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## Theoretical study of low-lying states of UH

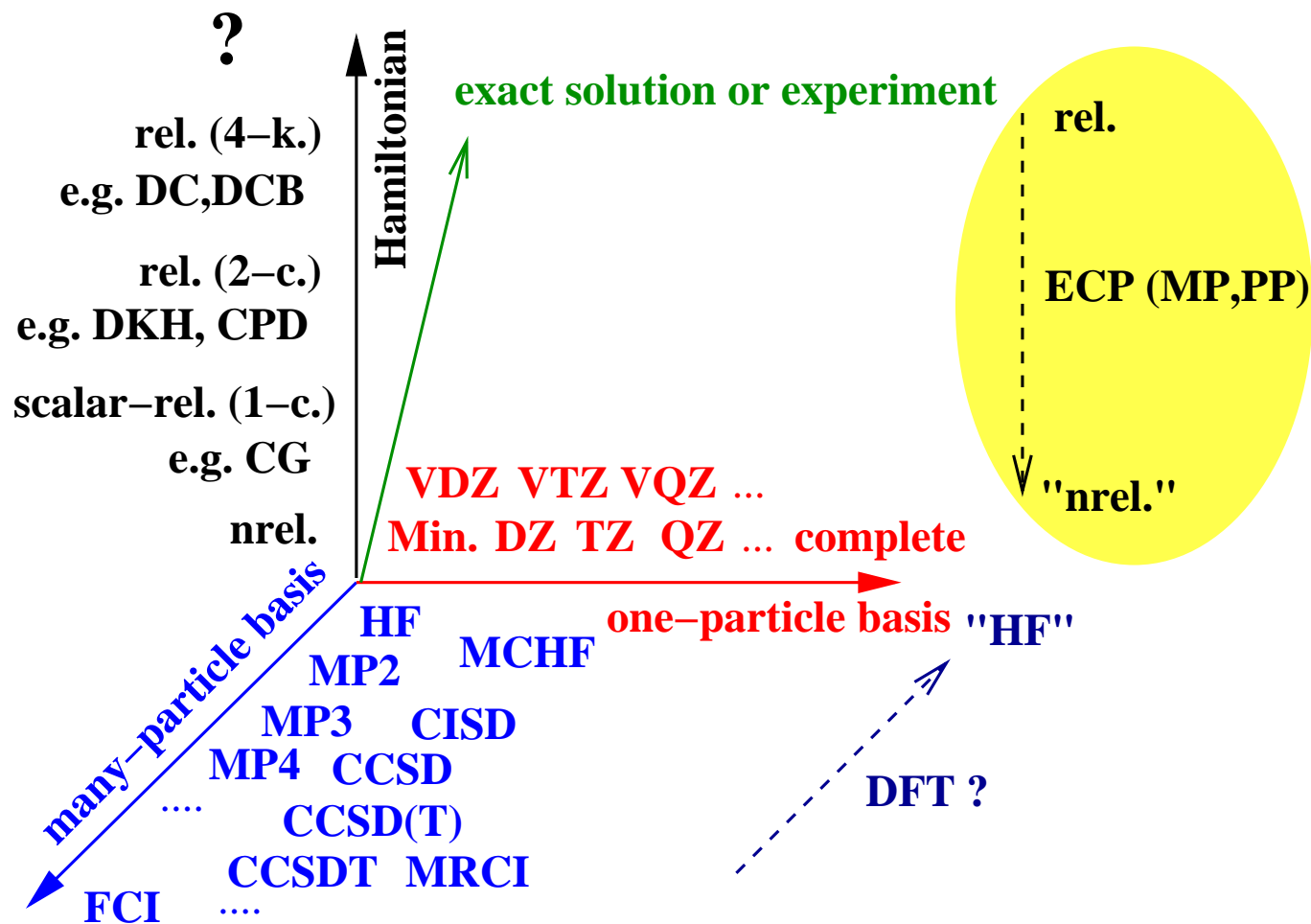
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### Contents:

- A new relativistic energy-consistent small-core pseudopotential\* for U supplemented by pVDZ, pVTZ and pVQZ generally contracted ANO valence basis sets
- Some preliminary results for UH and ‘calibration’ against all-electron data

\*‘Stuttgart-(Dresden→Bonn→Cologne)’ PPs and corresponding valence basis sets:

<http://www.theochem.uni-stuttgart.de>



**Wanted: suitable compromise between accuracy and computational effort !**

Note: ECPs lead to reductions in the sizes of the one- and many-electron basis sets and incorporates the most important relativistic effects at low cost !

all-electron case:

Dirac-Coulomb-Breit Hamiltonian

$$\mathcal{H} = \sum_i^n h(i) + \sum_{i<j}^n g(i, j) + V_{NN}$$

$$h_D(i) = c\vec{\alpha}_i\vec{p}_i + (\beta_i - \mathbf{I}_4)c^2 + V_{Nn}$$

$$V_{Nn}(i) = \sum_{\lambda}^N \left( -\frac{Z_{\lambda}}{r_{\lambda i}} \right)$$

$$g_{CB}(i, j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}} \left[ \vec{\alpha}_i \vec{\alpha}_j + \frac{(\vec{\alpha}_i \vec{r}_{ij})(\vec{\alpha}_j \vec{r}_{ij})}{r_{ij}^2} \right]$$

$$V_{NN} = \sum_{\lambda < \mu}^N \frac{Z_{\lambda} Z_{\mu}}{r_{\lambda \mu}} .$$

possibly augmented by finite nucleus effects, frequency dependence of electron interaction, vacuum polarization, electron self-energy, ...

valence-electron-only case:

