Atoms, Molecules, Dirac Theory and all that ... : Relativistic Many-Body "Standard Models" to Arbitrary Order

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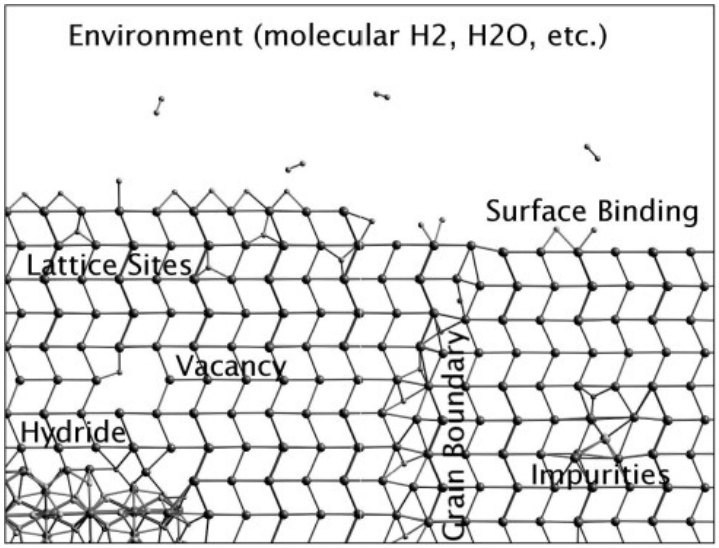
Scientific Motivation (1)

Actinide Sciences

- Materials sciences involving actinides
  E.g. uranium hydriding reaction
- Nuclear waste problem
  Small complexes
- **Actinide spectroscopy**
  Hydrides, oxides and hydroxides



C.D. Taylor, T. Lookman, R.S. Lillard, *Acta Materialia* **58** (2010) *1045*

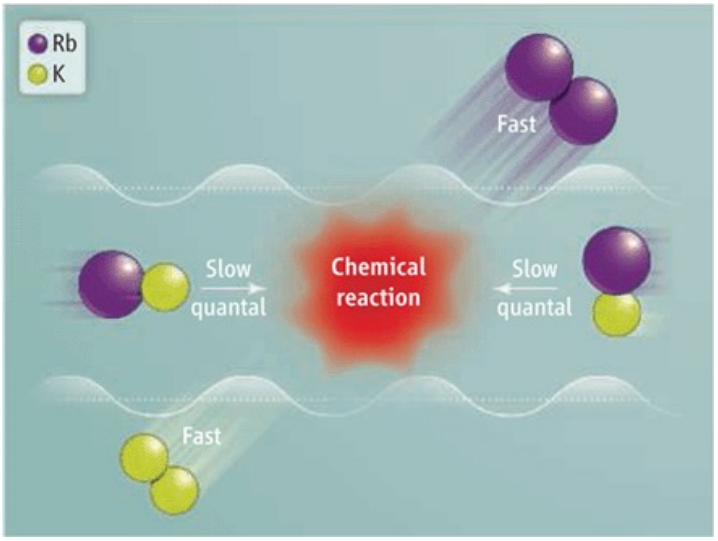
Persistent problems:

- Extremely complicated electronic structure
- Strong relativistic and electron correlation effects
- Protagonist systems: AcH_x, AcO_x, Ac_2, Ac^{n+}(complex), and many others

Scientific Motivation (2)

Ultracold Molecular Sciences

- Ultracold chemistry
  Quantum-controlled reactions
- Fundamental physics
  Electron EDM ?
- Quantum information
  e.g. Quantum computers



J. Hutson, *Science* **327** (2010) *788*

Persistent problems:

- Short- and long-range potentials required at very high accuracy
- Often considerable relativistic and electron correlation effects
- Protagonist systems: (A A'), (A EA), LiCs, KRb, Cs_2, RbYb, $RbBa^+$, and others

Motivation from Principles of Theory

Predictive power and falsifiability of theories/models

Avoid experimental data and fixed parameters

Generality and flexibility in application

General-order methods, adaptable multi-reference schemes

Pure "ab-initio" theory. Consequences:

Many (!) parameters

Large-scale algorithms required

Imperative "ingredients":

Creator-string based methodology

Modern representation of many-body methods

Exploit all the symmetry available !

Time-reversal, double point groups and quaternion algebra

Relativistic Many-Body Theory

What is different, what is new?

- (different) "Scalar relativistic" effects can be treated straightforwardly in a one-component formalism
  Many implementations available

- (new) Magnetic couplings (spin-orbit interaction) $\Rightarrow$
  Partial lifting of degeneracies, reduction of symmetry; much fewer methods/codes available

Consistent treatment by Dirac equation:

$$\begin{pmatrix} V\mathbf{1}_2 & c\boldsymbol{\sigma}\cdot\boldsymbol{p} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{p} & (V-2mc^2)\,\mathbf{1}_2 \end{pmatrix} \begin{pmatrix} \boldsymbol{\psi}^L \\ \boldsymbol{\psi}^S \end{pmatrix} = E \begin{pmatrix} \boldsymbol{\psi}^L \\ \boldsymbol{\psi}^S \end{pmatrix}$$

- Is a 4-component approach really necessary?
- Is a spinor-based approach necessary?

Relativistic Many-Body Theory

Methodology for treating electron correlation and spin-orbit interaction

Spinor–based models

Hartree–Fock		*Dynamic Correlation*
2– or 4–component Hamiltonian	+	2– or 4–component Hamiltonian

Double–group CI/CC (DIRAC)

Spinorbital–based models

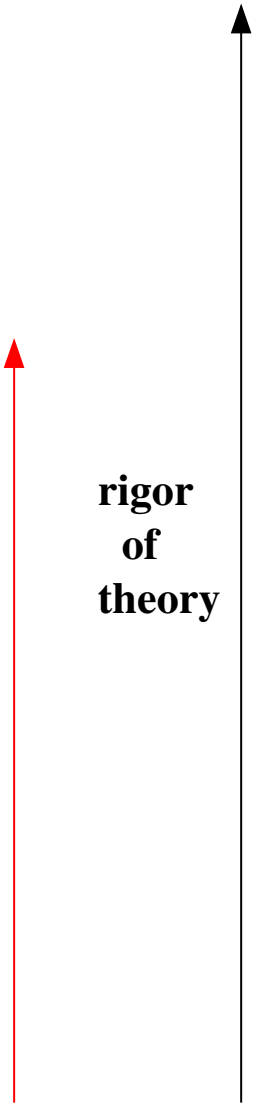
Hartree–Fock		*Dynamic Correlation*
scalar relativistic Hamiltonian	+	2–component Hamiltonian

Spin–orbit CI (EPCISO, COLUMBUS)
Spin–orbit Coupled Cluster (van Wuellen, Gauss)

Additive models

Hartree–Fock		*Dynamic Correlation*		*Magnetic Couplings*
scalar relativistic Hamiltonian	+	scalar relativistic Hamiltonian	+	2–component Hamiltonian

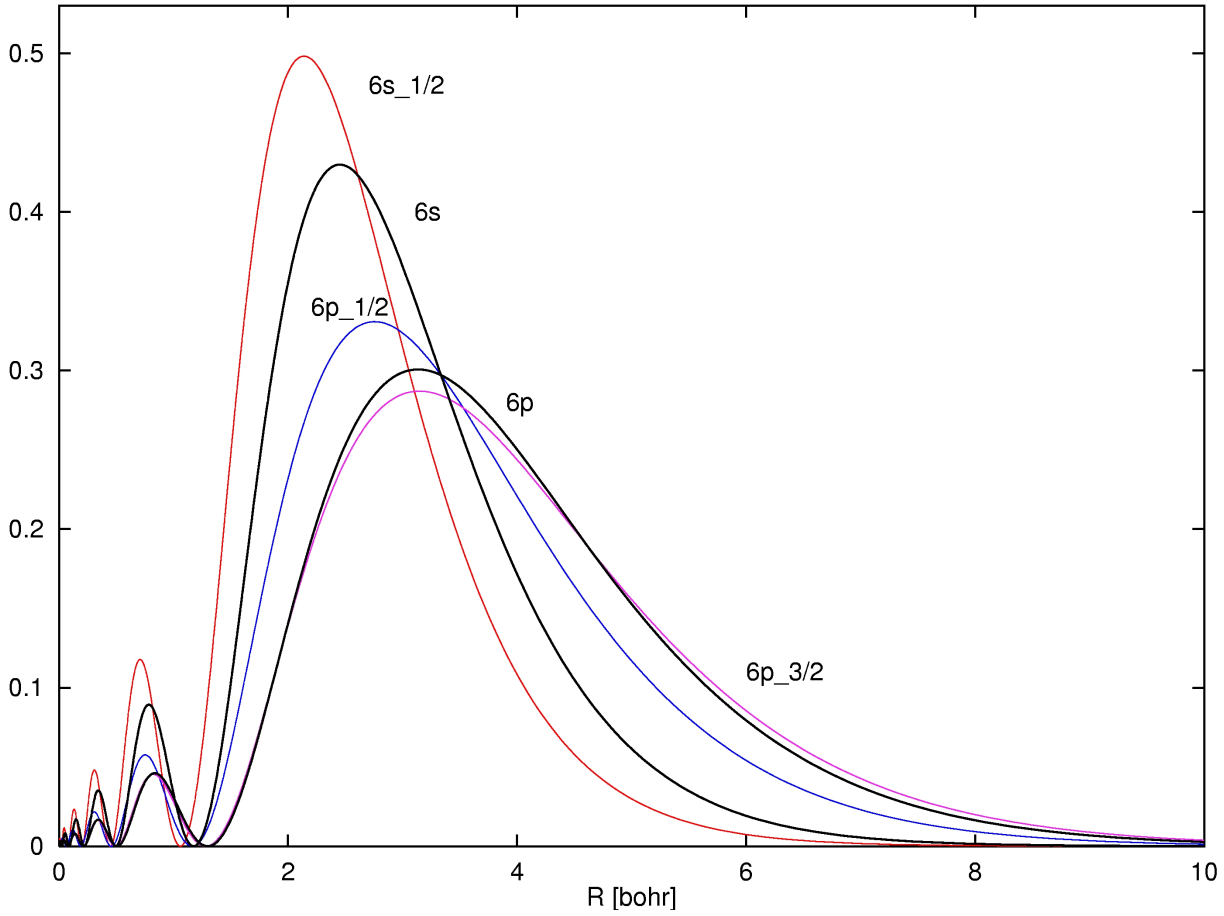
Spin–orbit QDPT (Hess, Marian)
CASPT2–Spin–orbit RASSI (MOLCAS)



Relativistic Effects

Tl atomic valence spinors

Radial probability density functions



Describe difference *a priori* or *a posteriori* ?

