

Study of T, P -nonconservation effects & hyperfine constants in diatomics and solids by the relativistic pseudopotential / core-restoration method

Anatoly V. Titov

A.N. Petrov, L.V. Skripnikov, A.D. Kudashov & N.S. Mosyagin



PNPI

QChem

Group

<http://qchem.pnpi.spb.ru>

**B.P. KONSTANTINOV PETERSBURG
NUCLEAR PHYSICS INSTITUTE
ST.-PETERSBURG STATE UNIVERSITY**

RUSSIA

The relativistic pseudopotential (RPP) [1] calculations of valence (spectroscopic, chemical etc.) properties of molecules are now most efficient in general because the modern two-component RPP methods allow one to treat very accurately both correlation and relativistic effects for the valence and outer-core electrons of a molecule and to reduce dramatically the computational cost. In particular, some combined computational schemes can be applied which include both fully relativistic and highly-correlated scalar-relativistic approaches. Such combined schemes are firstly important for studying compounds of d- and f-elements, many-atomic systems and crystals. To reduce efforts, valence molecular spinors are usually smoothed in atomic cores and, therefore, direct calculation of proper densities of valence electrons near heavy nuclei within such RPP approaches is impossible. The knowledge of electronic density matrices in atomic cores is required to study hyperfine constants and other magnetic properties, time-reversal (T) and space parity (P) nonconservation effects, which are described by the operators heavily concentrated in atomic cores. For such properties the electronic structure should be well evaluated in both valence and atomic core regions of studied systems. The relativistic one-center core-restoration technique [2] developed by the authors overcomes the restrictions of the RPP method and extends its applicability to core-concentrated properties while preserving the advantages of using RPPs. The features of the two-step method (RPP study of a system followed by the electronic structure restoration in atomic cores), presented in the lecture, are compared to those of the all-electron four-component approaches.

Study of both spectroscopic and core-concentrated properties (hyperfine constants, P- and T,P-nonconservation effects) is discussed for polar heavy-atom diatomics (HfF+ [3], RaO [4], WC [5], PtH+, PbF, RaF, YbF etc.), Eu^{2+} in an external electric field simulating Eu-in- $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ and solids (PbTiO_3 etc.), which are of interest for the experimental search of the electron electric dipole moment, Schiff and anapole moments of nuclei.

The work is supported by the SPbU Fundamental Science Research grant from Federal budget and RFBR grant #13-02-01406.

[1] N.S.Mosyagin, A.V.Zaitsevskii, A.V.Titov, *Int.Rev.At.Mol.Phys.*, 1(1), 63 (2010).

[2] A.V. Titov, N.S. Mosyagin, A.N. Petrov, T.A. Isaev, D.P. DeMille, *Progr. Theor. Chem. Phys. B* 15, 253 (2006).

[3] K.C. Cossel, D.N. Gresh, L.C. Sinclair, T. Coffey, L.V. Skripnikov, A.N. Petrov, N.S. Mosyagin, A.V. Titov, R.W. Field, E.R. Meyer, E.A. Cornell, J. Ye, *Chem. Phys. Lett.* 546 (Frontiers) 1-11 (2012).

[4] A.D. Kudashov, A.N. Petrov, L.V. Skripnikov, N.S.Mosyagin, A.V.Titov, V.Flambaum, <http://arxiv.org/abs/1211.5797>, PRA, in press.

[5] J. Lee, J. Chen, L.V. Skripnikov, A.N. Petrov, A.V. Titov, N.S. Mosyagin, A.Leanhardt, <http://arxiv.org/abs/1212.5744>, PRA in press.