pseudopotential Hamiltonian

$$\mathcal{H}_v = \sum_i^{n_v} h_v(i) + \sum_{i<j}^{n_v} g_v(i, j) + V_{cc}$$

$$h_v(i) = -\frac{1}{2}\Delta_i + V_{cv}(i)$$

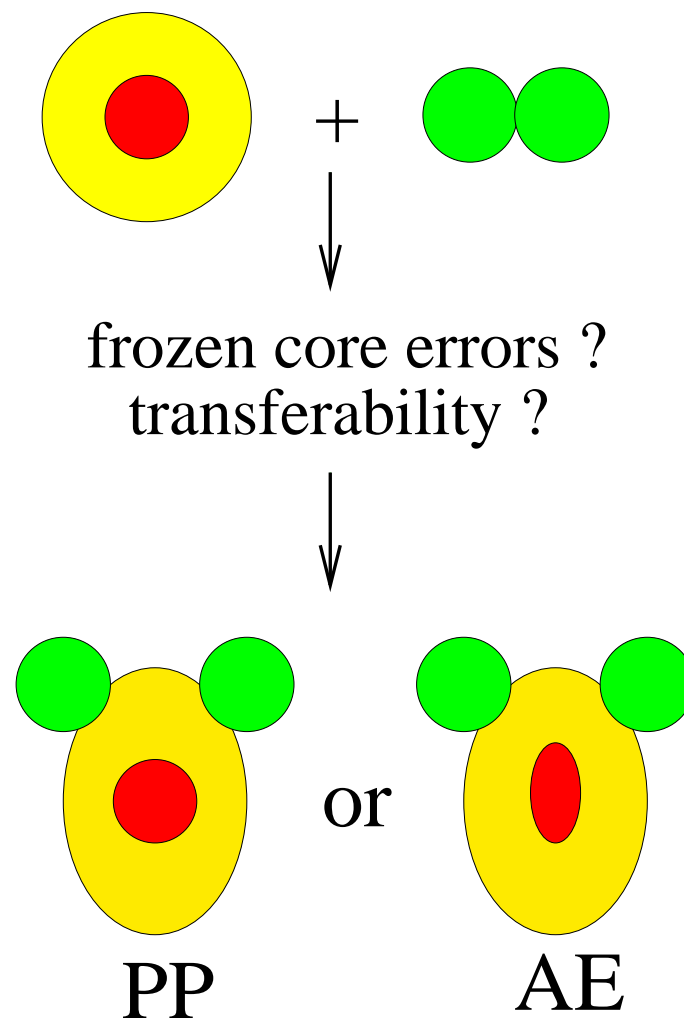
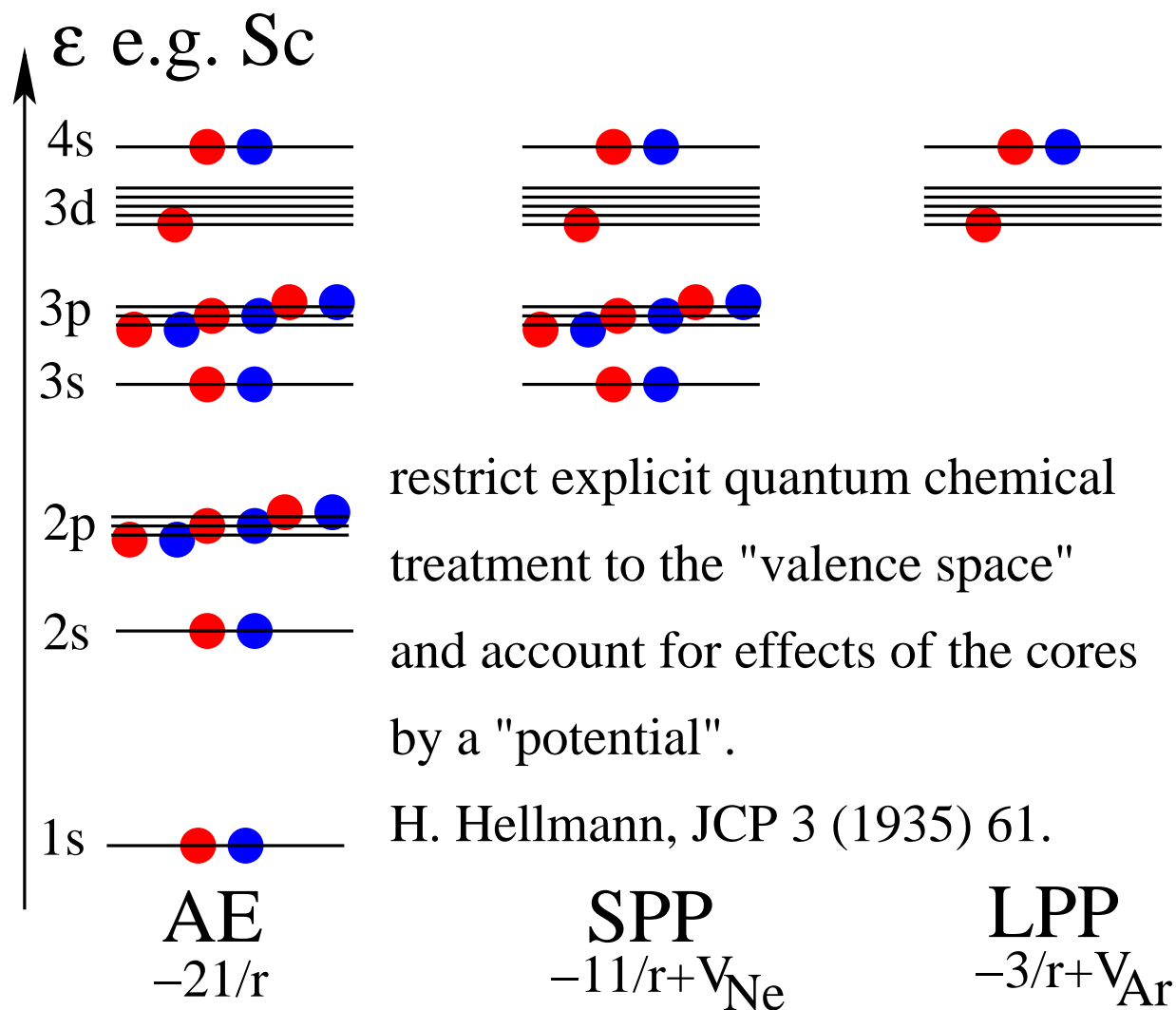
$$V_{cv}(i) = \sum_{\lambda}^N \left( -\frac{Q_{\lambda}}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i}) \right)$$

$$g_v(i, j) = g_C(i, j) = \frac{1}{r_{ij}}$$

$$V_{cc} = \sum_{\lambda < \mu}^N \frac{Q_{\lambda} Q_{\mu}}{r_{\lambda \mu}}$$

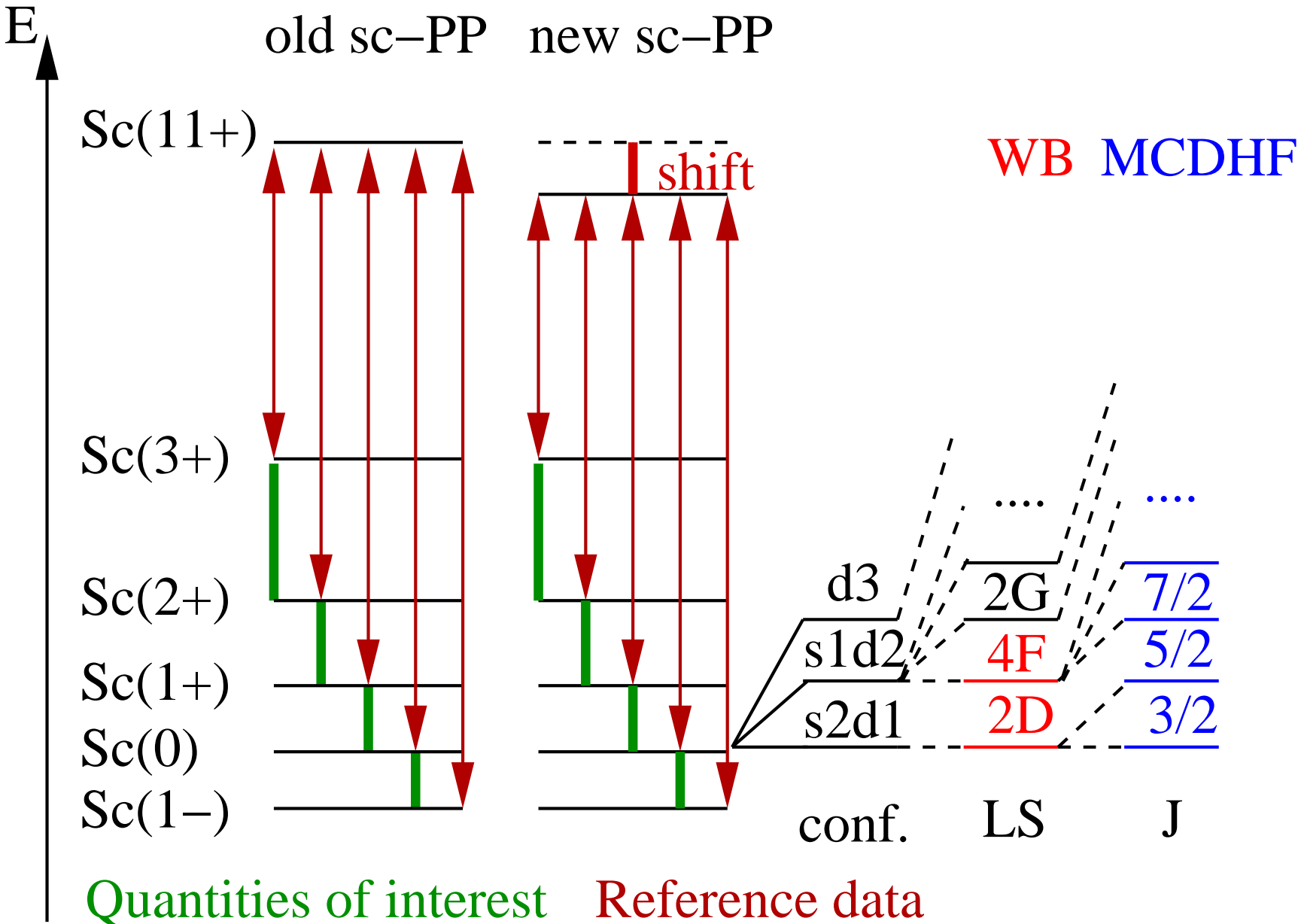
reduction of the computational effort, implicit incorporation of relativistic effects in formally non-relativistic electronic structure calculations.