Relativistic Many-Body Theory

Why do we prefer spinors over spin-orbitals?

Comparison of orbital-based and spinor-based relativistic CI for representative atoms[1]

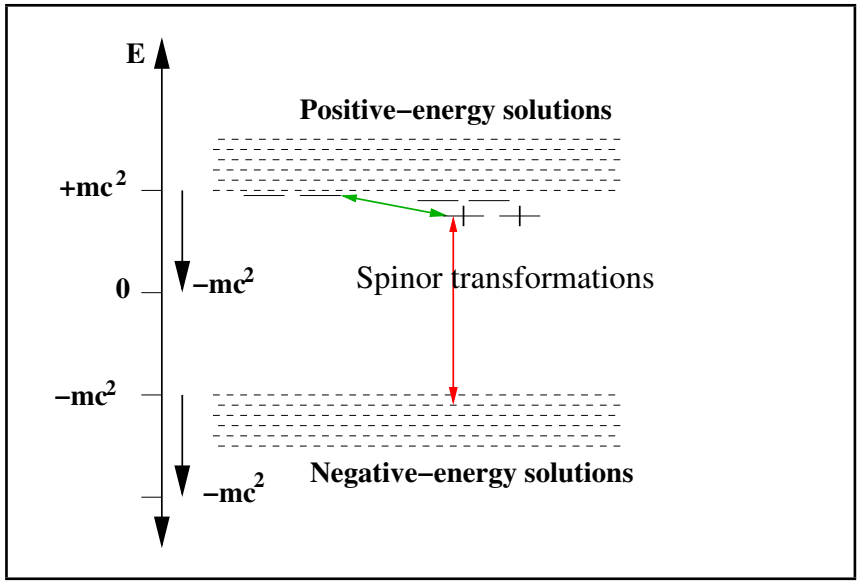
Atom	Tm (f^{13})		Lu (d^1)		Tl (p^1)	
Valence spinors	$f_{7/2} - f_{5/2}$		$d_{3/2} - d_{5/2}$		$p_{1/2} - p_{3/2}$	
$\Delta < r >$	0.018		0.085		0.496	
Approach	orbitals	spinors	orbitals	spinors	orbitals	spinors
rel. CASCI	9108	8996	2578	1687	6330	7709
rel. CISD	9817	9280	2450	1744		
rel. CISDT					7200	7286
Exp. (Martin, Moore)	8771.243		1993.32		7793	

- Spinor basis outperforms (scalar relativistic) orbital basis
- Reason: Spin-orbit splitting need not be described by correlation expansion
- How do we use spinors and are there any drawbacks?

[1] T. Fleig, J. Olsen, L. Visscher, *J Chem Phys* **119,6** (2003) *2963*

Dirac-Hartree-Fock and MCSCF

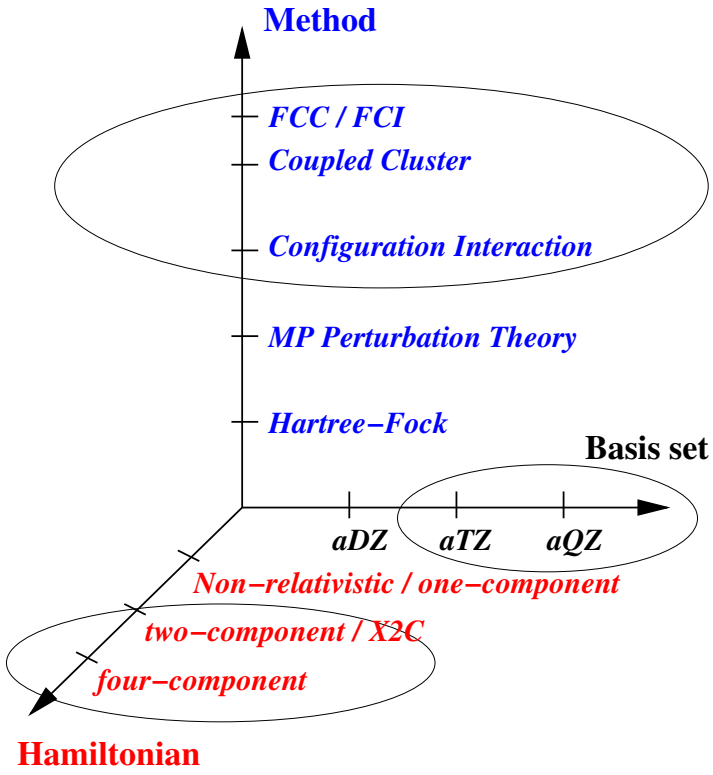
The "empty Dirac" picture



- **Occupied** positive-energy bound-state spinors Fermi vacuum state $|0\rangle$
- **Empty** continuum of negative-energy states
- Expectation value of parameterized state vector
  $\left\langle Ref|\hat{H}|Ref\right\rangle = \left\langle 0|e^{-\hat{\kappa}}\hat{H}e^{\hat{\kappa}}|0\right\rangle$

- Approximation of general expectation value to first order:
  $\left\langle 0|e^{-\hat{\kappa}}\hat{H}^{DC}e^{\hat{\kappa}}|0\right\rangle \approx \left\langle 0|\left[\hat{H}^{DC},\hat{\kappa}\right]|0\right\rangle = \sum_{pq}\kappa_{pq}\left[\left\langle 0|\hat{H}^{DC}a_p^\dagger a_q|0\right\rangle - \left\langle 0|\hat{H}^{DC}a_q^\dagger a_p|0\right\rangle^*\right]$
- Parameterized Dirac-spinor transformations:
  $\hat{\kappa} = \sum_{pq}\left[\kappa_{p_+q_+}a^\dagger_{p_+}a_{q_+} + \kappa_{p_+q_-}a^\dagger_{p_+}a_{q_-} + \kappa_{p_-q_+}a^\dagger_{p_-}a_{q_+} + \kappa_{p_-q_-}a^\dagger_{p_-}a_{q_-}\right]$
- Green terms: minimization of energy w.r.t. rotations
- Red terms: maximization of energy w.r.t. rotations
  $\Rightarrow$ **minimax** variation

Rigorous Relativistic Many-Body Approaches[2]



Computational scaling: yN^x

Relativistic MRCI[3]

GAS Ansatz, 4- or 2-spinors

$$\left|\Psi^{\mathrm{GASCI}}\right\rangle = \hat{T}^{\mathrm{rel}}_{\mathrm{GAS}} \left|\Psi^{\mathrm{Ref}}\right\rangle$$

$\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$ General-order excitations
Basis of 4- or 2-spinors

Relativistic MR Coupled Cluster[4]

Generalized-Active-Space Ansatz

$$\left|\Psi^{\mathrm{GASCC}}\right\rangle = e^{\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}} \left|\Psi^{\mathrm{Ref}}\right\rangle = exp(\sum_{\mu} t_\mu \hat{\tau}_{\mu_{\mathrm{GAS}}}) \left|\Psi^{\mathrm{Ref}}\right\rangle$$

Hamiltonians based on Dirac theory

4- and 2-component operators, e.g.

$$\hat{H}^{\mathrm{rel}} = \hat{H}^{\mathrm{Dirac}} + \hat{H}^{\mathrm{Coulomb}}$$

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[2] T. Fleig, **"Relativistic String-Based Electron Correlation Methods"** (2010) in "Challenges and Advances in Computational Chemistry and Physics, Vol. 10", *Eds. Barysz, Ishikawa*

[3] S. Knecht, H.J.Aa. Jensen, T. Fleig, *J Chem Phys* **132** (2010) *014108*

[4] L.K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*

Spinors and Strings

How do we parameterize $\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$?

General concept: Kramers-paired spinors

Time-reversal operator for a fermion:
$\hat{K} = e^{-\frac{\imath}{\hbar}\pi\left(\hat{\vec{s}}\cdot\vec{e}_y\right)}\,\hat{K}_0 = -\imath\Sigma_y\hat{K}_0$

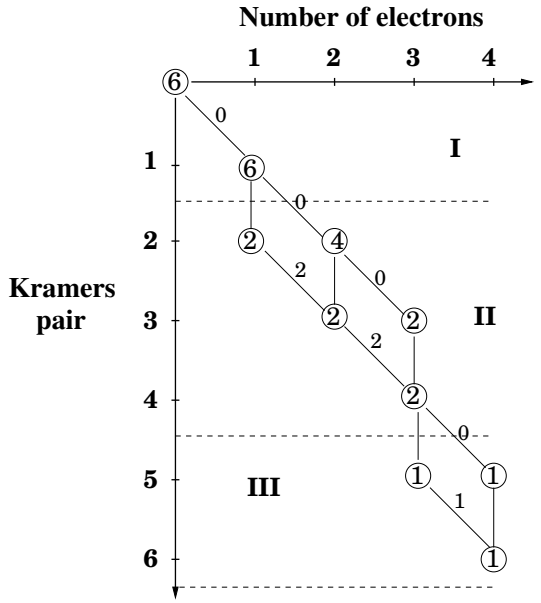
Spinorbitals	General spinors
$\hat{K}\,\varphi_i\,\alpha = \varphi_i^*\,\beta$	$\hat{K}\,\phi_i = \phi_{\bar{i}}$
$\hat{K}\,\varphi_i^*\,\beta = -\varphi_i\,\alpha$	$\hat{K}\,\phi_{\bar{i}} = -\phi_i$

General spinor basis:
$\phi_i = a_i^\dagger \mid\rangle \qquad \phi_{\bar{i}} = a_{\bar{i}}^\dagger \mid\rangle$

- Many-particle wavefunction defined as
  - 1 unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$
  - 1 barred (Kramers down) string $\overline{\mathcal{S}} = a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

- Configuration Interaction: **Slater determinants**

  Coupled Cluster: **Individual strings**

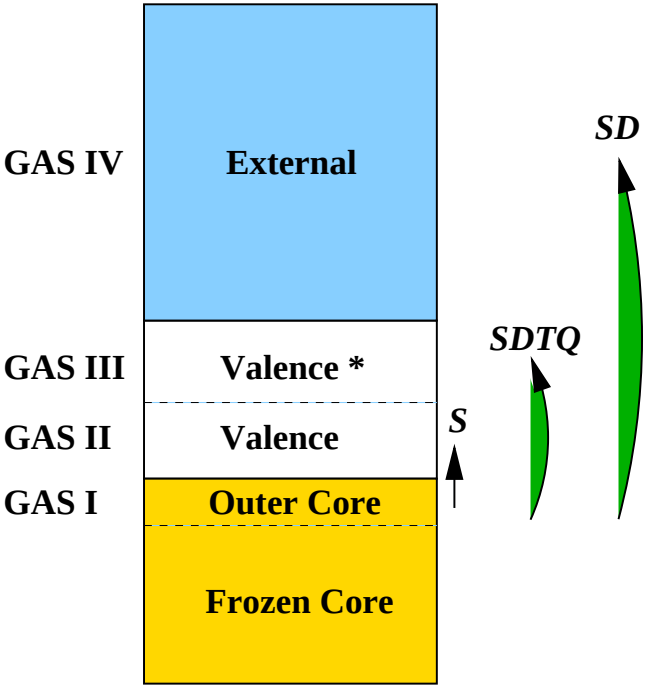


⊗ x: vertex weight
y: arc weight

Relativistic CI and CC

How do we parameterize $\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$?

