Breaching $|d_e| \approx 10^{-32}\, e$cm with Ultracold Molecules ?

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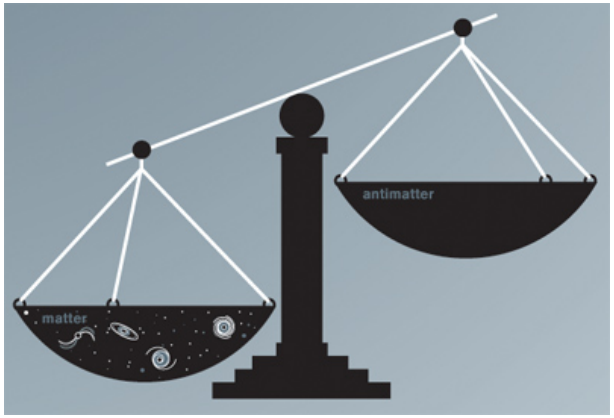
26 November 2018

Laboratoire de Chimie et Physique Quantiques

Université Paul Sabatier TOULOUSE III

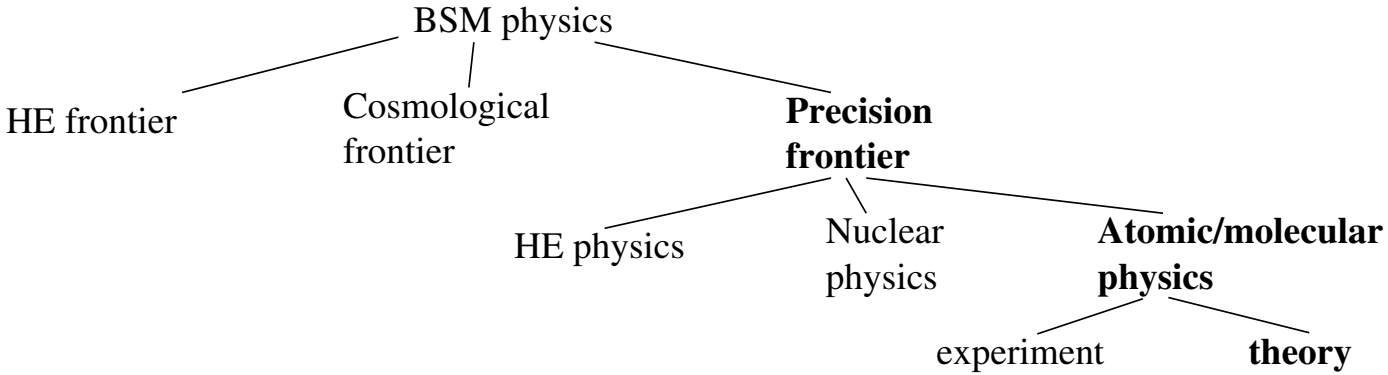
Yale

Motivation and Positioning



- **Matter-antimatter asymmetry** of the universe[1]
- Nature of **cold dark matter**
- Degree of $\mathcal{CP}$ **violation** in nature[2]

- Detection/constraint of **EDMs** as a powerful probe of possible explanations/consequences[3]

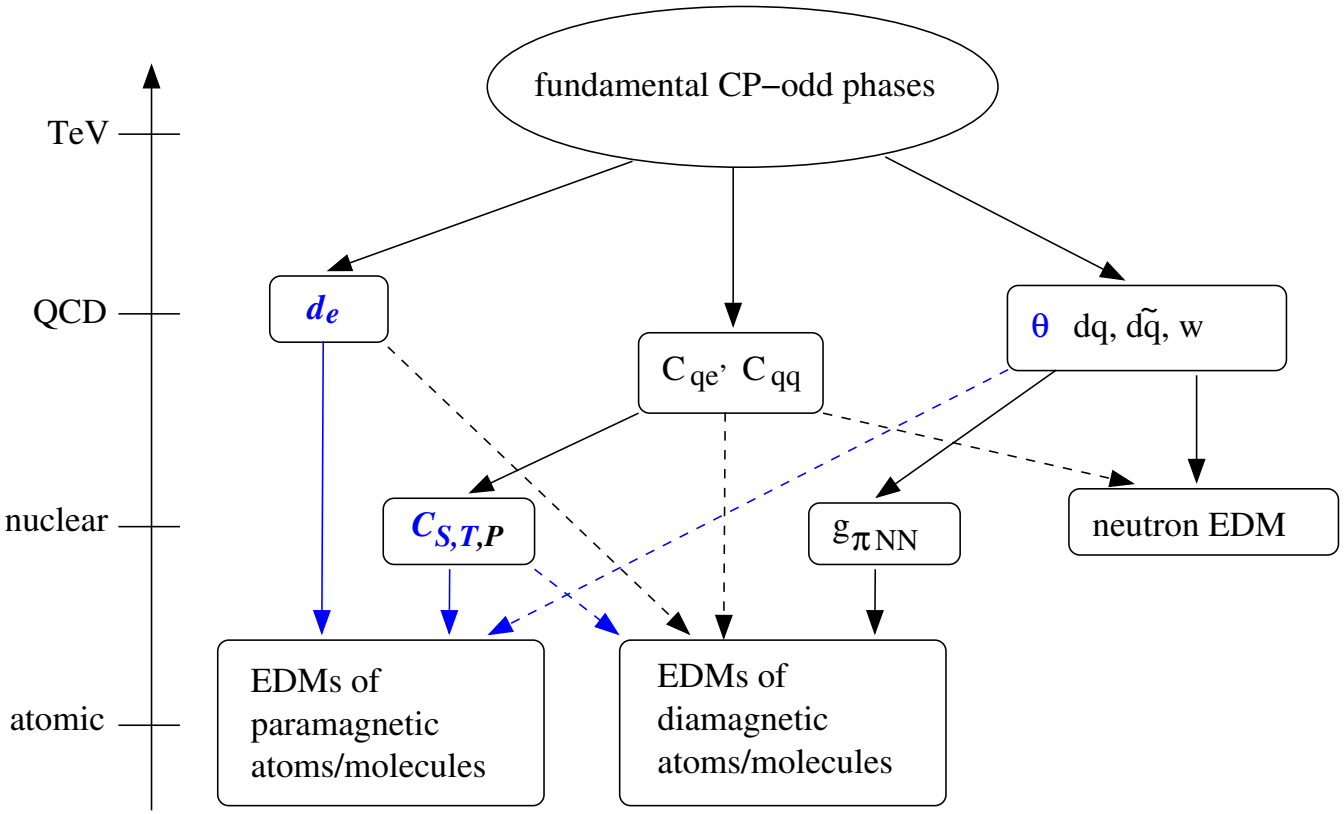


[1] M. Dine, A. Kusenko, *Rev. Mod. Phys.* **76** (2004) *1*

[2] G. C. Branco, R. G. Felipe, F. R. Joaquim, *Rev. Mod. Phys.* **84** (2012) *515*

[3] J. Engel, M. J. Ramsey-Musolf, U. van Kolck, *Prog. Part. Nuc. Phys.* **71** (2013) *21*

Electric Dipole Moments and Their Source Tree[4]



$\phi_{\not C\not P}^{(\mathrm{CKM})}$ or $\phi_{\not C\not P}^{(\mathrm{BSM})}$

give **electric dipole moments** (d_e, d_q, ...)

and $\mathcal{T}$**-violating piece** of weak interaction

Recent work on tensor interaction[5] C_T in ^{199}Hg and ^{225}Ra

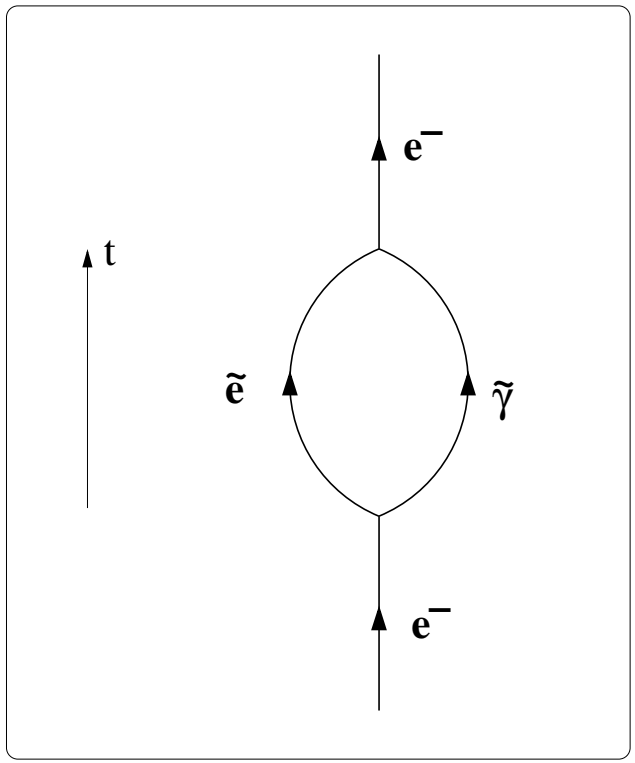
scalar-pseudoscalar interaction[6] C_S in ^{199}Hg

[4] M. Pospelov, A. Ritz, "Electric dipole moments as probes of new physics", *Ann. Phys.* **318** (2005) *119*

[5] TF, *arXiv:1811.01684* (2018)

[6] TF, M. Jung, *J. High Energy Phys.* **7** (2018) *012*

The Electron Electric Dipole Moment



$\tilde{e}$: ***s*electron**

Bosonic superpartner of the electron,
$s = 0$
Electric charge $q_{\tilde{e}} = -e$
Mass $m_{\tilde{e}} >> m_e$

$\tilde{\gamma}$: **photino** (a WIMP, gaugino).