*Relativistic effective core potentials. The relativistic energy-consistent ab initio pseudopotential approach and its application to lanthanide and actinide compounds.* M. Dolg, X. Cao, in: *Recent Advances in Computational Chemistry*, vol. 6, p. 1 - 35, eds. K. Hirao, Y. Ishikawa, World Scientific, New Jersey (2004).



Method of adjustment:

least-squares-fit of total valence energies (quantum mechanical observables !)



## MCDHF calculations for U: choice of reference data

U AE DHF results (in  $\text{cm}^{-1}$ ):

5f 6d 7s 7p	result ----- deviation ----				5f 6d 7s 7p	result -- deviation --				5f 6d 7s 7p	result ----- deviation ----				5f 6d 7s 7p	result -- deviation --			
	HFDB	HFDB	HFD+B	HFD		MCDHF/DC+B	MCDHF/DC+B(w)				HFDB	HFDB	HFD+B	HFD		MCDHF/DC+B	MCDHF/DC+B(w)		
	Fermi	Point	Fermi	Fermi		Fermi	Fermi nucleus				Fermi	Point	Fermi	Fermi		Fermi	Fermi nucleus		
	A=238		A=238	A=238		A=238	A=238				A=238		A=238	A=238		A=238	A=238		
	(*)	(*)	(*)	(*)		(**)	(**)				(*)	(*)	(*)	(*)		(**)	(**)		
5	99459	252	4	1126		99462.63	26.79			2 3 1	15120	28	-1	-675					
										2 3	59251	119	-1	-611		59248.83	-31.22		
4 2	49572	223	3	709						2 2 2	4640	-85	-1	-779		4638.54	-24.64		
4 1 1	30790	154	2	670		30792.34	17.68			2 2 1 1	23857	2	-1	-764					
4 1 1	47895	222	2	706		47896.84	11.76			2 2 1	49992	-10	-1	-729		49990.25	-30.11		
4 1	69159	224	2	735		69161.06	13.55			2 1 2 1	17449	-129	-1	-897		17447.06	-34.13		
4 2	15780	76	2	627		15782.04	20.13			2 1 2	47433	-156	-1	-862		47431.36	-28.98		
4 1 1	30712	138	2	648		30713.75	13.03			2 2 1						76494.09	-43.27		
4 1	54593	126	1	677		54594.01	15.82			2 1 1 1						74925.44	-42.91		
4						80130.98	5.36												
										1 4 1	38781	-49	-2	-1549		38779.68	-53.48		
3 2 1	13124	97	0	78						1 4	85256	54	-2	-1477		85254.51	-59.25		
3 2	54576	177	0	138		54575.18	-6.55			1 3 2	31450	-176	-2	-1673		31448.66	-52.56		
3 1 1 1	17200	75	0	14						1 3 1 1	52488	-78	-2	-1655					
3 1 2	0	0	0	0		0.00	0.00			1 3 1	79451	-89	-2	-1616		79449.36	-58.37		
3 1 1	42328	63	0	44		42327.62	-5.05			1 2 2	80779	-251	-2	-1769		80777.54	-57.39		
3 2 1	7516	-40	0	-93		7516.23	-8.28			1 2 2 1	49776	-224	-2	-1810					
3 2	36289	-68	0	-62		36288.95	-3.63			1 2 1 1						10350.39	-72.16		
3 1 1						61569.42	-16.62			1 1 2 1						16100.09	-72.68		
3 1						70265.01	-16.63												
										4 1						31966.53	-89.31		
										4 2						81605.91	-83.19		

(\*) Mosyagin, Petrov, Titov, Tupitsyn, in: Progress in Theoretical Chemistry and Physics, Vol. 15, Springer, 2006

(\*\*) GRASP; this work.

→ red contributions are included in the reference calculations: (Scalar relativistic effects > spin-orbit effects >) Breit interaction (up to  $O(10^3 \text{cm}^{-1})$ ) > finite nucleus effects (up to  $O(10^2 \text{cm}^{-1})$ ) > radiation corrections (up to  $O(10^1 \text{cm}^{-1})$ ) >> self-consistency of Breit term ( $O(1 \text{cm}^{-1})$ ).

still unclear: importance of vacuum polarisation and self-energy corrections !

**New:** U MCDHF/DC+B PP: 100 configurations (yielding 30190 J-levels) of U to  $U^{7+}$ :

[illegible]

## Small-core PPs for actinides: reference states used for U

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U(3+) ctnd.										U(5+) ctnd.									
5s2	5p6	5d10	5f1	6s2	6p6	6d1	7s1		39	5s2	5p6	5d10	6s2	6p6	7s1				2
5s2	5p6	5d10	5f1	6s2	6p6	6d1		7p1	113	5s2	5p6	5d10	6s2	6p6		7p1			2
5s2	5p6	5d10	5f1	6s2	6p6		7s2		2	5s2	5p6	5d10	6s2	6p6			8s1		1
5s2	5p6	5d10	5f1	6s2	6p6			7s1	24	5s2	5p6	5d10	6s2	6p6			9s1		1
5s2	5p6	5d10		6s2	6p6	6d3			19	5s2	5p6	5d10	6s2	6p6			8p1		2
5s2	5p6	5d10		6s2	6p6	6d2	7s1		16	5s2	5p6	5d10	6s2	6p6			9p1		2
5s2	5p6	5d10		6s2	6p6	6d1	7s2		2	5s2	5p6	5d10	6s2	6p6			7d1		2
5s2	5p6	5d10		6s2	6p6		7s2	7p1	2	5s2	5p6	5d10	6s2	6p6			8d1		2
U(4+)										5s2	5p6	5d10	6s2	6p6			9d1		2
5s2	5p6	5d10	5f2	6s2	6p6				13	5s2	5p6	5d10	6s2	6p6			6f1		2
5s2	5p6	5d10	5f1	6s2	6p6	6d1			20	5s2	5p6	5d10	6s2	6p6			7f1		2
5s2	5p6	5d10	5f1	6s2	6p6		7s1		4	5s2	5p6	5d10	6s2	6p6			8f1		2
5s2	5p6	5d10	5f1	6s2	6p6			7p1	12	5s2	5p6	5d10	6s2	6p6			9f1		2
5s2	5p6	5d10		6s2	6p6	6d2			9	U(6+)									
5s2	5p6	5d10		6s2	6p6	6d1	7s1		4	5s2	5p6	5d10	6s2	6p6					1
5s2	5p6	5d10		6s2	6p6	6d1		7p1	12	U(7+)									
5s2	5p6	5d10		6s2	6p6		7s2		1	5s1	5p6	5d10	6s2	6p6					1
5s2	5p6	5d10		6s2	6p6		7s1	7p1	4	5s2	5p5	5d10	6s2	6p6					2
U(5+)										6s2	6p6	5d9	6s2	6p6					2
5s2	5p6	5d10	5f1	6s2	6p6				1	5s2	5p6	5d10	6s1	6p6					1
5s2	5p6	5d10		6s2	6p6	6d1			2	5s2	5p6	5d10	6s2	6p5					2