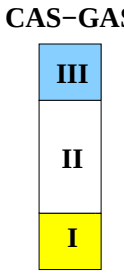
Space of orbitals / Kramers pairs



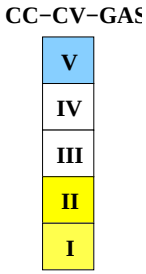
GAS concept

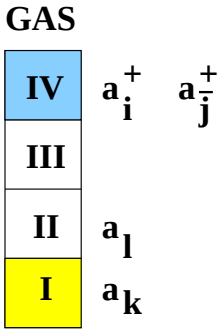
Full and restricted subspace expansions

Complete MR expansions
often impracticable



Flexible expansions
Adaptation to problem





Operator type
+
Occupation type

$\Longrightarrow$ Excitation class

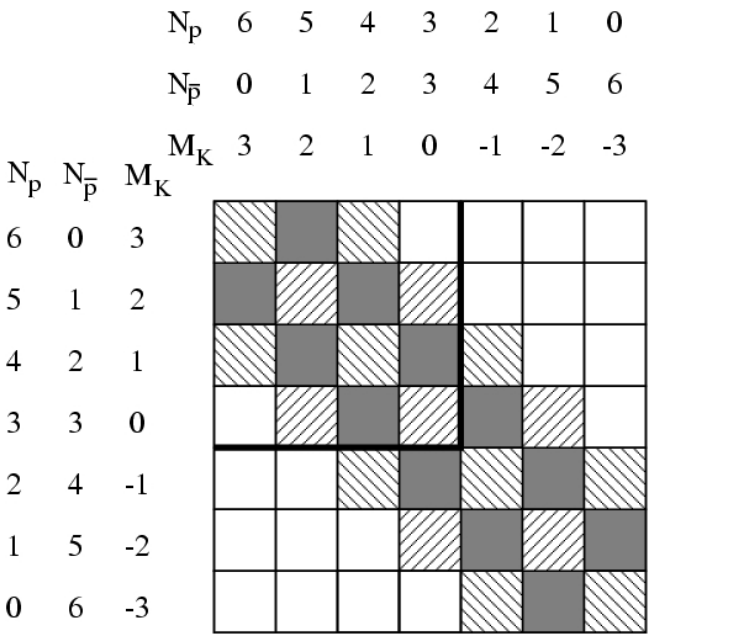
$\hat{T}^{\mathrm{rel}}_{\mathrm{GAS}}$ defined

Relativistic Symmetry

MCSCF and Configuration Interaction

T. Fleig, J. Olsen, H. J. Aa. Jensen, L. Visscher, J Chem Phys **124** (2006) *104106*

- Double point-group symmetry fully exploited
  Currently D_{2h}^* and subgroups
- Quaternion algebra at the integral level[5]
  $\Rightarrow$ For matrix groups $D_{2h}^*, D_2^*, C_{2v}^*$ entirely *real* algebra



- Only shaded blocks are non-vanishing
- Various shadings display block structure in quaternion/complex/real matrix groups[6]
- Square indicates many-particle Kramers symmetry

[5] T. Saue, H. J. Aa. Jensen, J Chem Phys **111** (1999) *6211*

[6] H. J. Aa. Jensen, K. G. Dyall, T. Saue, K. Fægri Jr., J Chem Phys **104** (1996) *4083*

Application of Parallel MRCI

BiH: Spin-Orbit Splitting of $0^+(^3\Sigma^-) - 1(^3\Sigma^-)$

S. Knecht, H. J. Aa. Jensen, T. Fleig, J Chem Phys **132** (2009) *014108*

Uncontracted Dyall basis sets (Bi) / (ANO-RCC: H)

aTZ $[30s26p17d11f1g]$

aQZ $[34s31p21d17f3g1h]$

Cutoff virtual spinors: 5 a.u.

4c-/2c-Hamiltonians

SD(2in2)MRSD6 (aQZ)	4655
SD(2in2)MRSD16 (aTZ)	4467
SD(2in2)MRSD16 (aQZ)	4689
IOTC-G SD(2in2)MRSD16 (aTZ)	4407
SD(2in2)MRSDTQ16 (aTZ)	4633
SD(6in5)MRSD16 (aTZ)	4509
SD(6in5)MRSD16 (aQZ)	4761
SD(2in2)MRSDTQ16 (aQZ)	$\approx$ 4950
Exp.[7]	4917

Basis set correction (TZ - QZ)	$+300$ cm^{-1}
Higher excitations (SD - SDTQ)	$+250$ cm^{-1}
$5d$ correlation	$+35$ cm^{-1}
Gaunt correction (spin-other-orbit)	-60 cm^{-1}

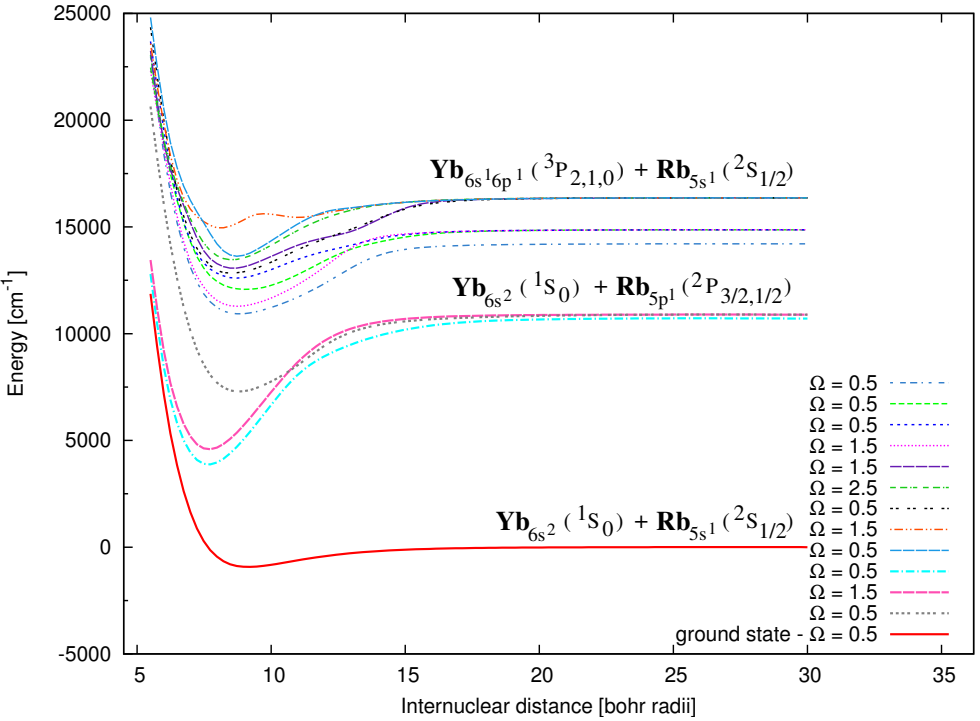
"Standard model"
SD(6in5)MRSD16 (aQZ)

"Benchmark model"
SD(2in2)MRSDTQ16 (aQZ)
$\approx 2.8 \times 10^9$ determinants

[7] NIST Standard Reference Database (2008)

Applications aux éléments lourds

Etudes 4c-CC / 4c-IC sur la molécule RbYb



- Prédictions théoriques sur une molécule inconnue, guidant l'expérience
- Démarche initiale: Formation de la molécule dans l'environnement ultrafroid

  N. Nemitz et al., *Phys Rev A* **79** (2009) *061403(R)*
- But à long terme: Recherche d'un moment dipolaire électrique de l'électron (violation de P et T)

- PECs et moment dipolaire de haute précision ($\mu_e^{\mathrm{4c-CCSD(T)23}} = 0.977$ D)
- Mécanisme supposé pour l'émission stimulée à l'état fondamental rovibronique via les facteurs de Franck-Condon

L.K. Sørensen, S. Knecht, T. Fleig, C.M. Marian, *J Phys Chem* **113** (2009) *12607*

Applications to Heavy Elements

4c-CI study of UH

- Motivation 1: UH plays a role in the uranium hydriding reaction

  T.C. Totemeier, *J Nuc Mater* **278** (2000) *301*

U–H

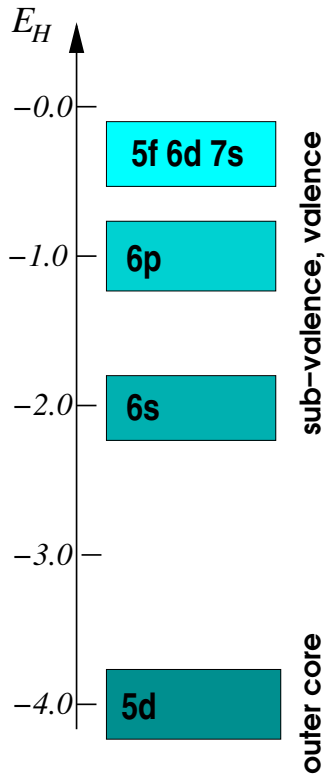
- Motivation 2: Can we accurately describe even the smallest conceivable uranium molecule?