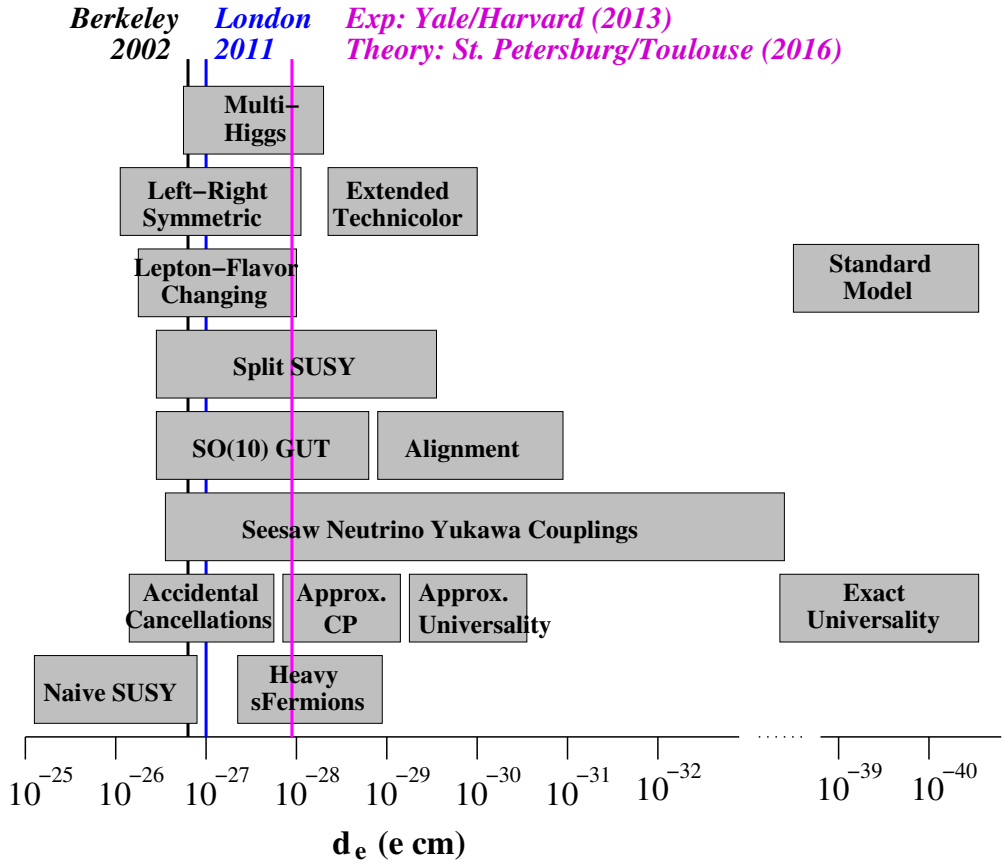
Fermionic superpartner of the photon,
$s = 1/2$
Electric charge $q_{\tilde{\gamma}} = 0$
Mass $m_{\tilde{\gamma}} > 0$

One-loop fermion EDM within MSSM ("naïve SUSY") prediction:[7]

$$|d_e| \approx 10^{-27}\,[e\ \text{cm}]$$

[7] J. Ellis, J.S. Lee, A. Pilaftsis, *J High Energy Phys* **10** (2008) *049*

eEDM Constraint on Beyond-Standard-Model Theories[8]
Single-source interpretation



Model	$\lvert d_e \rvert [e \cdot cm]$
Standard model	$< 10^{-38}$
Left-right symmetric	$10^{-28} \ldots 10^{-26}$
Lepton-flavor changing	$10^{-29} \ldots 10^{-26}$
Multi-Higgs	$10^{-28} \ldots 10^{-27}$
Supersymmetric	$\leq 10^{-25}$
Experimental limit (Tl)[9]	$< 1.6 \cdot 10^{-27}$
Experimental limit (YbF)[10]	$< 10.5 \cdot 10^{-28}$
Experimental limit (ThO)[11]	$< 9.6 \cdot 10^{-29}$

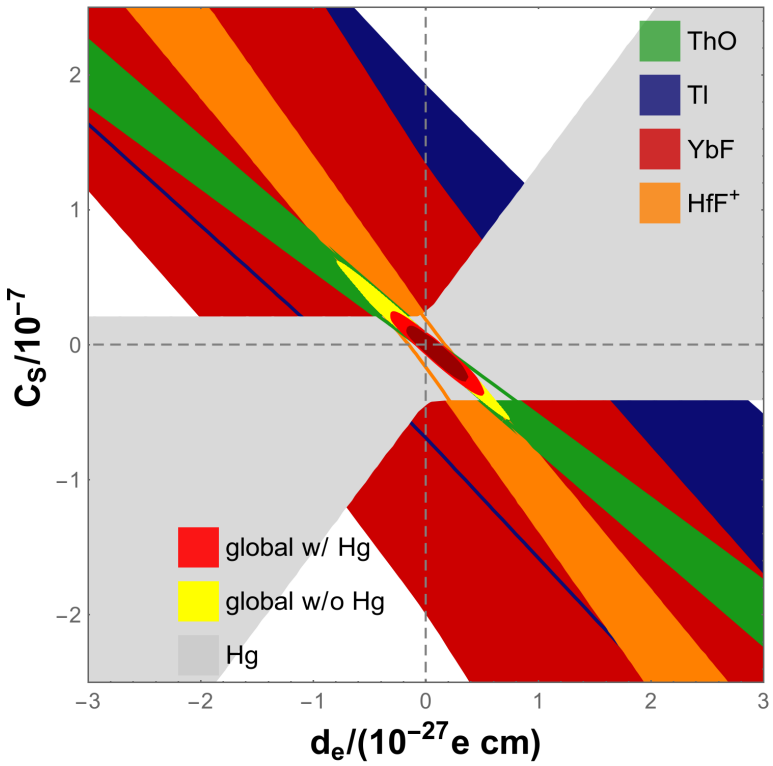
[8] Courtesy: DeMille (2005), Huliyar (2009)

[9] B.C. Regan, E.D. Commins, C.J. Schmidt, D.P. DeMille, *Phys Rev Lett* **88** (2002) *071805/1*

[10] J.J. Hudson, D.M. Kara, I.J. Smallman, B.E. Sauer, M.R. Tarbutt, E.A. Hinds, *Nature* **473** (2011) *493*

[11] D. DeMille, ICAP 2014, Washington D.C., ACME Collaboration, *Science* **6168** (2014) *269*, TF and M. K. Nayak, *J. Mol. Spectrosc.* **300** (2014) *16*, L. V. Skripnikov, A. N. Petrov, A. V. Titov, *J. Chem. Phys.* **139** (2013) *221103*, L. V. Skripnikov, A. V. Titov, *J. Chem. Phys.* **142** (2015) *024301*, M. Denis, TF, *J Chem Phys* **145** (2016) *214307*

New Bounds on (Semi-)Leptonic $\mathcal{CP}$-odd Parameters[12]



Multiple-source picture:

$$\Delta E_{\mathcal{P},\mathcal{T}} = -\langle \mathbf{d}_{\mathrm{sys}} \cdot \mathbf{E}_{\mathrm{ext}} \rangle$$
$$= \left(\alpha_{d_e}\, d_e + \alpha_{C_S}\, C_S\right) \langle \mathbf{n} \cdot \mathbf{z} \rangle \left(E_{\mathrm{ext}}\right)$$

Previous resulting bound:

