Role of Chemistry in Fundamental Physics

Geetha Gopakumar Nair
Tokyo Metropolitan University, Japan

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Outline

- **General aspects about molecular calculations**

❖ Importance of multi-reference correlation methods in molecules

❖ Relativistic effects in Quantum Chemistry

- **Application to fundamental physics**

❖ Photoassociation spectroscopy in ultracold polar molecules in an optical lattice

LiX (X-alkaline-earth-metal) – mp/me variation studies - open shell

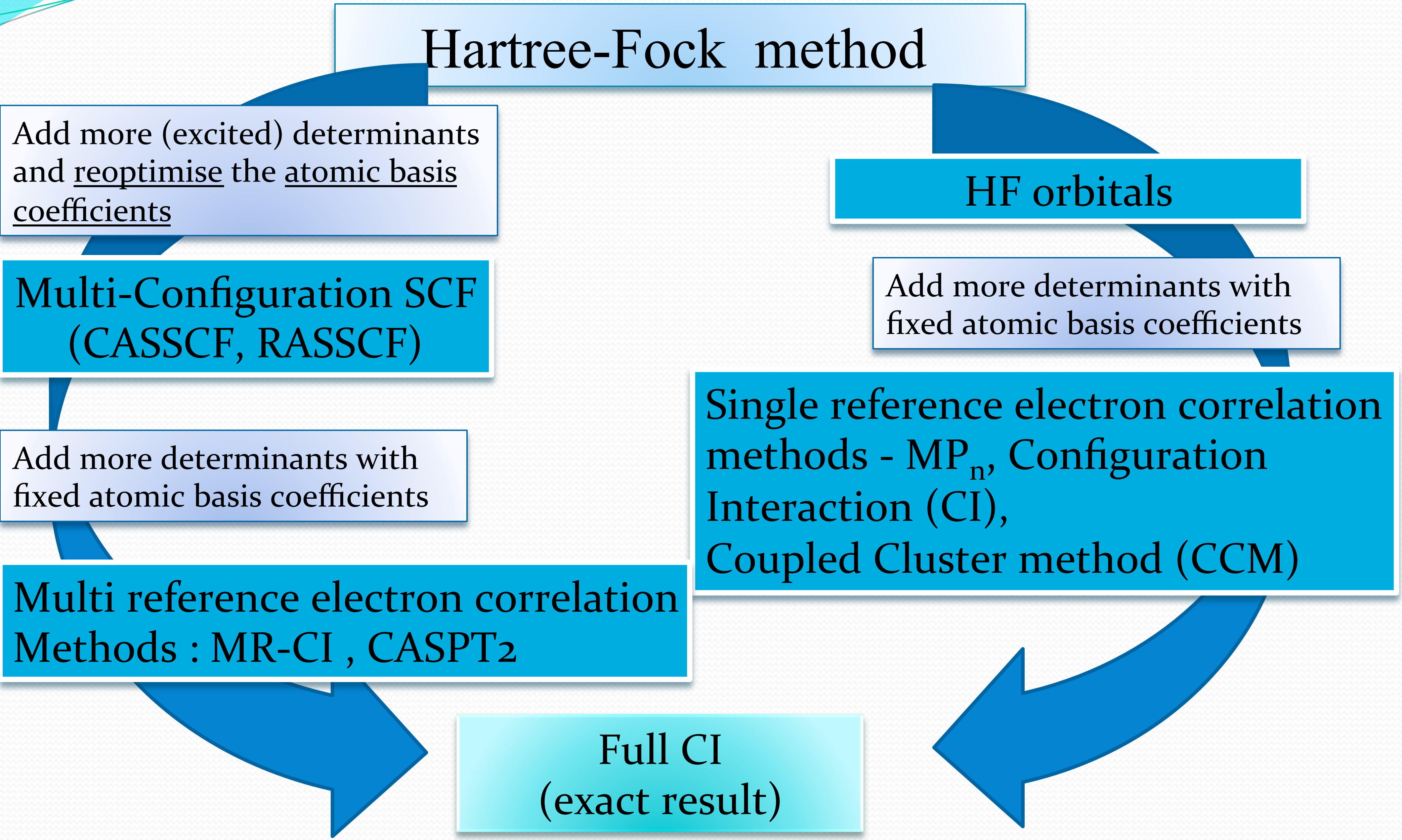
HgYb - Nuclear EDM measurement – closed shell

Importance of multi reference correlation methods in molecules

Reference

- Roland Lindh, The winter school, Helsinki, 12-16 Dec 2011
- Multiconfigurational and multireference methods, Peter R. Taylor and Jeppe Olsen, Sep 2011
- Electronic structure calculations, Attila G. Csaszar, Eotvos Universiy, Budapest, Hungary
- Introduction to nondynamical correlations, C. David Sherrill, School of Chemistry and Biochemistry, Georgia Institute of Technology
- Post HF methods lectures by Andrew S. Ichimura, CIT
- R. J. Bartlett, Int. J. Mol. Sci. 2002, 3, 579-603
- How accurate is the CASPT2 method? Zahra Azizi et al.,PCCP, 2006,8,2727-2732

Electron correlation -Post HF



Hartree-Fock method

Add more (excited) determinants and reoptimise the atomic basis coefficients

Multi-Configuration SCF (CASSCF, RASSCF)

Add more determinants with fixed atomic basis coefficients

Multi reference electron correlation Methods : MR-CI , CASPT2

HF orbitals

Add more determinants with fixed atomic basis coefficients

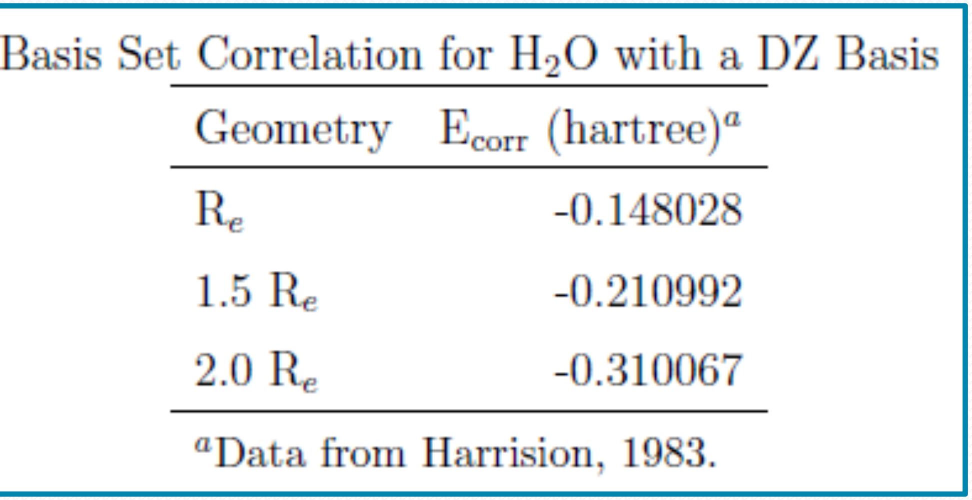
Single reference electron correlation methods - MP_n, Configuration Interaction (CI), Coupled Cluster method (CCM)

Full CI
(exact result)

Courtesy: Attilla G.Csaszar presentation

Dynamical and Non-dynamical Correlations

✓ HF level - Inter electronic repulsions are considered in an average way.
✓ HF neglects instantaneous electron-electron repulsions.
✓ Correlation energy is the difference between Full CI and HF.
✓ Correlation energy is obtained by fully allowing the electrons to see and avoid each other – correlation related to movement of electrons **–“Dynamic Correlation”**



Basis Set Correlation for H_2O with a DZ Basis

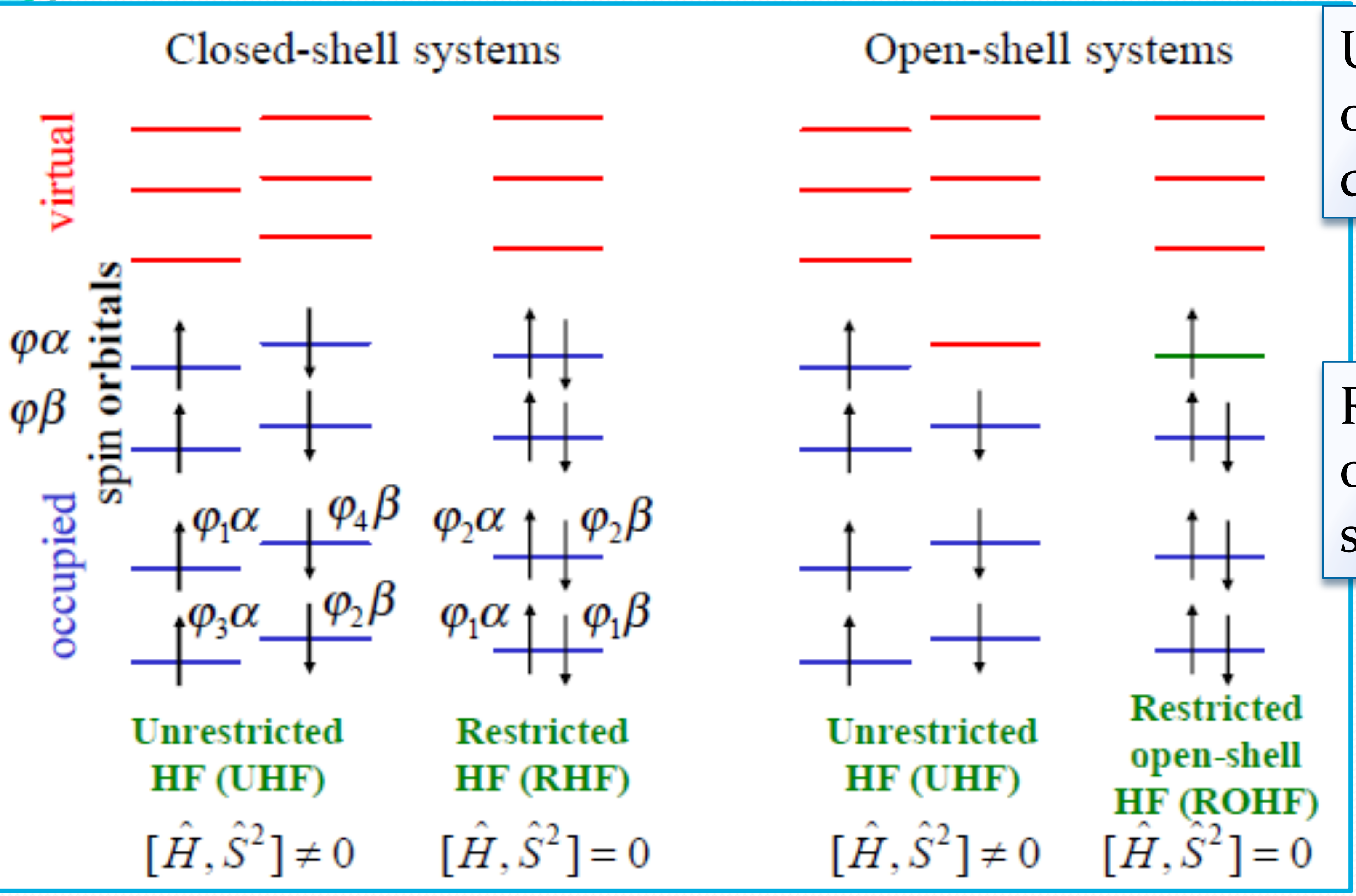
Geometry	E_{corr} (hartree)[a]
R_e	-0.148028
1.5 R_e	-0.210992
2.0 R_e	-0.310067

[a] Data from Harrision, 1983.

Courtesy: Prof. David Sherrill, Georgia Institute of Technology

✓ At R > Re, as electrons are further apart, dynamical correlation should become less important .
✓ Correlation increases with stretching..
✓ Some correlation is missing in HF. It does not account for nearly degenerate electron configurations – **“Non Dynamic Correlation”**

Restricted and Unrestricted HF methods



UHF: Different orbtials for different spins

RHF: Same orbital for both spin states

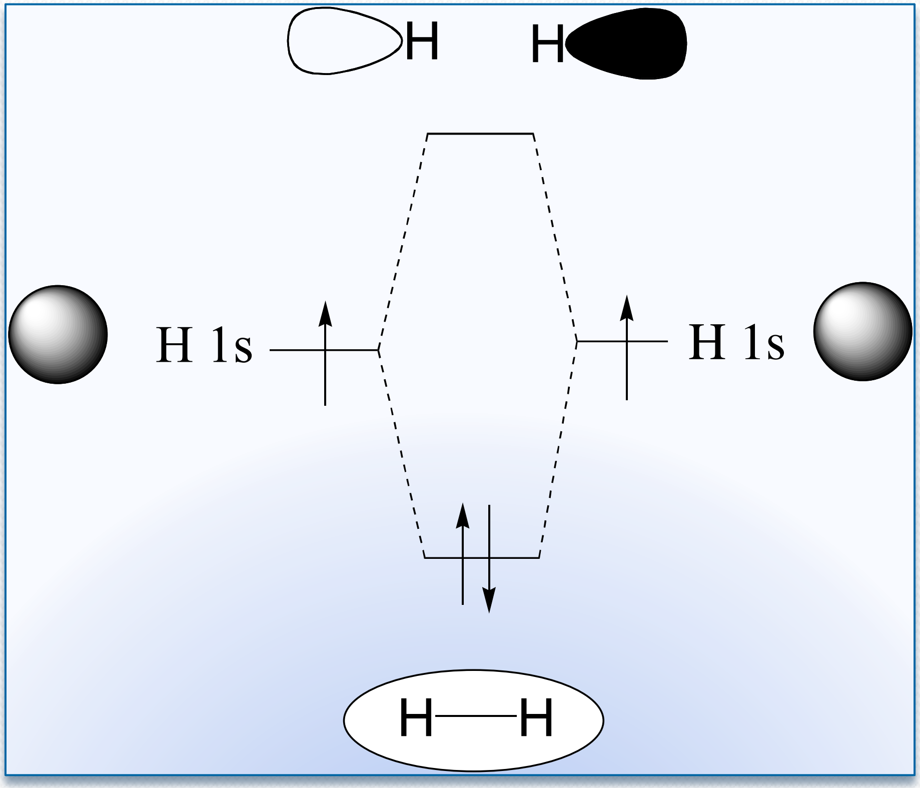
ROHF: Same orbital's for occupied α and β spin states
Different orbital for unmatched α spin state

H_2 molecule

Ground state in a minimal basis: one atomic 1*s* orbital on each atom

Two AOs leads to two MOs

$\Phi_2 = N_1 (\chi_A - \chi_B)$ - Anti bonding MO



$\Phi_1 = N_1 (\chi_A + \chi_B)$ - Bonding MO

Ground state wave function

$$\Phi_0 = \begin{vmatrix} \phi_1\alpha(1) & \phi_1\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) \end{vmatrix}$$

Slater determinant with two electrons in the bonding MO (ground state)

$$\begin{aligned} \Phi_0 &= \varphi_1\alpha(1)\varphi_1\beta(2) - \varphi_1\alpha(2)\varphi_1\beta(1) \\ &= \varphi_1(1)\,\varphi_1(2)\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\ &\sim (\chi_A(1) + \chi_B(1))(\chi_A(2)+\chi_B(2)) \end{aligned}$$

Expand the Slater determinant
Factor the spatial and spin part

$$\Phi_0 = (\chi_A(1)\chi_A(2) + \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2) + \chi_B(1)\chi_B(2)$$

Four terms in the AO basis

$(\chi_A(1)\chi_A(2)$ and $\chi_B(1)\chi_B(2)$

$(\chi_A(1)\chi_B(2)$ and $\chi_B(1)\chi_A(2)$

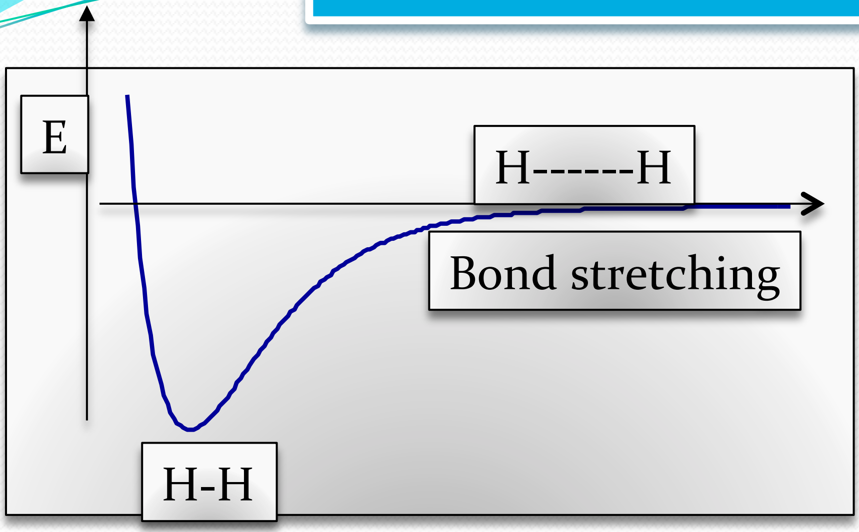
Ionic terms

Covalent terms

Two electrons in one AO

Two electrons shared between two AOs

H_2 Potential energy Surface



At dissociation limit, H_2 must separate into two neutral H atoms

At the RHF level, the wave function, ϕ is 50% ionic and 50% covalent at all bond lengths

H2 molecule does not dissociate correctly at the RHF level!!!

H_2 RHF dissociation consequences

✓Energies of stretched bonds too large - Affects transition state structures
✓Potential well steep hence (1) short equilibrium bond lengths
(2) large binding energy
✓Improper curvature of PEC – too high vibrational frequencies
✓Wave function is too ionic – dipole moments are too large

Remedy for this problem

- ❖Add flexibility by removing fixed ratio for each terms

[At large inter nuclear separations, the wave function should be 100% covalent (ionic terms should be zero)]

- ❖ Starting with a different trial function

$$\Phi_1 = \begin{vmatrix} \varphi_2\alpha(1) & \varphi_2\beta(1) \\ \varphi_2\alpha(2) & \varphi_2\beta(2) \end{vmatrix}$$

Slater determinant with two electrons in the anti bonding MO (excited state)

$$\Phi_0 \sim (\chi_A(1)\chi_A(2) - \chi_A(1)\chi_B(2) - \chi_B(1)\chi_A(2) + \chi_B(1)\chi_B(2)$$

Four terms in the AO basis

$(\chi_A(1)\chi_A(2)$ and $\chi_B(1)\chi_B(2)$

Ionic terms

Two electrons in one AO

$(\chi_A(1)\chi_B(2)$ and $\chi_B(1)\chi_A(2)$

Covalent terms

Two electrons shared between two AOs

New trial function: Linear combination of Φ_o and Φ_1 (Two Configuration SCF)

$$\Psi = a_0\Phi_0 + a_1\Phi_1 = a_0(\phi_1\phi_1) + a_1(\phi_2\phi_2)$$

$$\Psi = (a_0 + a_1)\left[\chi_A\chi_A + \chi_B\chi_B\right] + (a_0 - a_1)\left[\chi_A\chi_B + \chi_B\chi_A\right]$$

Ionic terms

Covalent terms

At R > R_e

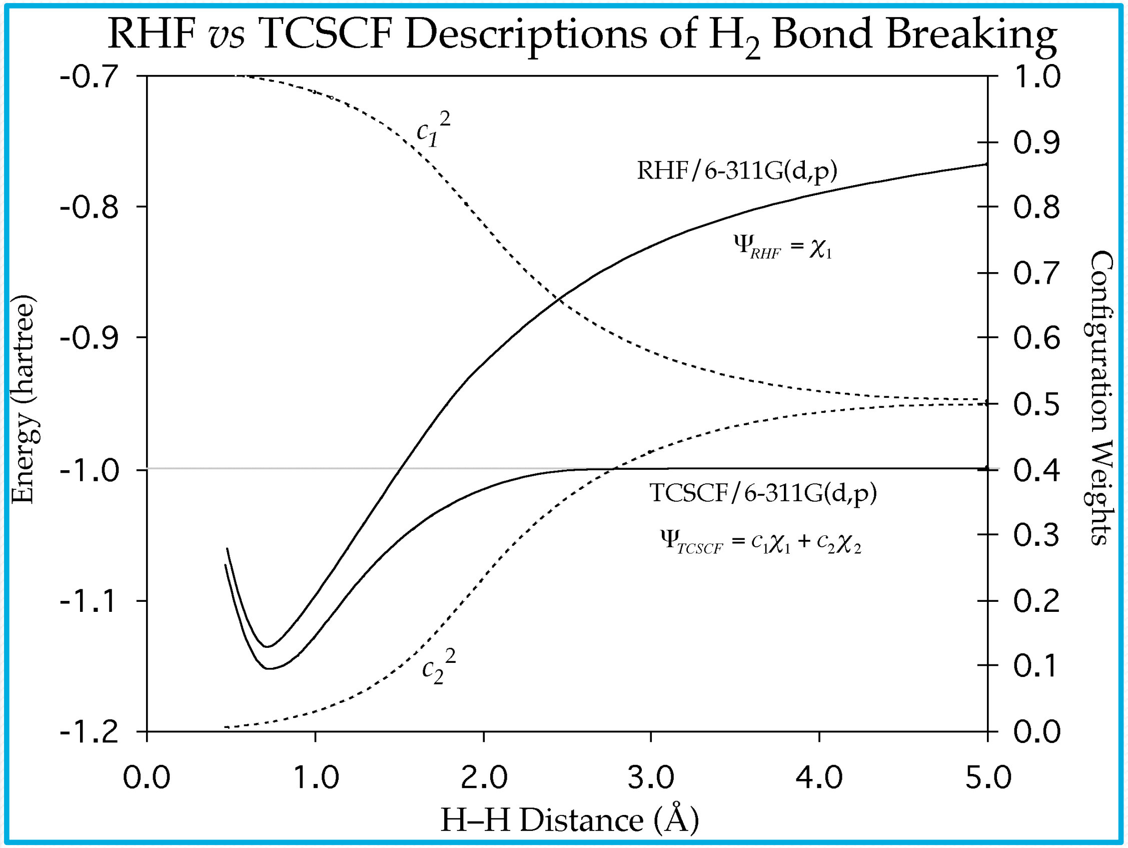
$a_1 = -a_o$ (ionic terms) ⟶ zero

$\Psi = \Psi_{CI}$, an example of ***CI***

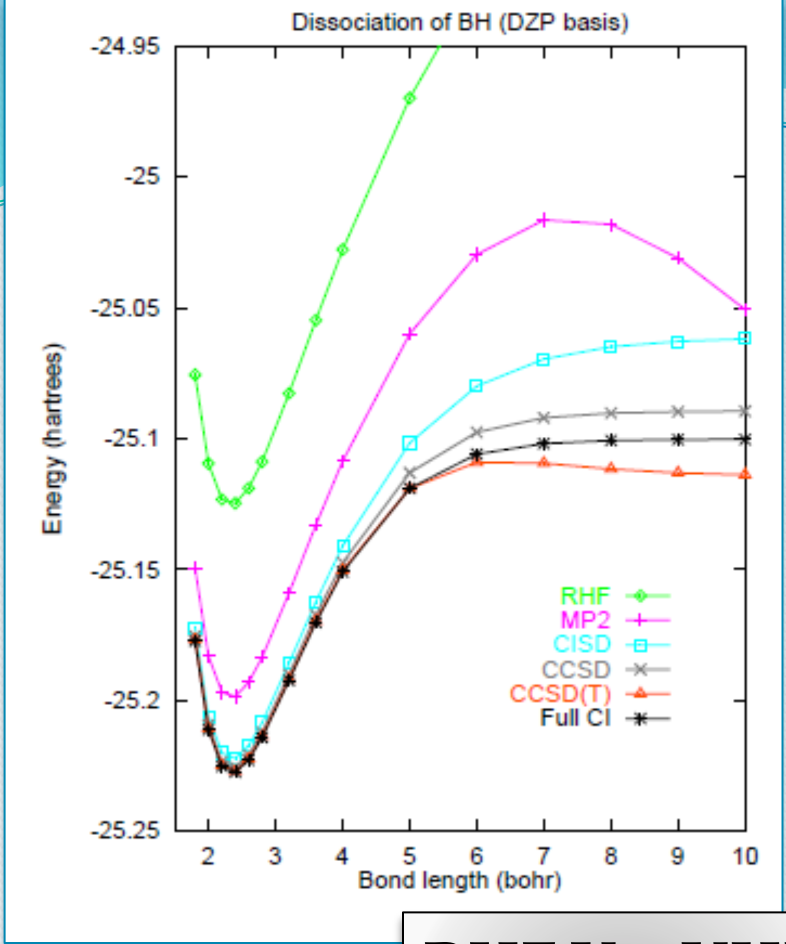
Incl. of *anti-bonding character*

-allows electrons to be farther apart – non dynamical correlation

Lower energy than RHF (two variational parameters).