Problems:

1. The uranium atom has several unpaired electrons

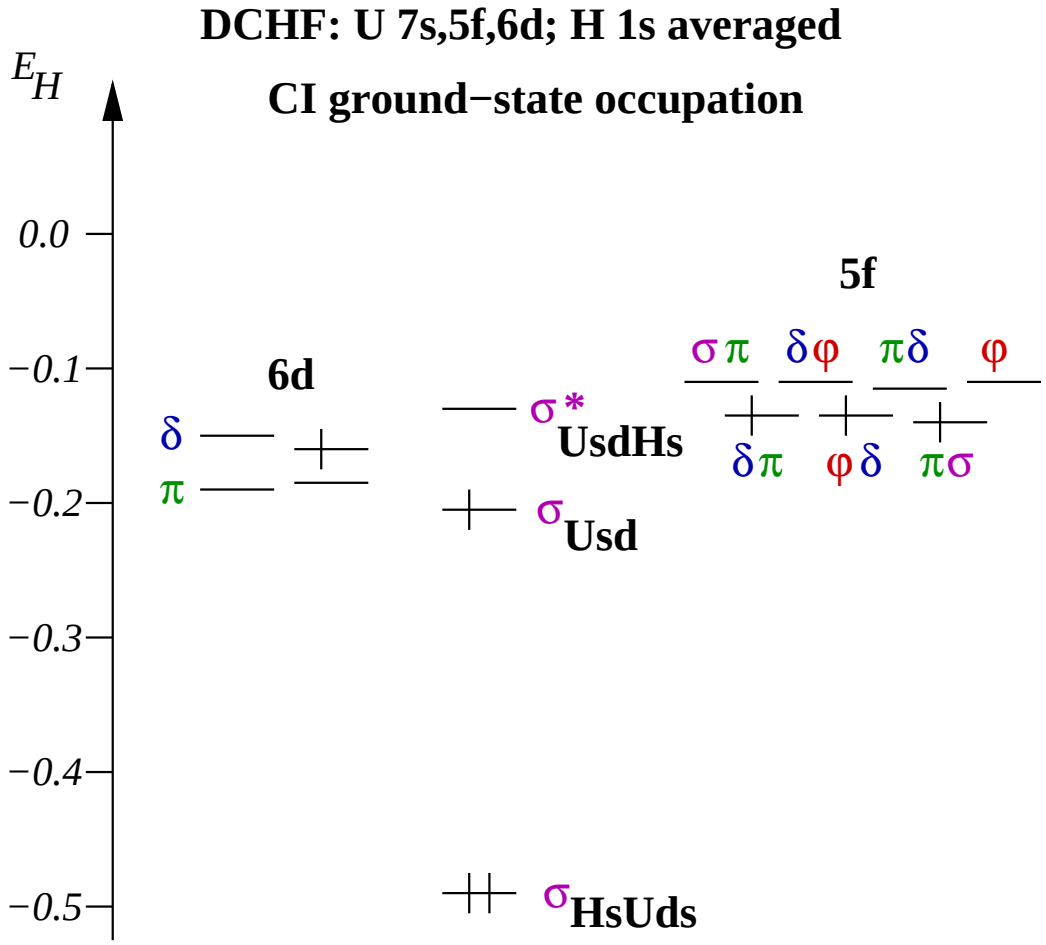
   ground-state configuration: $[Rn]5f^3 6d^1 7s^2$

2. Sub-valence and outer-core shells are energetically close
3. The reference space for a correlated calculation is expected to be huge
4. Electron correlation and relativistic effects are strong and likely to be coupled



Application of Parallel MRCI

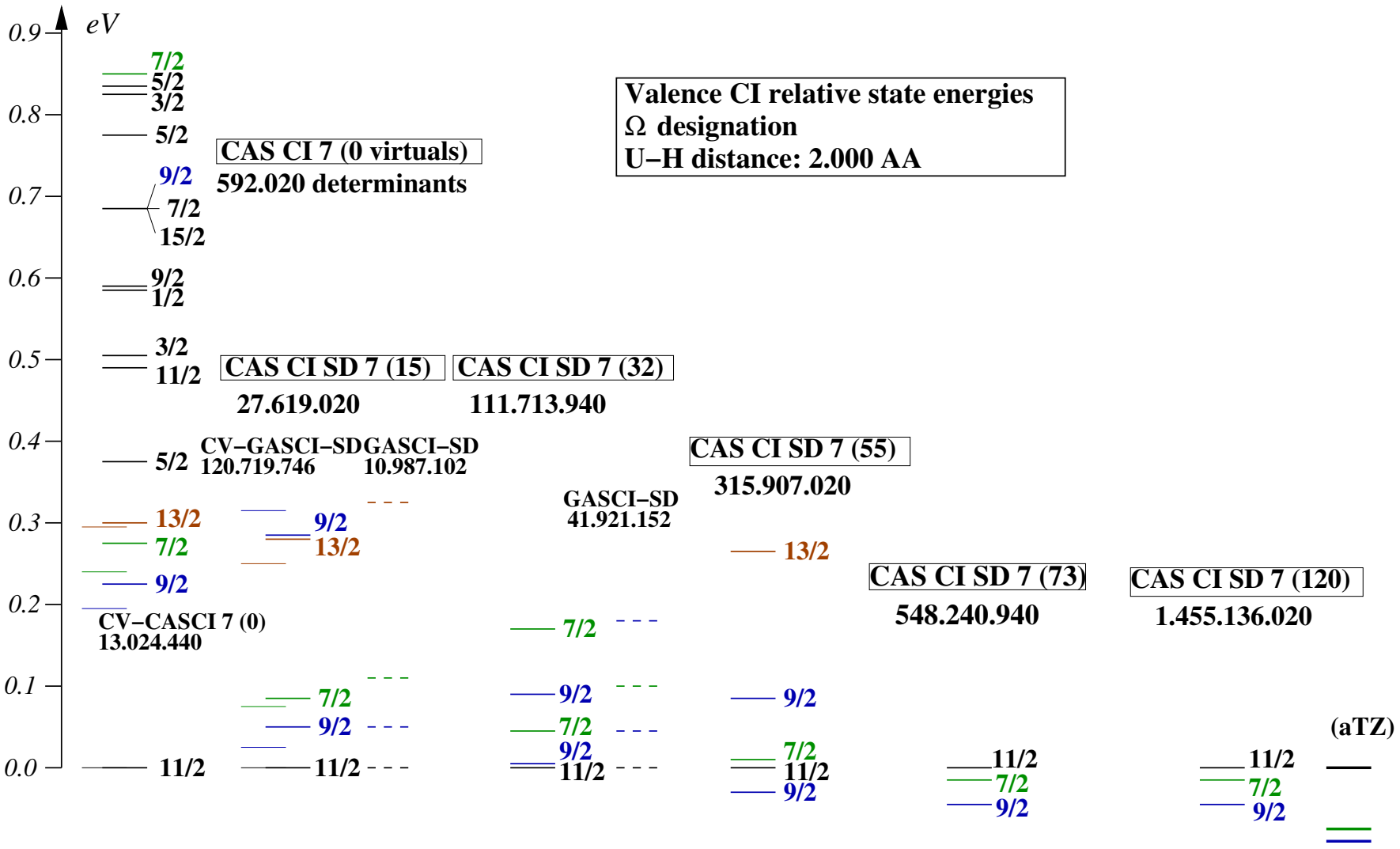
UH bonding and valence spinors; 2.0 Å



- Bonding mainly of $7s - 1s$ type, fairly ionic
- Strong spin-orbit mixing in (essentially atomic) $5f$ shell
- Lower excited states arise from different occupations *within* the $5f$ shell

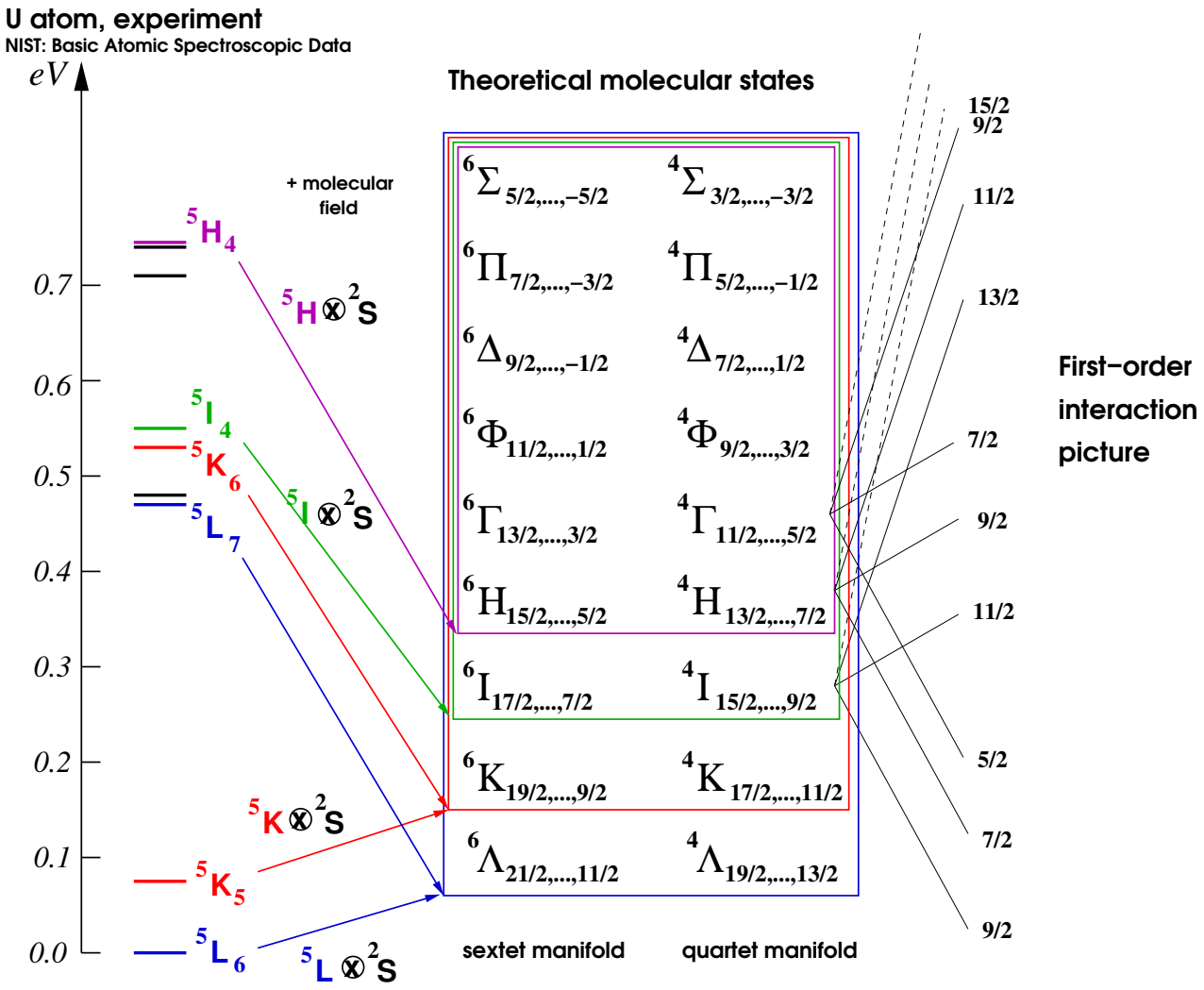
Application of Parallel MRCI

Vertical electronic spectrum of UH



Application of Parallel MRCI

Vertical electronic spectrum of UH



- Inferred from calculations of Dolg et al.

