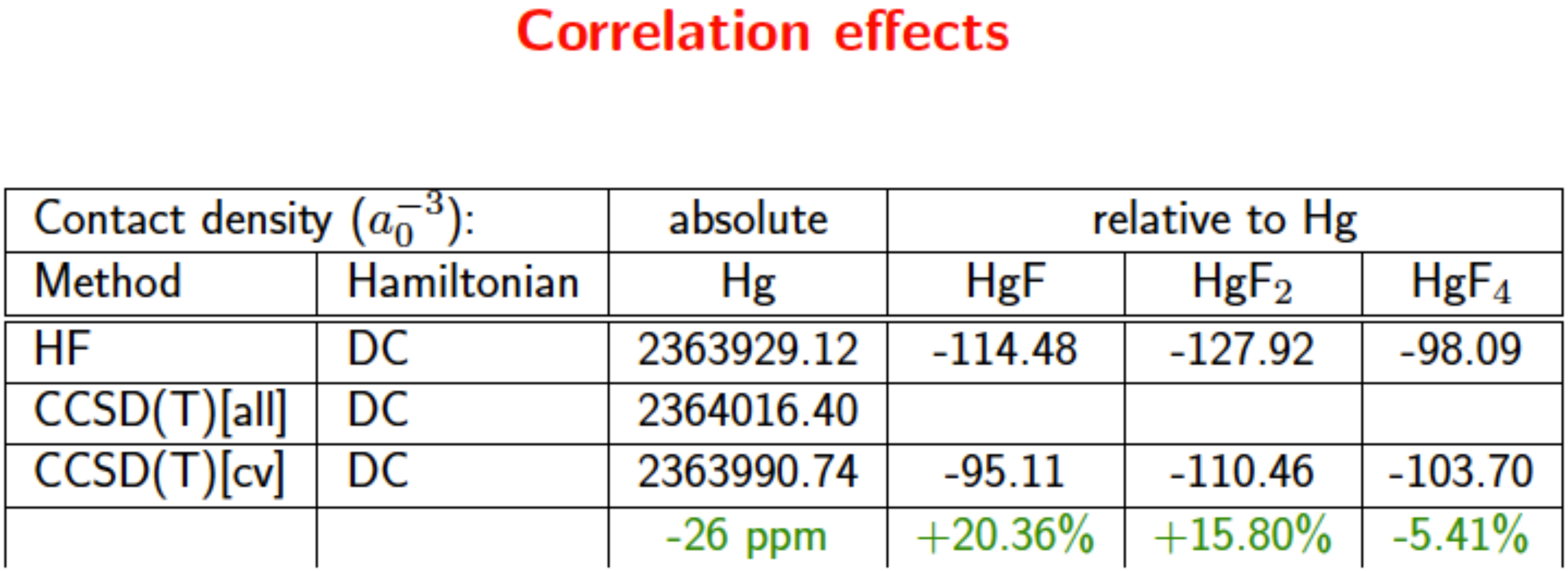
Mössbauer isomer shifts in Hg complexes

Relativistic effects on absolute and relative $\rho^{Hg}(0)$ (a.u.)



Contact density (a_0^{-3}):		absolute	relative to Hg		
Method	Hamiltonian	Hg	HgF	HgF_2	HgF_4
HF	DC	2363929.12	-114.48	-127.92	-98.09
HF	NR	361818.93	-11.92	-13.35	-6.77
		-84.69%	-89.59%	-89.56%	-93.10%

Mössbauer isomer shifts in Hg complexes



Correlation effects

Contact density (a_0^{-3}):		absolute	relative to Hg		
Method	Hamiltonian	Hg	HgF	HgF_2	HgF_4
HF	DC	2363929.12	-114.48	-127.92	-98.09
CCSD(T)[all]	DC	2364016.40			
CCSD(T)[cv]	DC	2363990.74	-95.11	-110.46	-103.70
		-26 ppm	+20.36%	+15.80%	-5.41%

- Correlation effect on the absolute contact density are small but relative contact densities are of the same order
- Correlation effect on relative densities therefore important

Nuclear size effects in rotational spectra

- Molecular field shift V^x arising from the finite size of the atomic nuclei as an additional correction factor to the Born-Oppenheimer approximation