From HfF^+, ThO, YbF, Tl

$$|d_e|_{2017} < 6.4 \times 10^{-28} e\ \mathrm{cm}$$

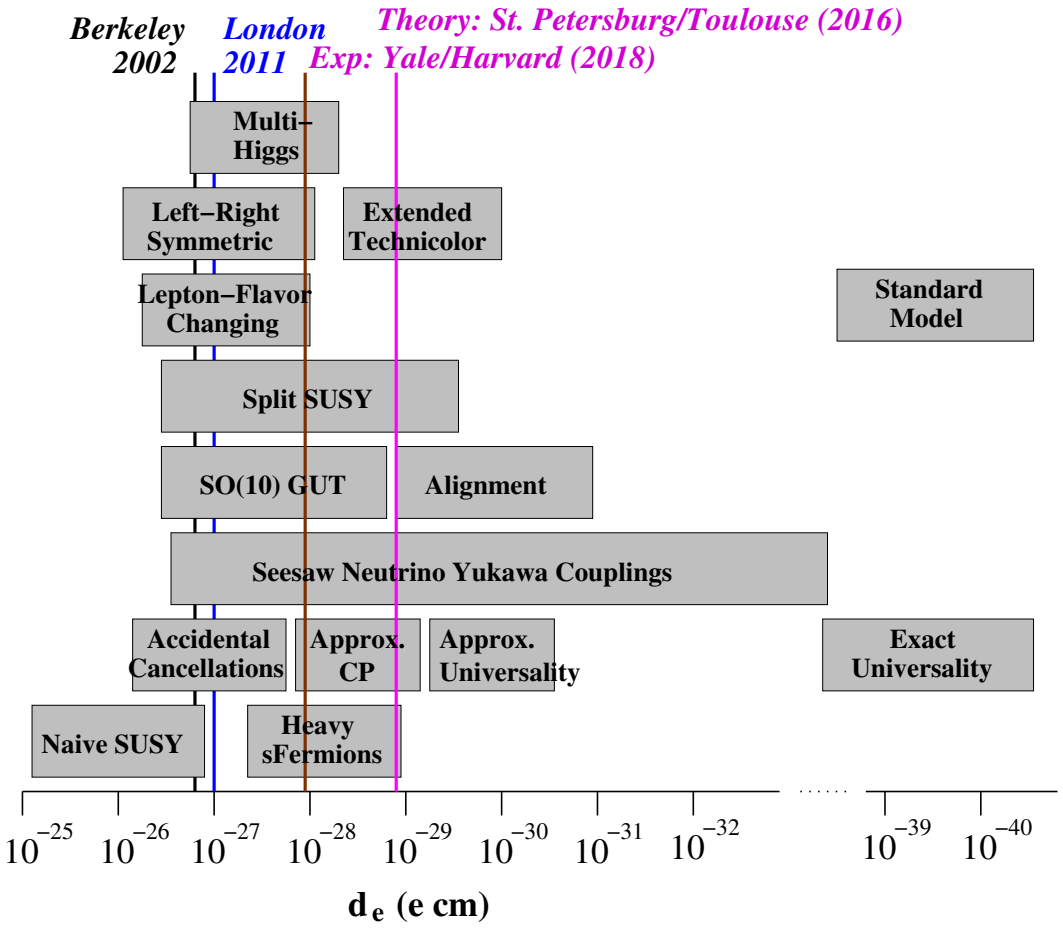
New resulting bounds:

From Hg, HfF^+, ThO, YbF, Tl

$$|d_e|_{2018} < 3.8 \times 10^{-28} e\ \mathrm{cm}$$
$$|C_S|_{2018} < 2.7 \times 10^{-8}$$

[12] TF, M. Jung, *J. High Energy Phys.* **7** (2018) *012*
J. Baron *et al.*, *Science* **343** (2014) *269*
M. Denis, T. F., *J. Chem. Phys.* **145** (2016) *214307*
L. Skripnikov, *J. Chem. Phys.* **145** (2016) *214301*
W.B. Cairncross, D.N. Gresh, M. Grau, K.C. Cossel, T.S. Roussy, Y. Ni, Y. Zhou, J. Ye, E.A. Cornell, *Phys. Rev. Lett.* **119** (2017) *153001*
T. F., *Phys. Rev. A (Rap. Comm.)*, **96** (2017) *040502(R)*
L.V. Skripnikov, *J. Chem. Phys.*, **147** (2017) *021101*

eEDM Constraint on Beyond-Standard-Model Theories
Single-source interpretation (2018)



ACME 2018 result[13] combined with 2016 theory

[13] ACME collaboration, *Nature*, **562** (2018) *355*

Going Ultracold: From beams to traps

PHYSICAL REVIEW A, VOLUME 63, 023405

Loading and compressing Cs atoms in a very far-off-resonant light trap

D. J. Han, Marshall T. DePue, and David S. Weiss
Department of Physics, University of California at Berkeley, Berkeley, California 94720-7300
(Received 25 May 2000; published 12 January 2001)

We describe an experiment in which 3×10^7 Cs atoms are loaded into a 400 μm crossed beam far-off-resonant trap (FORT) that is only 2 μK deep. A high-density sample is prepared in a magneto-optic trap, cooled in a three-dimensional far-off-resonant lattice (FORL), optically pumped into the lowest-energy state, adiabatically released from the FORL, magnetically levitated, and transferred to the final trap with a phase-space density of 10^{-3}. Spontaneous emission in the FORT is negligible, and we have compressed the atoms in the FORT to a spatial density of 2×10^{13} atoms/cm^3. Evaporative cooling under these conditions proceeds rapidly.

- Estimated sensitivity of Cs EDM measurement in DLT[14] is $|d_e| \approx 10^{-29}\, e\text{cm}$

  Cs atom: $\Delta E = R\, E_{\text{ext}}\, d_e$
  $E_{\text{int}} \approx 20\ \left[\frac{\text{MV}}{\text{cm}}\right]$

  Ultracold **XY** Molecule: $\Delta E = E_{\text{eff}}\, d_e$
  $E_{\text{eff}} \approx 50\ \left[\frac{\text{GV}}{\text{cm}}\right]$

- A factor of $\approx \mathbf{2500}$ gain in sensitivity!

[14] DLT: Dipole light trap; D. Weiss (Penn State), 2014: "Measuring the eEDM using laser-cooled Cs atoms in optical lattices"
S. Chu, J.E. Bjorkholm, A. Ashkin, A. Cable, *Phys. Rev. Lett.* **57** (1986) *314*
C. Chin, V. Leiber, V. Vuletić, A.J. Kerman, S. Chu, *Phys. Rev. A* **63** (2001) *033401*

Towards Ultracold DLT EDM Measurement

Picking the cherry

In the casting:
Alkali(-like) atoms: Li, Na, K, Rb, Cs; Ag, Au
Earth-alkaline atoms: Sr, Ba, Ra; Yb

Jury spreadsheet for X partner of Ra and some contenders:

X	EA(X) [eV]	$E_{\mathrm{eff}_{\max}}\left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$	$B_v = \left\langle v\left\vert\frac{1}{\mu R^2}\right\vert v\right\rangle\,[\mathrm{cm}^{-1}]$	D [D]	$E_{\mathrm{pol}} = \frac{B_v}{D}\left[\frac{\mathrm{kV}}{\mathrm{cm}}\right]$
Li	0.62	61	−	≈ 1.5	
Na	0.55	58	−	≈ 1	
K	0.50	50	−	≈ 1	
Rb	0.49	48	+	≈ 1	
Cs	0.47	44	+	≈ 1	
Ag	1.30	66	0.021	5.4	0.264
Au	2.31	60	+	≈ 6	
AgBa	1.30	6	+	≈ 3	
RbYb[15]		−0.7	0.001	0.21	5.5
CsYb[15]		0.54	0.007	0.24	3.5

[15] E. R. Meyer, J. L. Bohn, *Phys. Rev. A* **80** (2009) *042508*

Towards Ultracold DLT EDM Measurement

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RbYb		−0.7	0.001	0.21	5.5
CsYb		0.54	0.007	0.24	3.5

Au is forbidden fruit!

$(\mathcal{P},\mathcal{T})$-odd properties of AgRa

- Electron EDM effective electric field[16]

$$E_{\text{eff}} = \frac{2\imath c}{e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5 \, \vec{p}_j{}^{\,2} \right\rangle_{\psi^{(0)}}$$

- S-PS nucleon-electron interaction constant[17]

$$W_{\mathcal{S}} := \frac{\imath}{\Omega} \frac{G_F}{\sqrt{2}} Z_{\text{heavy}} \, \langle \Psi_\Omega | \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5 \, \rho_N(\vec{r}_j) \, | \Psi_\Omega \rangle$$

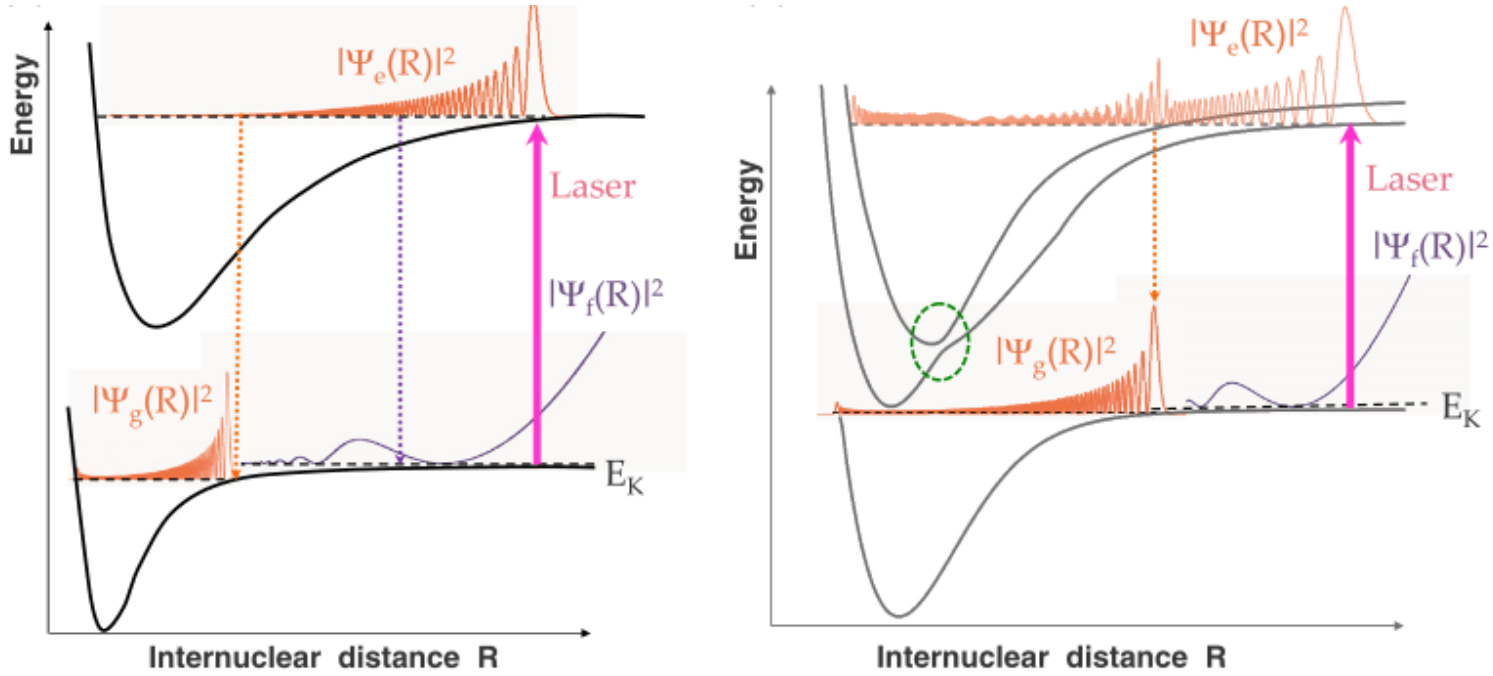
	$^3\Delta_1$			$^2\Sigma_{1/2}$		
	ThO	HfF^+	ThF^+	YbF	AgRa	
$\lvert E_{\text{eff}} \rvert$	78	23	35	25	64	$\left[\frac{\text{GV}}{\text{cm}}\right]$
$\lvert W_S \rvert$	106	20	51	40	175	[kHz]