Introduction of the core energy shift  $\Delta E_{shift}$  allows the inclusion of higher ionized states to the reference data set, including some with holes in 5s, 5p, 5d, 6s and 6p semi-core orbitals. Supplemented by pVDZ, pVTZ and pVQZ basis sets.

MD, in preparation.

**Old:** U WB PP +  $\Delta$ DHF SO: 13 LS states of U and U<sup>+</sup>; no holes in semi-core orbitals considered. Later augmented by multi-state multi-electron adjusted valence (5f, 6d, 7p) SO terms for use in either perturbation theory or variational calculations/spin-orbit CI and supplemented by pVDZ, pVTZ and pVQZ basis sets.

W. Küchle, MD, H. Stoll, H. Preuß, J. Chem. Phys. 100 (1994) 7535; X. Cao, MD, H. Stoll, J. Chem. Phys. 118 (2003) 487.

Nevertheless very good results are obtained using the WB PP, e.g., for UF<sub>6</sub>

cf. E. R. Batista, R. L. Martin, P. J. Hay, J. E. Peralta, G. E. Scuseria, J. Chem. Phys. 121 (2004) 2144.



Test case U  $IP_1$  to  $IP_4$

U  $5f^3 6d^1 7s^2$   $J=6 \rightarrow U^+ 5f^3 7s^2$   $J=9/2 \rightarrow U^{2+} 5f^4$   $J=4 \rightarrow U^{3+} 5f^3$   $J=9/2 \rightarrow U^{4+} 5f^2$   $J=4$

configurational averages (in eV)

	SPP, WB	AE, WB	AE, DC	AE, DC+B	SPP, DC+B	AE, HF
$IP_1$	4.5540	4.5267	4.4916	4.4993	4.4976	6.3872
$IP_2$	12.4644	12.5087	12.7351	12.6333	12.6324	3.7030
$IP_3$	16.3815	16.3693	16.1322	16.2146	16.2135	21.9880
$IP_4$	29.9814	29.8940	29.5774	29.6819	29.6844	36.6348

SPP, WB vs. AE, WB: errors of the SPP 0.1 eV or less !

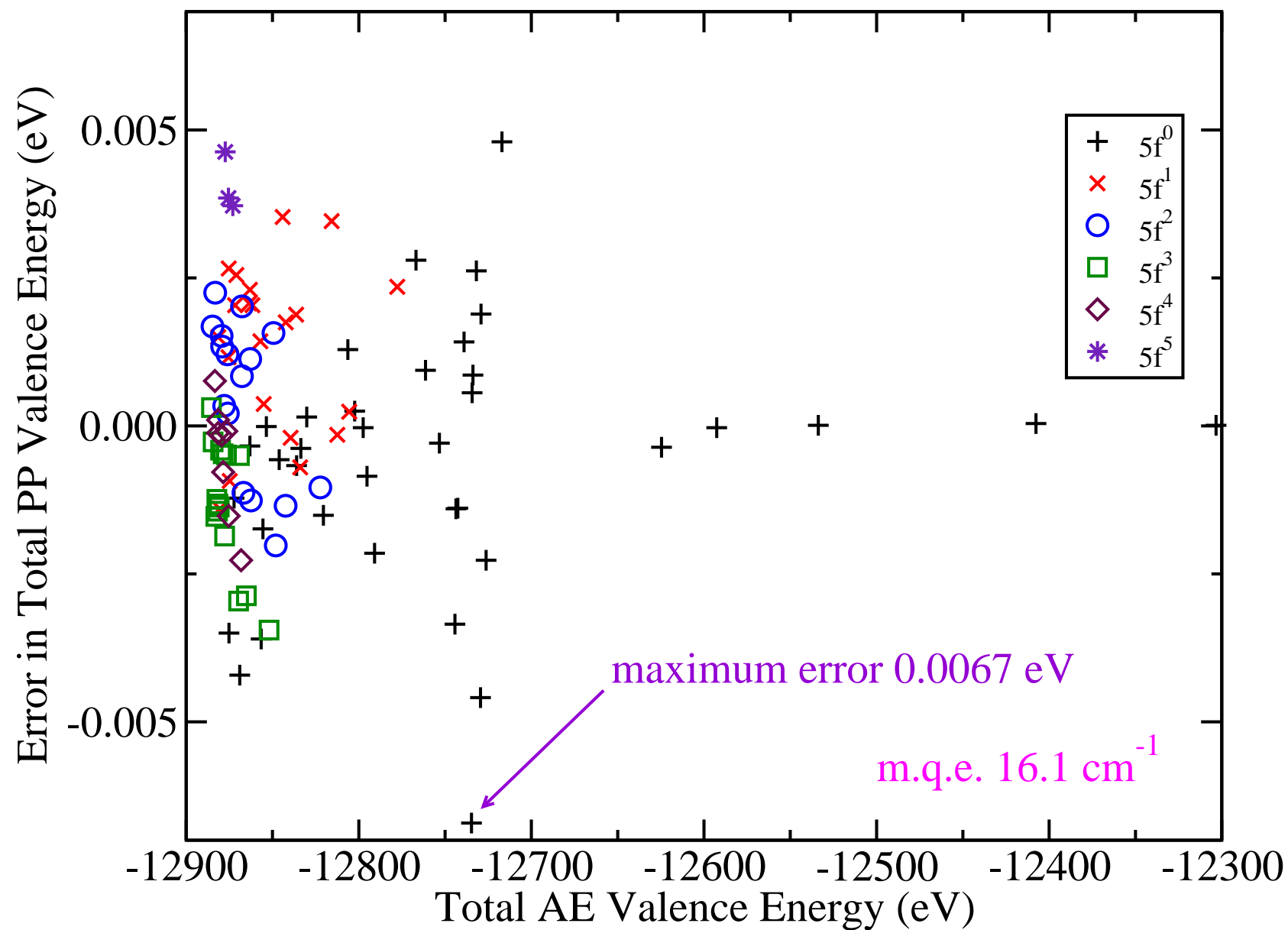
AE, WB vs. AE, DC: deviations of up to 0.3 eV ! Note:  $IP_2+IP_3$  AE, WB 28.8780 eV, AE DC 28.8673 eV  $\rightarrow$  The problems mainly arise for changing f occupation numbers ! AE, WB (usually) agrees even 'better' with AE, DC+B than with AE, DC.