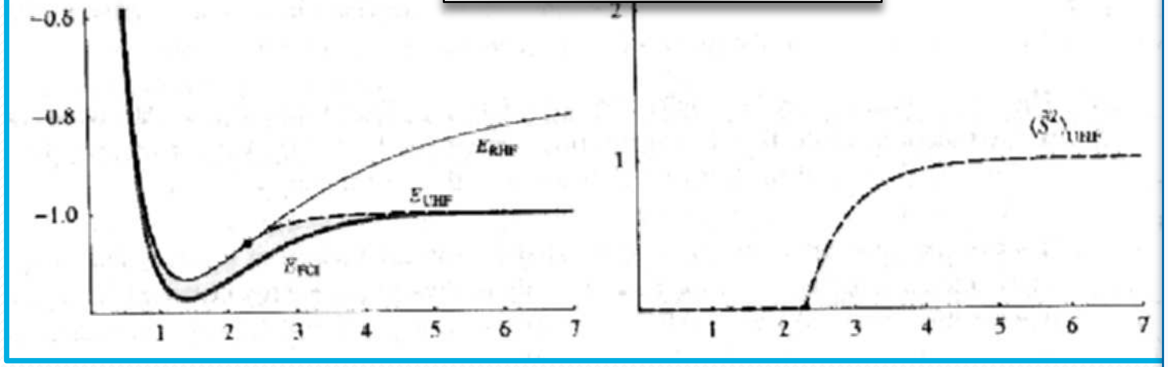
RHF *vs* TCSCF Descriptions of H_2 Bond Breaking



Near degeneracy at large distances between bonding and anti-bonding MOs is bad for energy denominators in MP2

With regular RHF orbitals, even correlated MP2, CISD, CCSD, CCSD(T) can fail

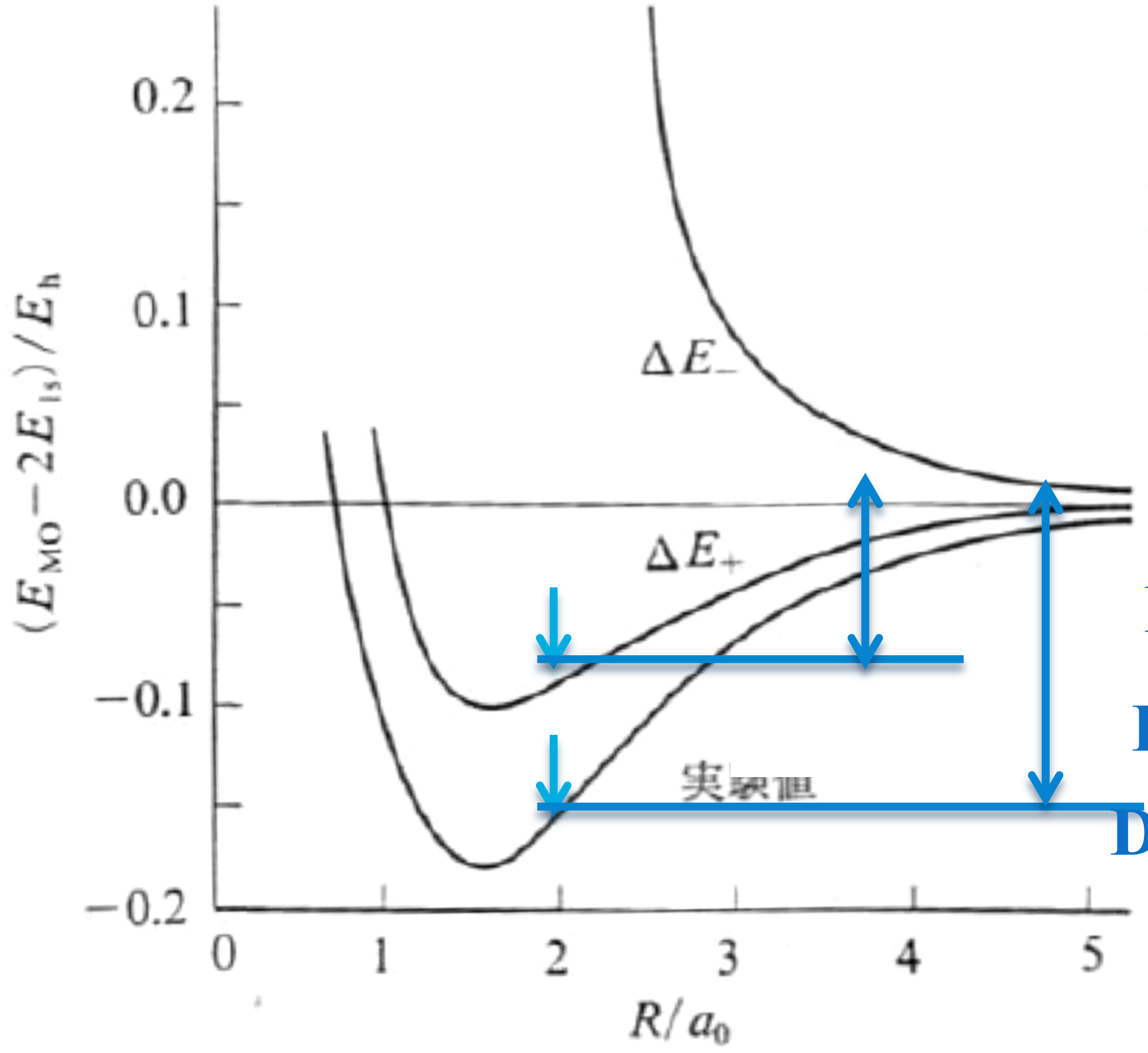
RHF Vz. UHF



H2 molecule – RHF, UHF, FCI

- RHF and UHF good at short R
- RHF not good at larger separations – UHF falls towards FCI
- RHF remains singlet
- UHF – incorrect spin – intermediate of a singlet and triplet

H_2 molecule



R_e (calculated) = 0.85 Å

R_e (HF limit) = 0.741 Å

R_e (experiment) = 0.741 Å

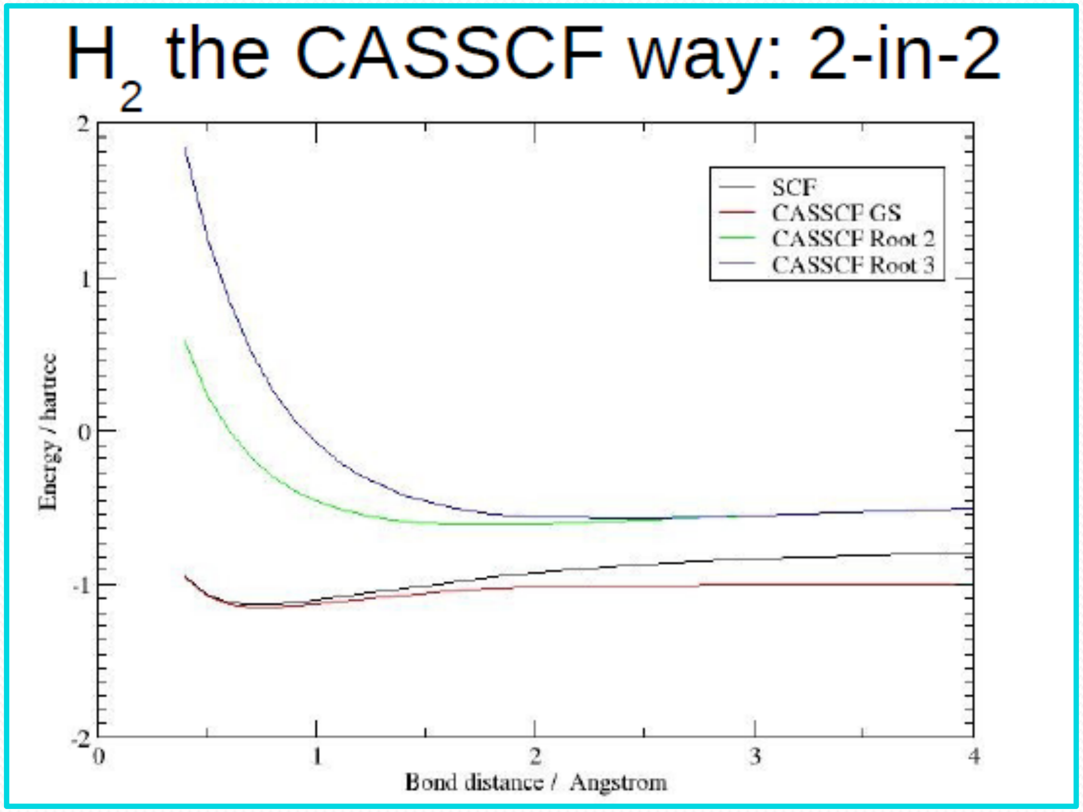
D_e (calculated) = 260 kJ/mol

D_e (HF limit) = 351 kJ/mol

D_e (experiment) = 457 kJ/mol

Ref: Abe san’s lecture

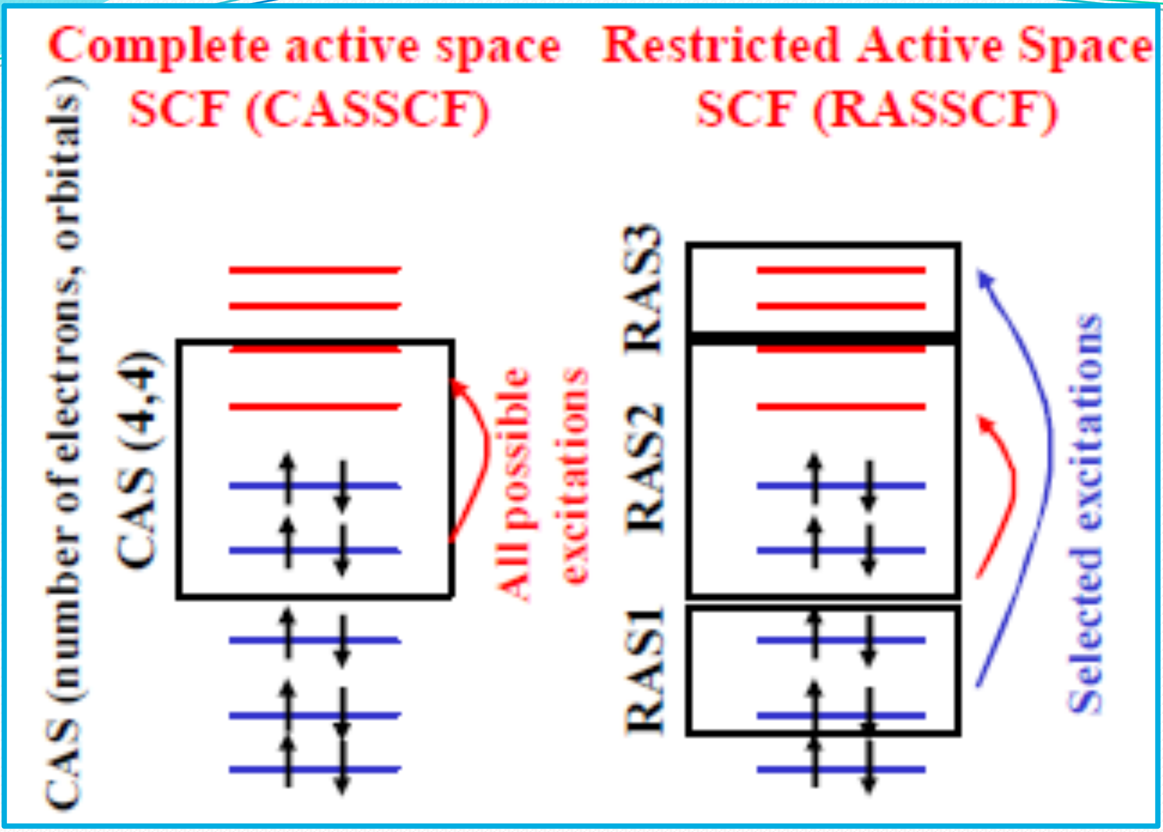
- We need to include all near degenerate determinants in our reference (non dynamical)
- Need to find orbital to minimize the energy of the mixture of near degenerate determinants (MCSCF)
- A special case of MCSCF which takes full CI in a given active space(CASSCF)
- Need to use multi-configurational references for subsequent treatment of dynamical correlation- MRPT, MRCI, MRCC, CASPT2


H_2 the CASSCF way: 2-in-2

The CASSCF wave function has the correct asymptotic behavior

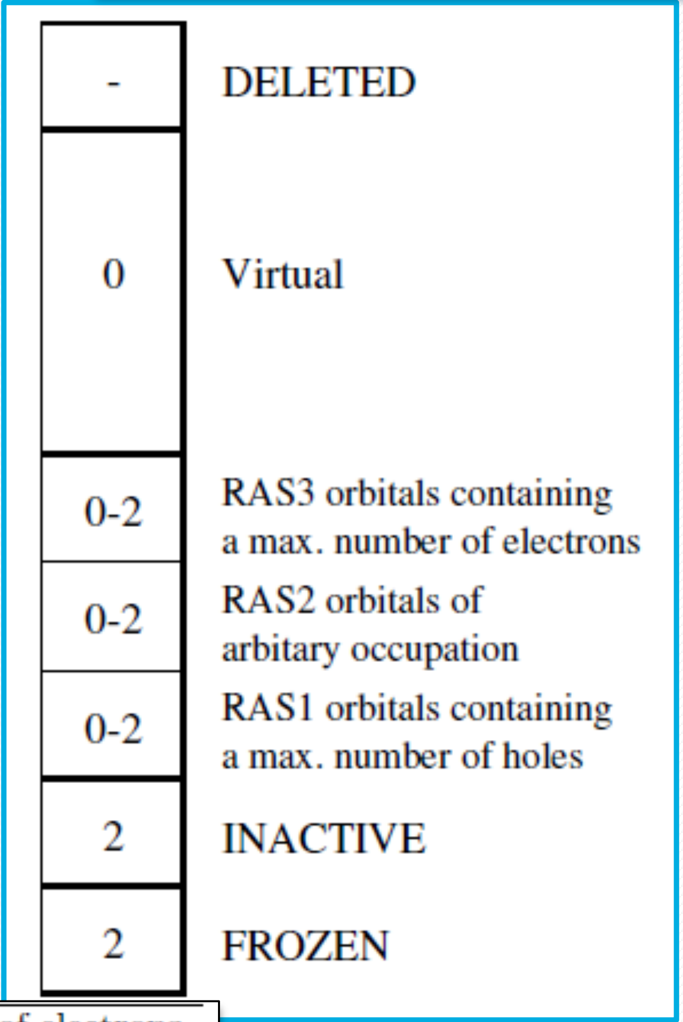
Prof. Lyndh, Winter school, Helsinki, 2011

What is CASSCF and RASSCF?

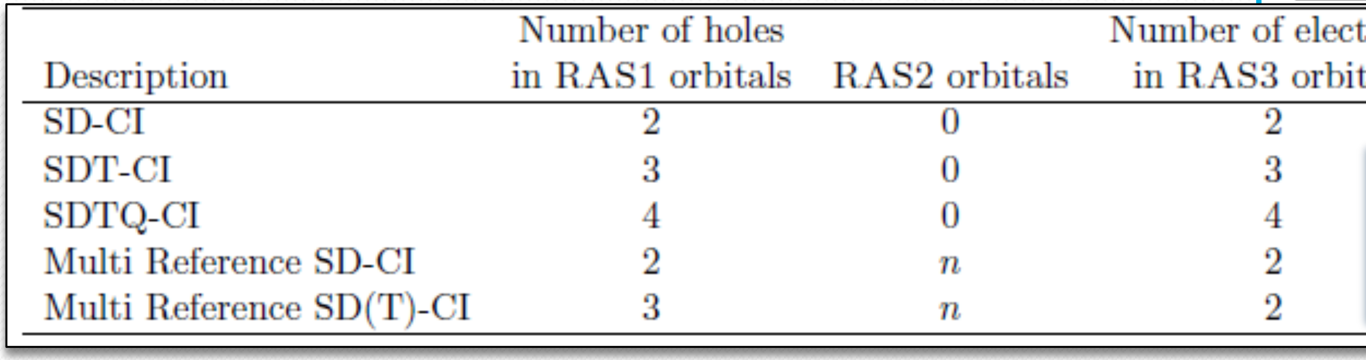


RASSCF = CASSCF when RAS1= RAS3 = zero

Electron occupancy in RASSCF



-	DELETED
0	Virtual
0-2	RAS3 orbitals containing a max. number of electrons
0-2	RAS2 orbitals of arbitary occupation
0-2	RAS1 orbitals containing a max. number of holes
2	INACTIVE
2	FROZEN

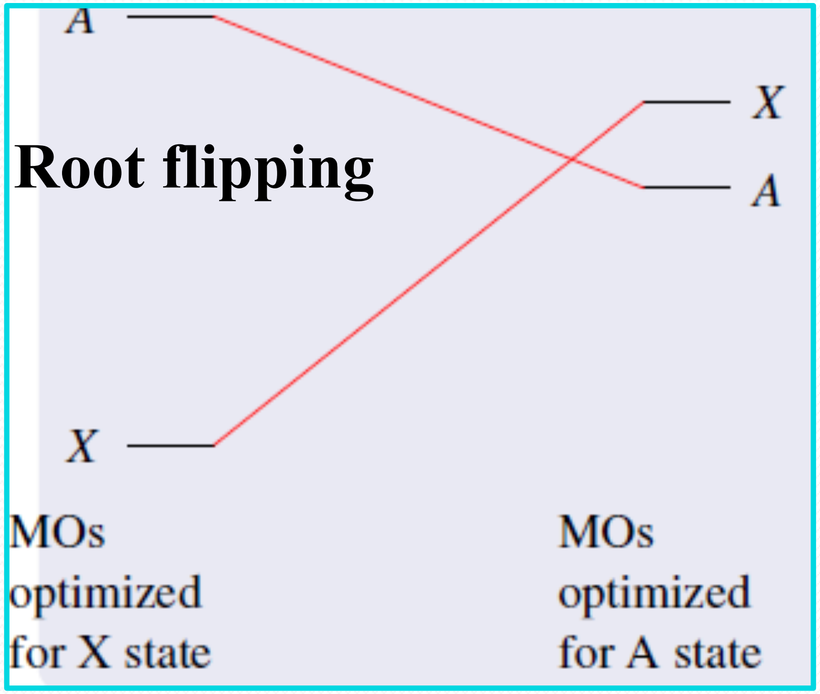


Description	Number of holes in RAS1 orbitals	RAS2 orbitals	Number of electrons in RAS3 orbitals
SD-CI	2	0	2
SDT-CI	3	0	3
SDTQ-CI	4	0	4
Multi Reference SD-CI	2	n	2
Multi Reference SD(T)-CI	3	n	2

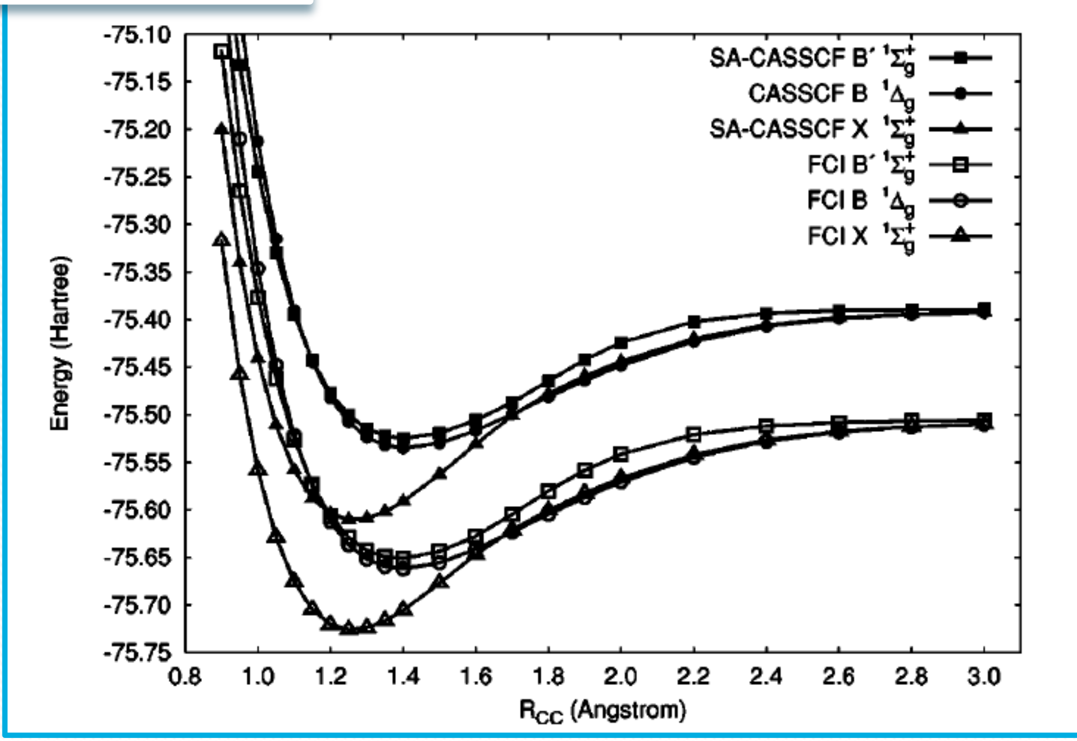
Types of wave functions using RASSCF

Ref. MOLCAS manual

MCSCF - excited state
Separate calculations on the individual states



Root flipping


herrill and P. Piecuch

SA-CASSCF – MO is optimized w.r.to (weighted)average energy of the states of a particular symmetry

Advantage :

- Single set of orbitals with different coefficients describe all the states
- CASSCF states are orthogonal to each other

How do we add dynamical correlations now?

- Multi reference Configuration Interaction (MR-CI)
- Multi reference Coupled Cluster (MR-CC) -
- Multi state Complete Active space Perturbation Theory (CASPT2)

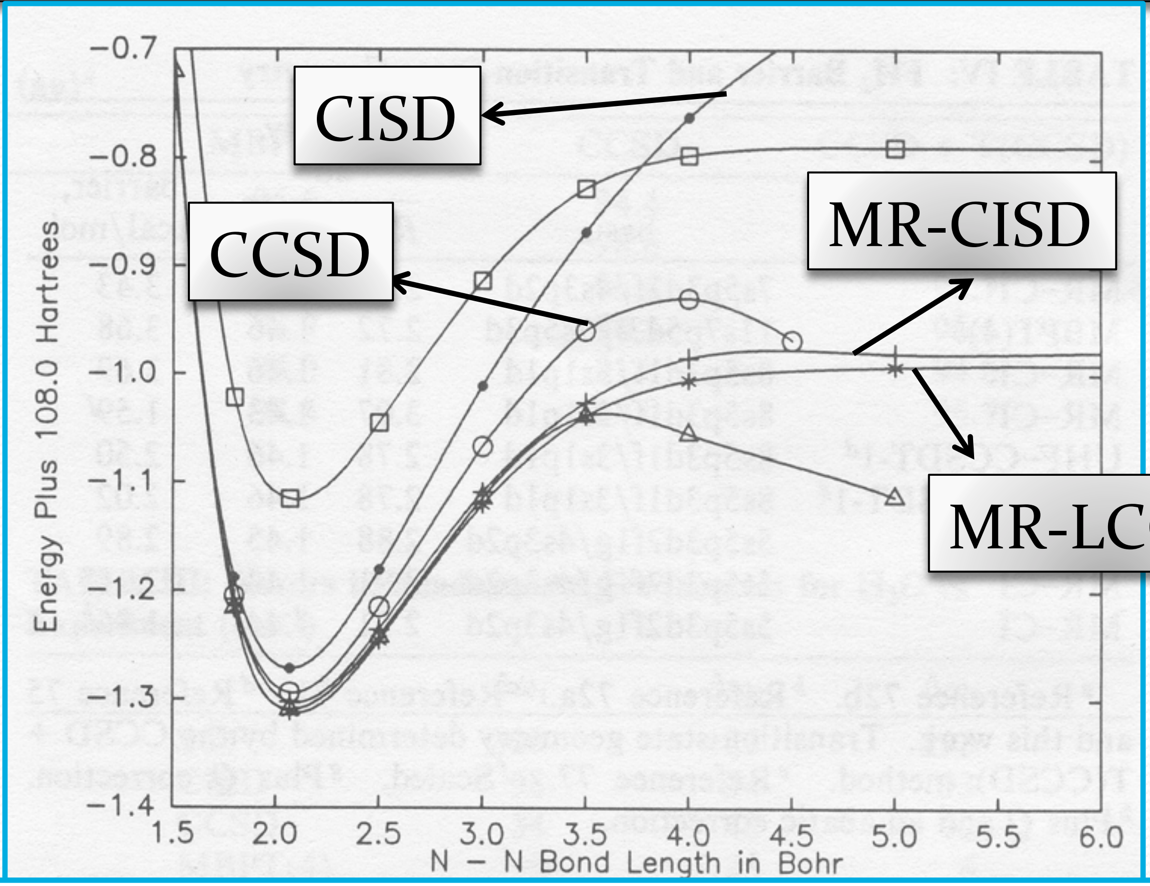


Figure 3: RHF-based CISD, CCSD, CCSDT-1, MCSCF, MR-CISD, and MR-LCCM potential curves for N_2 (absolute scale). The various curves are identified as follows: (•) CISD, (○) CCSD, (△) CCSDT-1, (□) MCSCF, (+) MR-CISD, and (*) MR-LCCM.

MR-CI

- Most accurate method for small molecules
- Computationally expensive

MR-CC

- SS CC + EOM-CC Multi-reference description on some target states
- Challenging area

Ref: R.J. Bartlett, To multi reference or not to multi reference: That is the question? – Int. J. Mol. Sci. 2002,3,579-603

Perturbation Theory : Partition of Hamiltonian : H = Ho + V

Hilbert space : P (reference space) + Q (secondary space) = 1

Wave operator **$\Omega^\alpha |\alpha> = |\Psi>$**

BLOCH equation

$$(E_0^\alpha - H_0)\Omega^\alpha|\alpha\rangle = QV\Omega^\alpha|\alpha\rangle - Q\Omega^\alpha|\alpha\rangle\langle\alpha|V\Omega^\alpha|\alpha\rangle$$

Single-State (SS-CASPT2)

$$P = |\alpha\rangle\langle\alpha|,$$

$$H_0|\alpha\rangle = E_0^\alpha|\alpha\rangle$$

We need **Ω_1^α and E_2^α**

$$H_0^\alpha = |\alpha\rangle\langle\alpha|\hat{F}^\alpha|\alpha\rangle\langle\alpha| + \sum_k |k\rangle\langle k|\hat{F}^\alpha|k\rangle \times \langle k| + Q_{sd}^\alpha\hat{F}^\alpha Q_{sd}^\alpha + Q_{tq\ldots}^\alpha\hat{F}^\alpha Q_{tq\ldots}^\alpha,$$

k : all states within the CAS orthogonal to α

Q^α_{sd} = states obtained by applying double excitation operator on α

$$(E_0^\alpha - \hat{F}^\alpha)\Omega_1^\alpha|\alpha\rangle = Q_{sd}^\alpha H|\alpha\rangle,$$

Multi-State (MS-CASPT2)

$$P = \sum_{\alpha=1}^{d} |\alpha\rangle\langle\alpha|$$

$$H_0^\alpha|\alpha\rangle = E_0^\alpha|\alpha\rangle \quad (\alpha = 1, 2, \cdots, d)$$

We need **Ω_1^α and E_2^α (α = 1,2, …..,d)**

$$H_0^\alpha = \sum_\beta |\beta\rangle\langle\beta|\hat{F}^\alpha|\beta\rangle\langle\beta| + \sum_k |k\rangle\langle k|\hat{F}^\alpha|k\rangle\langle k| + Q_{sd}^\alpha\hat{F}^\alpha Q_{sd}^\alpha + Q_{tq\ldots}^\alpha\hat{F}^\alpha Q_{tq\ldots}^\alpha + \cdots \quad (\alpha = 1, 2, \cdots, d), \tag{23}$$

β space : (1,2,…..,d)

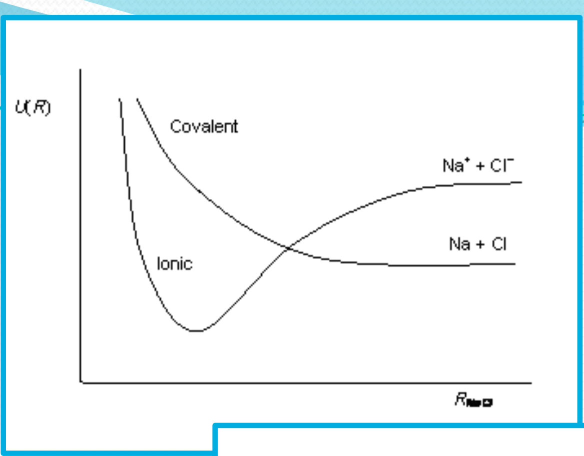
$$\Omega_1^P = \sum_\alpha \Omega_1^\alpha|\alpha\rangle\langle\alpha|.$$

MR- Ω : linear combination of SS Ω

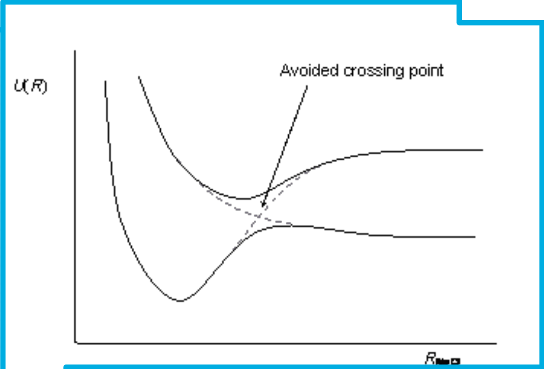
$$H_{2nd}^{\text{eff}} = PHP + PH\Omega_1^P P.$$

Why MS-CASPT2?