P, T-odd effects in molecules: historical background

- ✧ **1965: Sandars** suggests to use heavy atoms to search for EDMs.
*In the nonrelativistic case E_{eff} is zero in accord to the Schiff theorem;
relativistic eEDM enhancement $E_{\text{eff}}/E_{\text{ext}} \sim \alpha^2 Z^3$ [V.Flambaum, Sov.J.Nucl.Phys. **24** (1976)]*

EDMs of charged particles e^- , p etc. can be studied !
- ✧ **1967: Sandars:** in polar heavy-atom molecules $E_{\text{mol}}/E_{\text{ext}} \gg 1$.
- ✧ He initiated the search for the P, T-odd effects on ^{205}TlF and estimated these effects **semiempirically** ($E_{\text{eff}} \approx 20 \text{ kV/cm}$ on a valence proton).
- ✧ **1991:** The last series of the ^{205}TlF experiments is finished by **Hinds** group at Yale (USA) and the best limitation on the proton EDM, $d_p = (-4 \pm 6) \times 10^{-23} \text{ e}\cdot\text{cm}$, is obtained. In **2002 Petrov et al.** recalculated it with taking account of correlation and relativistic effects as
 $d_p = (-1.7 \pm 2.8) \times 10^{-23} \text{ e}\cdot\text{cm}$.

P, T-odd effects in molecules: historical backgr. (cont)

- ✧ **1967: Onischyuk** [Preprint JINR, Dubna]: first ideas to use close rotational levels of opposite parity in diatomics in search for *P*- and *T*-odd effects.
- ✧ **1978: Labzowskii**: ideas to use diatomic radicals CuO, CuS, CuSe due to additional enhancement of *P*-odd in Λ -doublets with $^2\Pi_{1/2}$ ground state, $E_{\text{mol}}/E_{\text{ext}} \sim 10^5$. Systematic study of heavy-atom diatomics is initiated.
- ✧ **1978: Sushkov & Flambaum**, and in **1979 Gorshkov, Labzowskii & Moskalev**: ideas to use diatomic radicals (Ω -doublets) to search for *P, T*-odd effects including EDM of electron due to additional enhancement.
- ✧ **1984: Sushkov, Flambaum & Khriplovich; Flambaum & Khriplovich**, and then **Kozlov** suggest to use diatomics with a $^2\Sigma_{1/2}$ ground state.
- ✧ Many new molecules, molecular cation and solids are considered up-to-date for the eEDM search by Novosibirsk, SPb and other groups.
- ✧ **2002: The last series of the ^{205}Tl beam experiment is finished at Berkeley (USA) and the best atomic limitation on d_e , $|d_e| < 1.6 \times 10^{-27} \text{ e}\cdot\text{cm}$, is obtained**
- ✧ **2002: The first results are obtained by Hinds group on the ^{174}YbF molecular beam at Sussex (UK) for the eEDM, $d_e = (-0.2 \pm 3.2) \times 10^{-26} \text{ e}\cdot\text{cm}$;**
- ✧ **2011: new limitation on d_e is obtained on YbF, $|d_e| < 1.05 \times 10^{-27} \text{ e}\cdot\text{cm}$.**

First calculations of PNC effects in heavy-atom molecules:

- First *ab initio* **nonrelativistic** calculations of *P, T*-parity nonconservation effects in **TIF** followed by the **relativistic scaling** were performed by **Hinds & Sandars** in **1980** and by Coveney & Sandars in 1983 (Oxford, UK).
- A series of **semiempirical** calculations was performed since 1978 by **Kozlov & Labzowskii** (St.Petersburg); **Sushkov, Flambaum & Khriplovich** (Novosibirsk) for heavy-atom molecules.
- **Two-step (RECP / one-center-restoration)** relativistic calculations at SPbSU, PNPI: **RECP** = Relativistic Effective Core Potential method without correlations: on **PbF** & **HgF** (1985-1991); with correlations: on **YbF** (1996, 1998, 2012), **BaF** (1997), **TIF** (2002), **PbO*** (2004), **Hf*** (2005), **liquid Xe** & **HfF*** (2006+); **PtH*** (2009) ...
- First **Dirac-Fock** calculations on **TIF** (1997) and **YbF** (1998) are performed by Parpia (USA) and by Quiney et al. (EU).
- In 2006-2009, **correlation four-component** calculation of **BaF** and **YbF** are performed by **Nayak & Chaudhuri**.
- ... **PtH***, **ThO** & **ThF*** (2008) are calculated “**semi-ab-initio**” by **Meyer & Bohn** (JILA, Boulder, USA).
-