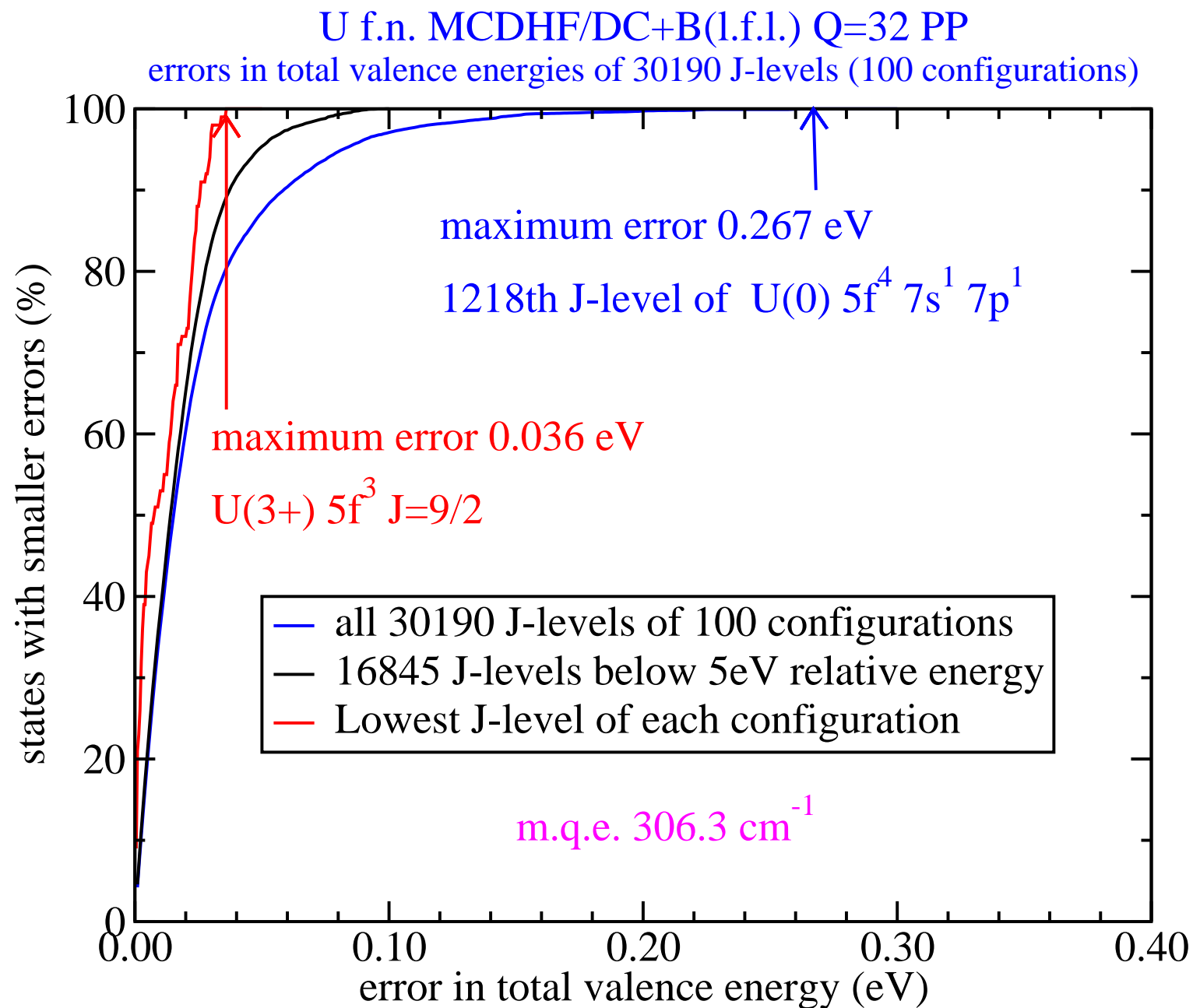
lowest J-levels (in eV)

	SPP, WB SO per.	SPP, WB SO var.	AE, DC	AE, DC+B	SPP, DC+B
$IP_1$	5.5625	5.5729	5.5380	5.5399	5.5108
$IP_2$	11.6142	11.5995	11.9457	11.8455	11.8451
$IP_3$	17.1710	17.1878	16.8616	16.9430	16.9372
$IP_4$	31.5465	31.5575	31.0744	31.1704	31.1853

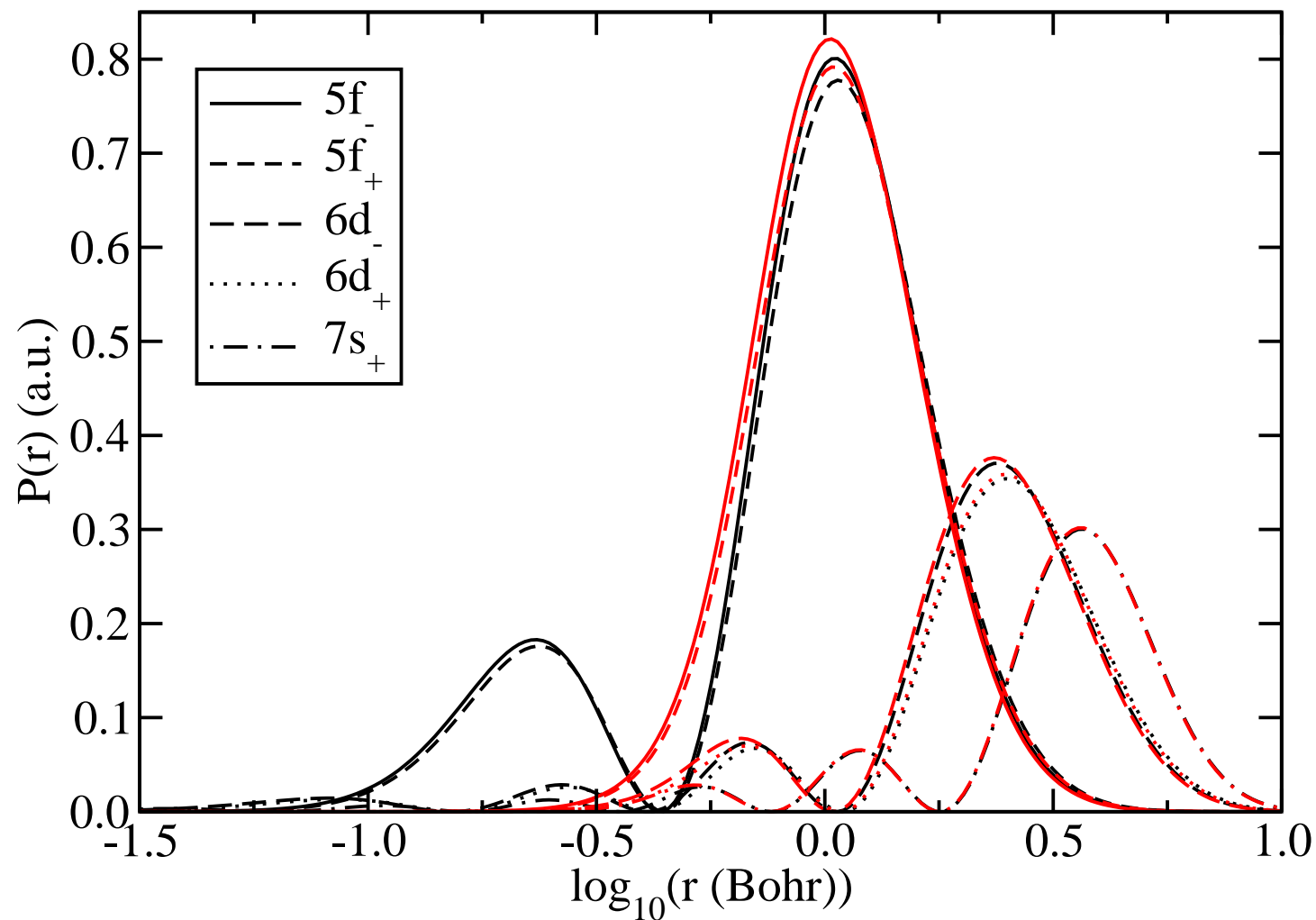
The errors in excitation energies are usually smaller than in IPs, e.g., U  $5f^3 6d^1 7s^2 \rightarrow U 5f^4 7s^2$  WB 1.8651 eV, DC 2.0342 eV, DC+B 1.9568 eV, SPP WB 1.8779 eV.