- CASSCF is not a good reference
  Strong mixing of reference with the secondary space - PT2 fails
- SS-CASPT2 can be inadequate at avoided crossings (same symmetry states cannot cross each other – adiabatic approximation)

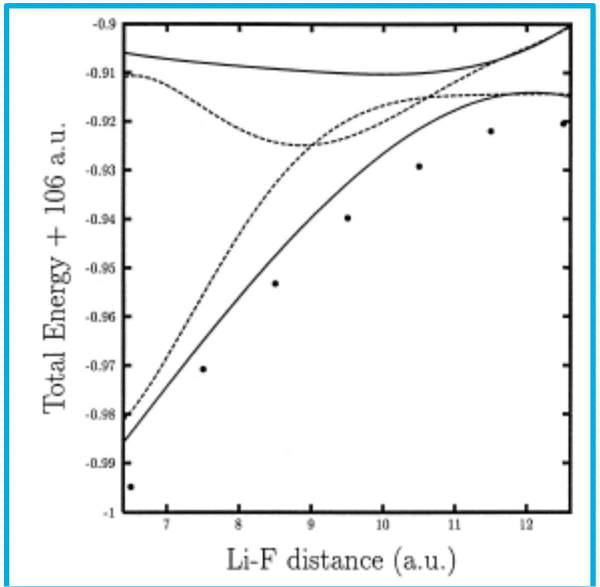


Mixing of ionic and covalent PECs of NaCl



Avoided crossing of mixed w.f of NaCl energies

Ionic-neutral curve crossing of LiF molecule



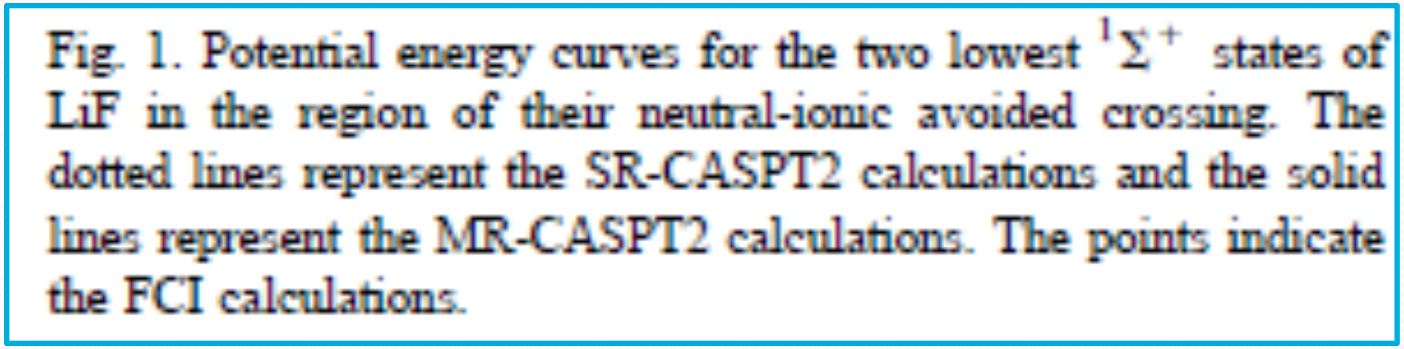
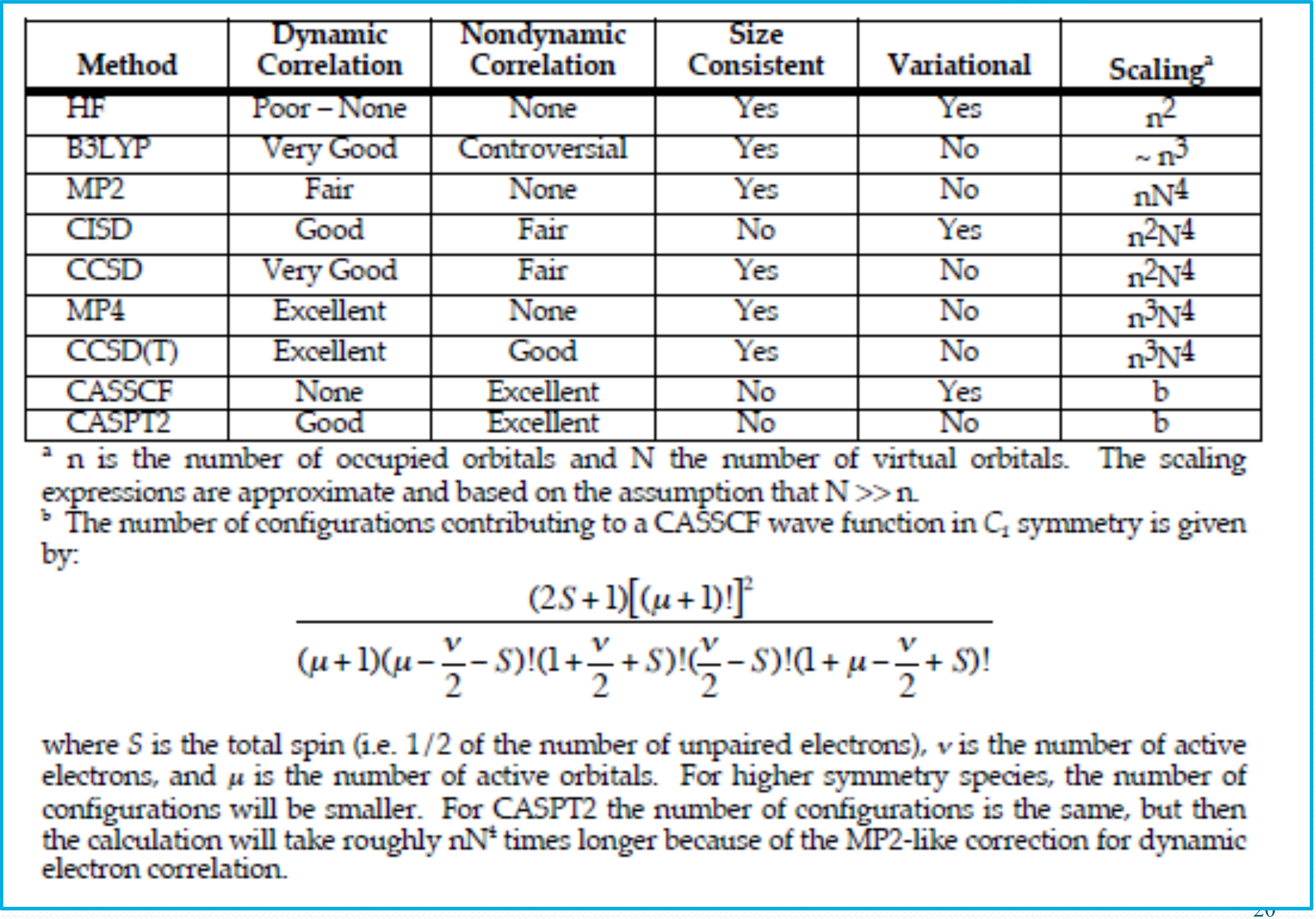


Fig. 1. Potential energy curves for the two lowest $^1\Sigma^+$ states of LiF in the region of their neutral-ionic avoided crossing. The dotted lines represent the SR-CASPT2 calculations and the solid lines represent the MR-CASPT2 calculations. The points indicate the FCI calculations.

Ref:J.Finley, Chhemical Physics Letters, 288, 299-306(1998)

Summery of methods for treating electron correlation



Method	Dynamic Correlation	Nondynamic Correlation	Size Consistent	Variational	Scaling[a]
HF	Poor – None	None	Yes	Yes	n^2
B3LYP	Very Good	Controversial	Yes	No	$\sim n^3$
MP2	Fair	None	Yes	No	nN^4
CISD	Good	Fair	No	Yes	n^2N^4
CCSD	Very Good	Fair	Yes	No	n^2N^4
MP4	Excellent	None	Yes	No	n^3N^4
CCSD(T)	Excellent	Good	Yes	No	n^3N^4
CASSCF	None	Excellent	No	Yes	b
CASPT2	Good	Excellent	No	No	b

[a] n is the number of occupied orbitals and N the number of virtual orbitals. The scaling expressions are approximate and based on the assumption that N >> n.

[b] The number of configurations contributing to a CASSCF wave function in C_1 symmetry is given by:

$$\frac{(2S+1)[(\mu+1)!]^2}{(\mu+1)(\mu-\frac{\nu}{2}-S)!(1+\frac{\nu}{2}+S)!(\frac{\nu}{2}-S)!(1+\mu-\frac{\nu}{2}+S)!}$$

where S is the total spin (i.e. 1/2 of the number of unpaired electrons), ν is the number of active electrons, and μ is the number of active orbitals. For higher symmetry species, the number of configurations will be smaller. For CASPT2 the number of configurations is the same, but then the calculation will take roughly nN^4 times longer because of the MP2-like correction for dynamic electron correlation.

Relativistic effects in Quantum Chemistry

<u>Reference</u>

- Relativistic effects in atoms and molecular properties, M. Illias, V. Kello, M. Urban, acta physica slovaca vol. 60, No.3, 259-391 (2010)
- An introduction to relativistic Quantum Chemistry, Bernd Hess
- Relativistic Electronic Structure calculations for atoms and molecules, Markus Reiher and Bernd A Hess, Modern Methods and Algorithms of Quantum Chemistry (2000)

Relativistic effects in atoms

$$m = m_0[1 - (v/c)^2]^{-1/2}$$

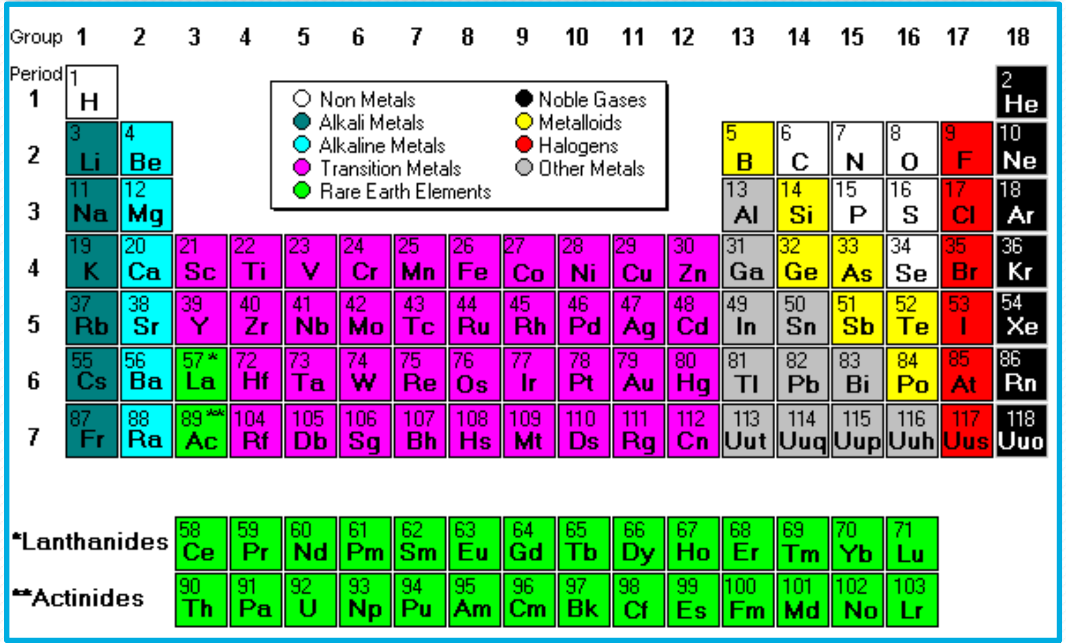
m, m_0 are the masses at velocity v and zero

Bohr's model for hydrogen like species

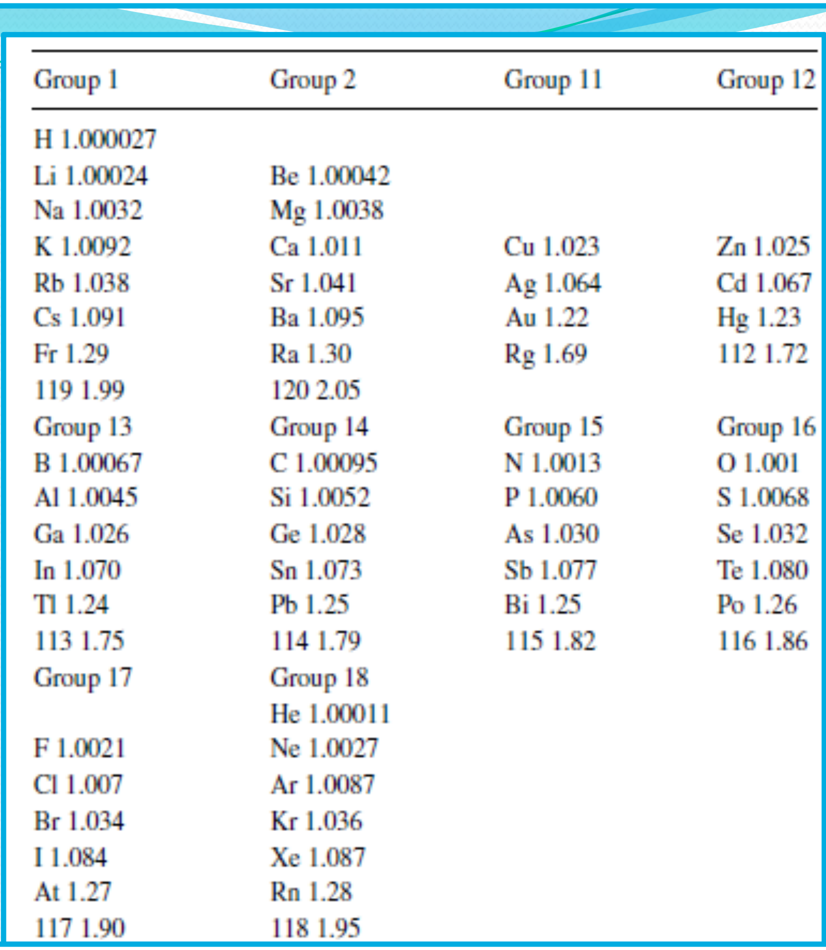
$$v = (2\pi e^2/nh)Z$$

$$E = -(2\pi^2 e^4/n^2h^2)mZ^2$$

$$r = Ze^2/mv^2$$



Calculated m/m_0 for ground state n=1



Group 1	Group 2	Group 11	Group 12
H 1.000027			
Li 1.00024	Be 1.00042		
Na 1.0032	Mg 1.0038		
K 1.0092	Ca 1.011	Cu 1.023	Zn 1.025
Rb 1.038	Sr 1.041	Ag 1.064	Cd 1.067
Cs 1.091	Ba 1.095	Au 1.22	Hg 1.23
Fr 1.29	Ra 1.30	Rg 1.69	112 1.72
119 1.99	120 2.05		
Group 13	Group 14	Group 15	Group 16
B 1.00067	C 1.00095	N 1.0013	O 1.001
Al 1.0045	Si 1.0052	P 1.0060	S 1.0068
Ga 1.026	Ge 1.028	As 1.030	Se 1.032
In 1.070	Sn 1.073	Sb 1.077	Te 1.080
Tl 1.24	Pb 1.25	Bi 1.25	Po 1.26
113 1.75	114 1.79	115 1.82	116 1.86
Group 17	Group 18		
	He 1.00011		
F 1.0021	Ne 1.0027		
Cl 1.007	Ar 1.0087		
Br 1.034	Kr 1.036		
I 1.084	Xe 1.087		
At 1.27	Rn 1.28		
117 1.90	118 1.95		

(H to Na) -1-3 : less than 1%

K – 4 : 0.9% to 3.6%

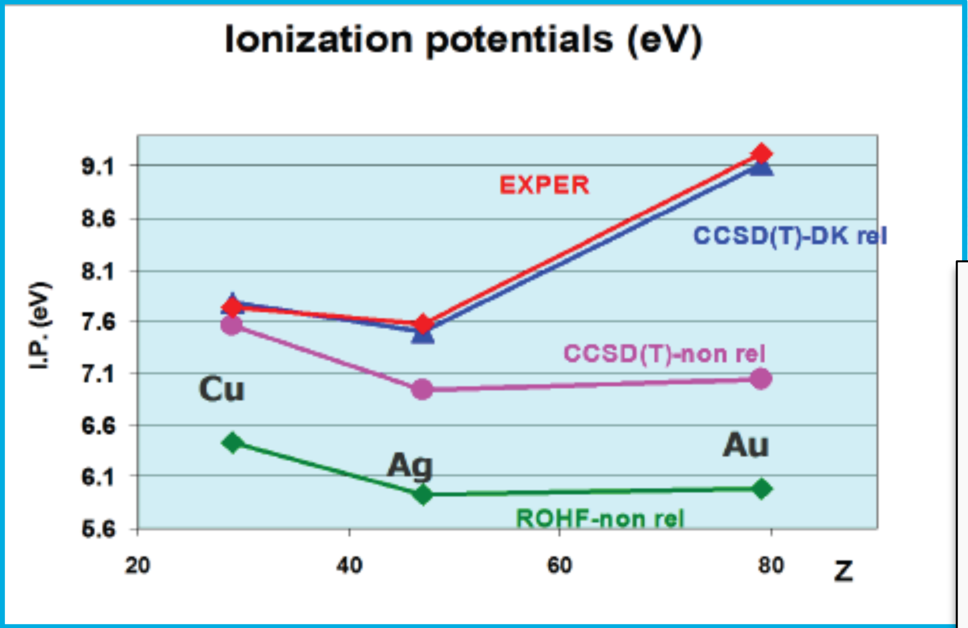
Rb – 5 : ~ 8%

Cs – 6 : ~ 10%

All other elements : more than 10%

Ref: Relativistic methods for Chemists, edited by M. Baryzs and Y. Ishikawa, Chapter 2 by John S. Thayer, Relativistic effects and the chemistry of the heavier main group elements

Relativistic effects in properties (coinage elements)-Group 11



^{29}Cu: [Ar]$3d^{10}4s^{1}$
^{47}Ag: [Kr]$4d^{10}\ 5s^{1}$
^{79}Au: [Xe]$5d^{10}4f^{14}6s^{1}$

- Cu, Ag, Au – ROHF and NR- CCSD(T)
  Electron correlation effects are similar
- Cu – NR CCSD(T) result is close to expt.
  Ag – NR CCSD(T) result is differing by 0.5eV
  Au – NR CCSD(T) result is misleading
- One component scalar relativistic DK – Close to experiment

Apart from electron correlation – relativistic treatment is also important

- ✓ Non-relativistic Hamiltonian
- ✓ Non-relativistic Hamiltonian + correlation
- ✓ Relativistic Hamiltonian (at different approximations)

Atoms and Molecules are neither Relativistic or Non Relativistic –
The magnitude of relativistic effects are related to the accuracy required for the property under consideration

Relativistic Calculations in Molecules

- **Z<40 – relativistic effects are small** (except nuclear dependent)

- **Computationally expensive**

  Molecular calculation: expansion techniques (Gaussians)

$$\Psi_S = \frac{1}{2mc}\bar{\boldsymbol{\sigma}}.\hat{p}\Psi_L \qquad \frac{\partial}{\partial x}\left(x^l e^{-\alpha r^2}\right) = \left(l x^{l-1} - 2\alpha x^{(l+1)}\right)e^{-\alpha r^2}$$

No. of small comp. = 2 * No. of large comp.

- **Coupling of spin and spatial wf – complex wf**

  - prevents handling of spin and point group symmetry separately

Decoupling schemes: 4 to 2 component Hamiltonians

- Unitary transformation of the Dirac Hamiltonian accurate to various orders of some expansion parameters

Attributes of approximate relativistic Hamiltonian

- Accurate results close to 4 component calculations
- Well balanced to treat heavy and light elements and molecules
- Variationally stable
  - (i) Foldy-Wouthuysen (FW) transformation
  - (ii) Douglas-Kroll (DK) transformation

Foldy-Wouthuysen (FW) transformation : PRA, 78, (1950) 29

$$\hat{H}'_{2comp} = U\hat{H}_{4comp}U^{\dagger}.$$

$$U = \ldots U_2 U_1 U_0$$

Product of series of transformations

$$\hat{H}_{DCB/DCG} = \sum_{i}^{n} \hat{h}_D(i) + \frac{1}{2}\sum_{i\neq j}^{n} \hat{g}_{ij}^{Breit/Gaunt}$$

FW

$$\hat{H}^{BP} = \sum_{i} \hat{h}^{BP}(i) + \sum_{i<j} \hat{g}_{ij}^{BP}$$

- Highly singular
- Variationally unstable

Coulomb, spin-orbit, spin-spin, orbit-orbit, higher order terms

First order relativistic Hamiltonian

Douglas-Kroll (DK) transformation

(Ann. Phys. 82(1974)89)

Expansion parameter:
FW transformation : (1/c)
DK transformation : V_{ext}

$$\hat{U}_n = (1+W_n^2)^{1/2} + W_n,$$

W_n is an anti-Hermitian operator

Idea: Block diagonalisation of the Dirac operator

$$\hat{H}^{decoupled} = U\hat{H}_D U^+ = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}$$

[Electronic bound + continuum states defined just by h+] - complete elimination of small component

Identify: odd operators (couples LS or SL) : $c\alpha p$
even operators (couples LL or SS) : $(\beta - 1)$, V

Find: A unitary matrix which removes the odd terms

$$H^{\text{decoupled}} \approx \beta E_p + \mathcal{E}_1 - \beta(W_1 E_p W_1 + \frac{1}{2}[W_1{}^2, E_p]),$$

2^{nd} order in V_{ext}
DK2 (good for chemical appli.)

DK2- Hess, PRA 32(1985) 756, Hess, PRA 33(1986) 3742
DK3- Nakajima, Hirao, JCP, 113 (2000) 7786
DKH – infinite order – Reiher, Wolf, JCP, 121 (2004) 2037; JCP, 121(2004) 10945

Transformed two component Hamiltonian

Hess et al., Modern electronic structure theory, Part I, ed. D.R. Yarkony, Advanced series in physical chemistry, Vol.2, p 152-278(1995)

$$\hat{H}^{DK} = \sum_{i}(E_i + \hat{V}^{sf}_{eff}(i) + \hat{h}^{DK}_{SO}(i)) + \sum_{i\neq j}(\hat{V}^{eff-sf}_{ij} + \hat{g}^{DK}_{SO\,ij}),$$

- Spin free terms (kinematics, scalar relativistic terms)
- Spin-orbit terms (spin-spin, spin-orbit terms)

How can we separate these terms?

$$(\hat{\sigma}\cdot\hat{\mathrm{a}})(\hat{\sigma}\cdot\hat{\mathrm{b}}) = \hat{\mathrm{a}}\cdot\hat{\mathrm{b}} + i\hat{\sigma}\cdot(\hat{\mathrm{a}}\times\hat{\mathrm{b}}),$$

Dirac relation

Why are we separating the terms into SF and SO terms?

- Many center 2-electron SO integrals are computationally expensive

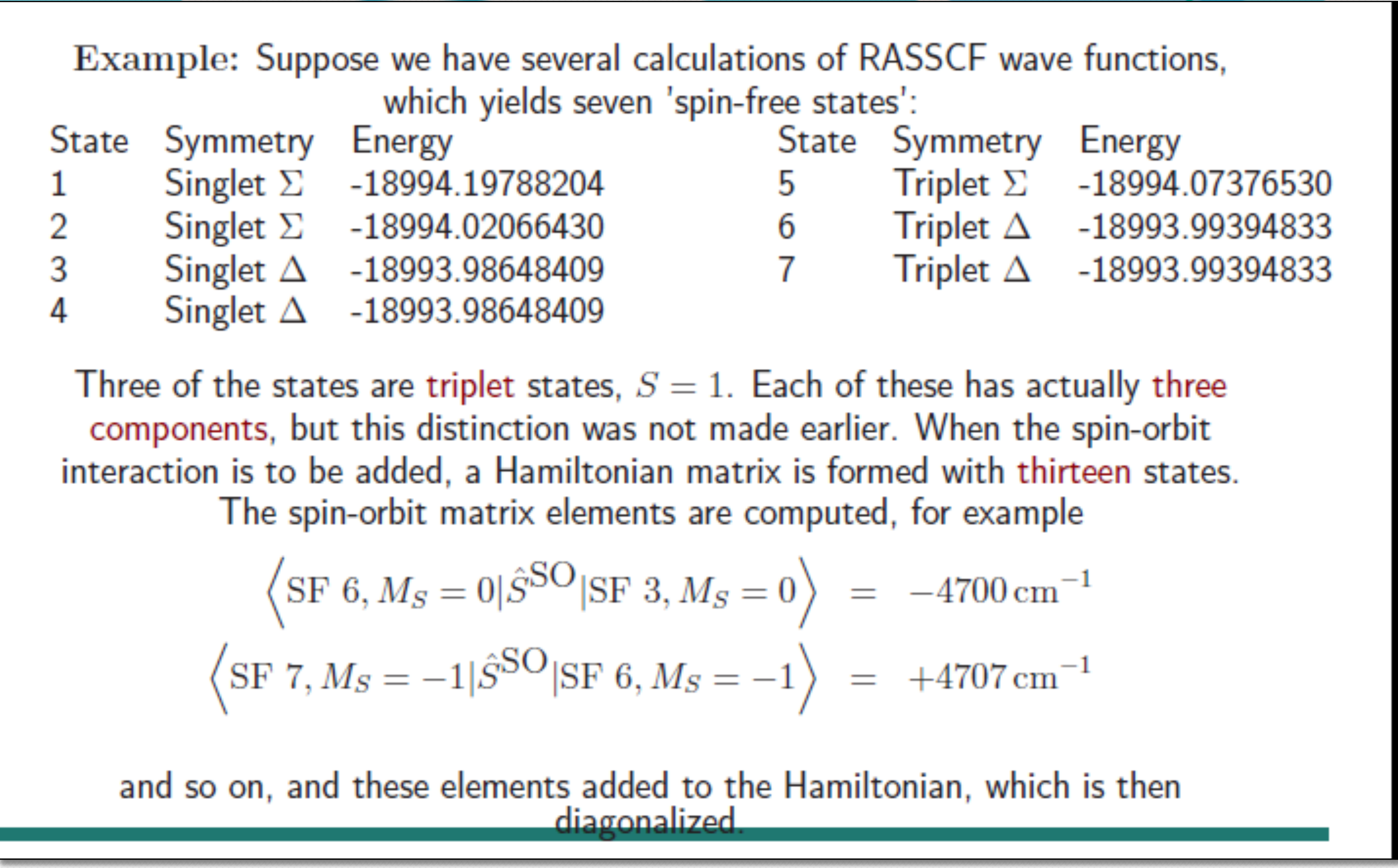
~ similar order - computation of 2 electron integrals over small basis

How do we compute SO effects in molecules? – first order Perturbation theory

- Define a pseudo **one-center** mean field SO operator (MFSO)
- RASSI-SO - MOLCAS

✓ Spin-free states are obtained first using scalar terms (Sz is not defined)

✓ Using H = scalar term + MFSO, Basis : spin-free states



Example: Suppose we have several calculations of RASSCF wave functions, which yields seven 'spin-free states':

State	Symmetry	Energy	State	Symmetry	Energy
1	Singlet Σ	-18994.19788204	5	Triplet Σ	-18994.07376530
2	Singlet Σ	-18994.02066430	6	Triplet Δ	-18993.99394833
3	Singlet Δ	-18993.98648409	7	Triplet Δ	-18993.99394833
4	Singlet Δ	-18993.98648409			

Three of the states are triplet states, $S = 1$. Each of these has actually three components, but this distinction was not made earlier. When the spin-orbit interaction is to be added, a Hamiltonian matrix is formed with thirteen states. The spin-orbit matrix elements are computed, for example

$$\begin{aligned}\left\langle \mathrm{SF}\ 6, M_S = 0 | \hat{S}^{\mathrm{SO}} | \mathrm{SF}\ 3, M_S = 0 \right\rangle &= -4700\,\mathrm{cm}^{-1} \\ \left\langle \mathrm{SF}\ 7, M_S = -1 | \hat{S}^{\mathrm{SO}} | \mathrm{SF}\ 6, M_S = -1 \right\rangle &= +4707\,\mathrm{cm}^{-1}\end{aligned}$$

and so on, and these elements added to the Hamiltonian, which is then diagonalized.