Experiments on the electron EDM search

Heavy-atom polar molecules and cations:

- ✦ **YbF**-radical *beam* (E.Hinds group);
- ✦ **HfF⁺** (& ThF⁺, PtH⁺ ...) *trapped cations* (E.Cornell & J.Ye groups);
- ✦ **WC** (³Δ₁ is the ground state) *molecular beam* (A.Leanhard group);
- ✦ **ThO*** *beam* [& **PbO*** in optic cell] (ACME collaboration: D.DeMille; J.Doyle & G.Gabrielse);
- ✦ **PbF** *radicals* in a Stark trap (N.Shafer-Ray & R.Mawhorter);

Solids:

- ✦ **Gd-Ga Garnet** (S. Lamoreaux; C.-Y. Liu);
- ✦ **Gd-Iron Garnet** (L. Hunter);
- ✦ **Eu_{0.5}Ba_{0.5}TiO₃** (*perovskite, ferroelectric*); (S. Lamoreaux group)
- ✦ there are also other proposals.

What is required for reliable relativistic calculation?

- Choosing a suitable *methods for calculating the electronic structure* taking account of the required accuracy of properties, complexity of the system (number of atoms and electrons, features of the valence structure, types of atoms: *s*-, *p*-, *d*- or *f*-elements, etc.), acceptable computational cost :
 - method of accounting for *electron correlation* (fixing the subset of correlated electrons);
 - optimal *effective Hamiltonian* (relativistic, scalar-relativistic=without SO) and related *one-electron basis set* (choosing / generation for all atoms treated)

Correlation methods

- *Configuration interaction (CI)*

Spin-Orbit Direct Configuration Interaction (**SODCI**)

[R. Buenker *et al.*, *Wuppertal*, Germany];

improvements with spin-orbit: [A.V. Titov *et al.*, *IJQC* **81**, 409 (2001)]

- works well for systems with rather small number of correlated electrons (<25), but with any number and nature of open shells (>10'000 selected reference states!);

single and double excitations on the reference states to form the *final CI space with up to* 75'000'000 selected configurations (plus corrections).

Correlation methods

- **Coupled-clusters (CC):**

$$\Psi = e^{\hat{T}} \Phi_0$$

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 \rightarrow \text{CCSD};$$

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \rightarrow \text{CCSDT}$$

relativistic coupled-clusters with single and double excitations (**RCCSD**)

[U.Kaldor, E.Eliav, A. Landau, *Tel-Aviv Uni.*, Israel;

N.S. Mosyagin *et al.*, JCP , 115, 2007 (2001)]

scalar-relativistic (without spin-orbit) **CCSDT (srCCSDT)** to use large basis sets:

within **CFOUR package** [www.cfour.de];

multi-reference CC code by M.Kállay (**MRCC**)

Pioneered by D. Mukherjee

- it is the most advanced approach now; allows one to achieve *the best accuracy* for relatively small systems with rather simple valence structure. There are many different single- and multi-reference developments and combined schemes including CI & many-body perturbation theory.

- *Effective Hamiltonian:*

Relativistic pseudopotential (Generalized relativistic PP or GRPP):

N.S. Mosyagin *et al.*, Int.Rev.At.Mol.Phys. **1**, 63 (2010).

Restoration of electronic structure in heavy-atom cores:

A.V. Titov *et al.*, PTCP **B15**, 253 (2006).

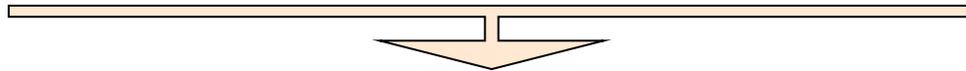
- *Basis Sets:* *GC-basis*: N.S. Mosyagin *et al.*, JPB **33**, 667 (2000).