J. Schlembach and E. Tiemann, Chem. Phys., 68, 21 (1982)

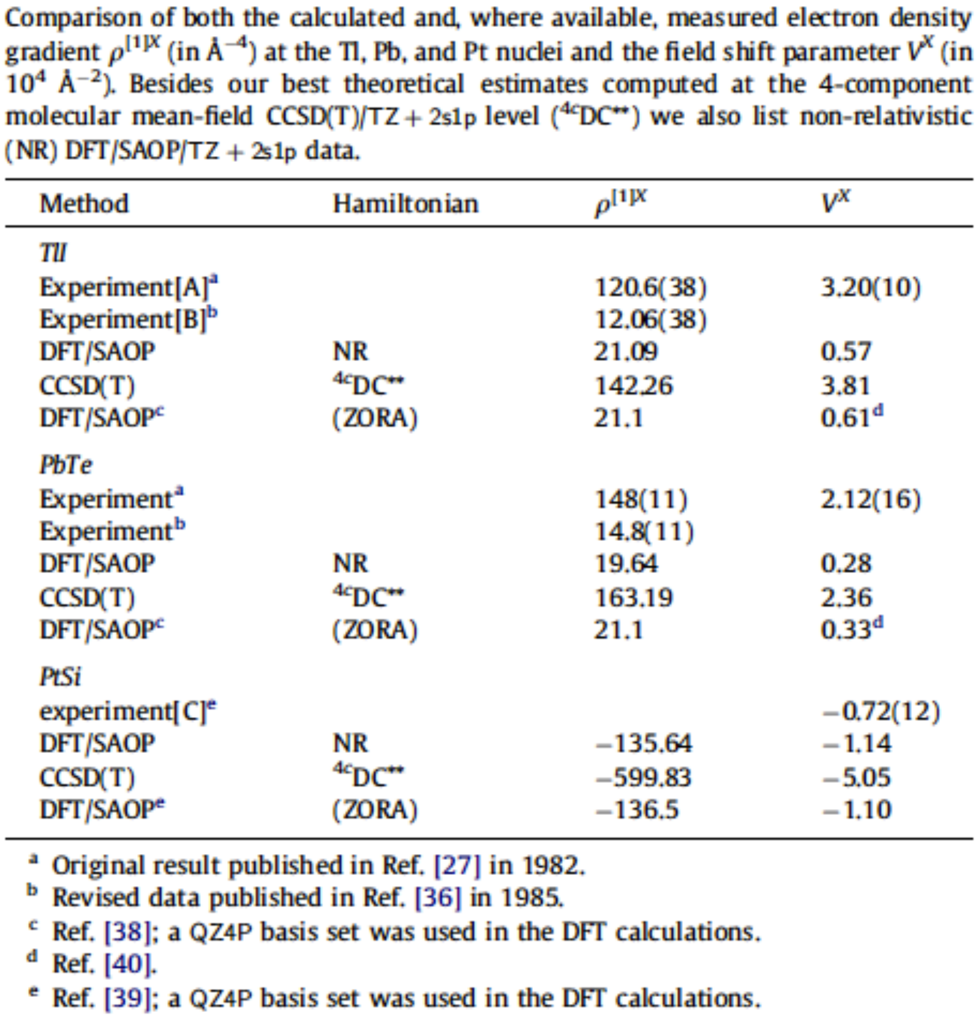
- Requires to compute the gradient of density at the nucleus

$$V^x \propto \left(\frac{d\rho(0)}{dR}\right)_{R_e}$$

- Computational benchmark for TlI, PtSi and PbTe

S. Knecht and T. Saue, Chem. Phys., 401, 103 (2012)

Nuclear size effects in rotational spectra



Comparison of both the calculated and, where available, measured electron density gradient $\rho^{[1]X}$ (in Å^{-4}) at the Tl, Pb, and Pt nuclei and the field shift parameter V^X (in 10^4 Å^{-2}). Besides our best theoretical estimates computed at the 4-component molecular mean-field CCSD(T)/TZ + 2s1p level (^{4c}DC**) we also list non-relativistic (NR) DFT/SAOP/TZ + 2s1p data.

Method	Hamiltonian	$\rho^{[1]X}$	V^X
TlI			
Experiment[A][a]		120.6(38)	3.20(10)
Experiment[B][b]		12.06(38)	
DFT/SAOP	NR	21.09	0.57
CCSD(T)	^{4c}DC**	142.26	3.81
DFT/SAOP[c]	(ZORA)	21.1	0.61[d]
PbTe			
Experiment[a]		148(11)	2.12(16)
Experiment[b]		14.8(11)	
DFT/SAOP	NR	19.64	0.28
CCSD(T)	^{4c}DC**	163.19	2.36
DFT/SAOP[c]	(ZORA)	21.1	0.33[d]
PtSi			
experiment[C][e]			−0.72(12)
DFT/SAOP	NR	−135.64	−1.14
CCSD(T)	^{4c}DC**	−599.83	−5.05
DFT/SAOP[e]	(ZORA)	−136.5	−1.10

[a] Original result published in Ref. [27] in 1982.

[b] Revised data published in Ref. [36] in 1985.

[c] Ref. [38]; a QZ4P basis set was used in the DFT calculations.

[d] Ref. [40].

[e] Ref. [39]; a QZ4P basis set was used in the DFT calculations.