Property Calculations (Change of Picture)

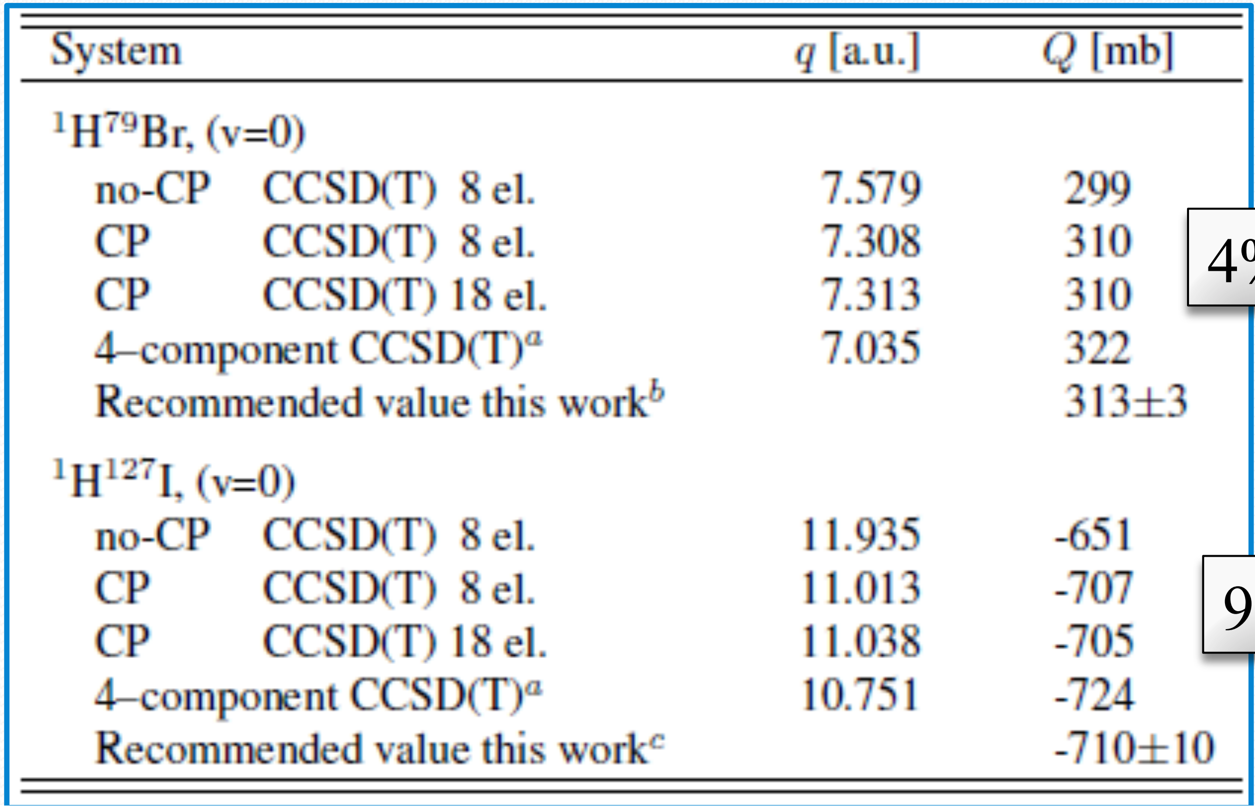
$$\langle \Psi | \hat{H}_D | \Psi \rangle = \langle \Psi | U^{+} U \hat{H}_D U^{+} U | \Psi \rangle = \langle U\Psi | U \hat{H}_D U^{+} | U\Psi \rangle = \langle \tilde{\Psi} | \hat{H}^{decoupled} | \tilde{\Psi} \rangle$$

$$\hat{H}^{decoupled} = U \hat{H}_D U^{+} = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}$$

$$U^{+} X_D U = X^{\text{decoupled}}$$

$$\tilde{\Psi} = U\Psi = \begin{pmatrix} \tilde{\Psi}_+ \\ 0 \end{pmatrix}$$

Nuclear quadruple moments

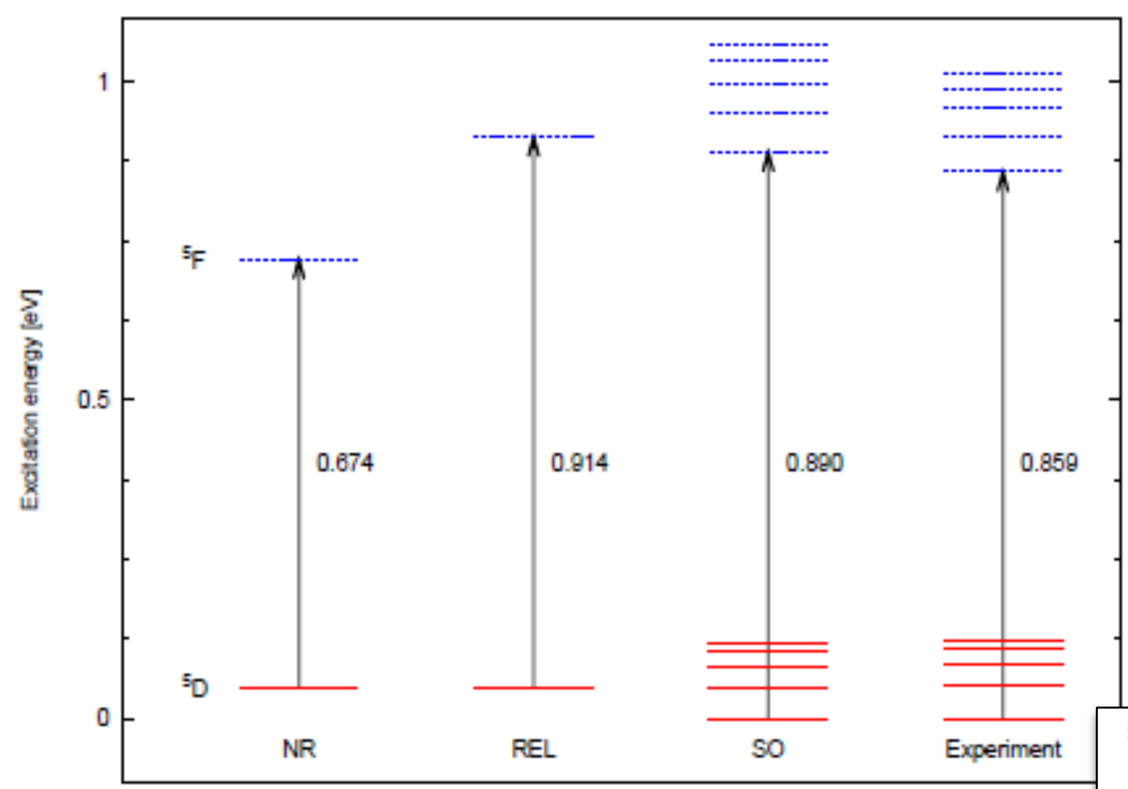


System		q [a.u.]	Q [mb]
$^{1}H^{79}Br$, (v=0)			
no-CP	CCSD(T) 8 el.	7.579	299
CP	CCSD(T) 8 el.	7.308	310
CP	CCSD(T) 18 el.	7.313	310
4–component CCSD(T)[a]		7.035	322
Recommended value this work[b]			313±3
$^{1}H^{127}I$, (v=0)			
no-CP	CCSD(T) 8 el.	11.935	-651
CP	CCSD(T) 8 el.	11.013	-707
CP	CCSD(T) 18 el.	11.038	-705
4–component CCSD(T)[a]		10.751	-724
Recommended value this work[c]			-710±10

4%

9%

Spin-orbit effects in atomic calculations



^{26}Fe atom

MRCI-SD method

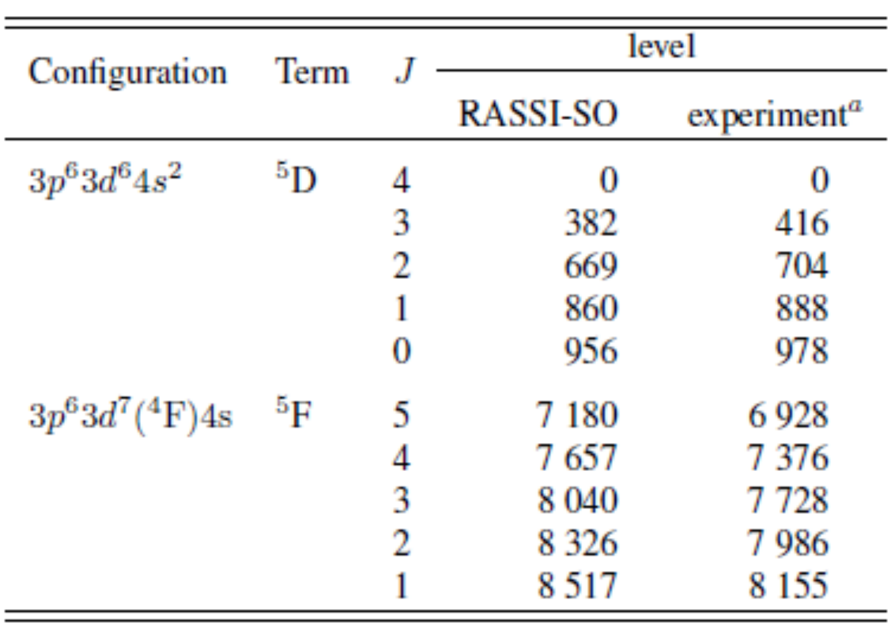
NR –non-relativistic

REL – DKH scalar

SO – RASSI-SO

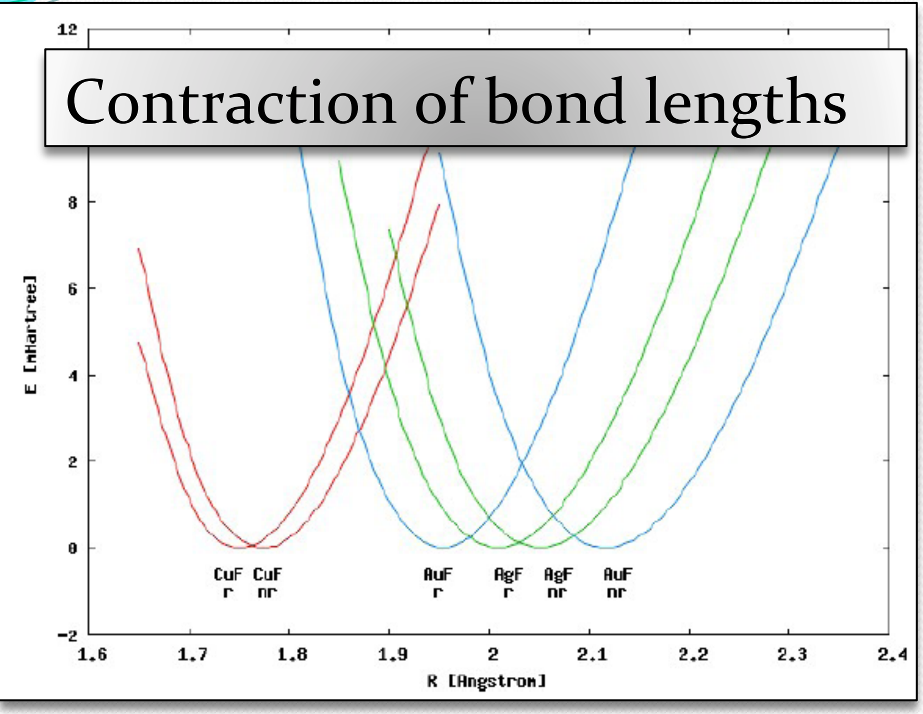
SO splitting ^{5}D ~ 22cm^{-1}

SO splitting ^{5}F ~ 110 cm^{-1}



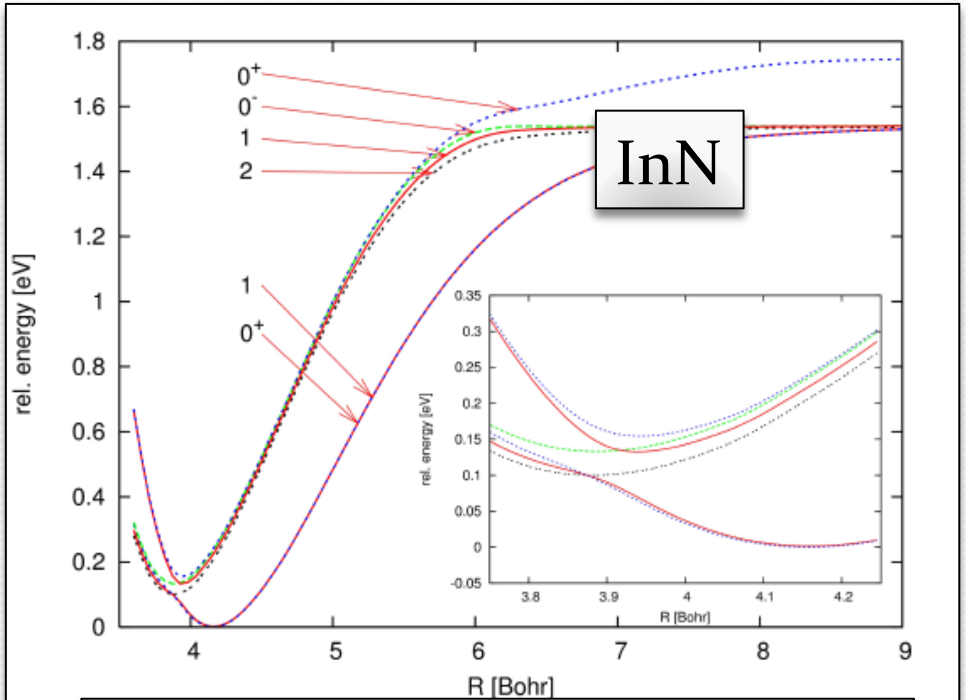
Configuration	Term	J	level	
			RASSI-SO	experiment^a
$3p^6 3d^6 4s^2$	^{5}D	4	0	0
		3	382	416
		2	669	704
		1	860	888
		0	956	978
$3p^6 3d^7 (^4\mathrm{F}) 4s$	^{5}F	5	7 180	6 928
		4	7 657	7 376
		3	8 040	7 728
		2	8 326	7 986
		1	8 517	8 155

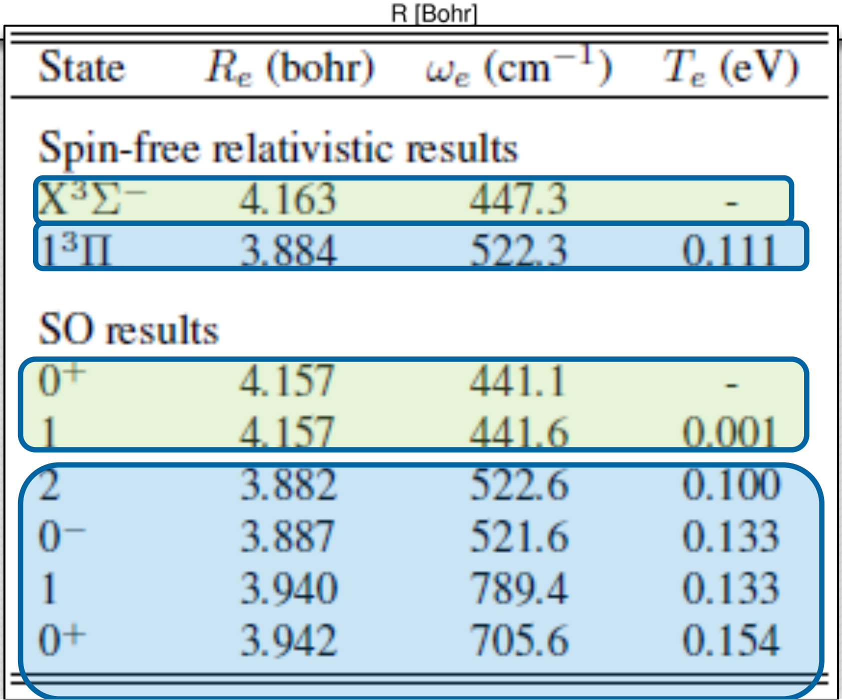
Spin-orbit effects in molecular geometries



Contraction of bond lengths

CuF R_e < AuF R_e < AgF R_e





State	R_e (bohr)	ω_e (cm^{-1})	T_e (eV)
Spin-free relativistic results			
$X^3\Sigma^-$	4.163	447.3	-
$1^3\Pi$	3.884	522.3	0.111
SO results			
0^+	4.157	441.1	-
1	4.157	441.6	0.001
2	3.882	522.6	0.100
0^-	3.887	521.6	0.133
1	3.940	789.4	0.133
0^+	3.942	705.6	0.154

Avoided crossings:
$^3\Sigma(0)$,$^3\Pi(0)$
$^3\Sigma(1)$,$^3\Pi(1)$

$^3\Sigma(2)$,$^3\Pi(0^-)$
Not affected

Photoassociation spectroscopy in ultracold polar molecules

Reference

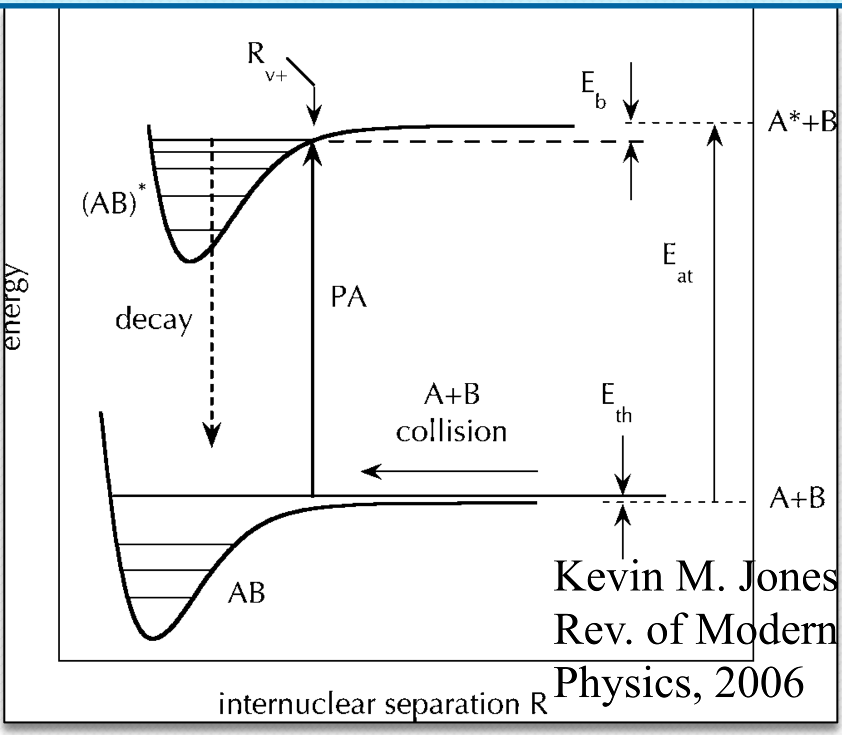
- Ultracold Photoassociation spectroscopy: Long range molecules and atomic scattering, Kevin M. Jones et al., Reviews of Modern physics, 78, 2006

Photo association (PA) of cold atoms : collision associated with light

(Collisions at long range / molecular binding energy/ scattering length / study on trap loss / A laser cooling method for molecules)

PA laser : S (ground) – P (excited)

$$A + B + h\nu \longrightarrow AB^*$$



Kevin M. Jones et al, Rev. of Modern Physics, 2006

Atomic ${}^{(2S+1)}L_J$	**Molecular** ${}^{(2S+1)}\Lambda_\Omega$
$X_s{}^2({}^1S_0)$ $+ \text{Li}\ {}_{2s}{}^1({}^2S_{1/2})$	${}^2\Sigma_{1/2}\mathbf{(1)}$ (ground)
$X_s{}^2({}^1S_0)$ $+ \text{Li}\ {}_{2s}{}^1({}^2P_{1/2,3/2})$	${}^2\Sigma_{1/2}\mathbf{(2)}$, ${}^2\Pi_{1/2,3/2}\ \mathbf{(1)}$
$X_{sp}({}^3P_{0,1,2})$ $+ \text{Li}\ {}_{2s}{}^1({}^2S_{1/2})$	${}^4\Pi_{5/2,3/2,1/2,1/2}\ \mathbf{(1)}$, ${}^2\Pi_{1/2,3/2}\mathbf{(2)}$, ${}^4\Sigma_{1/2,3/2}\mathbf{(1)}$, ${}^2\Sigma_{1/2}\mathbf{(3)}$
$X_{sp}({}^1P_1)$ $+ \text{Li}\ {}_{2s}{}^1({}^2S_{1/2})$	${}^2\Sigma_{1/2}\mathbf{(4)}$, ${}^2\Pi_{1/2,3/2}\mathbf{(3)}$

A pair of ultra cold ground-state atoms absorbs a photon, creating a molecule in an excited ro-vibrational electronic state. Thro spontaneous emission the molecule decays to high lying vibrational state of the ground/ excited meta stable state. Subsequently, through Raman pumping, stimulated emission brings the molecule to v=0 ground electronic state

Why polar molecules?

The interest in polar molecules stems from the fact that polar molecules have **permanent dipole moments**. This allows them to strongly interact with an **external electric fields** and with each other by **long range dipole-dipole forces**.

Long-range dipole-dipole interactions between molecules can create new types of **highly-correlated many-body states**.

Why ultra cold(< 1mK) polar molecules?

Slow molecules → Long measuring times → Narrow line widths → High resolution

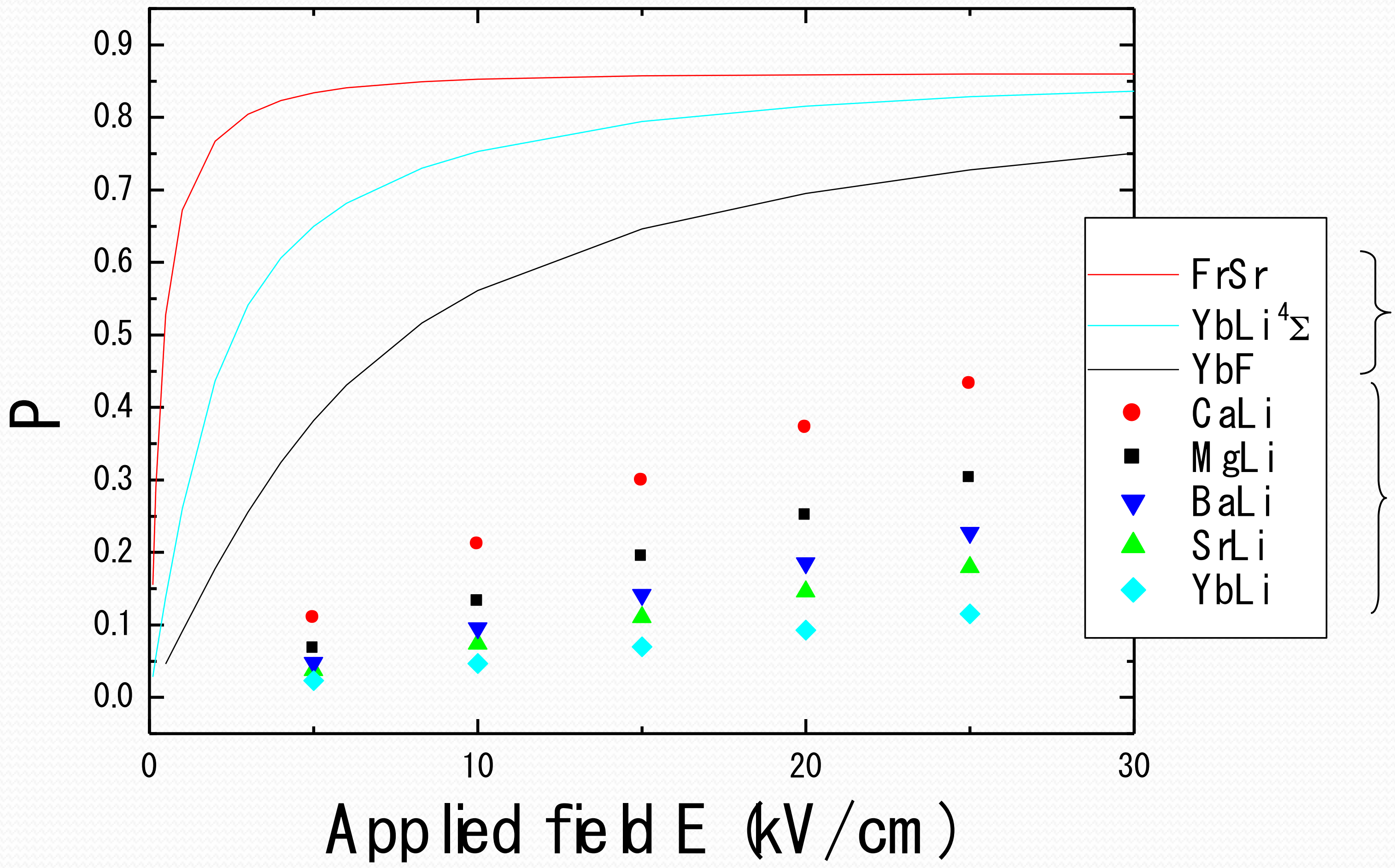
Dr. A. Vutha’s talk on reducing statistical uncertainty

What is the contribution from Quantum chemists?

- **Search of new types of ultracold polar molecule** as candidates for the study o long range dipole-dipole interactions - permanent dipole moment (PDM) is an indicator of the strength of these interactions.
- **Estimation of PDM** can lead to understanding of interactions between molecules, Bose-Einstein condensation, Fermi degeneracy etc
- **PDMs, TDMs and spontaneous emission rates** to determine the **type of lase for photoassociation spectroscopy** experiments
- Precise measurement of **molecular vibrational-rotational transition frequency**- **Measurement of variance of m_p/m_e** (proton to electron mass ratio and α (fine structure constant)
- **Frequency uncertainty** ~ **Stark effect** can be estimated from vibrational PDM and TDMs.
- **Lifetime of single vibrational quantum state** can be obtained from PDM - important requisite while designing experiments
- **Computation of molecular properties** – Parity violation/Parity-time violation
- **Non-radiative charge-transfer processes** – examining the **PDMs with avoided crossings**

Polarization factor of molecules

FrSr: d = 3.47 D, B = 0.36 GHz
Abe, Gopakumar, Hada
YbLi: $^4\Sigma$ d = 6.09 D, B = 3.6 GHz
Gopakumar, Abe, Hada
YbF: d = 3.7 D, B = 6.7 GHz



Aoki san's presentation

Why alkaline-earth-metal-Li molecules?