[16] E. Lindroth, E. Lynn, P.G.H. Sandars, *J. Phys. B: At. Mol. Opt. Phys.* **22** (1989) *559*
T.F., M.K. Nayak, *Phys. Rev. A* **88** (2013) *032514*

[17] V. G. Gorshkov, L. N. Labzovski, and A. N. Moskalev, *Zh. Eksp. Teor. Fiz.* **76** (1979) *414*
M. Denis *et al.*, *New J. Phys.* **7** (2015) *043005*

Devising a AgRa DLT EDM Experiment

- Photoassociating ultracold atoms into ultracold molecules[18]



- Does its electronic spectrum allow for efficient energy transfer (remove binding energy without heating) ?
- Which states are candidates for photoassociation ?

[18] L. D. Carr, D. DeMille, R. V. Krems, J. Ye, *New J. Phys.* **11** (2009) *055049*

AgRa - Electronic-structure model

		# of Kramers pairs	accumulated # of electrons min.	max.
III	*(4 a.u.)* *Virtual Kramers pairs*	71	21	21
II	*Ag: 5p,6s* *Ra: 7p,8p,6d* *Ag: 5s* *Ra: 7s* σ	18	19	21
I	*Ra: 6s, 6p* *Ag: 4d*	9	17	18
	Frozen core	(57)		

Determinant classes

$I^{18}\ II^{3}\ III^{0}$ (Reference space)

$I^{18}\ II^{2}\ III^{1}$ (Singles)

$I^{18}\ II^{1}\ III^{2}$ (Valence correlating)

$I^{17}\ II^{4}\ III^{0}$ (Singles)

$I^{17}\ II^{3}\ III^{1}$ (Singles)

$I^{17}\ II^{2}\ III^{2}$ (Core-val. correlating)

17.6×10^{6} expansion terms ($\Omega = 1/2$)

cvTZ bases[19] **KRCI** program[20]

[19] K.G. Dyall, *Theoret. Chim. Acta* **131** (2012) *1217*
K.G. Dyall, A.S.P. Gomes, *Theoret. Chim. Acta* **125** (2010) *97*

[20] S. Knecht, H.J.Aa. Jensen, T.F., *J. Chem. Phys.* **132** (2010) *014108*
DIRAC15 package (locally modified)

Atomic and Molecular Correlated Wavefunctions

- Solve relativistic equation of motion (yields wavefunctions)

- Dirac-Coulomb Hamiltonian operator (molecules)

$$\hat{H}^{DC} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \sum_A^N \frac{Z}{r_{iA}} \mathbb{1}_4 \right] + \sum_{i,j>i}^n \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_{A,B>A}^N V_{AB}$$

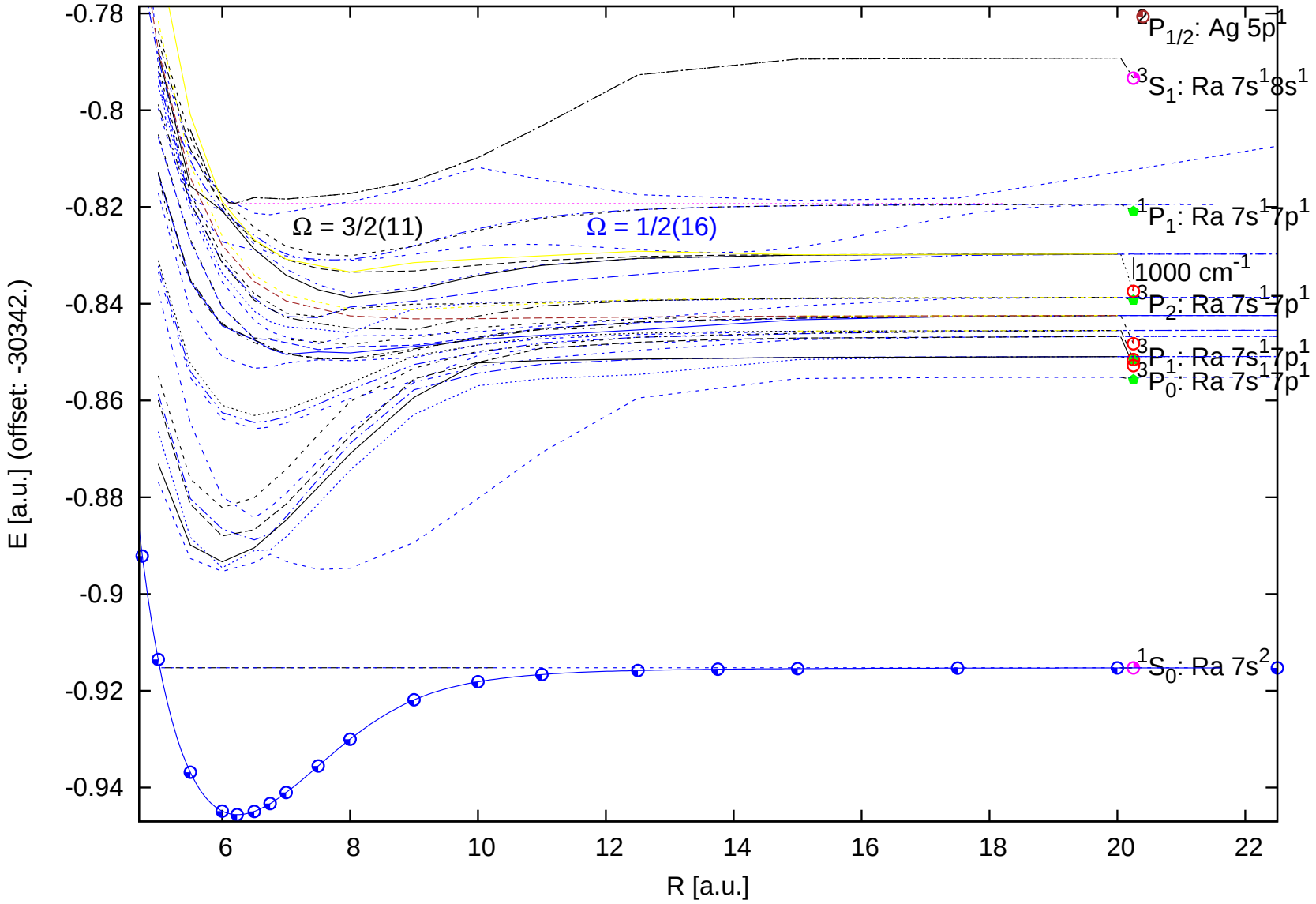
- Dirac-Coulomb-Gaunt Hamiltonian operator (molecules)

$$\hat{H}^{DCG} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \sum_A^N \frac{Z}{r_{iA}} \mathbb{1}_4 \right] + \sum_{i,j>i}^n \left(\frac{1}{r_{ij}} \mathbb{1}_4 + \frac{1}{2} \frac{\vec{\alpha}_i \vec{\alpha}_j}{r_{ij}} \right) + \sum_{A,B>A}^N V_{AB}$$