  X. Cao, A. Moritz, M. Dolg, *Chem Phys* **343** (2007) *250*

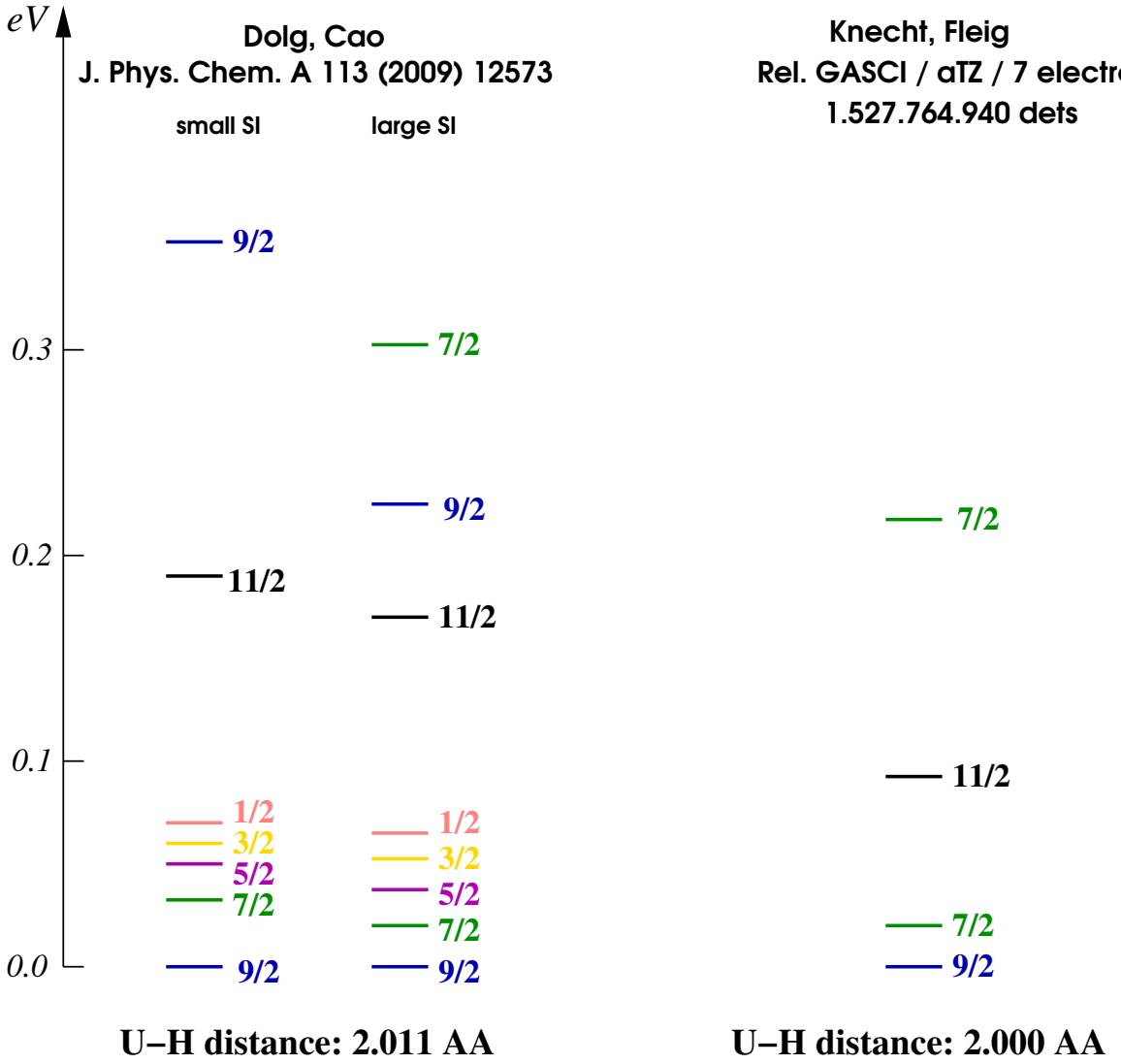
- Scalar relativistic calculations suggest strong state interactions

- Pattern corresponds to splitting of "particle" states

- Strong state interactions + strong SO splittings suggest a rigorous treatment of both

Application of Parallel MRCI

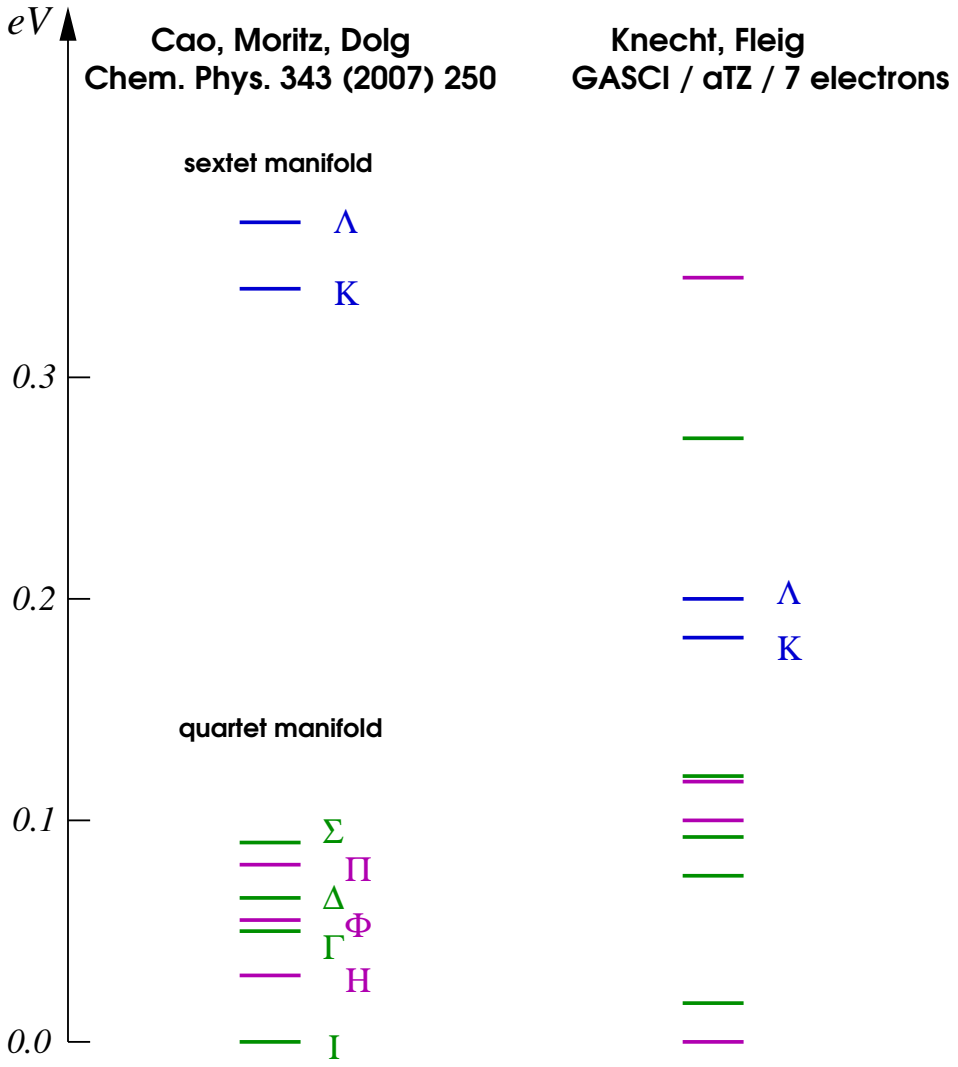
Vertical electronic spectrum of UH; 2.0 Å, Ω states



- Agreement on electronic ground state: $\Omega = 9/2$
- Strong dependency on state-interaction model
  which states to include in model space ?
- Disagreement on excited states $5/2, 3/2, 1/2$!
- Are there correlation errors ?

Application of Parallel MRCI

Vertical electronic spectrum of UH; spin-orbit free states



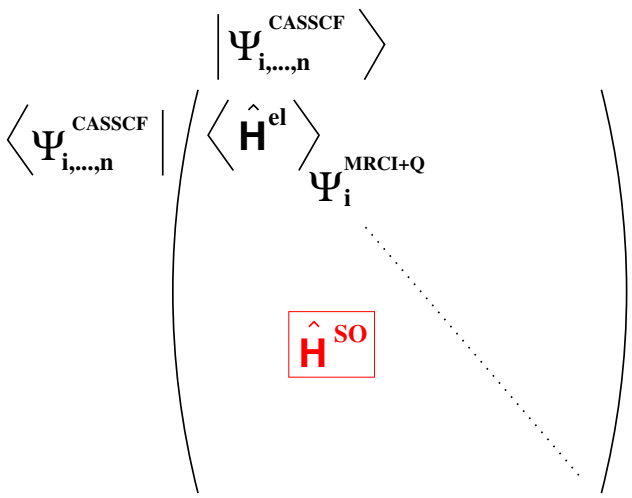
U–H distance: 2.000 AA

- Quartet manifold in energy window of 0.1 eV
- Sextet states significantly lower
- Somewhat different ordering, overall agreement
- Remaining discrepancies cannot be responsible for different excited-state structure including SO !

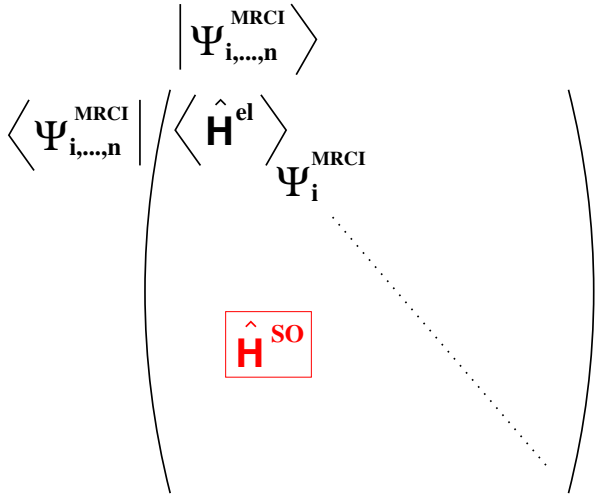
Discrepancies of Theories on UH

Analysis

First–order (quasidegenerate) interaction schemes



MRCI+Q scaled SO–CASSI



SO–MRCISI

- Differences for T of $\Omega = 5/2, 3/2, 1/2$ states ≈ 0.01 eV
- Choice of basis set of wave functions is not problematic

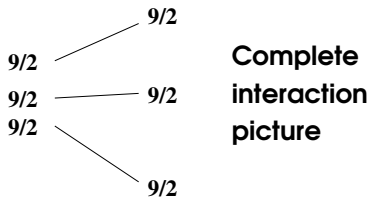
- Essential approximations:
  No reoptimization of expansion coefficients of $\Psi^{\mathrm{CASSCF/MRCI}}$ w.r.t. $\hat{H}^{\mathrm{SO}}$
  No higher-order couplings included
- Both models neglect correlation (and polarization) contributions of the type $\left\langle \Psi^{\mathrm{rel}}_{M_J} | \hat{H}^{\mathrm{el}} | \Psi'^{\mathrm{rel}}_{M_J} \right\rangle, \Delta M_J = 0$
- Is there a difference of this kind in UH for manifolds $9/2, 7/2$ and $5/2, 3/2, 1/2$?