- Li being the lightest atom can be easily laser-cooled in ground state
- Alkali-Li molecules - Large PDM hence lifetime of single quantum state is short - not advantageous for experiments

Molecule	PDM(Debye)
NaLi	0.56
KLi	3.6
RbLi	4.13
CsLi	5.45
FrLi	-

Molecule	PDM(Debye)
MgLi	0.90
CaLi	1.15
SrLi	0.33
BaLi	-0.42
YbLi	-0.04

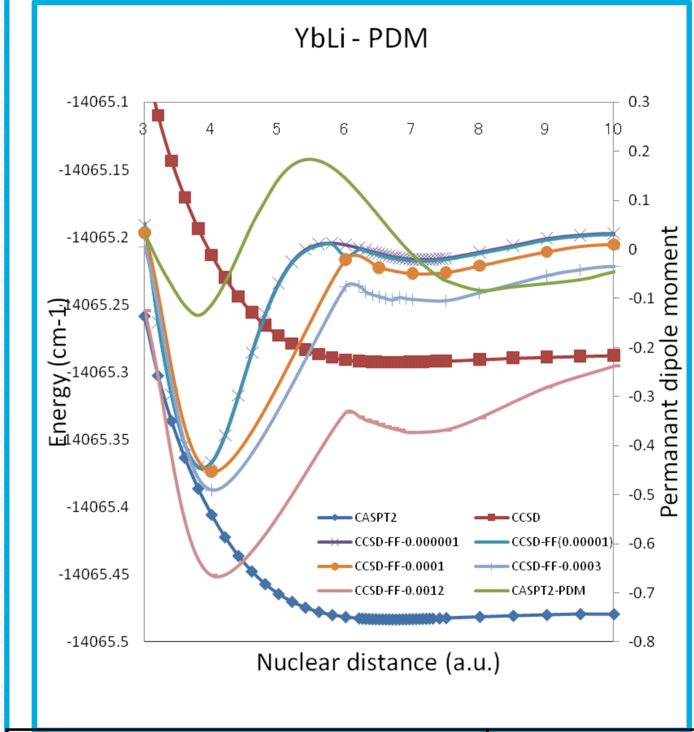
- Alkaline-earth –metal - Li molecules – PDM smaller than alkali-Li molecules ~ long lifetime of state advantageous for experimentalists
- Nuclear spin of X is zero – choosing ^{6}Li(nuclear spin =1)-fermionic or ^{7}Li (nuclear spin = 3/2) –bosonic molecules could be formed
- Simple energy structure due to zero nuclear spin of even alkaline-earth-metal atoms

Experiment/ theory work -LiYb molecule

- **Experiment**- simultaneous MOT of ^{174}Yb and ^{6}Li

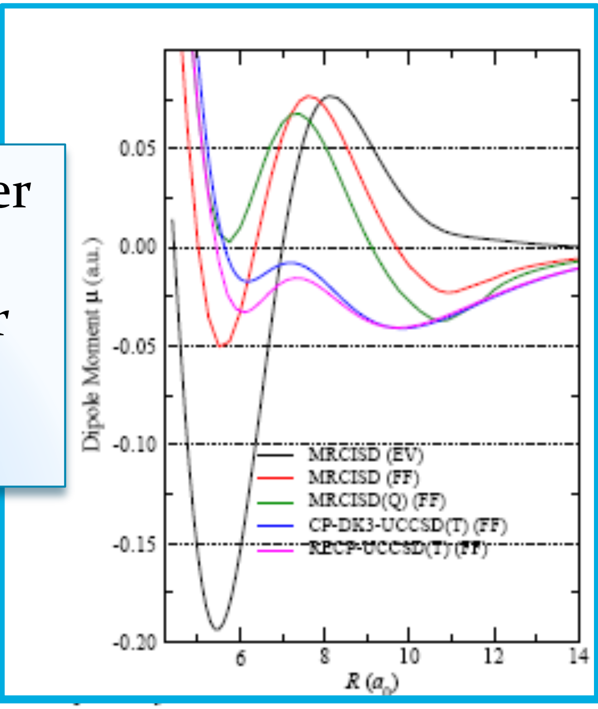
M. Okano et al, App. Phys,B, 98, 691 (**2010**) , Hideaki Hara al, PRL,106, 205304 (**2012**)

- **Computation** – Ground and excited states of LiYb molecule

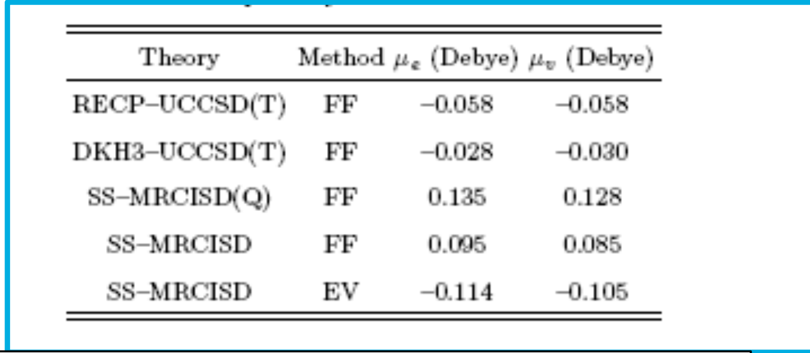


Absolute PDM is of same order by all correlation methods
- Not a probable candidate for long range dipole-dipole interaction studies

R_e (CASPT2) = 6.69 au,
R_e(CCSD(T)) = 6.70 au



Theory	μ_e (au)	μ_e (Debye)
SS-CASPT2	0.034	0.086
CCSD(T)-FF-0.000001	-0.0145	-0.037
CCSD(T)-FF-0.00001	-0.0172	-0.036

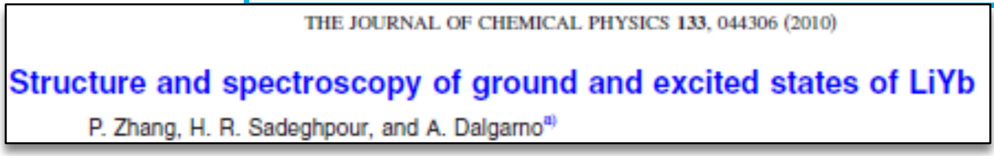


Theory	Method	μ_e (Debye)	μ_v (Debye)
RECP–UCCSD(T)	FF	−0.058	−0.058
DKH3–UCCSD(T)	FF	−0.028	−0.030
SS–MRCISD(Q)	FF	0.135	0.128
SS–MRCISD	FF	0.095	0.085
SS–MRCISD	EV	−0.114	−0.105

THE JOURNAL OF CHEMICAL PHYSICS 133, 124317 (2010)

Relativistic calculations of ground and excited states of LiYb molecule for ultracold photoassociation spectroscopy studies

Geetha Gopakumar,[1,a)] Minori Abe,[1] Bhanu Pratap Das,[2] Masahiko Hada,[1] and Kimihiko Hirao[3]



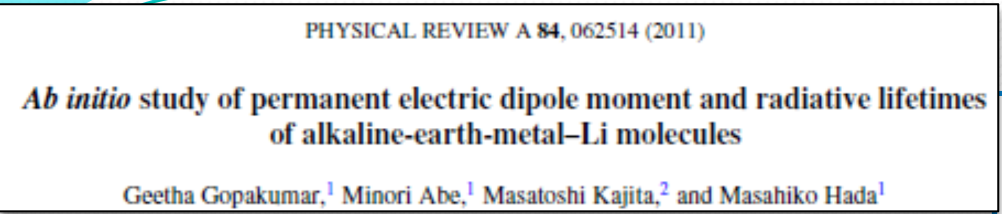
THE JOURNAL OF CHEMICAL PHYSICS 133, 044306 (2010)

Structure and spectroscopy of ground and excited states of LiYb

P. Zhang, H. R. Sadeghpour, and A. Dalgarno[a)]

PECs (CCSD(T)) and PDMs (FFPT)

Searching for other probable candidates : alkaline-earth-metal-Li molecules



PHYSICAL REVIEW A **84**, 062514 (2011)

Ab initio study of permanent electric dipole moment and radiative lifetimes of alkaline-earth-metal–Li molecules

Geetha Gopakumar,[1] Minori Abe,[1] Masatoshi Kajita,[2] and Masahiko Hada[1]

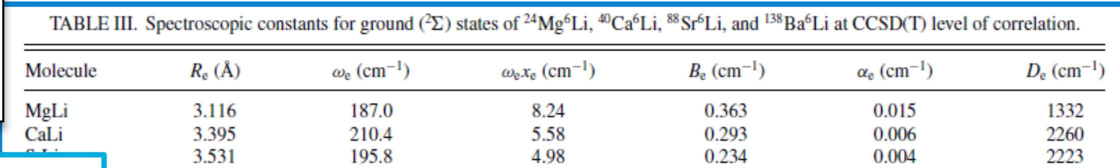
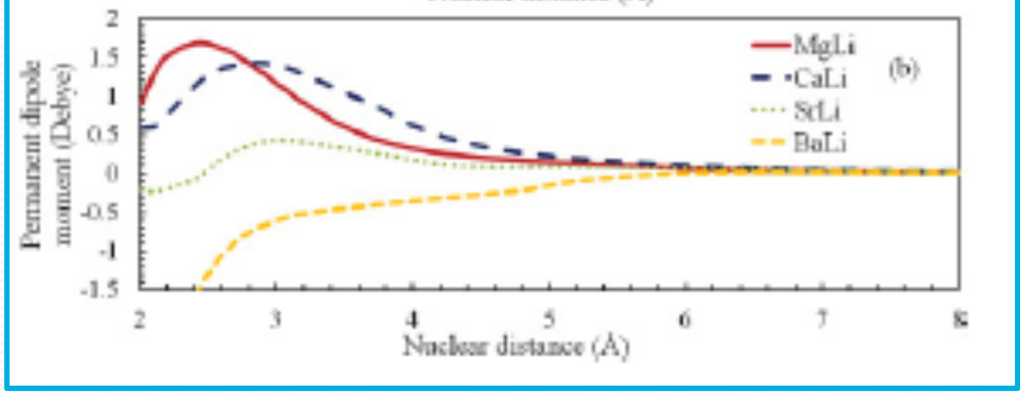


TABLE III. Spectroscopic constants for ground ($^2\Sigma$) states of ^{24}Mg^{6}Li, ^{40}Ca^{6}Li, ^{88}Sr^{6}Li, and ^{138}Ba^{6}Li at CCSD(T) level of correlation.

Molecule	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (cm^{-1})
MgLi	3.116	187.0	8.24	0.363	0.015	1332
CaLi	3.395	210.4	5.58	0.293	0.006	2260
	3.531	195.8	4.98	0.234	0.004	2223
	3.668	205.5	3.69	0.217	0.003	2871



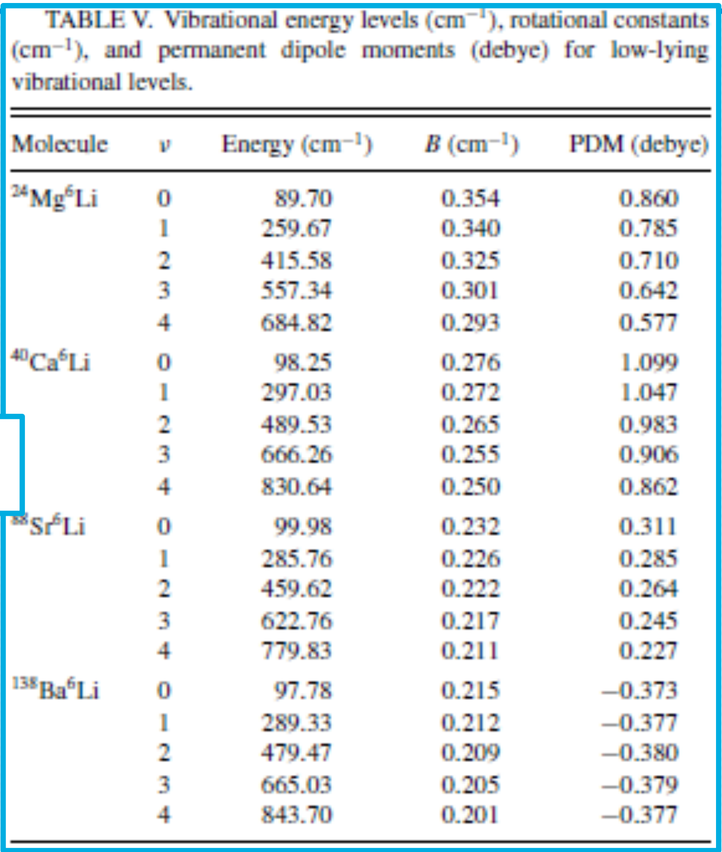


TABLE V. Vibrational energy levels (cm^{-1}), rotational constants (cm^{-1}), and permanent dipole moments (debye) for low-lying vibrational levels.

Molecule	v	Energy (cm^{-1})	B (cm^{-1})	PDM (debye)
^{24}Mg^{6}Li	0	89.70	0.354	0.860
	1	259.67	0.340	0.785
	2	415.58	0.325	0.710
	3	557.34	0.301	0.642
	4	684.82	0.293	0.577
^{40}Ca^{6}Li	0	98.25	0.276	1.099
	1	297.03	0.272	1.047
	2	489.53	0.265	0.983
	3	666.26	0.255	0.906
	4	830.64	0.250	0.862
^{88}Sr^{6}Li	0	99.98	0.232	0.311
	1	285.76	0.226	0.285
	2	459.62	0.222	0.264
	3	622.76	0.217	0.245
	4	779.83	0.211	0.227
^{138}Ba^{6}Li	0	97.78	0.215	−0.373
	1	289.33	0.212	−0.377
	2	479.47	0.209	−0.380
	3	665.03	0.205	−0.379
	4	843.70	0.201	−0.377

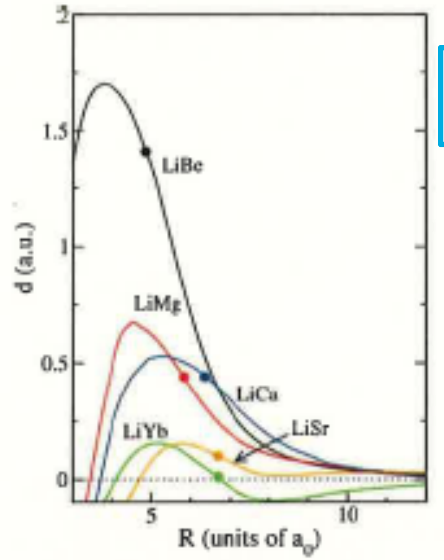
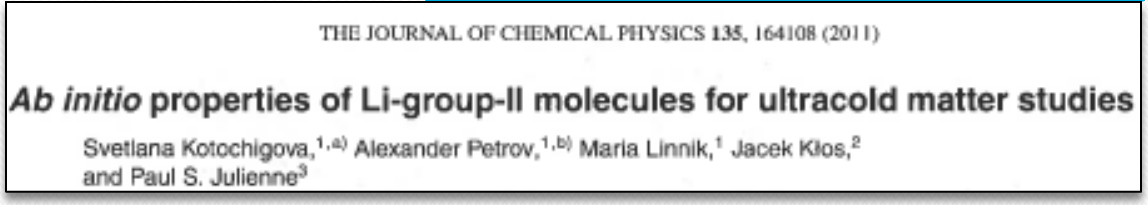


FIG. 7. Permanent dipole moment of the ground state of the Li-group II molecules and LiYb as a function of interatomic separation. Filled circles indicate dipole moment values at equilibrium separations of corresponding molecules.

Similar trend in PDM



THE JOURNAL OF CHEMICAL PHYSICS 135, 164108 (2011)

***Ab initio* properties of Li-group-II molecules for ultracold matter studies**

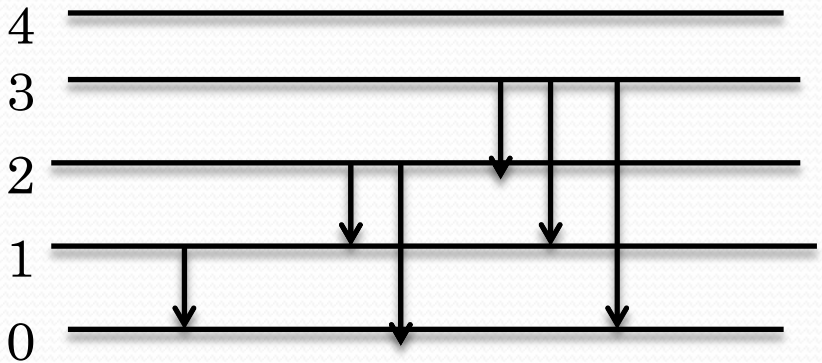
Svetlana Kotochigova,[1,a)] Alexander Petrov,[1,b)] Maria Linnik,[1] Jacek Klos,[2] and Paul S. Julienne[3]

Calculation details – Ground state of XLi molecules

- MOLCAS 7.2 software
- C_{2v} Point group symmetry
- Third order Douglas-Kroll-Hess (DKH) –relativistic Hamiltonian with relativistic basis set (ANO-RCC) – all molecules
- Potential energy curves and spectroscopic constants – CCSD(T) level of correlation
- Excitations are considered from Li(1s,2s), Mg(2p,3s), Ca(3p,4s), Sr(4p,5s) and Ba(5s,5p,6s)
- Electronic PDM using finite field perturbation theory - parameters (± 0.001 a.u to ± 0.0001 a.u.) - starting from CCSD(T) energy
- Electronic PDM at CASPT2 level – as expectation value as a check
- Numerical vibrational wave functions - Numerov method – vibrational PDM and TDM matrix elements
- BSSE (basis super position error) is negligible – largest ANO-RCC basis set

Spontaneous and black-body transition rates in alkali-earth-Li molecules

Black arrows – spontaneous emission



$$\Gamma_v^{spont} = \sum_{v'} \Gamma^{emis}\left(v \to v'\right)$$

$$\Gamma_v^{BB} = \sum_{v'} \bar{n}\left(\omega_{v'}\right)\Gamma^{emis}\left(v \to v'\right) + \sum_{v''} \bar{n}\left(\omega_{v''}\right)\Gamma^{abs}\left(v \to v''\right)$$

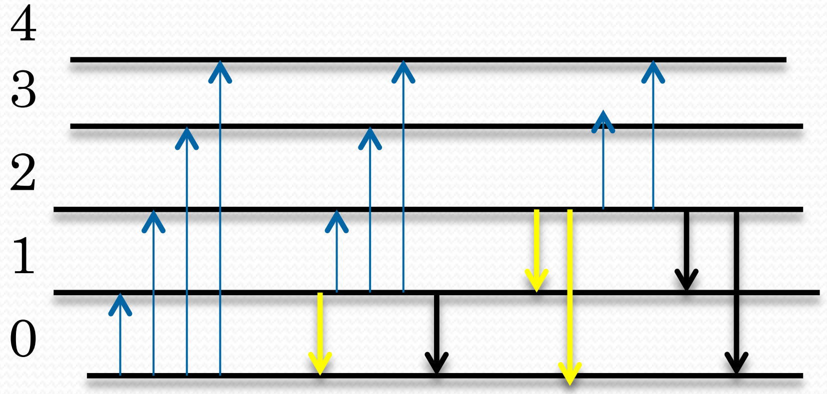
$$\bar{n}(\omega) = \frac{1}{e^{-\hbar\omega/k_B T} - 1}$$

$$\Gamma^{emis/abs}\left(v \to v'\right) = \frac{8\pi}{3}\frac{1}{\hbar c^3}\omega^3 \left|\left\langle v\right|d\left|v'\right\rangle\right|^2$$

$$\Gamma_v^{tot} = \Gamma_v^{spont} + \Gamma_v^{BB}$$

$$\tau_v^{tot} = \frac{1}{\Gamma_v^{tot}}$$

Yellow arrows – Black-body emission
Orange arrows – Black-body absorption



Additional checks : Radiative lifetimes, dipole polarizability

Radiative transition : Spontaneous emission + Black-body emission + Black-body absorption (300K)

Dipole polarizability (second derivative of energy)

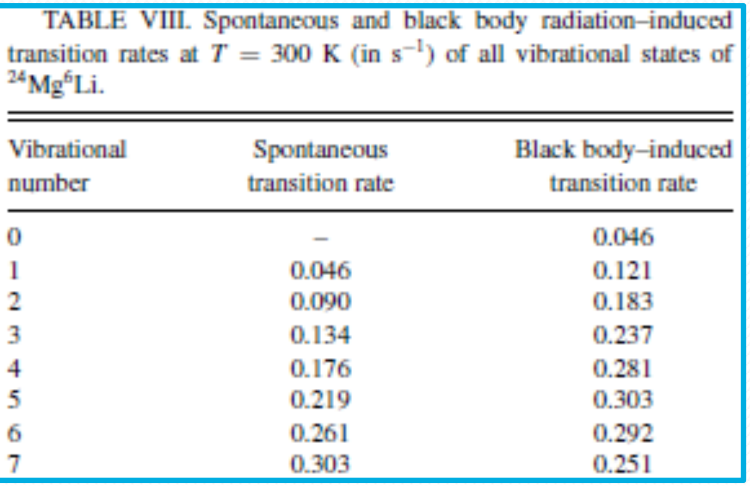


TABLE VIII. Spontaneous and black body radiation–induced transition rates at $T = 300$ K (in s^{-1}) of all vibrational states of $^{24}Mg^{6}Li$.

Vibrational number	Spontaneous transition rate	Black body–induced transition rate
0	–	0.046
1	0.046	0.121
2	0.090	0.183
3	0.134	0.237
4	0.176	0.281
5	0.219	0.303
6	0.261	0.292
7	0.303	0.251

Low lying vib levels

Spont. Tran. Rate < BB tran.rate

Lifetime is limited by BB trans. Rate

High lying vib levels

Spon. Tran. Rate > BB tran. Rate

Contribution from overtone transitions

(an-harmonicity of the PEC)

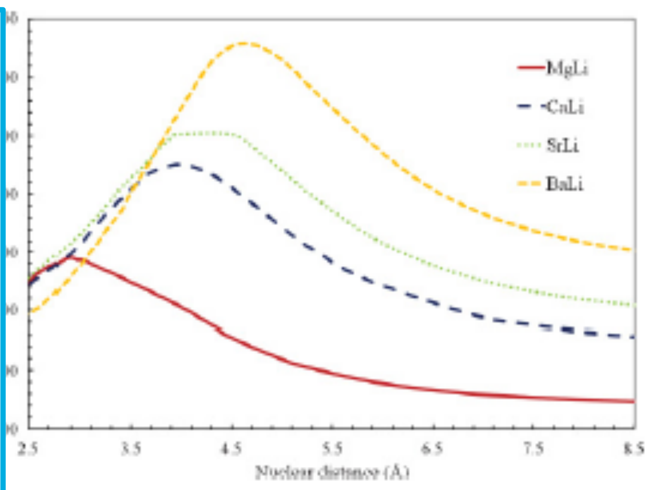
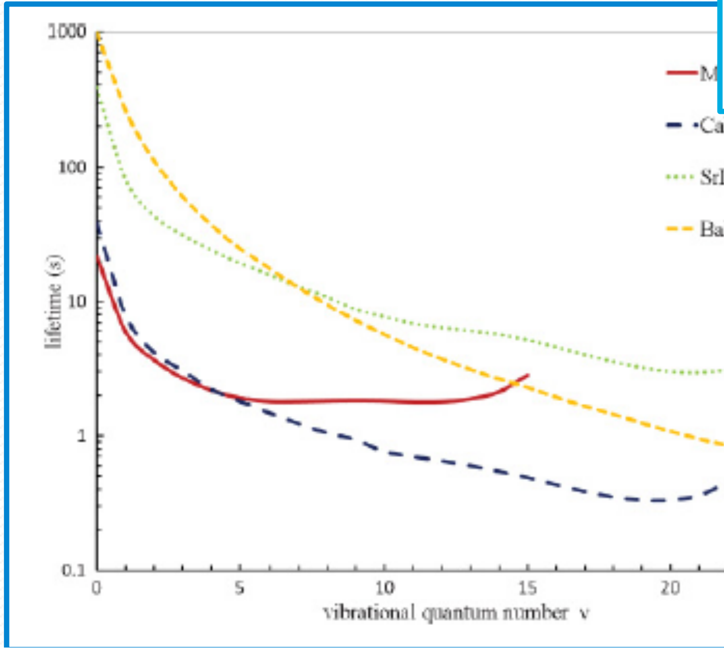
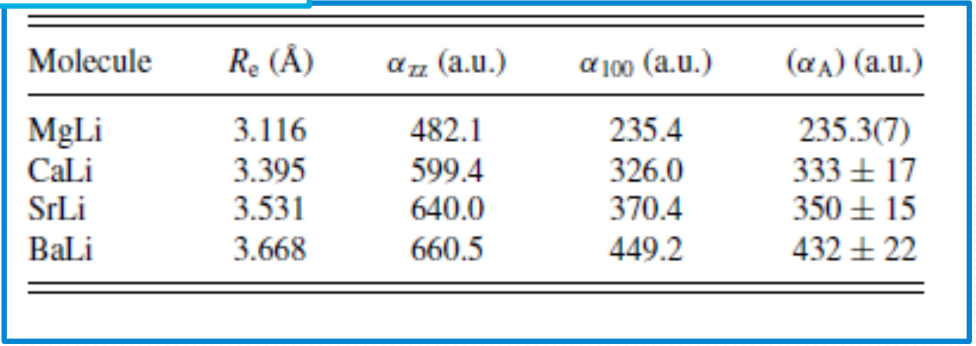


FIG. 3. (Color online) Dipole polarizability of the ground $^2\Sigma$ es for AEM-Li molecules [AEM: Mg (thick red line), Ca (blue g dashed line), Sr (green dotted line), and Ba (orange short dashed)] (in a.u.) at CCSD(T) levels of correlation.