U f.n. MCDF/DC+B(1.f.1.) PP Q=32  
errors in valence energies of 100 non-relativistic configurations

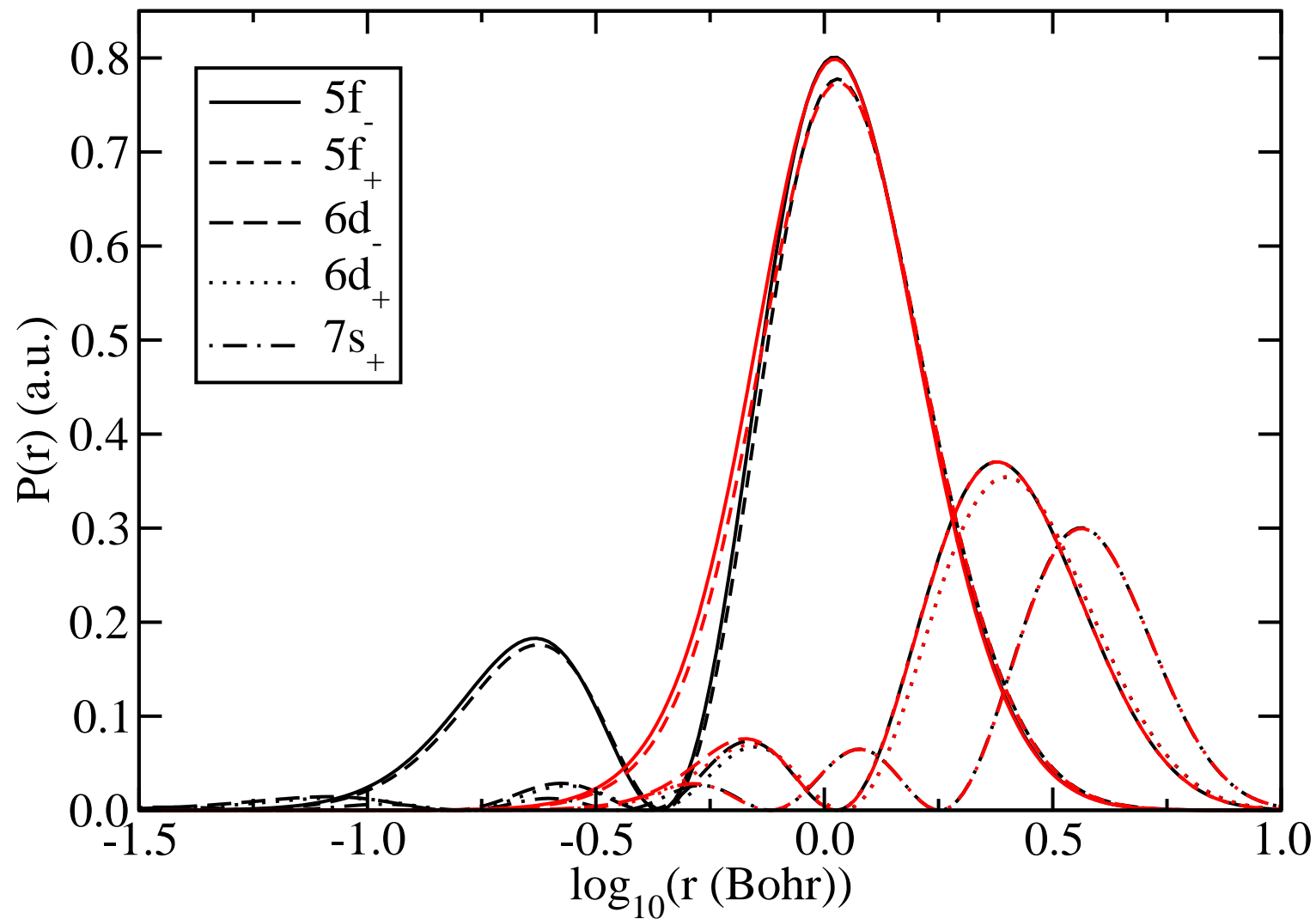




U  $5f^3 6d^1 7s^2$  (AE MCDHF vs. ECP60MWB + SO(5f,6d))  
 PP: state averaged relativistic MCHF (5s,5p,5d,6s,6p scalar-relativistic and frozen)



U  $5f^3 6d^1 7s^2$  (AE MCDHF vs. ECP60(MCDHF/DC+B))  
PP: state averaged relativistic MCHF



## Why UH ?

A ‘simple’ molecule suitable for calibration against relativistic all-electron treatments.

### Question of the ground state:

theory:

- Kraus, Stevens, 1983: RECP, SCF;  ${}^6\Lambda$  g.s. ( $R_e=2.16$  Å,  $\omega_e=1357$  cm $^{-1}$ ).
- Andrews et al., 1997; AE, DFT (ADF);  $S=3/2$  g.s. ( $R_e=2.03$  Å,  $\omega_e=1353$  cm $^{-1}$ ).
- Balasubramanian et al., 2003; RECP, CASSCF/SOCI;  ${}^4I$  g.s. ( $R_e=2.02$  Å,  $\omega_e=1538$  cm $^{-1}$ );  ${}^6\Lambda$  e.s. at 0.14 eV; **but**:  ${}^6\Lambda$  g.s. with  ${}^4I$  e.s. at 0.42 eV (CCSD(T)) and 0.72 eV (MP2).
- Andrews et al., 2007; RECP, PBE;  ${}^4\Phi$  g.s. ( $R_e=1.99$  Å,  $\omega_e=1480$  cm $^{-1}$ ).

→ **spin-orbit effects, Breit interaction, finite nucleus effects, ... not included !**

experiment:

- Andrews et al., 1997;  $\omega$  in Ar-matrix: 1424 cm $^{-1}$ .

### Low-lying electronic states (ground state candidates):

- $U^+ 5f^3 7s^2 {}^4I \ H^- 1s^2 {}^1S \rightarrow {}^4\Lambda$  ( $\Lambda = 0 - 6$ ; e.g.  ${}^4I$ ,  ${}^4H$ ,  ${}^4\Gamma$ ,  ${}^4\Phi$ ,  ${}^4\Delta$ ,  ${}^4\Pi$ ,  ${}^4\Sigma$ );  
lowest levels of  $U^+ 5f^3 6d^1 7s^1$ ,  $5f^3 6d^2$  and  $5f^4 7s^1$  at 289, 4585 and 4664 cm $^{-1}$ , respectively  
→ further possible low-lying states (sextet, quartet; doublet much higher).
- goal: calculation of  $\Omega$  states with term energies below 0.5 eV:  
exploratory calculations yield 9 low-lying  $\Lambda\Sigma$  states, i.e.,  ${}^4I$ ,  ${}^4H$ ,  ${}^4\Gamma$ ,  ${}^4\Phi$ ,  ${}^4\Delta$ ,  ${}^4\Pi$ ,  ${}^4\Sigma$ ,  ${}^6\Lambda$ ,  ${}^6K$   
→ 38  $\Omega$  states.