Spectroscopic constants of TlH

- TlH as “guinea pig” molecule for any new relativistic correlation method
- Comparison of our new relativistic DMRG implementation with CI and CC methods
- CAS space: 14 electrons in 94 spinors

S. Knecht, Ö. Legeza, and M. Reiher, J. Chem. Phys., 140, 041101 (2014)

Spectroscopic constants of TlH

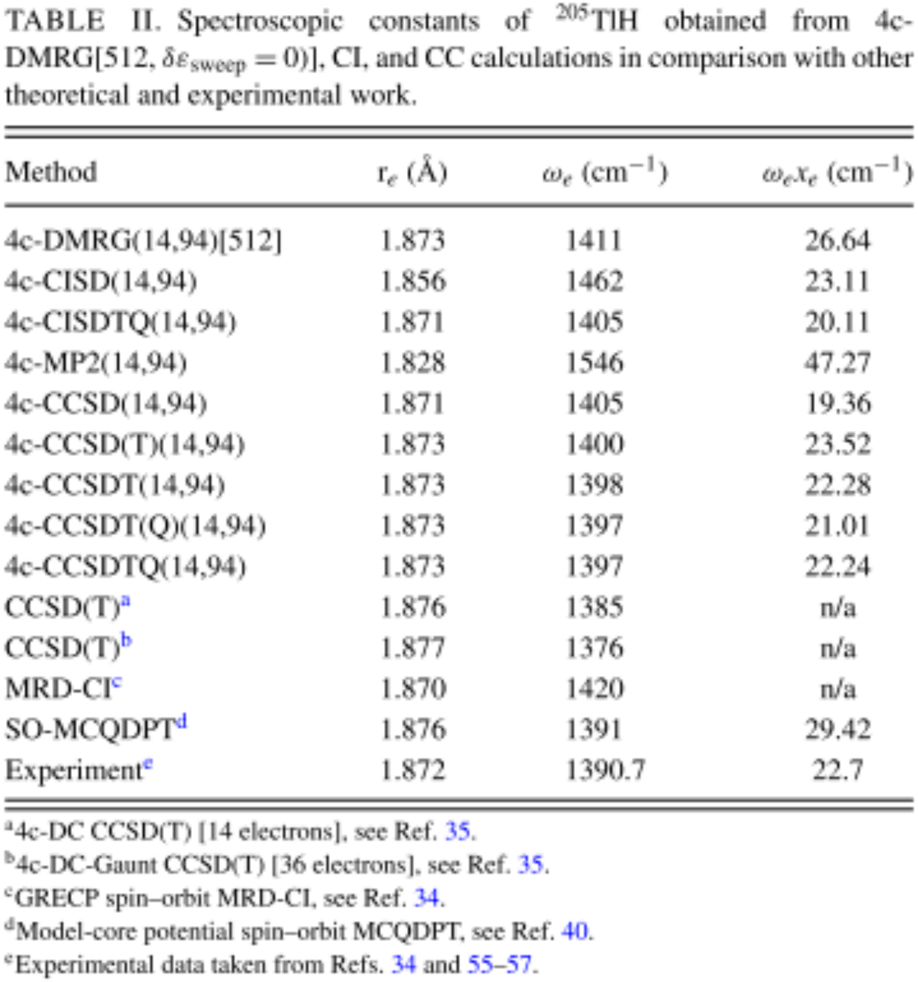


TABLE II. Spectroscopic constants of ^{205}TlH obtained from 4c-DMRG[512, $\delta\varepsilon_{\text{sweep}} = 0$)], CI, and CC calculations in comparison with other theoretical and experimental work.

Method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
4c-DMRG(14,94)[512]	1.873	1411	26.64
4c-CISD(14,94)	1.856	1462	23.11
4c-CISDTQ(14,94)	1.871	1405	20.11
4c-MP2(14,94)	1.828	1546	47.27
4c-CCSD(14,94)	1.871	1405	19.36
4c-CCSD(T)(14,94)	1.873	1400	23.52
4c-CCSDT(14,94)	1.873	1398	22.28
4c-CCSDT(Q)(14,94)	1.873	1397	21.01
4c-CCSDTQ(14,94)	1.873	1397	22.24
CCSD(T)[a]	1.876	1385	n/a
CCSD(T)[b]	1.877	1376	n/a
MRD-CI[c]	1.870	1420	n/a
SO-MCQDPT[d]	1.876	1391	29.42
Experiment[e]	1.872	1390.7	22.7

[a] 4c-DC CCSD(T) [14 electrons], see Ref. 35.

[b] 4c-DC-Gaunt CCSD(T) [36 electrons], see Ref. 35.

[c] GRECP spin–orbit MRD-CI, see Ref. 34.

[d] Model-core potential spin–orbit MCQDPT, see Ref. 40.

[e] Experimental data taken from Refs. 34 and 55–57.

Conclusions

- Electron correlation plays an important role in describing the electronic structure and properties of molecular systems
- Relativistic effects may not be non-negligible for light systems and are mandatory for heavy-element compounds
- Efficient and “new” wave-function based electron correlation methods are highly appreciated

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Thank you for your kind attention!