Discrepancies of Theories on UH

Analysis

States contributing to M_J subspace
in energy window of ≈ 0.5 eV

M_J	states
$9/2$	${}^4I, {}^4H, {}^4\Gamma, {}^6K$
$7/2$	${}^4H, {}^4\Gamma, {}^4\Phi$
$5/2$	${}^4\Gamma, {}^4\Phi$
$3/2$	${}^4\Phi$
$1/2$	${}^4\Delta$



- Decreasing number of interacting states
- Decreasing contributions to couplings $\left\langle \Psi^{\mathrm{rel}}_{M_J} | \hat{H}^{\mathrm{el}} | \Psi'^{\mathrm{rel}}_{M_J} \right\rangle, \Delta M_J = 0$

- Consequence: Complete interaction model (spinor-based rel. CI) should give lower-lying $9/2$ and $7/2$ states
- Is there a possibility of confirming this hypothesis ?
  $\longrightarrow$ exactly corresponding first-order state-interaction calculation (Thierry Leininger)

The UH Molecule

Some Conclusions and General Consequences for Other Actinide Species

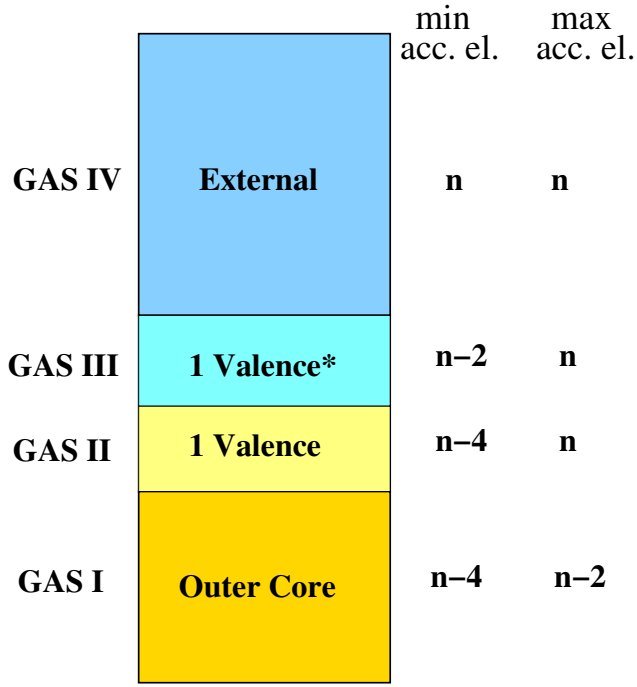
- Relativistic effects and electron correlation effects are important in actinide systems
- Their coupling is sizeable and crucial for describing the **excited-state** and **dissociation** energetics
- Simplified models are applied to many different actinide species; a word of warning
- TD-DFT in general too inaccurate in such situations
- Ground-state properties, e.g. R_e, ω_e, are often obtained satisfactorily with more approximate models

Relativistic Correlation Methods

Generalized Active Space Coupled Cluster

J. Olsen, *J Chem Phys* **113** (2000) *7140*
T. Fleig, L. K. Sørensen, J. Olsen, *Theo Chem Acc* **118,2** (2007) *347*
L. K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*

- "State-Selective" (SS) GAS-CC
  Simulation (SR-MRCC) of true multi-reference CC
- GAS-extended excitation manifold
  $\langle \mu_{\mathrm{GASCC}} | = \langle \Psi^{\mathrm{Ref}} | \, \hat{\tau}^{\dagger}_{\mu_{\mathrm{GAS}}}$
- $\hat{\tau}_{\mu_{\mathrm{GAS}}}$ contains "internal" higher excitations
  $|\Psi^{\mathrm{GASCC}}\rangle = exp(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu_{\mathrm{GAS}}}) \; |\Psi^{\mathrm{Ref}}\rangle$
- Relativistic generalization of cluster operators
  $\hat{T}_1 = \sum_{ia} \left\{ \; t_i^a \hat{\tau}_i^a + t_{\bar{i}}^a \hat{\tau}_{\bar{i}}^a + t_i^{\bar{a}} \hat{\tau}_i^{\bar{a}} + t_{\bar{i}}^{\bar{a}} \hat{\tau}_{\bar{i}}^{\bar{a}} \; \right\}$; $\hat{T}_2 = \ldots$



Example for constructed higher excitations:

$$\langle \mu_{\mathrm{GASCC}} | \quad = \quad \left\langle \mu^{S(\mathrm{III}^1)} \right| + \left\langle \mu^{S(\mathrm{IV}^1)} \right| + \left\langle \mu^{D(\mathrm{III}^2)} \right| + \left\langle \mu^{D(\mathrm{IV}^2)} \right| + \left\langle \mu^{D(\mathrm{III}^1+\mathrm{IV}^1)} \right|$$
$$+ \left\langle \boldsymbol{\mu}^{\mathbf{T}(\mathbf{III}^1+\mathbf{IV}^2)} \right| + \left\langle \boldsymbol{\mu}^{\mathbf{T}(\mathbf{III}^2+\mathbf{IV}^1)} \right| + \left\langle \boldsymbol{\mu}^{\mathbf{Q}(\mathbf{III}^2+\mathbf{IV}^2)} \right|$$

Relativistic Correlation Methods

Laboratoire de Chimie et Physique Quantiques

Rel. Kramers-Unrestricted GAS-CC

CI-based CC vector function

$$\Omega_\mu = \left\langle \mu \left| e^{-\hat{T}} \hat{H} e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$$

1. $|a\rangle = e^{\hat{T}} |\mathrm{Ref}\rangle = \left(\sum_{n=0} \frac{1}{n!} \hat{T}^n \right) |\mathrm{Ref}\rangle$
2. $|b\rangle = \hat{H} |a\rangle$ (CI sigma vectors)
3. $|c\rangle = e^{-\hat{T}} |b\rangle = \left(\sum_{n=0} \frac{(-1)^n}{n!} \hat{T}^n \right) |b\rangle$
4. $\Omega_\mu = \langle \mu | c \rangle = \left\langle \mathrm{Ref} \left| \hat{\tau}_\mu^\dagger \right| c \right\rangle$ (CI density matrices)

T. Fleig, L. K. Sørensen, J. Olsen, *Theo Chem Acc* **118,2** (2007) *347*

Commutator-based CC vector function

$$\Omega_\mu = \left\langle \mu \left| \left(\hat{H} + \left[\hat{H}, \hat{T} \right] + \tfrac{1}{2} \left[\left[\hat{H}, \hat{T} \right], \hat{T} \right] \ldots \right) \right| \mathrm{Ref} \right\rangle$$

- ↻ Loop over rel. excitation class of $\hat{H}$
  - ↻ Loop over commutator type, e.g. $\left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right]$
    - ↻ Loop over rel. excitation types $\hat{T}_i$ of $\hat{T}$ operators
      - ! Check for coupling with $\langle \mu |$
      - Yes? Contract with integrals
    - ↙ End loop
  - ↙ End loop
- ↙ End loop

L. K. Sørensen, T. Fleig, J. Olsen, *Z Phys Chem* **224** (2010) *999*

CI-based linear response (LR) function

$$A_{\mu\nu} = \left\langle \mu \left| e^{-\hat{T}} \left[\hat{H}, \hat{\tau}_\nu \right] e^{\hat{T}} \right| \mathrm{Ref} \right\rangle$$

Commutator-based LR function

$$A_{\mu\nu} = \left\langle \mu \left| \left(\left[\hat{H}, \hat{\tau}_\nu \right] + \left[\left[\hat{H}, \hat{\tau}_\nu \right], \hat{T} \right] + \tfrac{1}{2} \left[\left[\left[\hat{H}, \hat{\tau}_\nu \right], \hat{T} \right], \hat{T} \right] \ldots \right) \right| \mathrm{Ref} \right\rangle$$

Properties of the implementation:

- Very general approach
- Increased "N-scaling": $O^{n+2}V^{n+2}$

- General approach, currently some limitations
- Conventional "N-scaling": $O^n V^{n+2}$

Application of GAS-CC

BiH: Spectral constants of $0^+(^3\Sigma^-)$ ground state

L. K. Sørensen, J. Olsen, T. Fleig, *J Chem Phys* (2010) *in preparation.*

- Setup:

  Unc. cc-pCVTZ (Bi) / cc-pVTZ (H)
  $[30s26p17d13f1g]$ / $[5s2p1d]$
  Cutoff virtual spinors: 5.6 a.u.

  Dirac-Coulomb Hamiltonian (no SOO)

  $\sigma_{1/2}$, $\pi_{1/2}$, $\pi_{3/2}$ occupied

CC model	R_e[Å]	ω_e[cm^{-1}]
CCSD 6	1.822	1694
MRCCSD (6in5)	1.826	1676
CCSD(T) 6	1.824	1685
CCSDT 6	1.824	1681
CCSDTQ 6	1.825	1681
CCSD 16	1.792	1726
CCSD(T) 16	1.793	1709
CCSDT 16	1.793	1709
Exp.[8]	1.809	1700

- R_e, ω_e:
  outer-core $(5d)$ correlation $>$ Higher excitations
- CCSDT 16 feasible for complete potential curves
- Alternative: MRCCSD (6in5) active-space model (GAS problem)

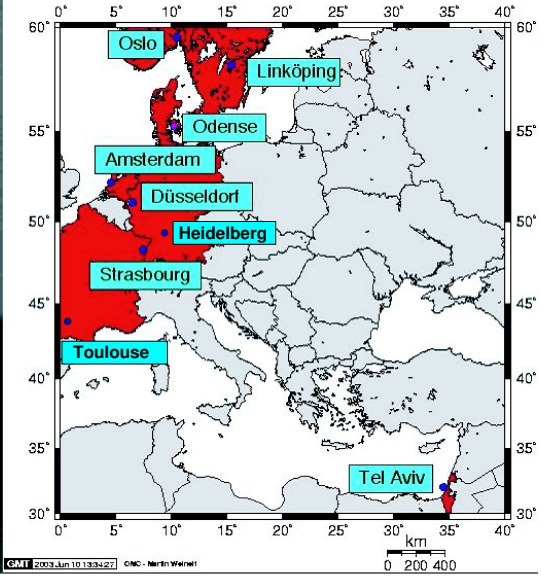
[8] Diode laser / IR Spectroscopy, Bernath et al. (1991), Urban et al. (1989)

DIRAC –

a European metalaboratory for the development of relativistic 4- and 2-component quantum-physical and -chemical methodology

P rogram
• for
A tomic
• and
M olecular

D irect
I terative
R elativistic
A ll-electron
C alculations



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Projets concernant ...