## How ?

### Hamiltonian and basis sets:

- U: AE DKH (30s26p18d14f7g)/[10s9p7d5f3g] ANO;  
SPP, WB and MCDF/DC+B (14s13p10d8f6g)/[6s6p5d4f3g] ANO.\*
- H: aug-cc-pVQZ (spdf) Dunning.

\*(adding U (3h)/[1h]: MRCI  $\Delta R_e = -0.005 \text{ \AA}$ ,  $\Delta\omega_e = +12 \text{ cm}^{-1}$ ; no change in CASSCF).

### CASSCF reference wavefunction (for MRCI and SOCI(state interaction)):

- Minimum active space: U 5f  $\rightarrow$  3 electrons in 7 orbitals !
- Ideal active space: U 5f, 6d, 7s and 7p, H 1s  $\rightarrow$  7 electrons in 17 orbitals !
- Applied reduced active space: lower  $\sigma^2$  kept doubly occupied, 4 weakly occupied orbitals excluded  $\rightarrow$  5 electrons in 12 orbitals !\*\* 1282 CSFs leading to  $36 \times 10^6$  contracted ( $498 \times 10^6$  uncontracted) configurations in MRCI.

\*\* (CASSCF 5,12 $\rightarrow$ 7,17:  $\Delta R_e = -0.003 \text{ \AA}$ ,  $\Delta\omega_e = -11 \text{ cm}^{-1}$ ).

Selected results for the UH  $5f^3 \sigma^2 \sigma^2 {}^4I$  ( $\Omega = 9/2$ ) ground state

method	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
SPP WB/CASSCF <sup>a</sup>	2.159	1330	
SPP WB/CASSCF <sup>b</sup>	2.076	1442	
SPP WB/CASSCF <sup>c</sup>	2.073	1431	
SPP WB/MRCI+Q	2.008	1501	2.97, 3.06 <sup>f</sup>
SPP MCDF/DC+B/MRCI+Q	2.021	1499	?.??., 3.04 <sup>f</sup>
DKH/MRCI+Q	2.019	1495	2.87, 2.99 <sup>f</sup>
SPP WB/MRCI+Q/SO	2.011	1497	2.85
<b>SPP MCDF/DC+B/MRCI+Q/SO</b>	<b>2.025</b>	<b>1505</b>	<b>2.81</b>
DKH/MRCI+Q/SO <sup>g</sup>	2.021	1483	2.79
<b>exp.<sup>d</sup></b>		<b>1424</b>	
PP/SOCI <sup>e</sup>	2.022	1538	2.26

<sup>a</sup> Minimum active space in CASSCF: 3 electrons in 7 orbitals (U 5f).

<sup>b</sup> Applied active space in CASSCF: 5 electrons in 12 orbitals.

<sup>c</sup> Ideal active space in CASSCF: 7 electrons in 17 orbitals (U 5f, 6d, 7s, 7p, H 1s)

<sup>d</sup> Andrews and coworkers (1997), UH in Argon matrix.

<sup>e</sup> Balasubramanian et al. (2003); active space 7 electrons in 8 orbitals.

<sup>f</sup> calculated wrt neutral atoms (U, H) in separate calculations and ions (U<sup>+</sup>, H<sup>-</sup>) at large distance in one calculation.

<sup>g</sup> new SO results (bigger basis set) still missing !

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## Termenergies (eV) from calculations with spin-orbit coupling (state interaction approach)

		SPP	SPP		AE DKH	
		WB	WB	DCB	bas. 1	bas. 2
No.	$\Omega$	LS(%)	$\Delta E$	$\Delta E$	$\Delta E$	$\Delta E$
1	4.5	$^4\text{I}(80)+^4\text{H}(17)+^4\text{G}(3)$	0.000	0.000	0.000	0.000
2	3.5	$^4\text{H}(60)+^4\text{G}(30)+^4\text{F}(9)+^4\text{D}(1)$	0.032	0.029	0.039	0.032
3	2.5	$^4\text{G}(43)+^4\text{F}(38)+^4\text{D}(16)+^4\text{P}(3)$	0.046	0.046	0.056	0.049
4	1.5	$^4\text{D}(40)+^4\text{F}(31)+^4\text{P}(23)+^4\text{S}(6)$	0.057	0.058	0.066	0.060
5	0.5	$^4\text{P}(49)+^4\text{S}(30)+^4\text{D}(21)$	0.068	0.070	0.077	0.071

term energies agree within 0.010/0.003 eV, LS contributions deviate by at most 1%

6	5.5	$^4\text{I}(72)+^4\text{H}(22)+^6\text{L}(3)+^4\text{G}(1)+^4\text{K}(1)$	0.336	0.380	0.419	0.419
8	4.5	$^4\text{H}(38)+^4\text{G}(36)+^4\text{I}(18)+^4\text{F}(8)$	0.363	0.405	0.455	0.447
9	3.5	$^4\text{F}(39)+^4\text{H}(32)+^4\text{D}(16)+^4\text{G}(13)$	0.378	0.424	0.469	0.464
10	2.5	$^4\text{G}(40)+^4\text{D}(35)+^4\text{P}(23)+^4\text{F}(2)$	0.392	0.436	0.484	0.480
11	1.5	$^4\text{F}(43)+^4\text{S}(30)+^4\text{P}(27)$	0.402	0.454	0.494	0.491
12	0.5	$^4\text{P}(43)+^4\text{D}(42)+^4\text{S}(15)$	0.404	0.452	0.496	0.494