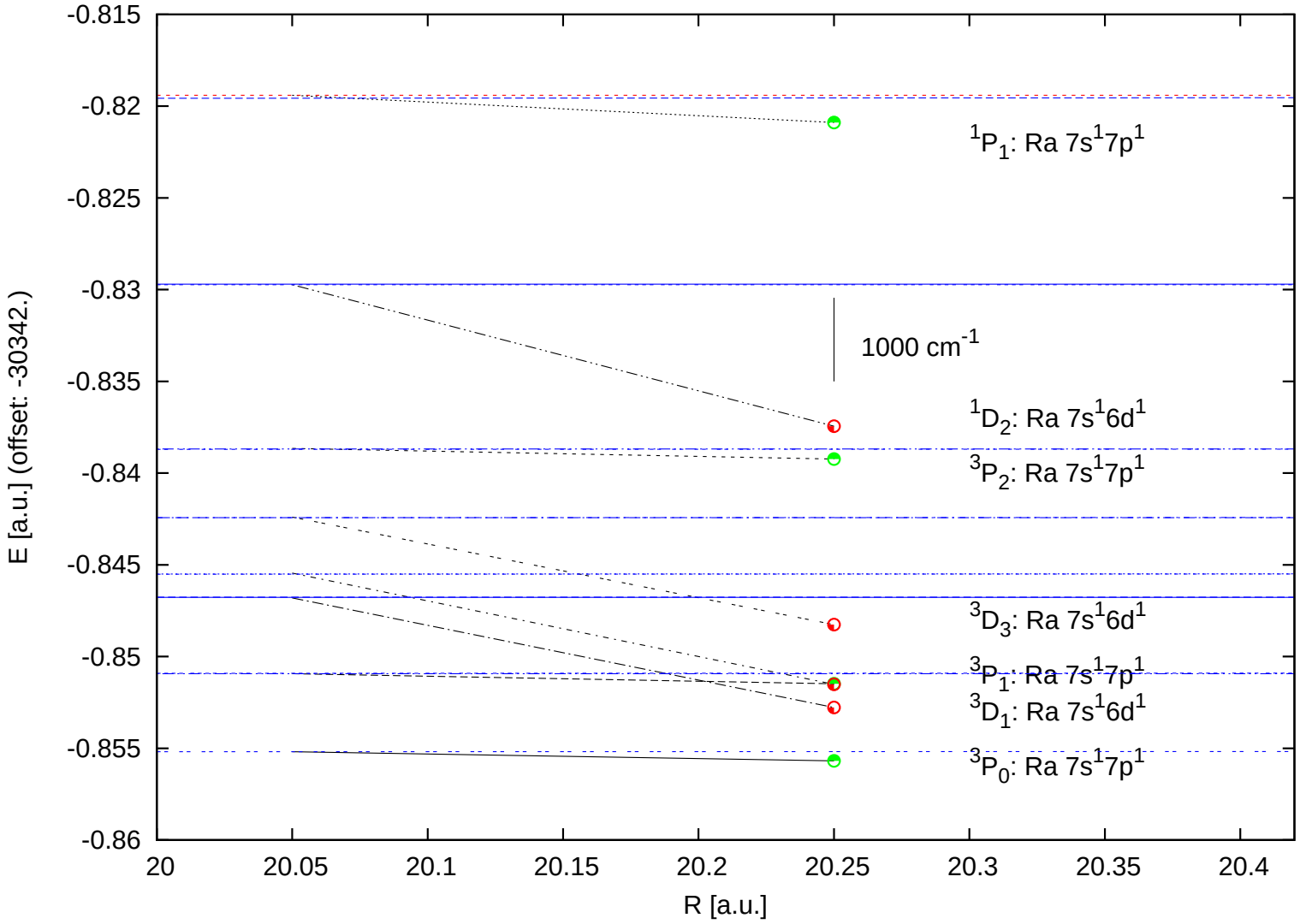
- Dirac-Coulomb Hamiltonian + external electric field (atoms)

$$\hat{H}^{\text{Dirac-Coulomb}} + \hat{H}^{\text{Int-Dipole}} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \frac{Z}{r_i} \mathbb{1}_4 \right] + \sum_{i,j>j}^n \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_i^n \mathbf{r}_i \cdot \mathbf{E}_{\text{ext}}\, \mathbb{1}_4$$

AgRa - PECs

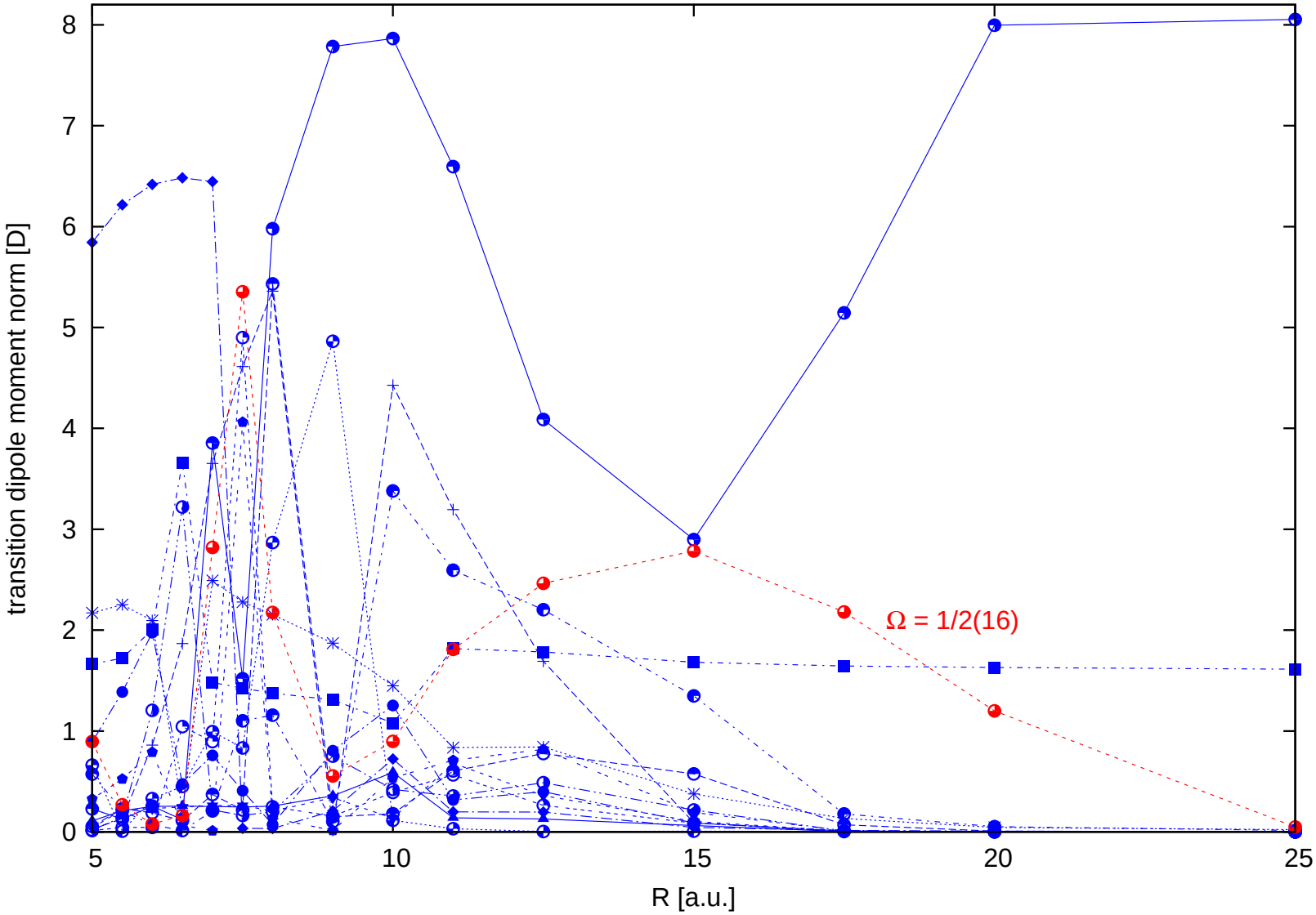

-0.78
-0.8
-0.82
-0.84
-0.86
-0.88
-0.9
-0.92
-0.94
E [a.u.] (offset: -30342.)
6
8
10
12
14
16
18
20
22
R [a.u.]
Ω = 3/2(11)
Ω = 1/2(16)
1000 cm-1
2P1/2: Ag 5p1
3S1: Ra 7s18s1
1P1: Ra 7s17p1
3P2: Ra 7s17p1
3P1: Ra 7s17p1
3P0: Ra 7s17p1
1S0: Ra 7s2

Radium excited states - Comparison with experiment[21]