la relativité et la théorie à N corps

Haute précision:

Théorie de la réponse linéaire pour des fonctions d'onde CC relativiste
(Mickael Hubert et Timo Fleig)

Interaction de Gaunt pour des méthodes corrélées à 4 composantes
(Timo Fleig, collaboration avec Trond Saue)

Systèmes de plus grande taille:

Implémentation d'une approximation du type GAS-CC(n) dans le cadre relativiste
(?? et Timo Fleig)

Physique fondamentale:

Nonconservation de la parité dans les systèmes moléculaires
(Timo Fleig, collaboration avec Trond Saue)

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Comparison of Methods

Vertical electronic spectrum of I_3^-; 2.93 Å, Ω states

A.S.P. Gomes, L. Visscher, H. Bolvin, T. Saue, S. Knecht, T. Fleig, E. Eliav, *J Chem Phys* **XXX** (2009) *to be submitted.*

$$[\,I-I-I\,]^-$$

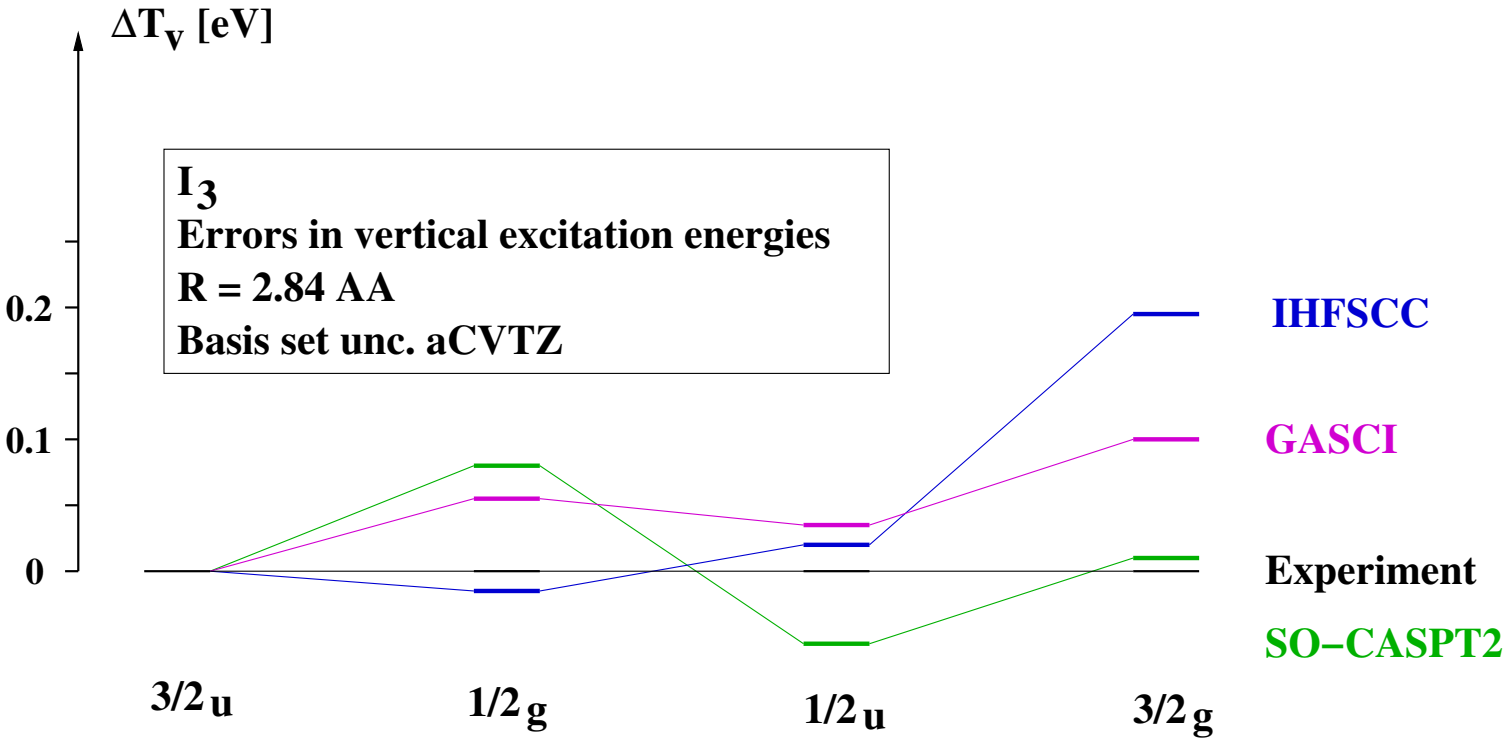
- Prototype for S_N2 reactions
- Example of hyperconjugation

- Excited states involved in photodissociation dynamics[9]
- High-accuracy PEC/Ss for subsequent wave-packet dynamics
- **Comparison of methodologies:**
  - Efficient description of dynamic electron correlation
  - Proper description of spin-orbit interaction
  - Method yields correct dissociation limits
  - Contestants: rel. IHFSCC, SO-CASPT2, rel. MRCI, rel. TDDFT

[9] J. Vala, R. Kosloff, J.N. Harvey, J Chem Phys **114** (2001) *7413*
R. Nakanishi, N. Saitou, T. Ohno, S. Kowashi, S. Yabushita, T. Nagata, J Chem Phys **126** (2007) *204311*

Comparison of Methods

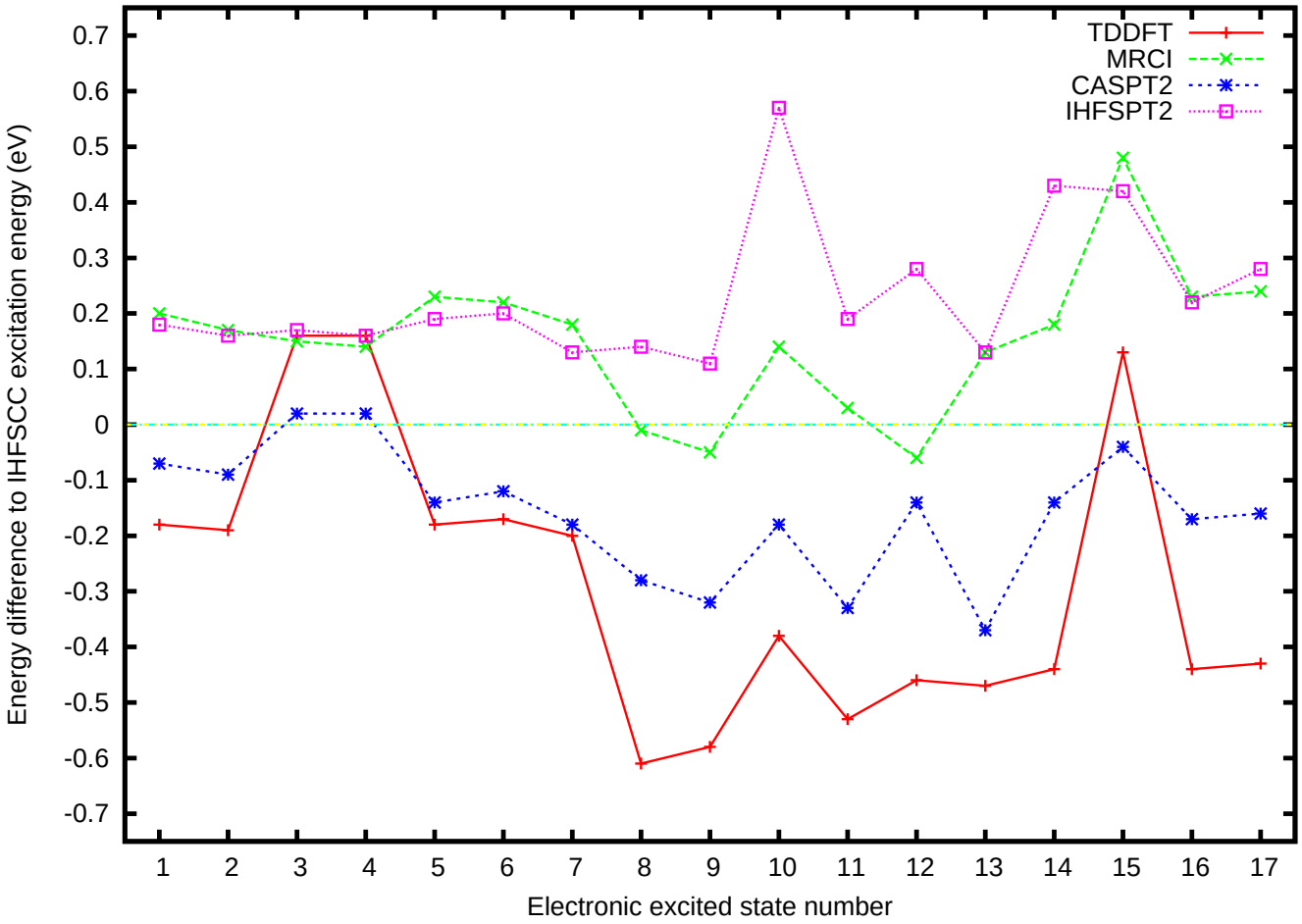
Vertical electronic spectrum of I_3; 2.84 Å, Ω states



- Errors of rel. MRCI systematic and < 0.1 eV
- SO-CASPT2 less systematic but also with small errors
- Error of IHFSCC likely due to linear parameterization for excited states (in this case)

Comparison of Methods

Vertical electronic spectrum of I_3^-; 2.93 Å, Ω states



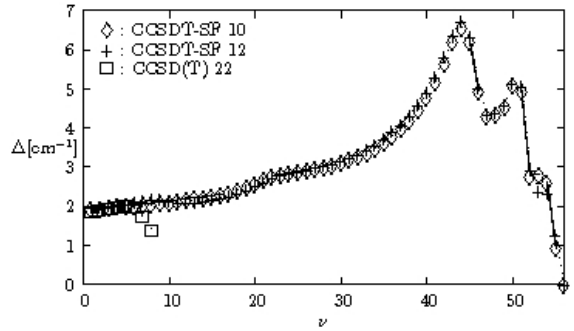
- TDDFT: large spread; CASPT2, MRCI: Similar quality, MRCI more systematic, IHFSPT2 inferior