Molecule	R_e (Å)	α_{zz} (a.u.)	α_{100} (a.u.)	(α_A) (a.u.)
MgLi	3.116	482.1	235.4	235.3(7)
CaLi	3.395	599.4	326.0	333 ± 17
SrLi	3.531	640.0	370.4	350 ± 15
BaLi	3.668	660.5	449.2	432 ± 22

Lifetime of v=0, J=0 vibrational state

$^6Li^{24}Mg$ =22s , $^6Li^{40}Ca$ = 39s ,

$^6Li^{88}Sr$ = 380s and $^6Li^{138}Ba$ = 988s

Candidates suitable for ultracold matter studies

MgLi : Ground state PDM - large but cooling of Mg atom difficult

CaLi : Ground state PDM – large; cooling of Ca already achieved

(T. Binnewies et al, PRL, 87, 123002 (2001)

SrLi : Ground state PDM – moderate ; cooling of Sr already achieved

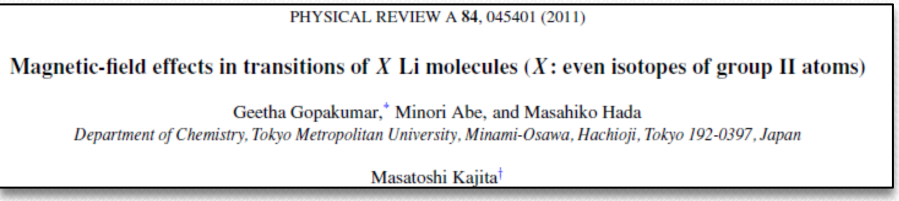
(H. Katori et al, PRL, 82, 1116 (1999)

Simultaneous cooling and trapping of Li and Sr for electron EDM measurements

(Torri et al, 5th International workshop on FPUA 2011, p-121-123)

BaLi: Ground state PDM – small – cooling of Ba already achieved

(De Subhadeep, Phd Thesis, TRIuP facility at KVI, Netherlands)



PHYSICAL REVIEW A **84**, 045401 (2011)

Magnetic-field effects in transitions of *X* Li molecules (*X*: even isotopes of group II atoms)

Geetha Gopakumar,* Minori Abe, and Masahiko Hada

Department of Chemistry, Tokyo Metropolitan University, Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Masatoshi Kajita†

PHYSICAL REVIEW A **84**, 022507 (2011)

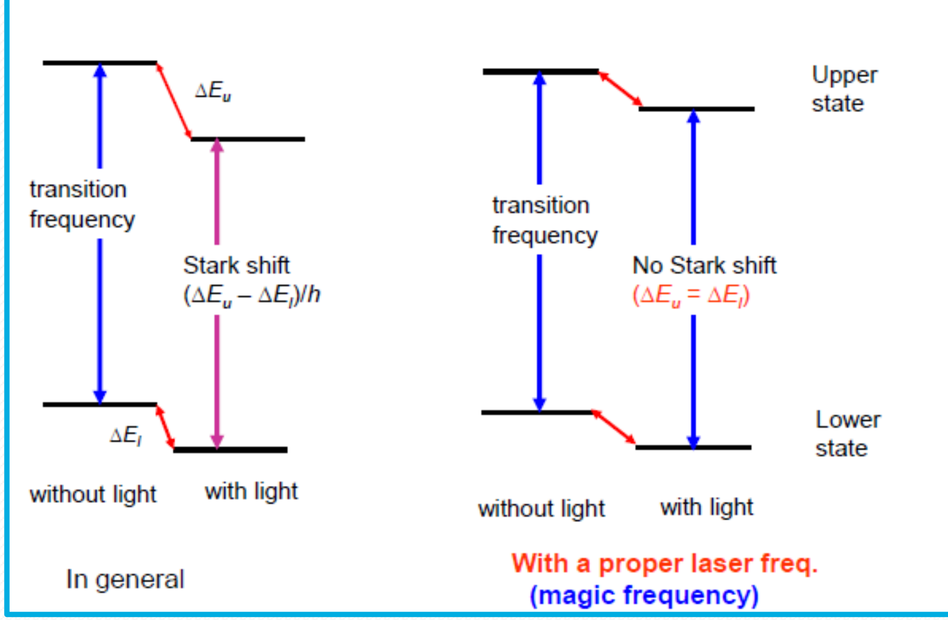
Elimination of the Stark shift from the vibrational transition frequency of optically trapped ^{174}Yb^{6}Li molecules

Masatoshi Kajita*

nal Institute of Information and Communications Technology, Koganei, Tokyo 184-8795,

Geetha Gopakumar, Minori Abe, and Masahiko Hada

Stark shift in the transition frequency



In general

With a proper laser freq.
(magic frequency)

Vibrational transition frequency

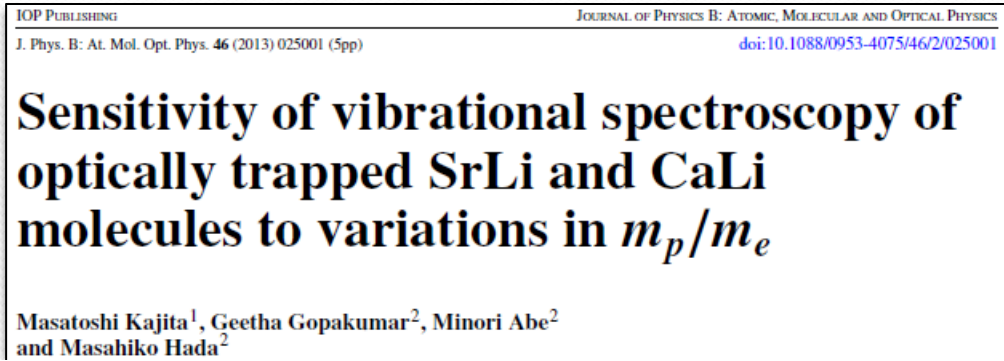
PHYSICAL REVIEW A **85**, 062519 (2012)

Accuracy estimations of overtone vibrational transition frequencies of optically trapped ^{174}Yb^{6}Li molecules

Masatoshi Kajita*

National Institute of Information and Communications Technology, Koganei, Tokyo 184-8795, Japan

Geetha Gopakumar, Minori Abe, and Masahiko Hada



IOP PUBLISHING | JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **46** (2013) 025001 (5pp) | doi:10.1088/0953-4075/46/2/025001

Sensitivity of vibrational spectroscopy of optically trapped SrLi and CaLi molecules to variations in m_p/m_e

Masatoshi Kajita[1], Geetha Gopakumar[2], Minori Abe[2] and Masahiko Hada[2]

Implication of variance of m_p/m_e and α in Grand Unification Theory (GUT)

- Grand unification theory implies the possibility of variance of various natural fundamental dimensionless constants.
- One example

  $[d(m_p/m_e)/dt] /m_p/m_e = R_c\ [d\alpha /dt]/\alpha$

  $20 < R_c < 40$: depends on the detail of GUT

  where α is the fine structure constant $\alpha = e^2/ hc4\pi\varepsilon_o$
- To determine R_c , information of variation of α and m_p/m_e is required.

Calculation details – Ground and excited states of CaLi molecule

- **Program** : MOLCAS 7.2 version.
- **Hamiltonian** : Relativistic spin free 3rd Order Douglas-Kroll Hamiltonian
- **Correlation** : Spin free multi-state CASPT2 followed by first order Spin-Orbit effect using RASSI (RAS State Interaction Program) – SO-MS-CASPT2
- **Symmetry :** C_{2v}
- **Active Space for CASSCF :** 3 electrons in 8 orbitals (4s and 5p of Ca and 2s and 2p of Li) – (4,2,2,0)

  [**a1**: (Ca -4s, 4pz; Li – 2s, 2pz) **b1/b2** : Ca – 4px/4py; Li 2px/2py; **a2** - 0]
- **Number of roots for state averaged CASSCF** :

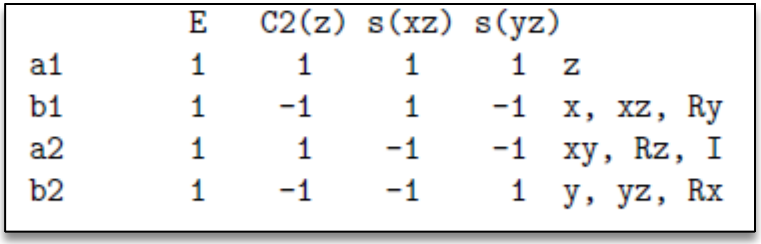
  $({}^2a_1 : 3, {}^2b_1 : 2, {}^2b_2 : 2 : {}^4a_1 : 1, {}^4b_1 : 1, {}^4b_2 : 1)$
- **Number of roots for spin-orbit CASPT2**

  $({}^2a_1 : 4, {}^2b_1 : 3, {}^2b_2 : 3 : {}^4a_1 : 1, {}^4b_1 : 1, {}^4b_2 : 1)$
- **Basis** : ROOS-ANO-RCC

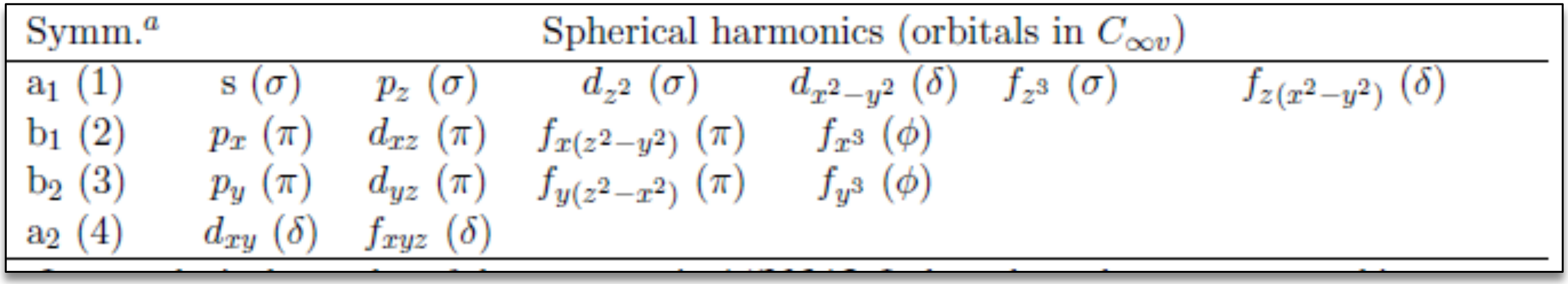
  (Ca) 20s16p6d4f – 10s9p6d4f

  (Li) 14s9p4d3f1g - 8s7p4d2f 1g

Character table for C_{2V}

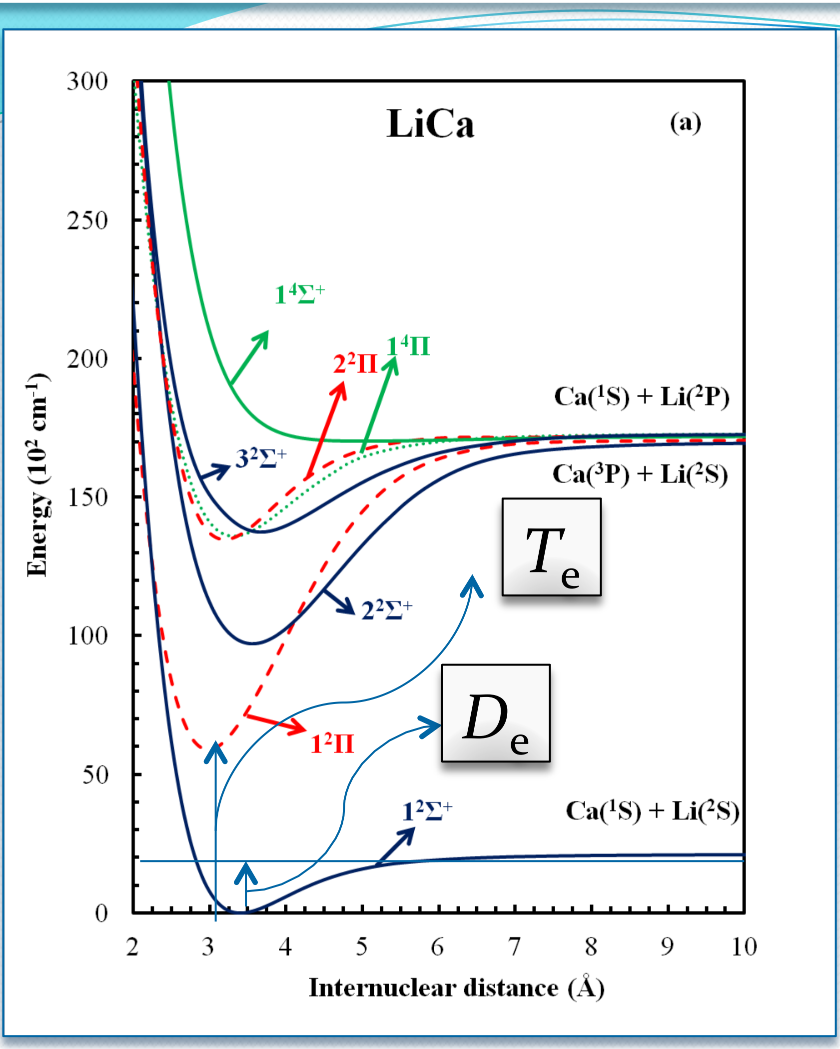


```
          E   C2(z) s(xz) s(yz)
a1        1     1     1     1   z
b1        1    -1     1    -1   x, xz, Ry
a2        1     1    -1    -1   xy, Rz, I
b2        1    -1    -1     1   y, yz, Rx
```



Symm.[a]	Spherical harmonics (orbitals in $C_{\infty v}$)					
a_1 (1)	s (σ)	p_z (σ)	d_{z^2} (σ)	$d_{x^2-y^2}$ (δ)	f_{z^3} (σ)	$f_{z(x^2-y^2)}$ (δ)
b_1 (2)	p_x (π)	d_{xz} (π)	$f_{x(z^2-y^2)}$ (π)	f_{x^3} (ϕ)		
b_2 (3)	p_y (π)	d_{yz} (π)	$f_{y(z^2-x^2)}$ (π)	f_{y^3} (ϕ)		
a_2 (4)	d_{xy} (δ)	f_{xyz} (δ)				

CaLi spin-free CASPT2 PECs + spectroscopic constants



Molecular $^{(2S+1)}\Lambda_\Omega$	Atomic $^{(2S+1)}L_J$
$^2\Sigma^+{}_{1/2}$	Li ($^2S_{1/2}$) + Ca/Sr ($^1S_0$)
$^2\Pi_{3/2,1/2}$, $^2\Sigma^+{}_{1/2}$	Li ($^2P_{1/2,3/2}$) + Ca/Sr ($^1S_0$)
$^4\Pi_{5/2,3/2,1/2,1/2}$, $^2\Pi_{3/2,1/2}$, $^4\Sigma^+{}_{3/2,1/2}$, $^2\Sigma^+{}_{1/2}$	Li ($^2S_{1/2}$) + Ca/Sr ($^3P_{0,1,2}$)

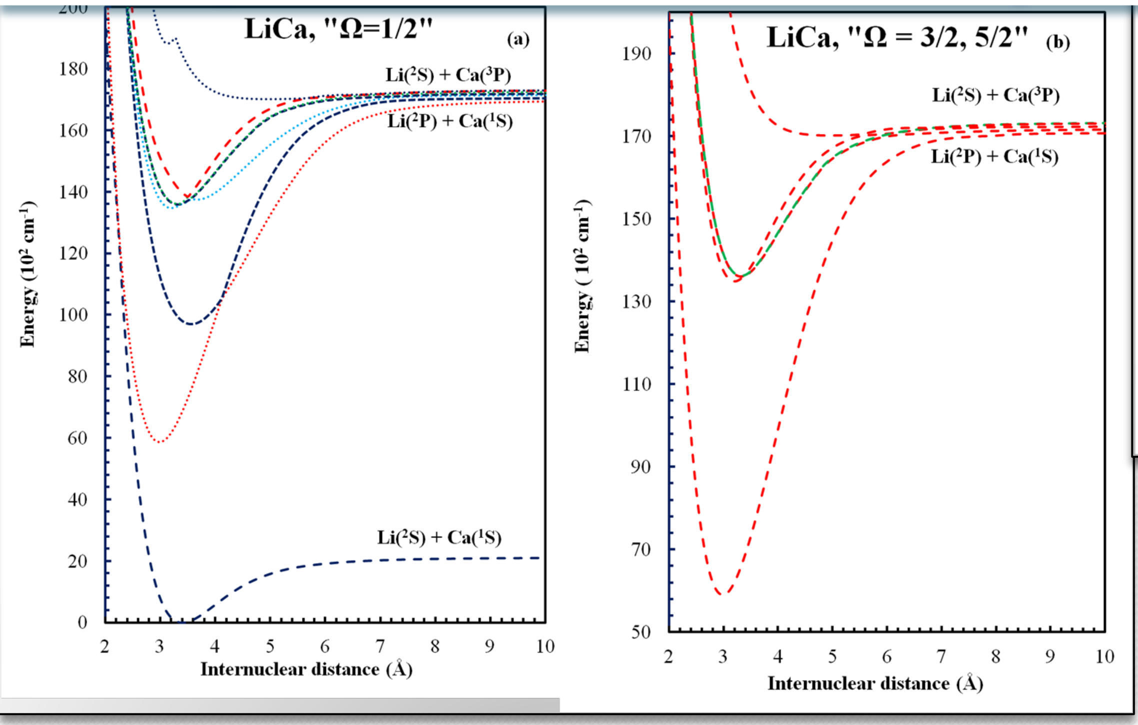
LiCa (Λ–S)	R_e (Å)	D_e (cm⁻¹)	ω_e (cm⁻¹)	B_e (cm⁻¹)	T_e (cm⁻¹)
$1^2\Sigma^+$	3.40	2131	206.2	0.28	–
$1^2\Pi$	2.98	11225	305.7	0.35	5882.05
$2^2\Sigma^+$	3.56	7280	208.7	0.25	9702.61
$2^2\Pi$	3.20	3759	254.8	0.30	13479.71
$1^4\Pi$	3.32	3721	223.2	0.29	13603.72
$3^2\Sigma^+$	3.67	3572	174.5	0.23	13745.06
	5.01	265	29.6	0.13	17227.63

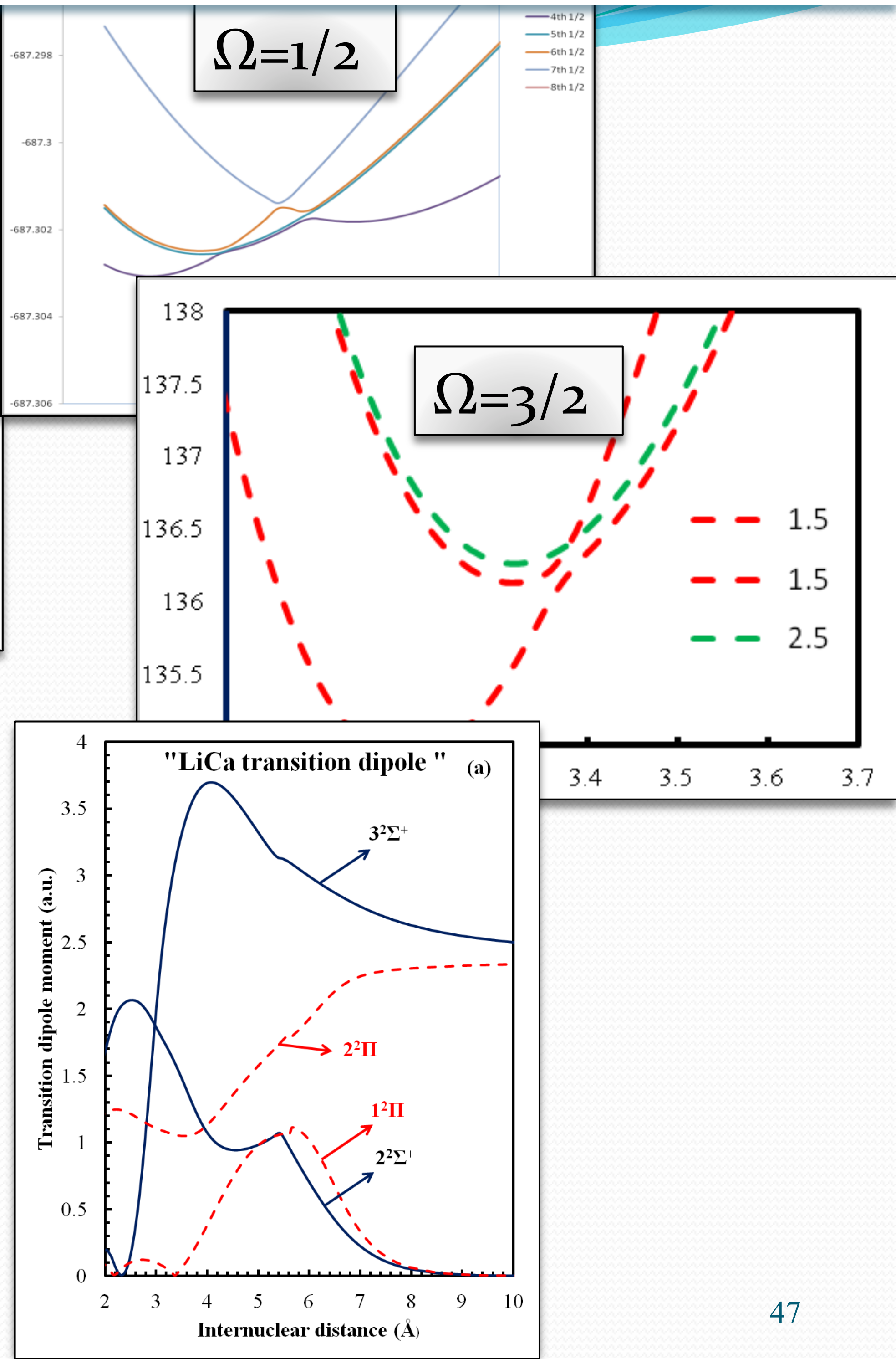
Spin-free excitation energies

Calcium			Lithium		
State	Present	Expt.	State	Present	Expt.
³P	14956	15263	²P	15212	14904

Inclusion of 3d in CAS space
EE of ³P = 15310 cm⁻¹

CaLi spin-orbit CASPT2 PECs + spin-free Transition dipole moment





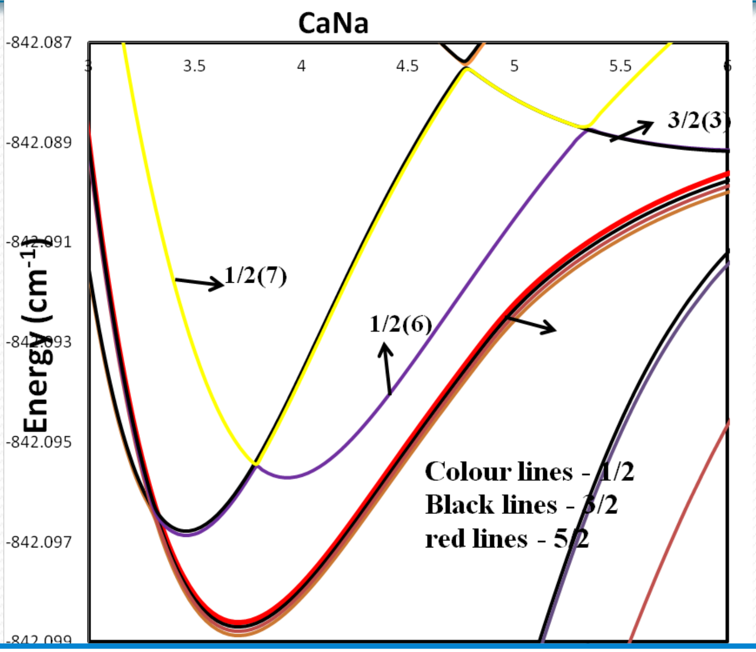
Spin-orbit effects leads to several states with double minima due to avoided crossings

- ➢**Atomic limits** - Order of ³P and ²P states are not obtained - (325 cm⁻¹)
- ➢**Molecular regions** - character of states are obtained as expected
- ➢ Excitation energy error < 3%
- ➢ spectroscopic constant error <1%

²P (2s-2p) transition dipole moment
100 a.u - 2.37 a.u. NIST – 2.36 a.u.

Spin-free

	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	T_e (cm^{-1})
$1^2\Sigma$	3.72	1242.09	92.03	0.08	–
$1^2\Pi$	3.24	9144.71	167.07	0.11	7203.71
$2^2\Sigma$	3.83	6245.15	117.62	0.08	10211.57
$1^4\Pi$	3.70	2367.24	109.24	0.07	14092.04
$3^2\Sigma$	3.93	3364.94	102.24	0.07	14754.62
$2^2\Pi$	3.45	3763.38	136.16	0.10	14510.57
$1^4\Sigma$	6.36	271.81	11.31	0.03	16173.07

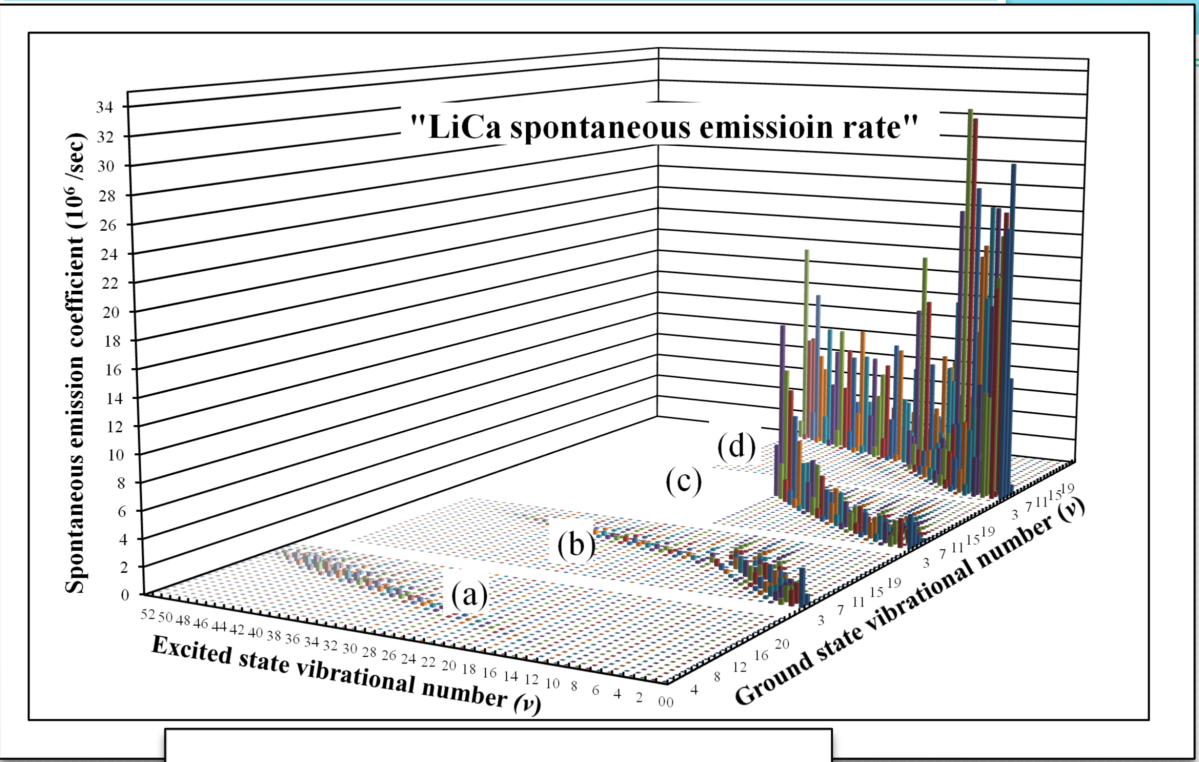


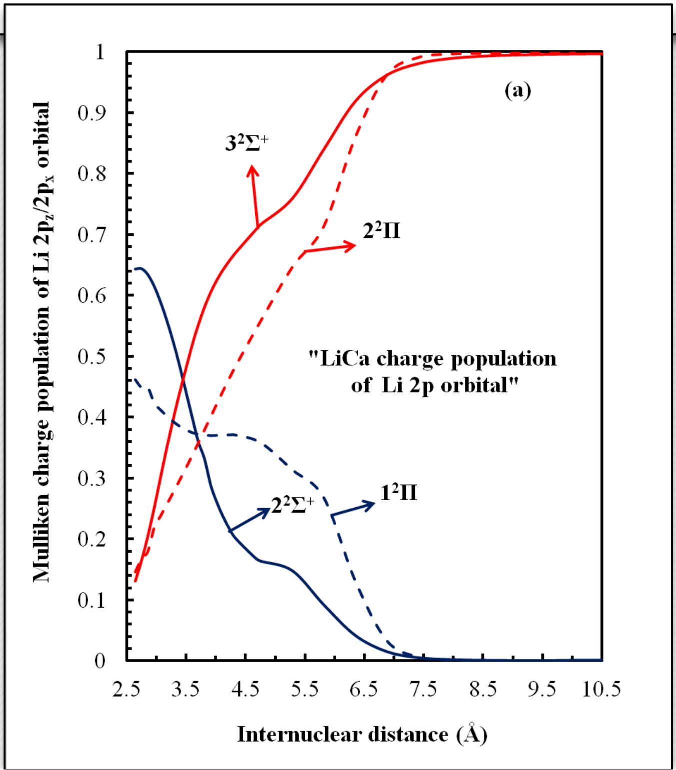
Spin-orbit

Ω	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	T_e (cm^{-1})
1/2(1)	3.72	1242.09	92.03	0.08	–
1/2(2)	3.24	9088.25	177.83	0.11	7180.45
3/2(1)	3.24	9056.79	167.65	0.50	7227.19
1/2(3)	3.82	6104.00	121.85	0.08	10212
1/2(4)	3.70	2290.61	103.93	0.08	14063.29
5/2(1)	3.70	2319.65	107.67	0.47	14121.01
3/2(2)	3.70	2287.39	105.68	0.08	14101.70
1/2(5)	3.70	2318.84	108.86	0.08	14082.38
1/2(6)(1m)	3.45	1920.41	91.99	0.09	14501.79
1/2(6)(2m)	3.93	-	-	-	14755.50
3/2(3)(1m)	3.45	1905.08	156.48	0.22	14520.67
3/2(3)(2m)	6.10	-	-	-	16188.65
1/2(7)(1m)	3.78	3311.71	169.17	0.08	14816.08
1/2(7)(2m)	5.32	-	-	-	16297.07
1/2(8)	4.76	1721.99	124.49	0.05	19343.77
3/2(4)	4.76	1717.15	124.11	0.05	16585.67