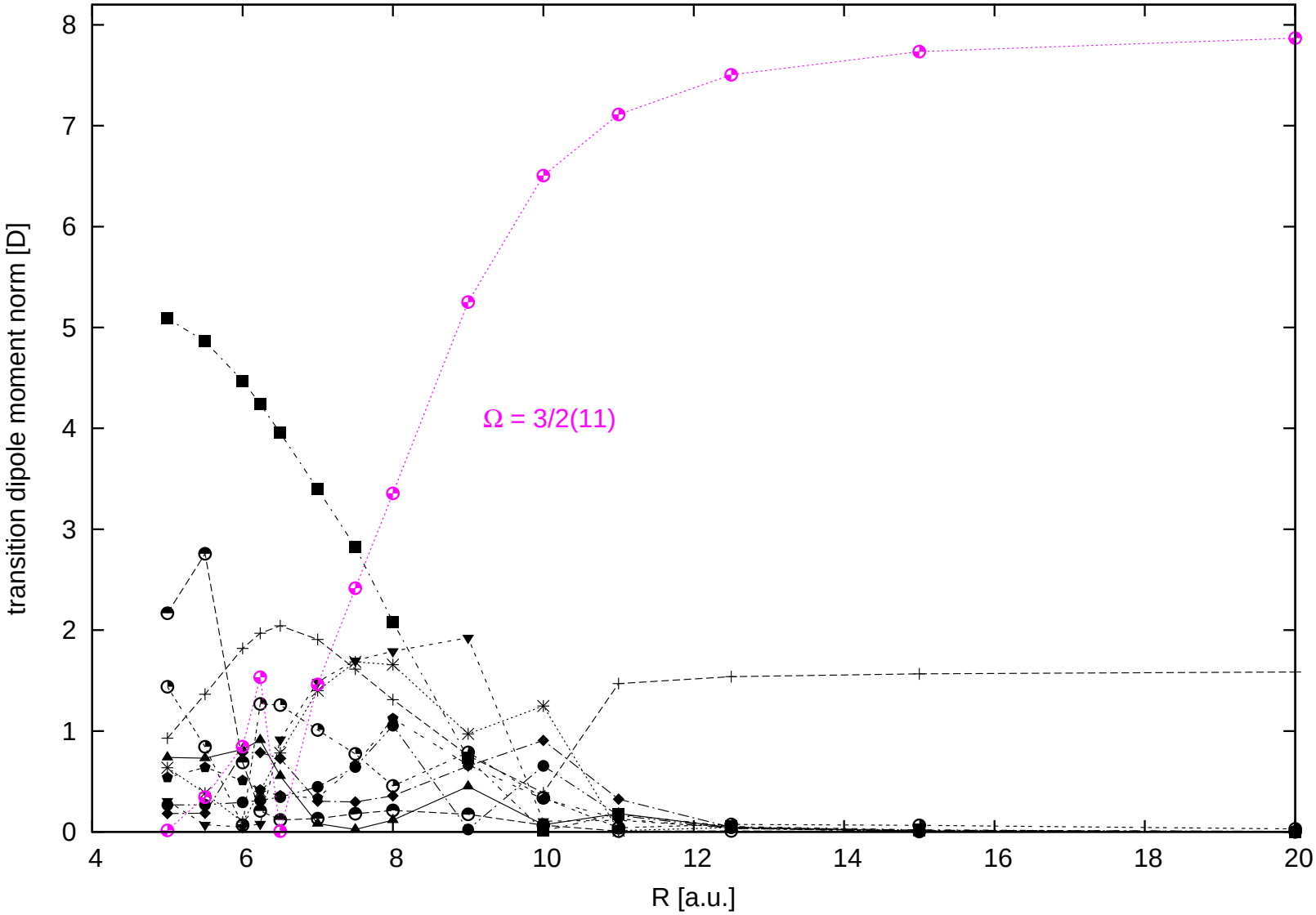


[21] NIST Atomic Spectra Database (ver. 5.5.1)

Electronic Transition Dipole Moments : $\Omega = 1/2$ states



Electronic Transition Dipole Moments : $\Omega = 3/2$ states



Long-range interactions : theory

- Motivation: Find least-bound vibrational level of ground potential
- Problem: PECs at long range not sufficiently accurate, even with very large basis sets !
- Solution: Go "back" to atomic physics

Dispersion interaction for two neutral heteronuclear atoms

Van der Waals interaction potential:

$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots$

Dispersion coefficients from oscillator strengths[22]

Ground state:

$$C_6^{\Omega=1/2(1)} = \sum_{n_c(\ell_c=1),n_d(\ell_d=1)} \frac{3}{2} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} \, (\Delta E_{ca} + \Delta E_{db})}$$

$a = {}^2S_{1/2}(5s^1)$ for Ag and $b = {}^1S_0(7s^2)$ for Ra

$$f_{KL}^{(1)} = 2 \, (E_L - E_K) \, || \, \langle \psi_K | \sum_{k=1}^{n} \hat{r}(k) \, | \psi_L \rangle \, ||^2$$

$|\psi_L\rangle = \left|{}^2P\right\rangle = \left|1, M_L; \frac{1}{2}, \frac{1}{2}\right\rangle$ are expanded as

$$\left|1, 0; \tfrac{1}{2}, \tfrac{1}{2}\right\rangle = \left\langle \tfrac{3}{2}, \tfrac{1}{2} | 1, 0; \tfrac{1}{2}, \tfrac{1}{2} \right\rangle \, \left|\tfrac{3}{2}, \tfrac{1}{2}\right\rangle + \left\langle \tfrac{1}{2}, \tfrac{1}{2} | 1, 0; \tfrac{1}{2}, \tfrac{1}{2} \right\rangle \, \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle$$

where $\langle J, M_J | L, M_L; S, M_S \rangle$

[22] J.-Y. Zhang, J. Mitroy, *Phys. Rev. A* **76** (2007) *022705*

Testing the approach: LiBe and RbSr

LiBe ($^2\Sigma_{1/2}$)	lin. CCSD[23]	KRCI(FCI)
C_6[a.u.]	$478(3)$	454

RbSr ($^2\Sigma_{1/2}$)	lin. CCSD[23]	KRCI MR-SD	KRCI MR-SD +TQ
C_6[a.u.]	$3697(10)$	3995	3849

5% residual deviation!

AgRa ($\Omega = 1/2(1)$)	KRCI(MR-SD)
C_6[a.u.]	1163

[23] A. Derevianko, S.G. Porsev, J.F. Babb, *At. Data Nucl. Data Tables* **96** (2010) *323*
M.S. Safronova, W.R. Johnson, A. Derevianko, *Phys. Rev. A* **60** (1999) *4476*

Connecting LR- and SR-Potentials

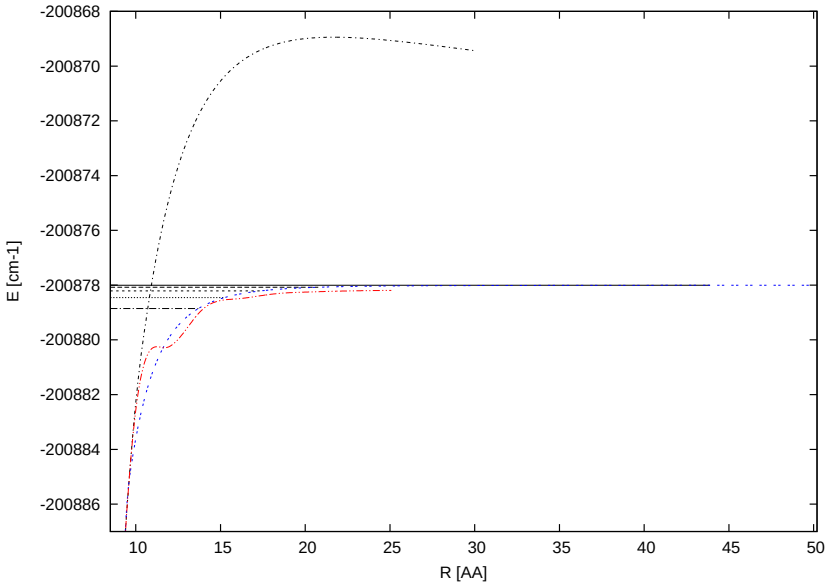
Ground potential $\Omega = 1/2(1)$

LeRoy radius[24]:

$$R_{\mathrm{LR}} = 2\left(\langle\hat{r}^2\rangle_A^{1/2} + \langle\hat{r}^2\rangle_B^{1/2}\right)$$

$$\langle\hat{r}^2\rangle_{\mathrm{Ag}_{5s}} = 13.90 \text{ a.u.} \qquad \langle\hat{r}^2\rangle_{\mathrm{Ra}_{7s}} = 28.71 \text{ a.u.}$$

$$\Rightarrow R_{\mathrm{LR}}^{\Omega=1/2(1)} = 18.2\,\text{a.u.}$$



- Pure short-range potentials produce artefacts!
- $V(R) \approx -\frac{C_6}{R^6}$ and fit long-range to short-range curves
- Correct physics from careful fitting

[24] R.J. LeRoy, *Can. J. Phys.* **52** (1974) *246*
R.J. LeRoy, R. B. Bernstein, *J. Chem. Phys.* **52** (1970) *3869*

Dispersion coefficients from oscillator strengths

Ra(7p) excited states:

$$C_6^{\Omega=1/2(16)} = C_6^{\Omega=3/2(11)} = \sum_{n_c(\ell_c=1),n_d(\ell_d=0)} \frac{3}{4} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} \left(\Delta E_{ca} + \Delta E_{db}\right)}$$

$$+ \sum_{n_c(\ell_c=1),n_d(\ell_d=1)} \frac{15}{8} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} \left(\Delta E_{ca} + \Delta E_{db}\right)}$$

$$+ \sum_{n_c(\ell_c=1),n_d(\ell_d=2)} \frac{57}{40} \frac{f_{ac}^{(1)} f_{bd}^{(1)}}{\Delta E_{ca} \Delta E_{db} \left(\Delta E_{ca} + \Delta E_{db}\right)}$$

AgRa $(\Omega = 1/2(16), \Omega = 3/2(11))$	KRCI(MR-SD)
C_6[a.u.]	773

Connecting LR- and SR-Potentials

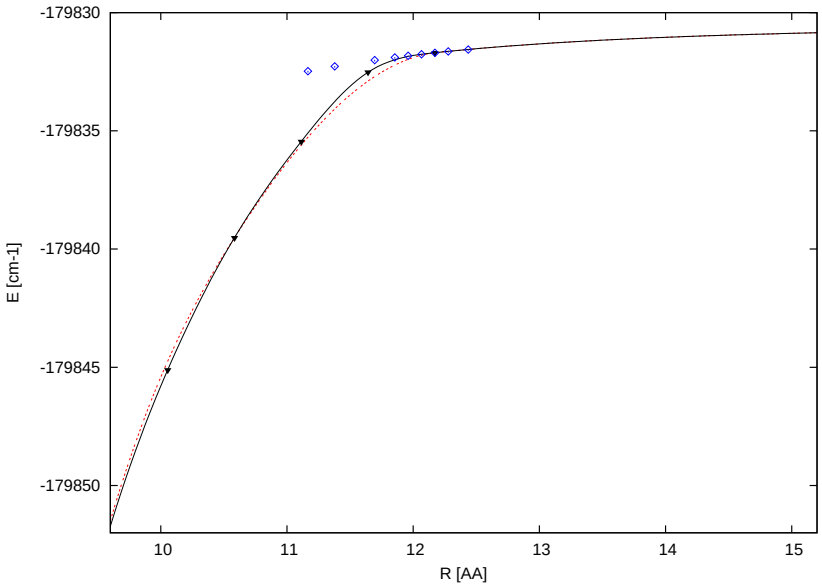
Excited potentials $\Omega = 1/2(16), \Omega = 3/2(11)$