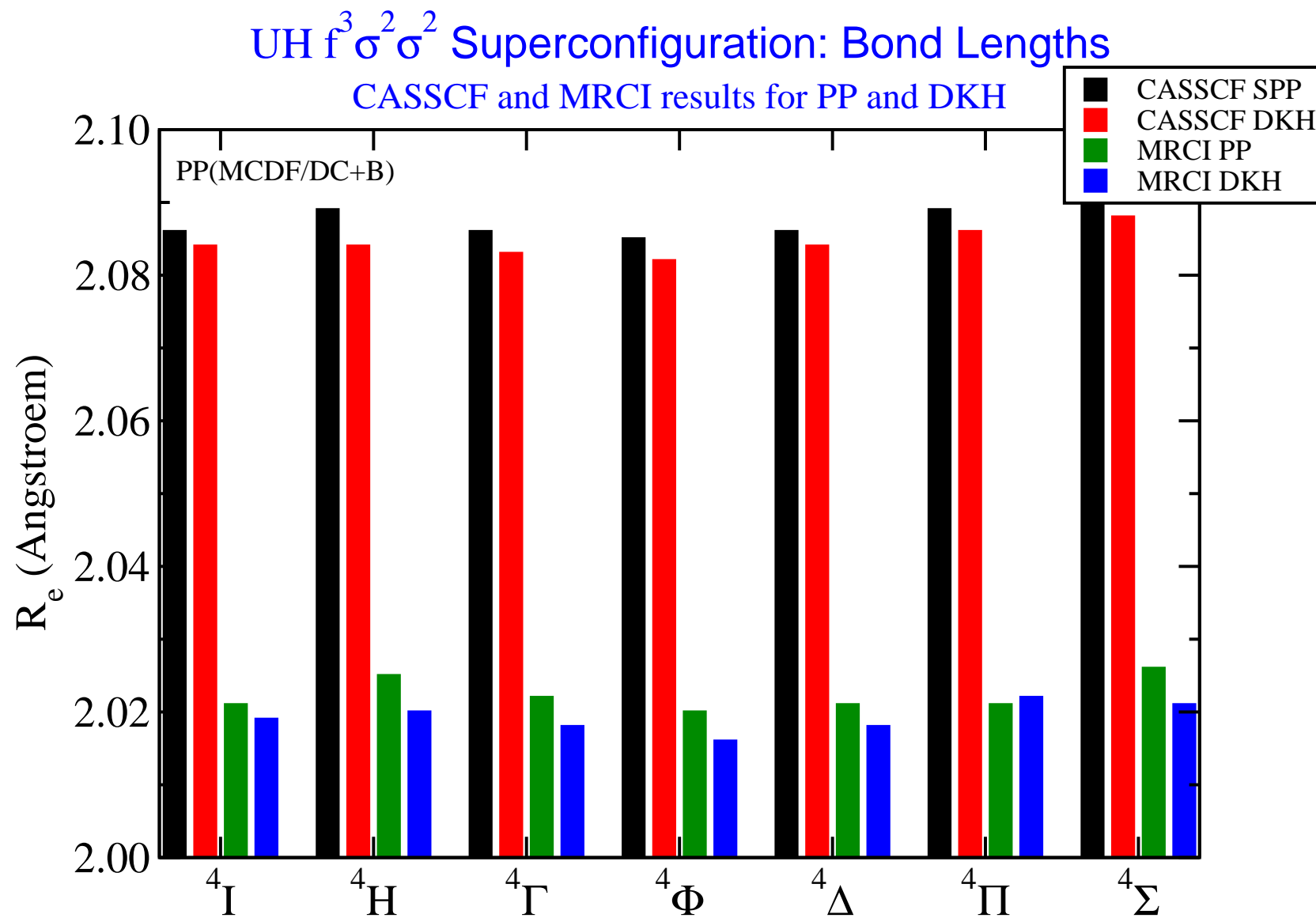
term energies agree within 0.10/0.09 eV, LS contributions deviate by at most 2%

7	5.5	$^6\text{L}(83)+^6\text{K}(13)+^4\text{I}(3)+^4\text{H}(1)$	0.341	0.271	0.145	0.190
13	4.5	$^6\text{K}(100)$	0.463	0.412	0.307	0.353
14	6.5	$^6\text{L}(79)+^6\text{K}(21)$	0.579	0.562	0.492	0.517

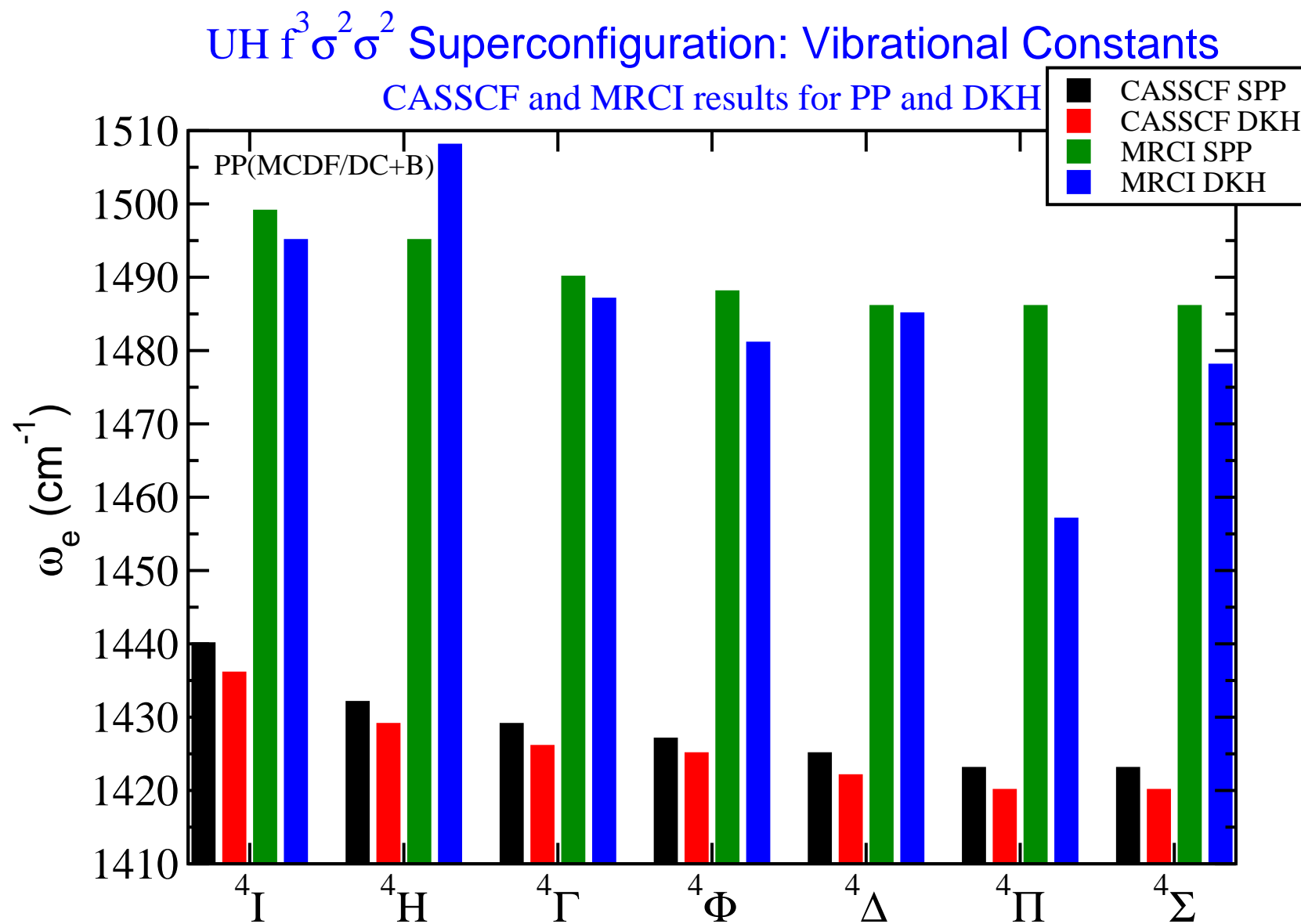
term energies agree within 0.15/0.08 eV, LS contributions deviate by at most 5%

basis set 1: U (21s18p12d16f), H (7s); due to limitations in MOLPRO 2002

basis set 2: U (30s26p18d14f7g)/[10s9p7d5f3g]; H aug-cc-pVQZ; MOLPRO 2006



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## Conclusions

- A first step towards an understanding of the UH low-lying states has been taken, however much more could be done !
- Accurate experimental data would be beneficial for calibration of theoretical methods.
- The main problem of ab initio calculations is electron correlation, not so much relativity.

## Contributions of R. M. Pitzer to this (and other) work of our group

- ATMSCF code for basis set optimization at the SCF level (used for exponent optimization)
- ARGOS integral code (used to evaluate PP integrals)

**Thanks Russ !**

**Thank you for your attention !**