Moderate spin-orbit effect – crossing of $^4\Sigma$, $^2\Sigma$ and $^2\Pi$

Spontaneous emission rate (sec^{-1})





- (a) – $1^2\Sigma$ to $1^2\Pi$
  – 140000 /sec –not easy experimentally

- (b) – $1^2\Sigma$ to $2^2\Sigma$
  – 600000 /sec – not easy but ok
  (sensitive detectors in UV)
- (c) – $1^2\Sigma$ to $2^2\Pi$
  – 14000000 /sec - good observe fluorescence

- (d) – $1^2\Sigma$ to $3^2\Sigma$
  - 30000000 /sec - very good
  - more than 10^7 /sec

Observe LIF spectrum using laser diode or Ti: Sapphire laser

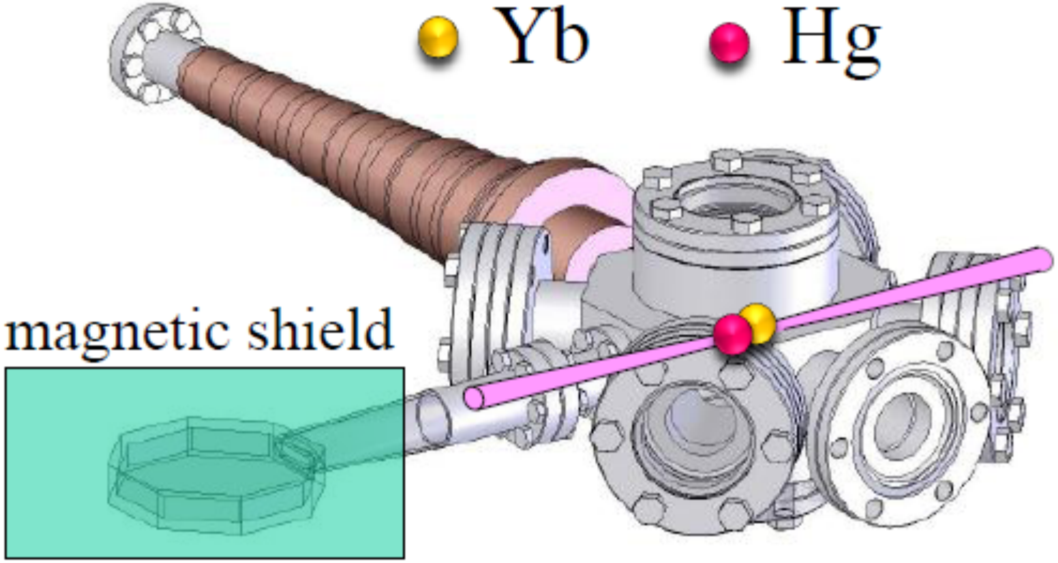
Measuring EDM using ultracold HgYb molecules

1. Dual MOT of Yb and Hg:

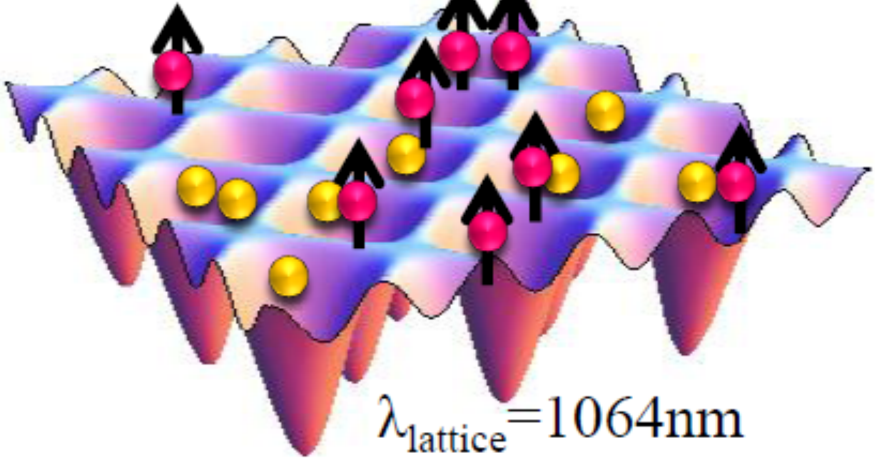
loaded from Zeeman Slower for Yb
Vapor Cell for Hg

2. Transfer of atoms
by Optical Tweezer:

215 mm travel, 1.7 s, 12% loss
(demonstrated)



3. Optical Pumping(F=1/2 ↔ F=1/2)
& Loading into 3D Optical Lattice:

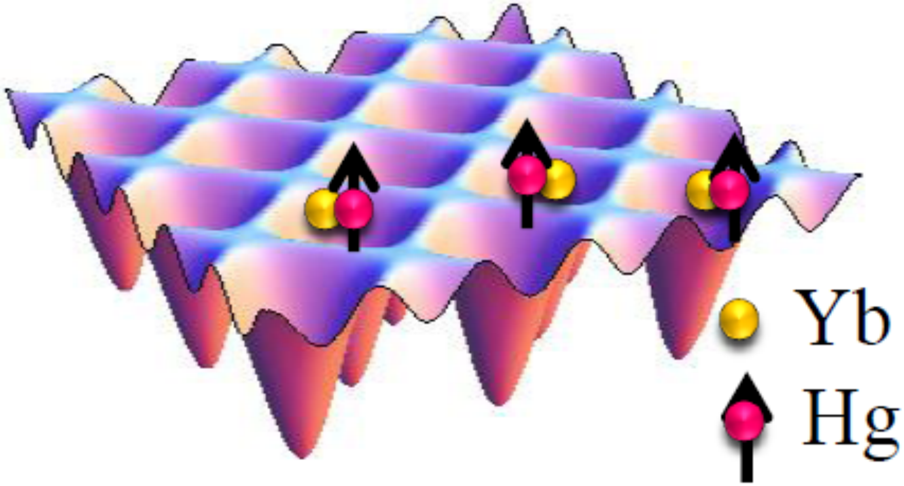


Optical Tweezer

Takahashi sensei – talk @
FPAU – 19-20-May-2012

Measuring EDM using ultracold HgYb molecules

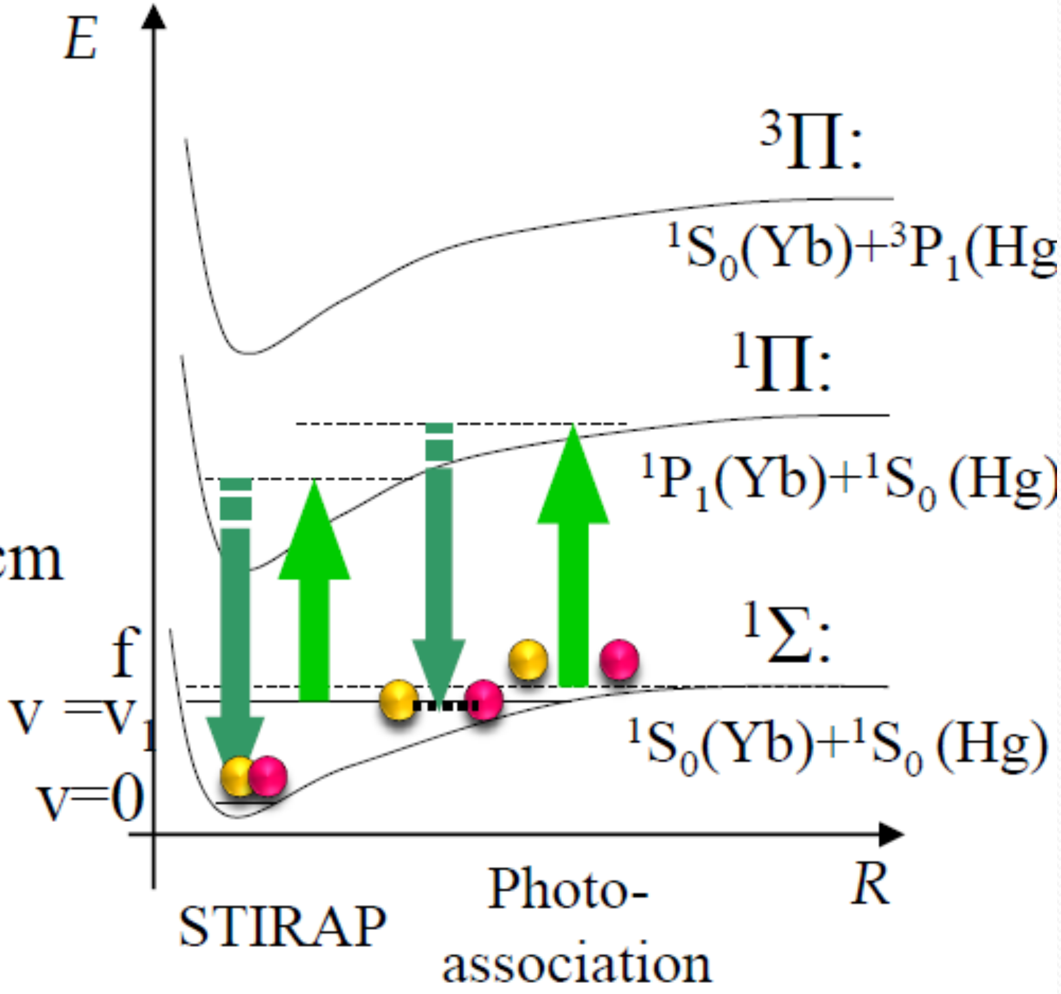
4. Photo-Association($f \rightarrow v=v_1$) and STIRAP($v=v_1 \rightarrow v=0$)
(Nuclear-Spin-Preserving)



5.Apply Electric Field:~10 kV/cm

3 sec. coherence time

6. STIRAP($v=0 \rightarrow v=v_1$) and
Photo-Dissociation($v=v_1 \rightarrow f$)
(Nuclear-Spin-Preserving)



Takahashi sensei – talk @
FPUA – 19-20-May-2012

Atomic calculations (validating whether the basis sets can represent the ground and excited states of atoms) – MS-CASPT2 – largest ANO-RCC basis sets

Yb			
^{1}S	0	ground	6s^2
^{3}P	0	17288.44	6s6p
	1	17992.01	
	2	19710.39	
^{3}D	1	24489.10	6s5d
	2	24751.95	
	3	25270.90	
^{1}P	1	25068.22	6s6p
^{1}D	2	27677.67	6s5d
^{3}S	1	32694.69	6s7s
^{1}S	0	34350.65	6s7s

	1st Calc	**2nd Calc**	**3rd Calc**
RAS	**2110**	**3110**	**5221**
A1	6s,6p_z(2)	6s,*s,6p_z(3)	6s,*s,6p_z,*d_{z2},*d_{x2-y2} (5)
B1	6p_x(1)	6p_x(1)	6p_x, *d_{xz}(2)
B2	6p_y(1)	6p_y(1)	6p_y,*d_{yz}(2)
A2	-	-	*d_{xy}(1)
States	^{1}S, ^{3}P and ^{1}P	^{1}S, ^{3}P, ^{1}P, ^{3}S and ^{1}S	^{1}S, ^{3}P, ^{1}P, ^{3}D, ^{1}D, ^{3}S and ^{1}S
States obtained in calc.	^{1}S, part of (^{3}P and ^{1}P) and ^{1}S and ^{3}S	^{1}S, ^{3}P, ^{1}P, ^{3}S and ^{1}S	^{1}S, ^{3}P, ^{1}P, ^{3}D, ^{1}D, ^{3}S and ^{1}S
Reason/ Problem	A1 RAS space – 6s, *s (not 6pz)	(1)6s*s and 6s6p excited states are mixed (2) Order is wrong	(1) Character of all states as expected (2) All states in order as obtained in NIST data

Excitation energy error estimate (3rd Calculation)
^{1}S, ^{3}P, ^{1}P, ^{3}D, ^{3}S and ^{1}S < 4%
1D < 5%

Hg			
^1S	0	ground	$7s^2$
^3P	0	37645.08	7s7p
	1	39412.30	
	2	44042.98	
^1P	1	54068.78	7s7p

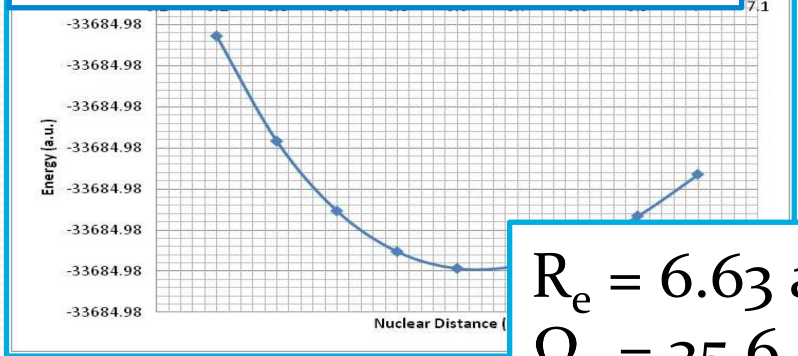
RAS	**2110**	States	All states obtained with required character
A1	7s,$7p_z$(2)	^1S, ^3P and ^1P	
B1	$7p_x$(1)		
B2	$7p_y$(1)		Excited states in order
A2	-		

Excitation energy error estimate
^3P < 5% and ^1P < 2%

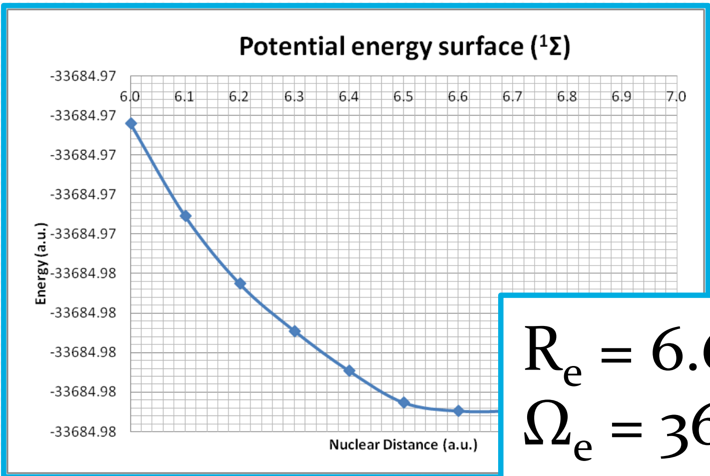
HgYb Ground state - State specific CASPT2 method

RAS space: 4220 (8 orbitals – 6s,6p – Yb and 7s,7p - Hg) – 4 electrons

RAS space: 5220 (9 orbitals – 6s,*s, 6p – Yb 7s,7p - Hg) – 4 electrons

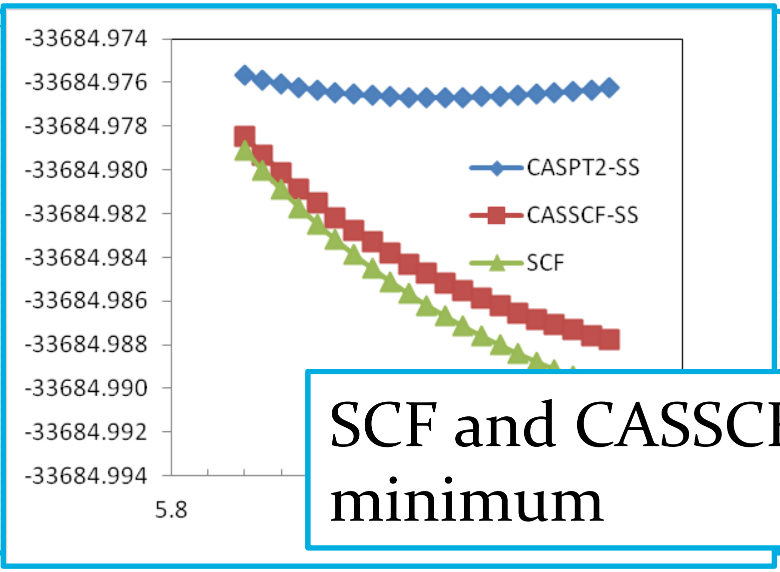


R_e = 6.63 a.u.
Ω_e = 35.6 cm-1
D_e = 2397.14 cm-1

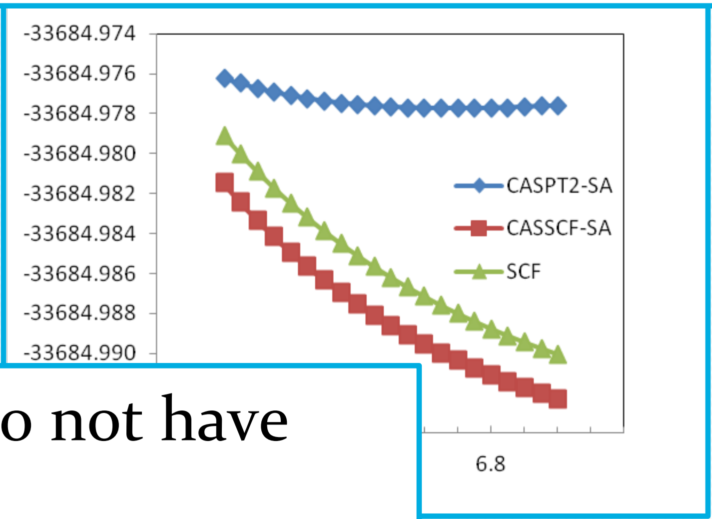

Potential energy surface ($^1\Sigma$)

R_e = 6.62 a.u.
Ω_e = 36.7 cm-1
D_e = 2340.39 cm-1

CASPT2 (7331)-State specific – ground state

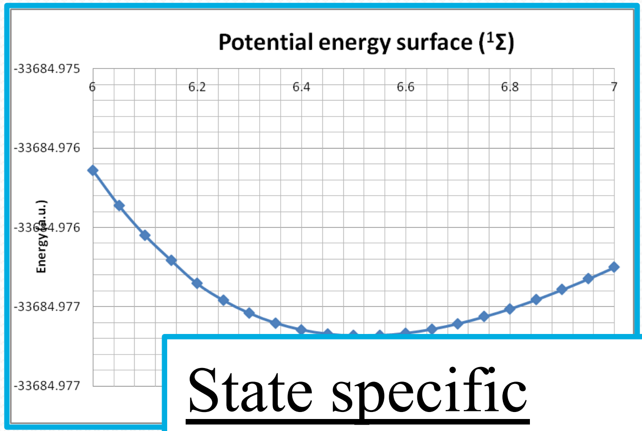


CASPT2 (7331) – State average – ground state



SCF and CASSCF (scaled) do not have minimum

Comparison of CASPT2 (7331)(state specific/average) with CCSD(T) – ground state of HgYb molecule

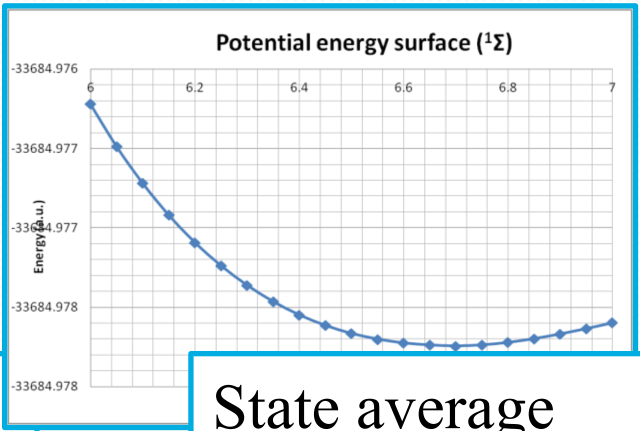


State specific

$R_e = 6.52$ a.u.

$\Omega_e = 38.7$ cm-1

$D_e = 2349.46$ cm-1

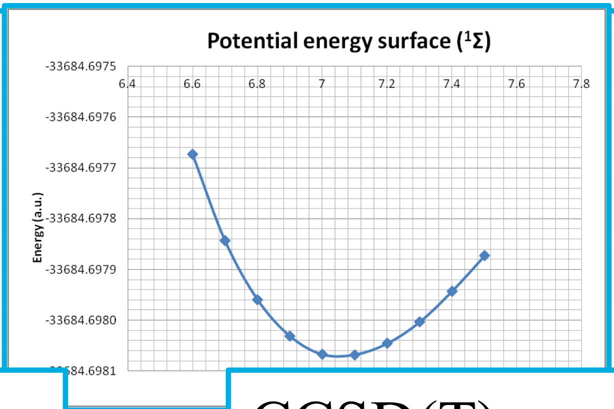


State average

$R_e = 6.70$ a.u.

$\Omega_e = 29.59$ cm-1

$D_e = 2213.23$ cm-1



CCSD(T)

$R_e = 7.06$ a.u.

$\Omega_e = 28.3$ cm-1

$D_e = 1064.80$cm-1

Computation of excited states: What should we check?

- Order of excited states with respect to energy in comparison with NIST atomic data
- How many states to be included in optimization at CASSCF level?
- How many states to be included at CASPT2 level?
- Smooth curves starting from binding regions to dissociation regions !
- Molecular excitation energy @100 a.u. in comparison with atomic excitation energies?

Atomic calculations RAS space: Yb (5221) + Hg (2110) >>>> YbHg (7331)

- **Program** : MOLCAS 7.2 version.
- **Method : Spin free** 3rd Order Douglas-Kroll Hamiltonian **Correlation** : Spin free multi-state CASPT2 followed by first order Spin-Orbit effect using RASSI (RAS State Interaction Program) – SO-MS-CASPT2
- **Symmetry :** C2v
- **Active Space for CASSCF :** 4 electrons in 14 orbitals (6s, 6p, 7s and 5d of Yb and 7s and 7p of Hg) – addition of 5d to get good Yb atomic limits
- **Frozen core** : 46 orbitals (1s to 4d of Yb (en ~7.561 au) and 1s to 4d of Hg (en ~ 14.352 au)
- **Active orbitals in CASPT2:** 5s,6s,5p,4f (Yb) and 5s,6s,5p, 4f, 5d(Hg)
- **Basis :** ROOS-ANO-RCC – 379 basis functions

  (Yb) 25s22p15d11f4g2h – 12s11p8d7f4g2h

  (Hg) 25s22p16d12f4g2h – 10s10p9d6f4g2h

	Singlet states	Triplet states
A1	(1) $^1\Sigma$,(2) $^1\Sigma$,(3) $^1\Sigma$,(4) $^1\Sigma$,(1) $^1\Delta$ [5]	(1)$^3\Sigma$, (2) $^3\Sigma$, (3) $^3\Sigma$,(4) $^3\Sigma$, (1) $^3\Delta$ [5]
B1	(1) $^1\Pi$, (2) $^1\Pi$ [2]	(1) $^3\Pi$, (2) $^3\Pi$, (3) $^3\Pi$ [3]
B2	(1) $^1\Pi$, (2) $^1\Pi$ [2]	(1) $^3\Pi$, (2) $^3\Pi$, (3) $^3\Pi$ [3]
A2	(1) $^1\Delta$ [1]	(1)$^3\Delta$ [1]

22 spin-free states

Order of excited states **7331- RAS space**

	Atomic limits	States
Ground	Yb($^1S_0$) + Hg ($^1S_0$)	$^1\Sigma$
1st	Yb($^3P_{0,1,2}$) + Hg($^1S_0$)	$^3\Sigma$, $^3\Pi$
2nd	Yb($^3D_{0,1,2}$) + Hg($^1S_0$)	$^3\Sigma$, $^3\Pi$, $^3\Delta$
3rd	Yb($^1P_1$) + Hg($^1S_0$)	$^1\Sigma$, $^1\Pi$
4th	Yb($^1D_{1,2,3}$) + Hg($^1S_0$)	$^1\Sigma$, $^1\Pi$, $^1\Delta$
5th	Yb($^3S_1$) + Hg ($^1S_0$)	$^3\Sigma$
6th	Yb($^1S_0$) + Hg ($^1S_0$)	$^1\Sigma$
7th	Yb($^1S_0$) + Hg($^3P_{2,1,0}$)	$^3\Sigma$, $^3\Pi$
8th	Yb($^1S_0$) + Hg($^1P_1$)	$^1\Sigma$, $^1\Pi$

How many states at CASSCF level of optimization?