What makes the core pseudopotential (PP)?

PP reduces the electronic structure calculation to an explicit treatment of only valence electrons (and outer-core electrons for better accuracy).

The problems which are solved within the PP method:

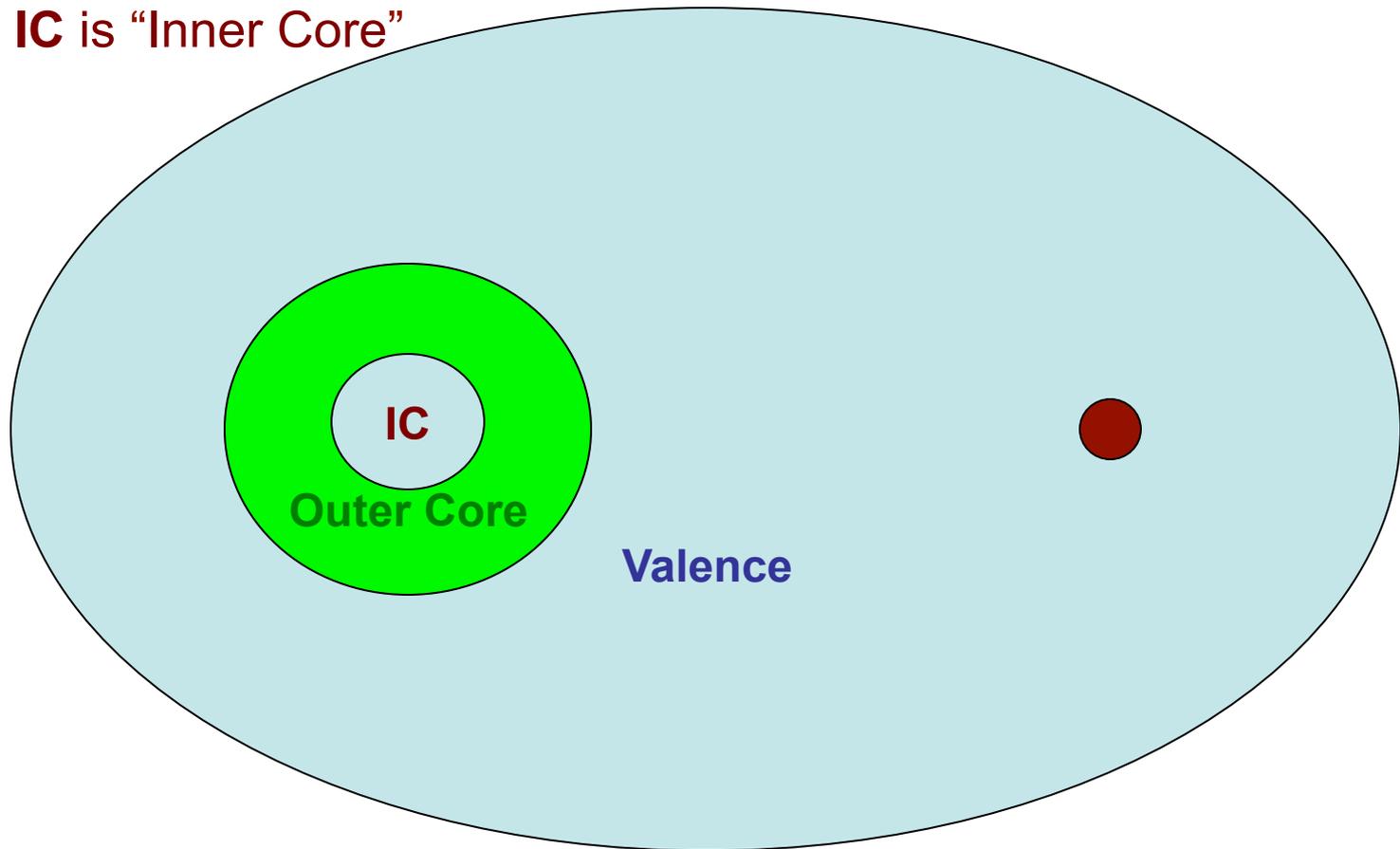
- elimination of chemically inactive (core) electrons from the calculation, while maintaining a sufficiently accurate description of the electronic structure and interactions in the valence region;
- providing Pauli orthogonality with respect to the occupied (explicitly excluded) core states, i.e., prevent the “collapse” of valence electrons into core;
- efficient treatment of relativistic effects (scalar-relativistic , spin-orbit , **Breit**);
- smoothing the pseudospinors to minimize atomic basis set size and reduce the computational cost that can be done depending on the task .