LeRoy radius:

$$R_{\mathrm{LR}} = 2\left(\langle \hat{r}^2 \rangle_A^{1/2} + \langle \hat{r}^2 \rangle_B^{1/2}\right)$$

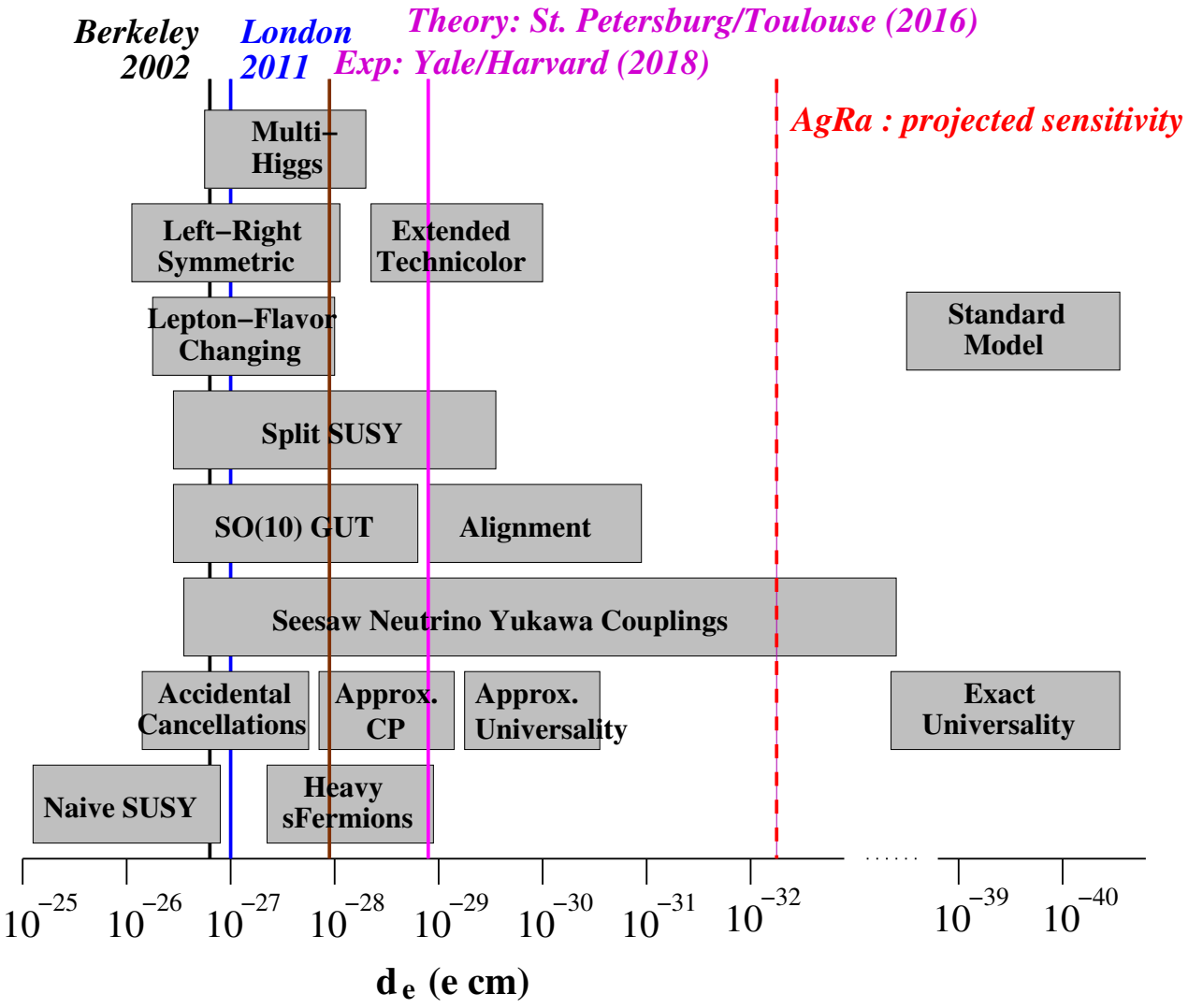
$$\langle \hat{r}^2 \rangle_{\mathrm{Ag}_{5s}} = 13.90 \text{ a.u.} \qquad \langle \hat{r}^2 \rangle_{\mathrm{Ra}^+_{7p_{3/2}}} = 60.63 \text{ a.u.}$$

$$\Rightarrow R_{\mathrm{LR}}^{\Omega=1/2(1)} = 23.0\,\text{a.u.}$$



- $V(R) \approx -\frac{C_6}{R^6}$ and fit long-range to short-range curves

eEDM Constraint on Beyond-Standard-Model Theories
Single-source interpretation (20??)

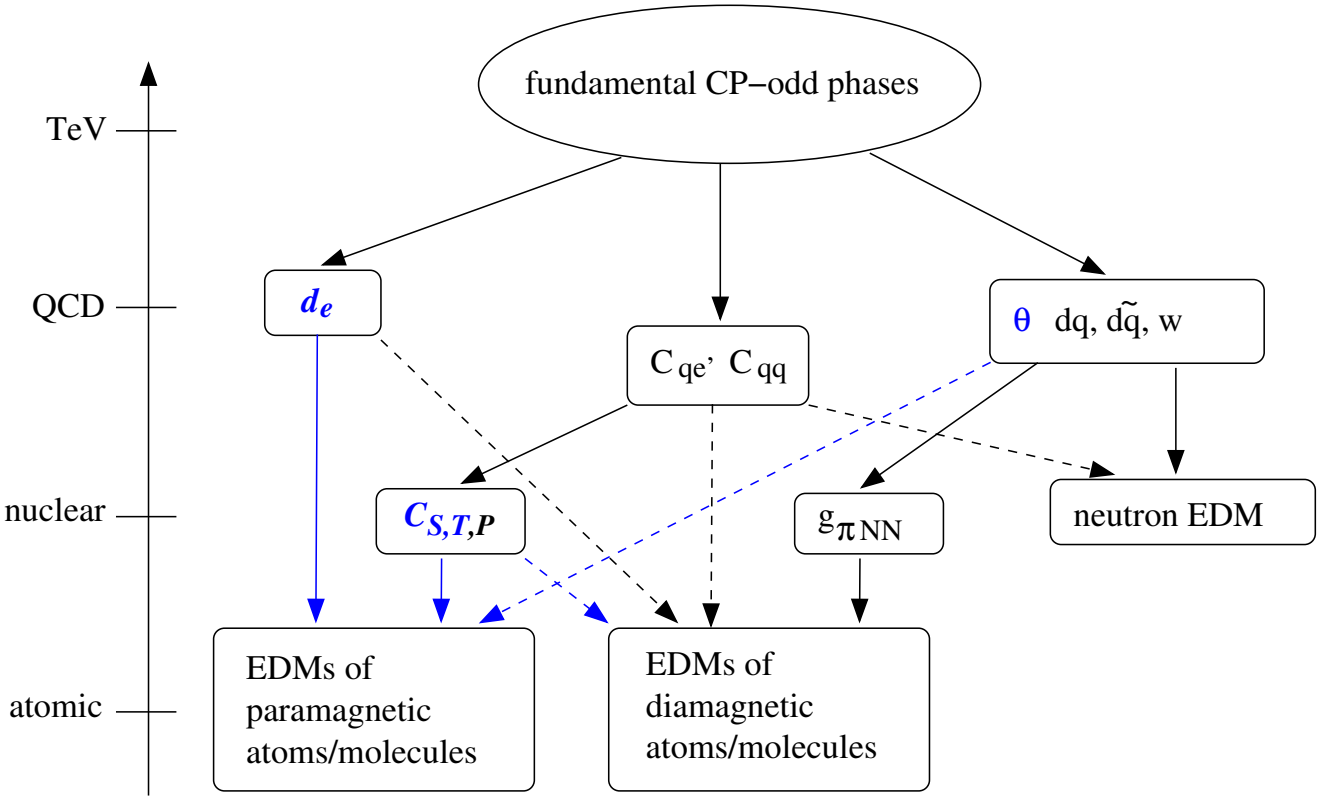


Conclusion.[25] Where do we go from here ?