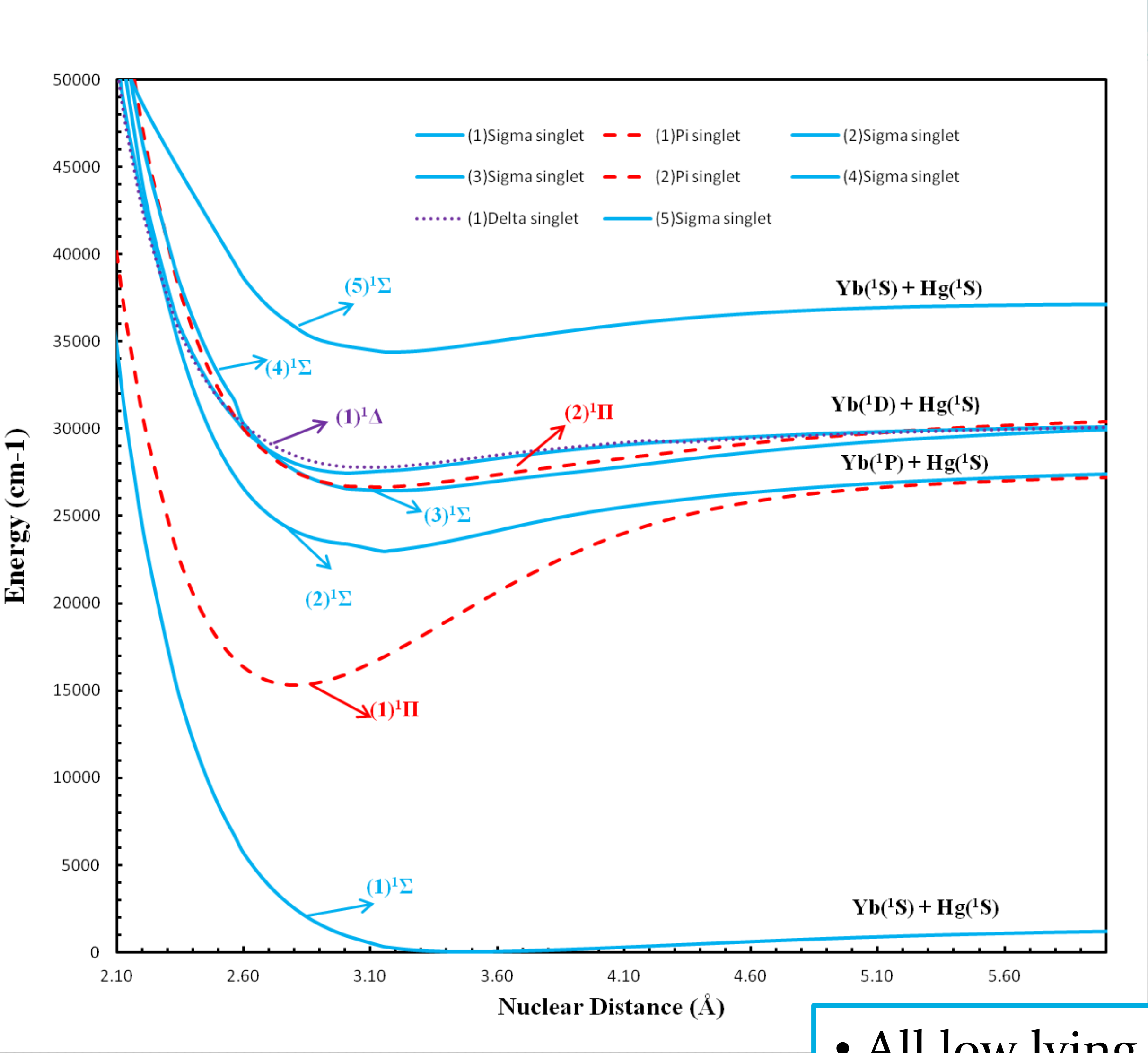
55232311: Between 6 to 5 a.u unsmooth PECs for 1-$^1\Sigma$, 2-$^3\Sigma$ and 1-$^3\Pi$ states

43222211: Ground ($^1\Sigma$) has discontinuity at 6.5a.u.

53222211: (used this CASSCF calculation for CASPT2 (55232311)

- lowest 20 spin-free states

Spin-free-HgYb singlet excited states

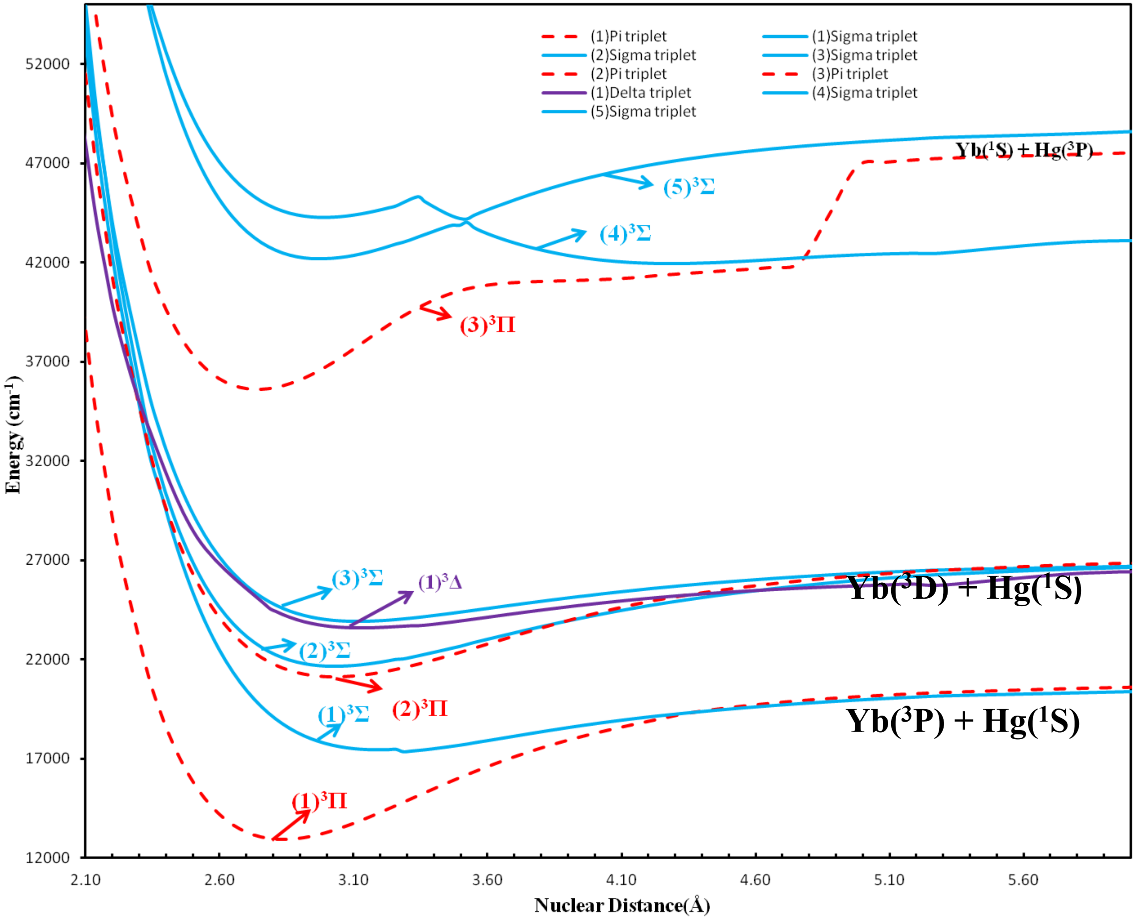


Symmetry A1 singlet(5)	configuration	Character	Dissociation channel
(1)$^1\Sigma$	2200000	Hg6s^{2}Yb6s^2	Yb(^{1}S) + Hg(^{1}S)
(2)$^1\Sigma$	2u0d000	Hg6s2Yb6s6p	Yb(^{1}P) + Hg(^{1}S)
(3)$^1\Sigma$	2u000d0	Hg6s2Yb6s5d	Yb(^{1}D) + Hg(^{1}S)
(4)$^1\Sigma$	2u0000d	Hg6s2Yb6s5d	Yb(^{1}D) + Hg(^{1}S)
(5)$^1\Sigma$	2ud0000	Hg6s2Yb6s7s	Yb(^{1}S) + Hg(^{1}S)
Symmetry B1/B2 singlet(2)	**configuration**	**Character**	**Dissociation channel**
(1)$^1\Pi$	2u00000 d00	Hg6s2Yb6s6p	Yb(^{1}P) + Hg(^{1}S)
(2)$^1\Pi$	2u00000 00d	Hg6s2Yb6s5d	Yb(^{1}D) + Hg(^{1}S)
Symmetry A2 singlet(1)	**configuration**	**Character**	**Dissociation channel**
(1)$^1\Delta$	2u00000 0 0 d	Hg6s2Yb6s5d	Yb(^{1}D) + Hg(^{1}S)

Blue lines: Singlet Sigma states
Dotted red lines : Singlet Pi states
Purple lines : Singlet Delta states

- All low lying Yb excited states required are reproduced correctly
- Due to state averaging procedure(optimization) some states may not be accurate (5) singlet Sigma, (2) singlet Pi and (1) singlet Delta

Spin-free-HgYb triplet excited states



Symmetry A1 triplet(5)	**configuration**	**Character**	**Dissociation channel**
(1)$^3\Sigma$	2u0u000	Hg6s^{2}Yb6s6py	Yb(^{1}P) + Hg(^{1}S)
(2)$^3\Sigma$	2u0000u	Hg6s2Yb6s5d	Yb(^{3}D) + Hg(^{1}S)
(3$^3\Sigma$	2u000u0	Hg6s2Yb6s5d	Yb(^{3}D) + Hg(^{1}S)
(4)$^3\Sigma$	200u00d	Hg6s2Yb6p5d	Yb(^{3}D) + Hg(^{1}S)
(5)$^3\Sigma$	200u0u0	Hg6s2Yb6p5d	Yb(^{3}S) + Hg(^{1}S)
Symmetry B1/B2 triplet(3)	**configuration**	**Character**	**Dissociation channel**
(1)$^3\Pi$	2u00000 u00	Hg6s2Yb6s6pz	Yb(^{3}P) + Hg(^{1}S)
(2)$^3\Pi$	2u00000 00u	Hg6s2Yb6s5d	Yb(^{3}D) + Hg(^{1}S)
(3)$^3\Pi$	u200000 0u0	Hg6s1Yb6s2Hg 6pz	Yb(^{1}S) + Hg(^{3}P)
Symmetry A2 triplet(1)	**configuration**	**Character**	**Dissociation channel**
(1)$^3\Delta$	2u00000 0 0 u	Hg6s2Yb6s5d	Yb(^{3}D) + Hg(^{1}S)

Blue lines: Triplet Sigma states
Dotted red lines : Triplet Pi states
Purple lines : Triplet Delta states

- All low lying Yb excited states are not reproduced correctly (red shaded)
- Hg excited (triplet Pi states) are obtained but triplet Sigma states are missing.

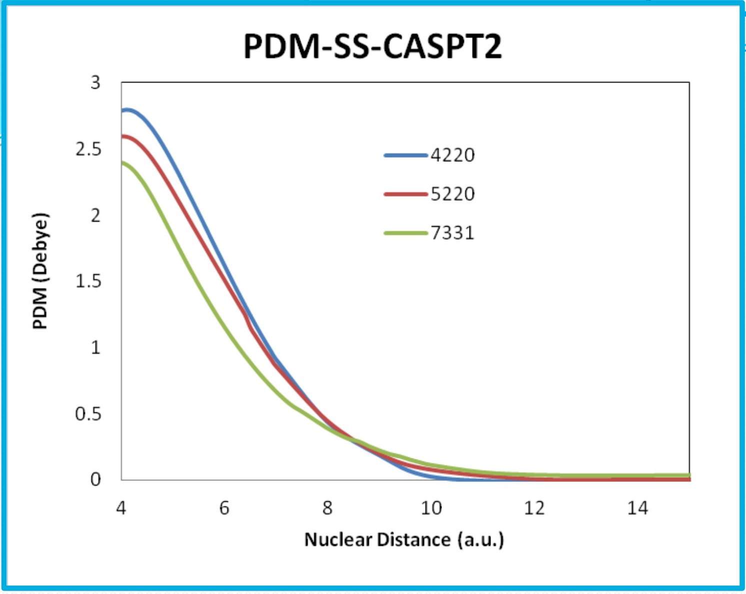
- Yb (triplet Sigma) states dissociating to ^{3}S are missing.
- (4) triplet Sigma and (5) triplet Sigma are not the states required.

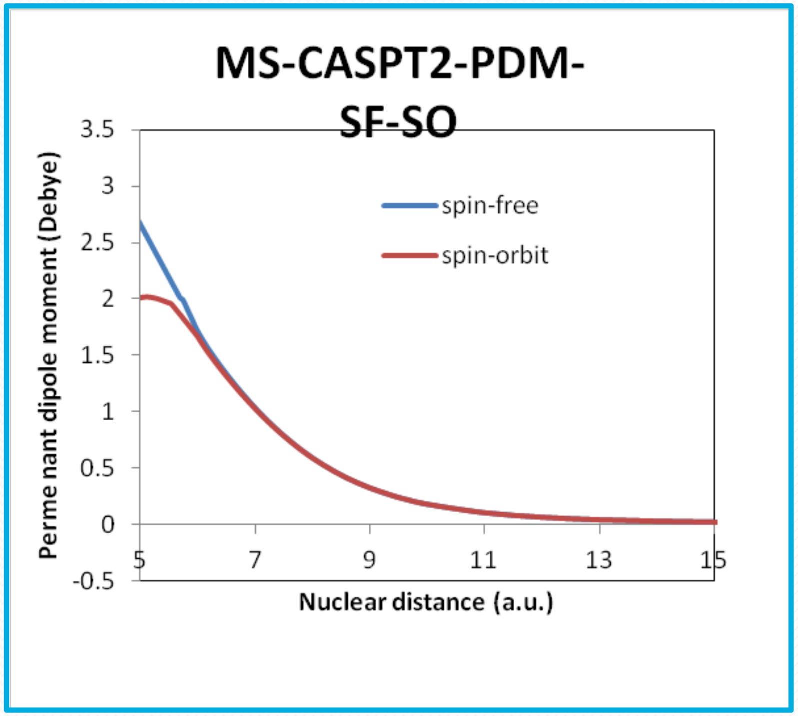
Spin-free spectroscopic constants

HgYb (Λ–S)	R_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	Dissociation
$(1)^1\Sigma$	3.49	1977.67	34.9	Yb(^{1}S) + Hg(^{1}S)
$(1)^3\Pi$	2.83	8172.81	109	Yb(^{3}P) + Hg(^{1}S)
$(1)^3\Sigma$	3.29	3848.07	106	Yb(^{1}P) + Hg(^{1}S)
$(2)^3\Sigma$	3.03	5479.72	82.6	Yb(^{3}D) + Hg(^{1}S)
$(3)^3\Sigma$	3.11	3184.28	63.1	Yb(^{3}D) + Hg(^{1}S)
$(2)^3\Pi$	3.02	6227.40	82.3	Yb(^{3}D) + Hg(^{1}S)
$(1)^1\Pi$	2.81	12414.48	119	Yb(^{1}P) + Hg(^{1}S)
$(2)^1\Sigma$	3.16	5189.37	213	Yb(^{1}P) + Hg(^{1}S)
$(3)^1\Sigma$	3.12	4298.93	74.1	Yb(^{1}D) + Hg(^{1}S)
$(2)^1\Pi$	3.11	4413.46	65.8	Yb(^{1}D) + Hg(^{1}S)
$(4)^1\Sigma$	3.05	3328.65	82.6	Yb(^{1}D) + Hg(^{1}S)
$(1)^1\Delta$	3.09	2867.30	63.7	Yb(^{1}D) + Hg(^{1}S)
$(3)^3\Pi$	2.737	13564.63	127	Yb(^{1}S) + Hg(^{3}P)

- $(3)^1\Sigma$ and $(4)^1\Sigma$ has avoided crossing at smaller nuclear distance
- 5th $^1\Sigma$ and $(3)^3\Pi$ state has a broad maximum ~ due to non inclusion of higher excited states
- All states are strongly bound in comparison with the ground state

Permanent dipole moment, ground state dissociation energy





Ground state pdm ~ 1.1 D to 1.3 D

Method	Re (a.u.)	PDM@Re (Debye)
SS-CASPT2-4220	6.63	1.15
SS-CASPT2-5220	6.62	1.09
SS-CASPT2-7331	6.52	1.15
MS-CASPT2 (spin-free)	6.59	1.27
MS-CASPT2 (spin-orbit)	6.57	1.29

Method	Re (a.u.)	De (cm-1)
CCSD(T)	7.06	1064.80
CCSD(T)-CP	6.71	1845.59
CASPT2-SA	6.69	2213.24
CASPT2-SA-CP	6.36	3277.46
MS-CASPT2 (spin-free)	6.59	1977.67
MS-CASPT2 (spin-orbit)	6.57	1538.10

CASPT2 method produces more bound molecule in comparison with CCSD(T)

HgYb spin orbit excited stat

First check: Atomic excitation energy with 100 a.u. data

Yb: $1s^2$.....$5s^25p^64f^{14}6s^2$

Hg : $1s^2$.....$5s^25p^64f^{14}6s^2\ 5d^{10}7s^2$

Hg ($7s^2$) ground + Yb ($6s^2$) ground
(j=0) (j=0)

Total Mj values possible: 0

Hg ($7s^2$) ground + Yb ($6s^16p^1$) excited
(j=0) (j= 0,1,2)

Total Mj values possible: 0,±1,0,±2,±1,0

Hg($7s^2$) ground + Yb($6s^15d^1$) excited
(j=0) (j= 1,2,3)

Total Mj values possible: ±1,0,±2, ±1,
0,±3,±2,±1,0)

Hg ($7s^2$) ground + Yb($6s^16p^1$) excited
(j=0) (j=1)

Total Mj values possible: 0,±1

Hg ($7s^2$) ground + Yb($6s^15d^1$) excited
(j=0) (j=2)

Total Mj values possible: 0, ±2,±1

Hg ($7s^2$) ground + Yb ($7s^2$) excited
(j=0) (j=0)

Total Mj values possible: 0

Hg ($7s^2$) ground + Yb ($7s^2$) excited
(j=0) (j=1)

Total Mj values possible: 0,±1

Hg (7s7p) excited + Yb ($6s^2$) ground
(j=0,1,2) (j= 0)

Total Mj values possible: 0,±1,0,±2,±1,0

Hg (7s7p) excited + Yb ($6s^2$) ground
(j=0,1) (j= 0)

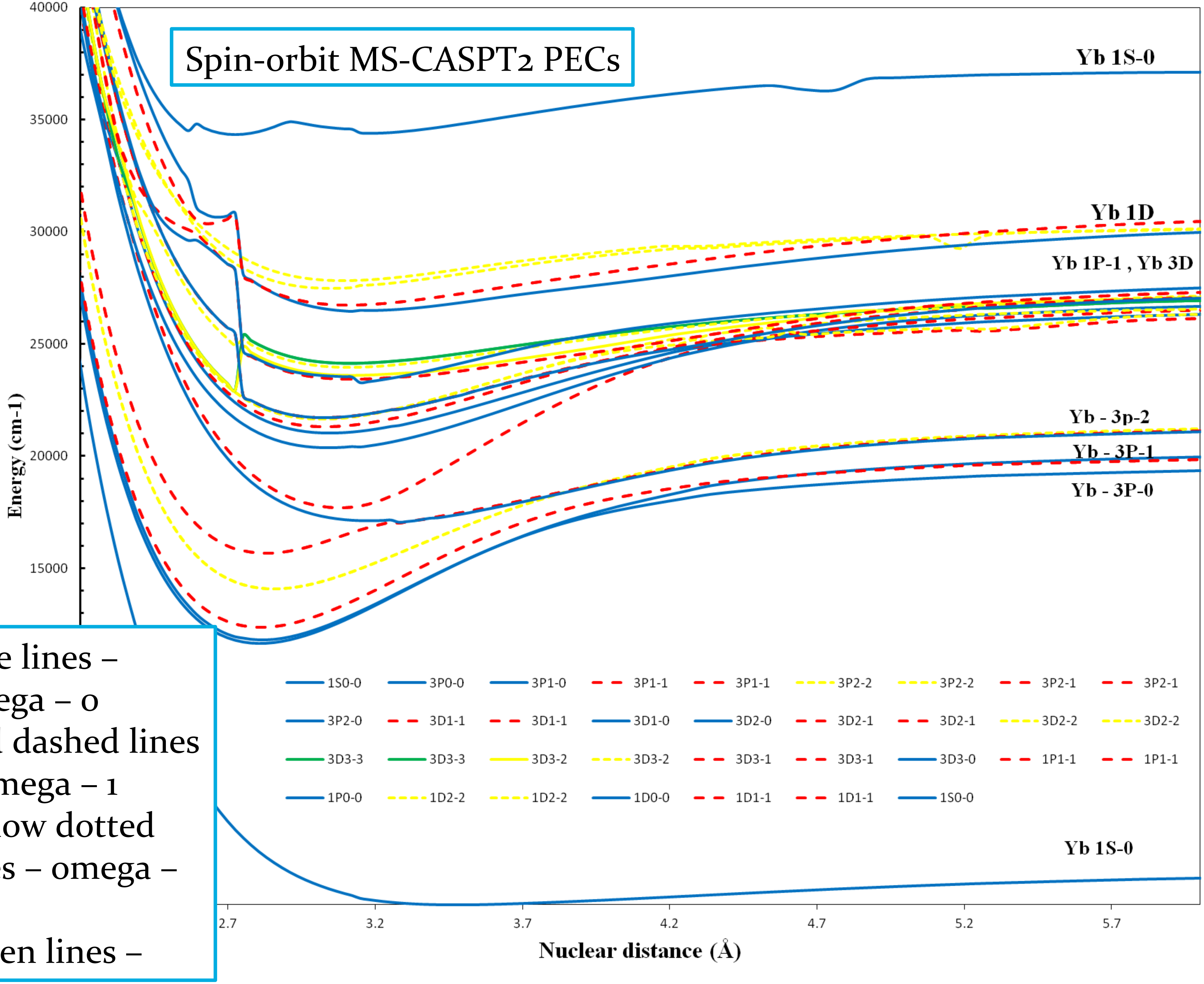
Total Mj values possible: 0,±1

states	NIST data	100 a.u.data	Accuracy (%)
1S0-0	0	0	
3P0-0	17288.44	17934.01	3.7
3P1-0	17992.01	18437.81	2.5
3P1-1	17992.01	18477.64	2.7
3P1-1	17992.01	18477.67	2.7
3P2-0	19710.39	19690.28	-0.1
3P2-1	19710.39	19690.31	-0.1
3P2-1	19710.39	19761.13	0.3
3P2-2	19710.39	19761.14	0.3
3P2-2	19710.39	19782.94	0.4
3D1-0	24489.1	24597.62	0.4
3D1-1	24489.1	24597.73	0.4
3D1-1	24489.1	24793.83	1.2
3D2-0	24751.95	25045.43	1.2
3D2-1	24751.95	25053.81	1.2
3D2-1	24751.95	25238.74	2.0
3D2-2	24751.95	25238.86	2.0
3D2-2	24751.95	25376.21	2.5
3D3-0	25270.9	25377.58	0.4
3D3-1	25270.9	25378.02	0.4
3D3-1	25270.9	25769.8	2.0
3D3-2	25270.9	25792.44	2.1
3D3-2	25270.9	25813.11	2.1
3D3-3	25270.9	25813.52	2.1
3D3-3	25270.9	25815.38	2.2
1P1-0	25068.22	25938.55	3.5
1P1-1	25068.22	25938.55	3.5
1P1-1	25068.22	26342.68	5.1
1D2-0	27677.67	28672.51	3.6
1D2-1	27677.67	28709.59	3.7
1D2-1	27677.67	28873.16	4.3
1D-2	17288.44	17934.01	3.7
1D2-2	17992.01	18437.81	2.5
1S0-0	17992.01	18477.64	2.7

Proper dissociation channel for the lowest 31 states out of 46 spin-orbit states

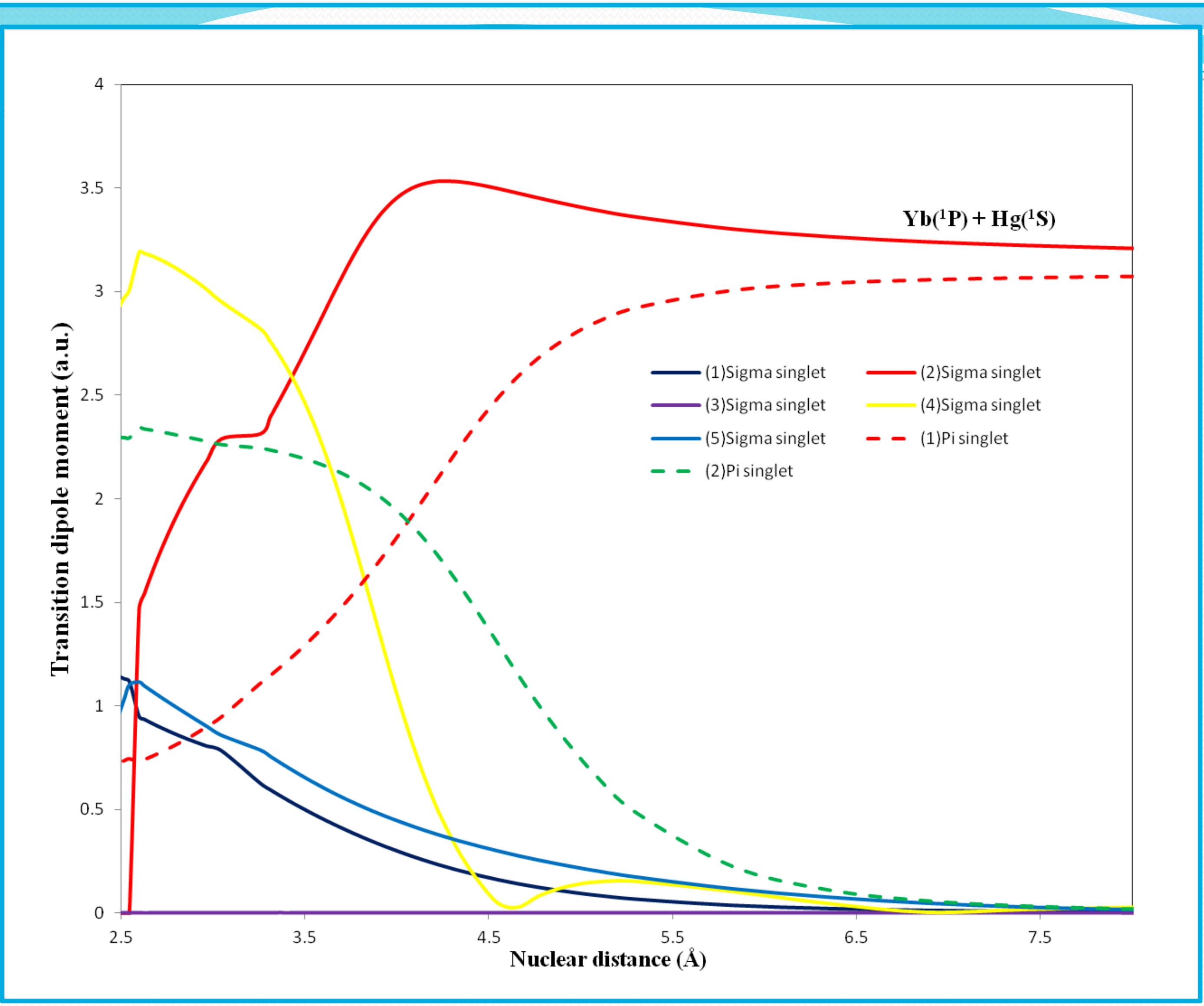
Excitation Energy < 5%

Spin-orbit MS-CASPT2 PECs



Blue lines – omega – 0
Red dashed lines – omega – 1
Yellow dotted lines – omega – 2
Green lines –

Transition Dipole moment – spin free level – check (lifetime calculations)



- Electric dipole transition possible from ground (^{1}S) to (^{1}P) state (at dissociation limits)
- All other transitions are forbidden at spin-free level.
- TDM ~ 3.114 a.u.
- **Lifetime of ^{1}P state (expt.) ~ 5.7 nsec**
- **100 a.u calculations ~ 4.5nsec**

- **Molecular regions:**
  Large TDM connecting ground(^{1}S) with (4)$^1\Sigma$ (yellow) and (2)$^1\Pi$(green) states at binding regions ((4)$^1\Sigma$ and (2)$^1\Pi$ dissociates to Yb ^{1}D excited state)
- Possible candidate for stabilization step in photo association experiment

Fundamental Physics applications starting from chemistry

✓Lifetime of excited meta stable states for the possibility of PA experiment in excited states

✓ Fitting the theoretical PECs with experiment to obtain accurate values of long range parameters (C6, C8..)

✓ With long range parameters find scattering length – important parameter in laser cooling experiments

✓ Parity Non Conservation in Chiral molecules – PNC NMR properties

✓ Electron EDM in open shell molecules

✓ Nuclear EDM in closed shell molecules

so on….

Thank you