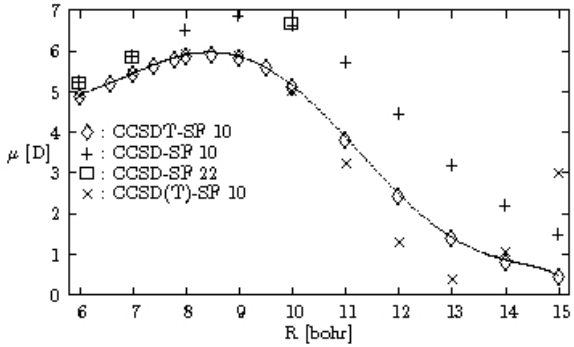
Application of GAS-CC

LiCs $^1\Sigma$: Vibrational levels and electric properties

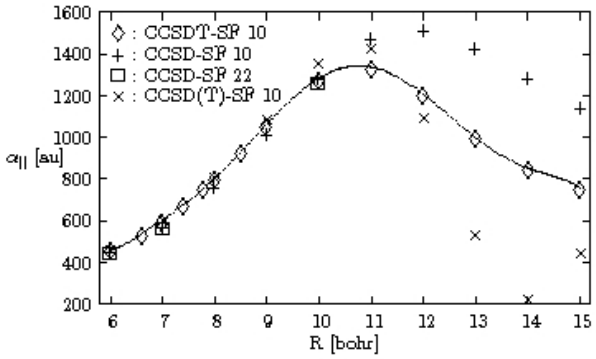
L. K. Sørensen, T. Fleig, J. Olsen, *J Phys B: At Mol Opt Phys* **42** (2009) *165102*

- Vibrational levels up to dissociation limit
  Change of level distance
  - criterion for quality of full curve
  - perturbative triples models deteriorate early
  - full triples yield balanced description
  - CCSDTQ for highest accuracy required





- Dipole moment and static polarizability
  - required in studies on ultracold molecules
  - CCSD insufficient
  - perturbative models insufficient beyond bonding region
  - CCSDT balanced and yields accurate results

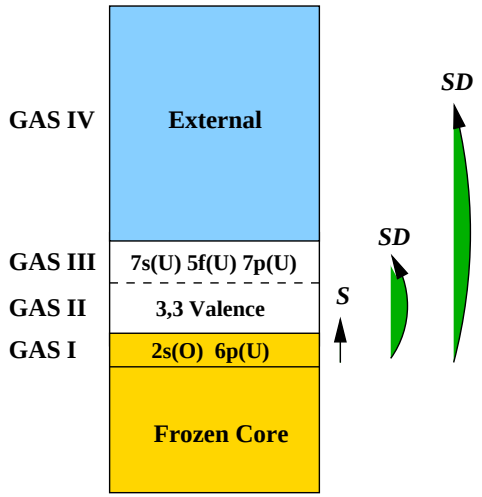


Application of Relativistic CI/MCSCF

UO_2 vertical excitation energies

T. Fleig, H. J. Aa. Jensen, J. Olsen, L. Visscher, J Chem Phys **124,10** (2006) *104106*

- u state manifold $\mathrm{U}(5\mathrm{f}^1\ 7\mathrm{s}\sigma_\mathrm{g}^1)\mathrm{O}_2$
  g state manifold $\mathrm{U}(5\mathrm{f}^2)\mathrm{O}_2$
- Weak dependence of excitation energies on internuclear distance (ca. 200 cm^{-1})
- Differential matrix effect unclear
  (est. $<< 500\,\mathrm{cm}^{-1}$)



State (Ω_{par}) U-O separation	SOCI(Col.)[8] 3.402 a_0	SO/CASPT2[9] 3.452 a_0	GASCI 14$^{(DCHF)}$ 3.372 a_0	^{3g1h} CV-GASCI 24 3.372 a_0	Exp. [cm^{-1}]
2_u	0	0	0	0	0
3_u	431	378	427		360[10]
1_u	1088	2567	1089		*1094*[11]
2_u	1566	2908	1542	2042	*1401*[11]

[8] Thesis by Q. Chang, Ohio State University (2002); COLUMBUS program

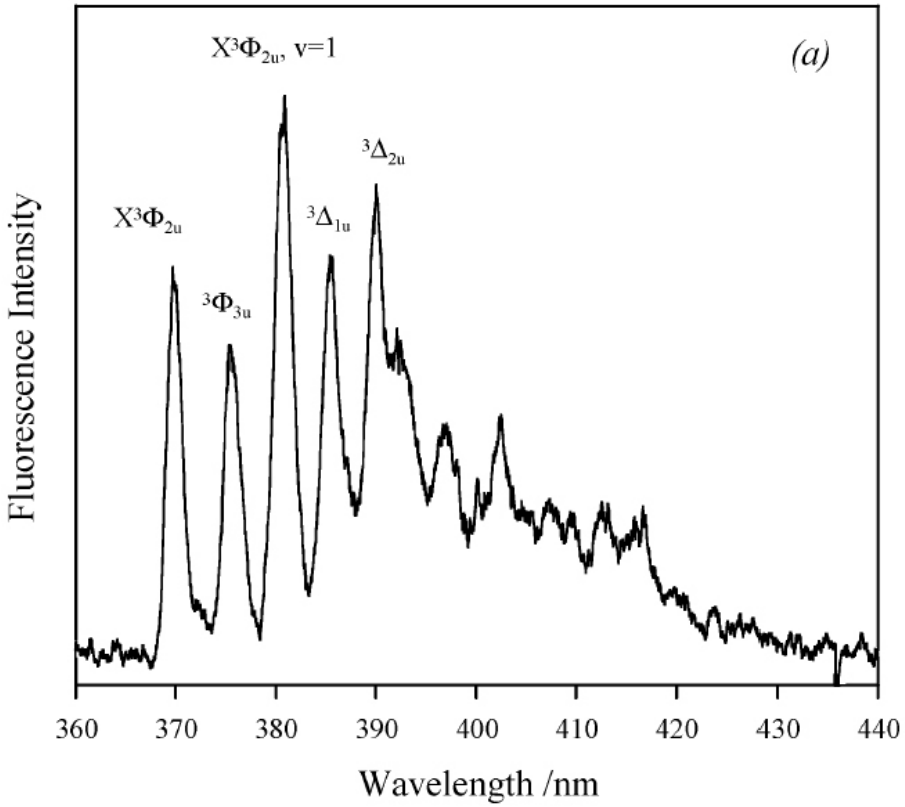
[9] L. Gagliardi, M. C. Heaven, J. W. Krogh, B. O. Roos, J Am Chem Soc **127** (2005) 86

[10] J. Han, V. Goncharov, L.A. Kaledin, A.V. Komissarov, M.C. Heaven, J Chem Phys **120** (2004) 5155

[11] C.J. Lue, J. Jin, M.J. Ortiz, J.C. Rienstra-Kiracofe, M.C. Heaven, J Am Chem Soc, **126** (2004) 1812

Application of Relativistic CI/MCSCF

UO_2 vertical excitation energies, theory/experiment



- Matrix emission spectrum[12] (argon)
- $^3\Delta_{1u,2u}$: Assignment based on inexact calculations !
- $2_u, 3_u$: Nearly parallel PECs
- New assignment:[13] Vibrational progression of $^3\Phi_{2u,3u}$ states

Matrix shift remains unresolved

More advanced experiments (and calculations) in progress

[12] C.J. Lue, J. Jin, M.J. Ortiz, J.C. Rienstra-Kiracofe, M.C. Heaven, J Am Chem Soc, **126** (2004) 1812

[13] M.C. Heaven, Phys. Chem. Chem. Phys., **8** (2006) 4497

Application MRCI

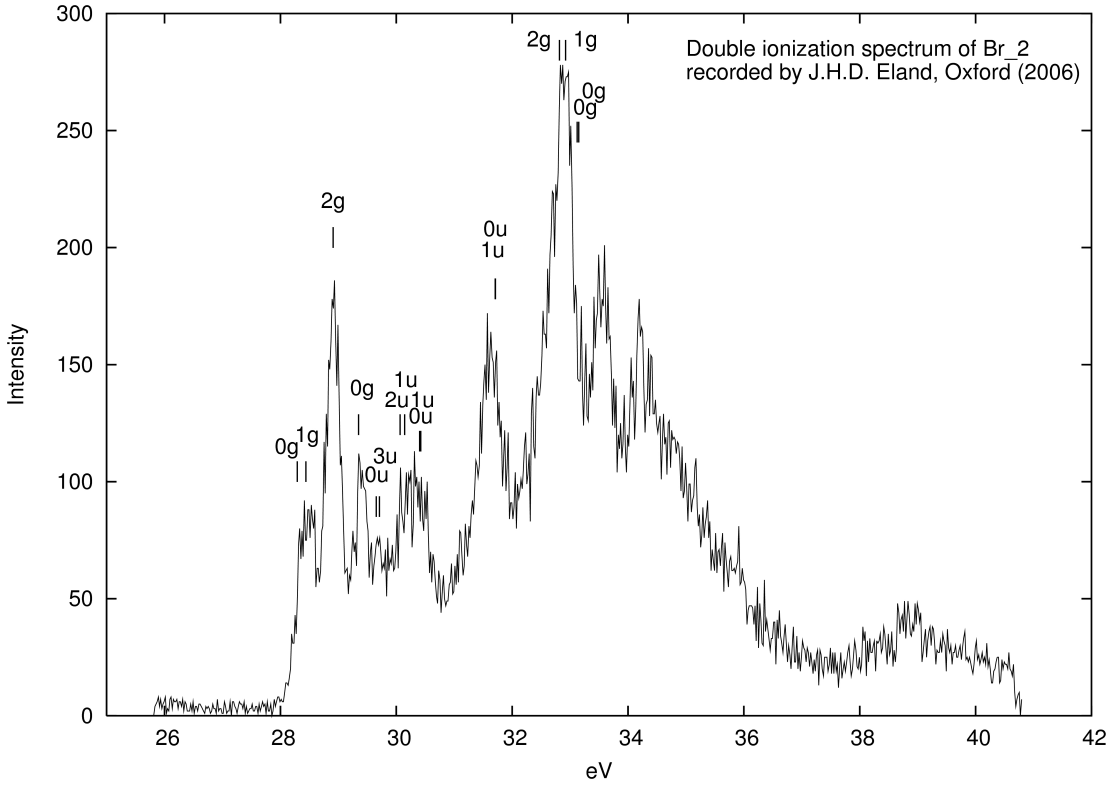
Double photoionisation of Br_2

T. Fleig, D. Edvardsson, S. T. Banks, J. H. D. Eland, *Chem Phys* **343** (2008) *270*

Process: $Br_2 \xrightarrow{h\nu} Br_2^{2+}$, various types of ionizations
Double ionisation spectra via TOF-PEPECO[15]

Characteristics:

- High accuracy:
  est. vertical errors: < 0.03 eV
- Main part of
  spectrum assigned
- PECs de Br_2^{2+} and Br_2
  aid for experimental
  studies
  R_e, ω_e, D_e, $T_{e,v}$, FCFs



[15] J.H.D. Eland, O. Vieuxmaire, T. Kinugawa, P. Lablanquie, R.I. Hall, F. Penent, Phys Rev Lett **90** (2003) *053003*