- AgRa can be trapped and cooled to ultracold temperatures
- $\mathcal{P}, \mathcal{T}$-odd properties are competitive
- Electronic spectrum is complex, but not hopeless for PA
- FCFs for $\Omega = 1/2(1) - \Omega = 1/2(16)$ and $\Omega = 1/2(1) - \Omega = 3/2(11)$ look promising
- One remaining question: Is predissociation possible?
- AgRa seems prime candidate among ultracold "contenders"

[25] TF, D. DeMille, manuscript in preparation

Ne-TPT Interaction in Atoms and Molecules



Effective Hamiltonian[26]

$$\hat{H}_{Ne}^{T-PT} = \frac{\imath G_F}{\sqrt{2}} 2\, C_T\, \gamma_e \cdot \boldsymbol{\sigma}_N\, \rho(\mathbf{r})$$

Important in closed-shell atomic systems, Hg, Ra, *et al.*

[26] E.A. Hinds, C.E. Loving, P.G.H. Sandars, *Phys. Lett. B* **62** (1976) *97*

Ne-TPT Interaction in Atoms and Molecules

With nuclear state expressed as $|I, M_I = I\rangle$ it follows

$$\hat{H}_{Ne}^{T-PT} = \frac{\imath G_F}{\sqrt{2}} 2\, C_T\, (\gamma_e)^3\, \langle \sigma_N \rangle_{\Psi_N}\, \rho(\mathbf{r})$$

Defining an electronic matrix element[27]

$$M_{Ne}^{T-PT} := \left\langle \psi_e | \imath\, (\gamma_e)^3\, \rho(\mathbf{r}) | \psi_e \right\rangle$$

The Ne-TPT interaction constant is

$$R_T = \sqrt{2} G_F \langle \sigma_N \rangle_{\Psi_N}\, M_{Ne}^{T-PT}$$

with $d_a = R_T C_T$.

[27] TF, *arXiv:1811.01684* (2018)
DIRAC15 package (locally modified)

Ne-TPT Interaction in Atoms and Molecules

^{199}Hg

Model/virtual cutoff [*a.u.*]	α_d [*a.u.*]		R_T [10^{-20} $\langle\sigma_N\rangle$ e cm]	
	Basis set		Basis set	
	vDZ	vTZ	vDZ	vTZ
RPA/-	44.5	45.5	−4.70	−4.94
SD12/22	35.0	33.5	−4.05	−4.25
SD18/22	30.7	34.2	−5.52	−5.82
SD12_SDT18/22			−5.35	
SD34/22			−4.77	−5.16
SD34/50	30.0	34.8	−4.95	−5.19
S8_SD42/50			−5.14	
S10_SD44/50			−5.00	
SDT12/22	37.9	34.4	−3.65	−3.71
SDTQ12/22			−3.40	
vTZ/SD34/50 +Δ	**35.7**		**−4.43**	
Singh *et al.*[28] CCSD$_p$T	34.27		−4.30	
Dzuba *et al.*[29] RPA/MBPT+CI	44.9		−5.1	
Experiment[30]	33.91			

[28] Y. Singh, B.K. Sahoo, *Phys. Rev. A* **91** (2015) *030501(R)*

[29] V.A. Dzuba, *Phys. Rev. A* **93** (2016) *032519*
V.A. Dzuba, V.V. Flambaum, S.G. Porsev, *Phys. Rev. A* **80** (2009) *032120*

[30] D. Goebel, U. Hohm, *J. Phys. Chem* **100** (1996) *7710*

Ne-TPT Interaction in Atoms and Molecules

^{225}Ra

Model/virtual cutoff [*a.u.*]	R_T [10^{-20} $\langle\sigma_N\rangle$ e cm]		
	Basis set		
	vDZ	vTZ	vQZ
RPA/-	-14.5	-14.7	-14.7
SD10/23	-12.5	-13.6	-13.7
SD10/50	-12.5		
SD20/23	-13.6	-13.9	-14.0
SD28/23	-14.7	-15.0	-14.9
SD28/50		-14.9	
S8_SD36/50		-15.4	
S14_SD42/50		-15.1	
SDT10/23	-11.3	-13.1	-13.2
SDTQ10/23	-10.7		
vTZ/SD28/50 $+\Delta R_T$		**-15.0**	
Dzuba et al.[32] MBPT+CI		-18	

Using Argonne result[31] for $d_{^{225}\mathrm{Ra}}$

$$|C_T| < \left|\frac{d_{^{225}\mathrm{Ra}}}{R_T}\right| = 9.3\times10^{-5}\,\frac{1}{\langle\sigma_N\rangle} < 10^{-3}$$

[31] M. Bishof et al., *Phys. Rev. C* **94** (2016) *025501*

[32] V.A. Dzuba, V.V. Flambaum, S.G. Porsev, *Phys. Rev. A* **80** (2009) *032120*

Atomic and Molecular Correlated Wavefunction

- All-electron Dirac-Coulomb Hartree-Fock (DC(G)HF) calculation
  set of time-reversal paired 4-spinors $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

$$\hat{K}(n) := e^{-\frac{i}{2}\pi\left(\sum_{j=1}^{n} \boldsymbol{\sigma}\otimes\mathbb{1}_2(j)\right)\cdot\vec{e}_y} \prod_{j=1}^{n} \hat{K}_0(j)$$

- Expansion and variation[33] in n-electron sector of Fock space

$$|\psi_k\rangle = \sum_{I=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{M},\mathrm{n})} c_{kI}\,(\mathcal{S}\overline{\mathcal{T}})_I\,|\ \rangle$$

unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$

barred (Kramers down) string $\overline{\mathcal{S}} = a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

Linear expansion: **Configuration Interaction**

Exponential expansion: Coupled Cluster

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

$\mathcal{P}$,$\mathcal{T}$-odd Property Calculations

using correlated wavefunctions

Expectation values over relativistic Configuration Interaction wavefunctions[34]

$$\left\langle \hat{H}' \right\rangle_{\psi_k^{(0)}} = \sum_{I,J=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{M,n})} c_{kI}^* c_{kJ} \left\langle \, | \, (\mathcal{S}\overline{\mathcal{T}})_I^\dagger \left| \hat{H}' \right| (\mathcal{S}\overline{\mathcal{T}})_J \, | \, \right\rangle$$

Property operator in basis of Kramers-paired molecular spinors

$$\hat{H}' = \sum_{p,q=1}^{P_u} h'_{pq} \, a_p^\dagger a_q + \sum_{p=1}^{P_u} \sum_{q=P_u+1}^{P} h'_{p\overline{q}} \, a_p^\dagger a_{\overline{q}} + \sum_{p=P_u+1}^{P} \sum_{q=1}^{P_u} h'_{\overline{p}q} \, a_{\overline{p}}^\dagger a_q + \sum_{p,q=P_u+1}^{P} h'_{\overline{p}\overline{q}} \, a_{\overline{p}}^\dagger a_{\overline{q}}$$

First-term contribution to expectation value

$$W'(\Psi_k)_1 = \sum_{I,J=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{P,N})} c_{kI}^* c_{kJ} \sum_{m,n=1}^{P_u} h_{mn}^M$$
$$\left\langle \, | \, \prod_{p=1}^{N_p\in\mathcal{S}_I} \prod_{\overline{p}=N_p+1}^{N_p\in\mathcal{S}_I+N_{\overline{p}}\in\overline{\mathcal{T}}_I} a_{\overline{p}} a_p \, a_m^\dagger a_n \prod_{q=1}^{N_p\in\mathcal{S}_J} \prod_{\overline{q}=N_p+1}^{N_p\in\mathcal{S}_J+N_{\overline{p}}\in\overline{\mathcal{T}}_J} a_q^\dagger a_{\overline{q}}^\dagger \, | \, \right\rangle$$

[34] S. Knecht, Dissertation, HHU Düsseldorf 2009

$\mathcal{P},\mathcal{T}$-odd Effects in Closed-Shell States ?

- Atomic electronic state in $E_{\text{ext}} \neq 0$:
  $|M_J\rangle$
- In the closed-shell subcase ($p_{1/2}^2 \neq$ closed shell) it follows:
  $|M_S = 0\rangle$
- Then it is straightfoward to show that
  $\langle M_S = 0| \sum_j \gamma^0(j)\, \Sigma_3(j)\, E_3\, |M_S = 0\rangle = 0$ and
  $\langle M_S = 0| \sum_j \gamma^0(j)\, \Sigma_\pm(j)\, E_\pm\, |M_S = 0\rangle = 0$
- The electron EDM Hamiltonian can be reformulated as
  $$-\left\langle \sum_{j=1}^{n} \gamma_j^0\, \boldsymbol{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_{\psi^{(0)}} \approx \tfrac{2\imath c}{e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \vec{p}_j{}^{\,2} \right\rangle_{\psi^{(0)}}$$
- which has the same transformation properties as the ne-SPS Hamiltonian.
- No $\mathcal{P},\mathcal{T}$-odd effects in closed-shell states (in $E_{\text{ext}} \neq 0$).

EDMs in paramagnetic atoms:

Nucleon-electron SPS interaction

- Effective interaction Hamiltonian

  $$\hat{H}_{\text{ne-SPS}}(S) = \frac{\imath G_F}{\sqrt{2}} A C_S \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e)$$

- To first order in perturbation theory

  $$(\Delta\varepsilon)_J = \left\langle \imath \frac{G_F}{\sqrt{2}} A C_S \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \right\rangle_{\psi_J^{(1)}}$$

  ψ_J: atomic many-particle state

- Atomic EDM is defined as

  $$d_a = - \lim_{E_{\text{ext}} \to 0} \left[\frac{\partial(\Delta\varepsilon)}{\partial E_{\text{ext}}} \right]$$

- Definition of an ne-SPS ratio

  $$S := \frac{d_a}{A C_S \frac{G_F}{\sqrt{2}}}$$

- from which follows

  $$S = - \lim_{E_{\text{ext}} \to 0} \left[\frac{\partial}{\partial E_{\text{ext}}} \left\langle \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \right\rangle_{\psi_J^{(1)}(E_{\text{ext}})} \right]$$