Being universal in applications, the PP method is the most flexible approach for calculating the electronic structures.

Inner-core / outer-core / valence regions

IC is "Inner Core"



Molecular ions for $eEDM$ search

[R.Stutz & E.Cornell, *Bull.Am.Phys.Soc.* **49**, 46 (2004)]

- Ions are easy to trap (in RF quadrupole trap);
- Potential for long spin coherence times (ion-ion repulsion);
- Can get $E_{\text{eff}}/E_{\text{lab}} = 10^9$ (for $\Omega > 1/2$ there are closely spaced levels of opposite parity fully polarized with $E \sim 10$ V/cm);
- Rotating external electric field can be used for $eEDM$ measurements keeping the cold ions in the trap.

However, accurate theoretical study of spectroscopic and other properties of such ions is required to speed up their experimental identification of their spectra since they are not stable under ambient conditions.

HfF⁺ study for eEDM search

Proposal: HfH⁺: [L.Sinclair *et al.*, *Bull.Am.Phys.Soc.* **450**, 134 (2005)];
HfF⁺ & ThF⁺: [E.Cornell & A.Leanhardt, private communication].

Calculation: HfF⁺: [A.Petrov *et al.*, *PRA* (2007, 2009),
L.Skripnikov *et al.*, *Pisma ZhETF* (2009),
K.Cossel *et al.*, *CPL(frontier)* (2012)]

- HfF⁺ working state - ³Δ₁; config.: [...] $\sigma_1^2 \sigma_2^1 \delta^1$,

- Hf²⁺: [...4f¹⁴]5s²5p⁶ 5d¹ 6s¹ + F⁻: 1s² 2s² 2p⁶
[outer core] [valence] [core] [valence]

HfF⁺ study for eEDM search

Proposal: HfH⁺: [L.Sinclair et al., *Bull.Am.Phys.Soc.* **450**, 134 (2005)];
HfF⁺ & ThF⁺: [E.Cornell & A.Leanhardt, private communication].

Calculation: HfF⁺: [A.N.Petrov et al., *PRA* (2007, 2009),
L.Skripnikov et al., *Pisma ZhETF* (2009),
K.Cossel et al., *CPL(frontier)* (2012)]

- HfF⁺ working state - ${}^3\Delta_1$; config.: $[...] \sigma_1^2 \sigma_2^1 \delta^1$,

- Hf²⁺: $[...4f^{14}]5s^25p^6 5d^1 6s^1$ + F⁻: $1s^2 2s^2 2p^6$
[outer core] [valence] [core] [valence]
- 1st question: which state is the ground one,
 ${}^3\Delta_1$ or ${}^1\Sigma^+$ (configuration: $[...] \sigma_1^2 \sigma_2^2$)?!
(and if ${}^3\Delta_1$ is not the ground one, how to populate it?)
- 2nd question: which is the effective field on e⁻, E_{eff} ?
- 3rd question: which transitions to excited states (${}^3\Pi$, ${}^1\Pi$) can be used to measure the EDM signals?

Potential curves of lowest-lying states of HfF^+

20e-GRPP / SODCI

basis set:

Hf: GC [6, 5, 5, 3, 1],

F: ANO [4, 3, 2, 1]

+correlation corrections:

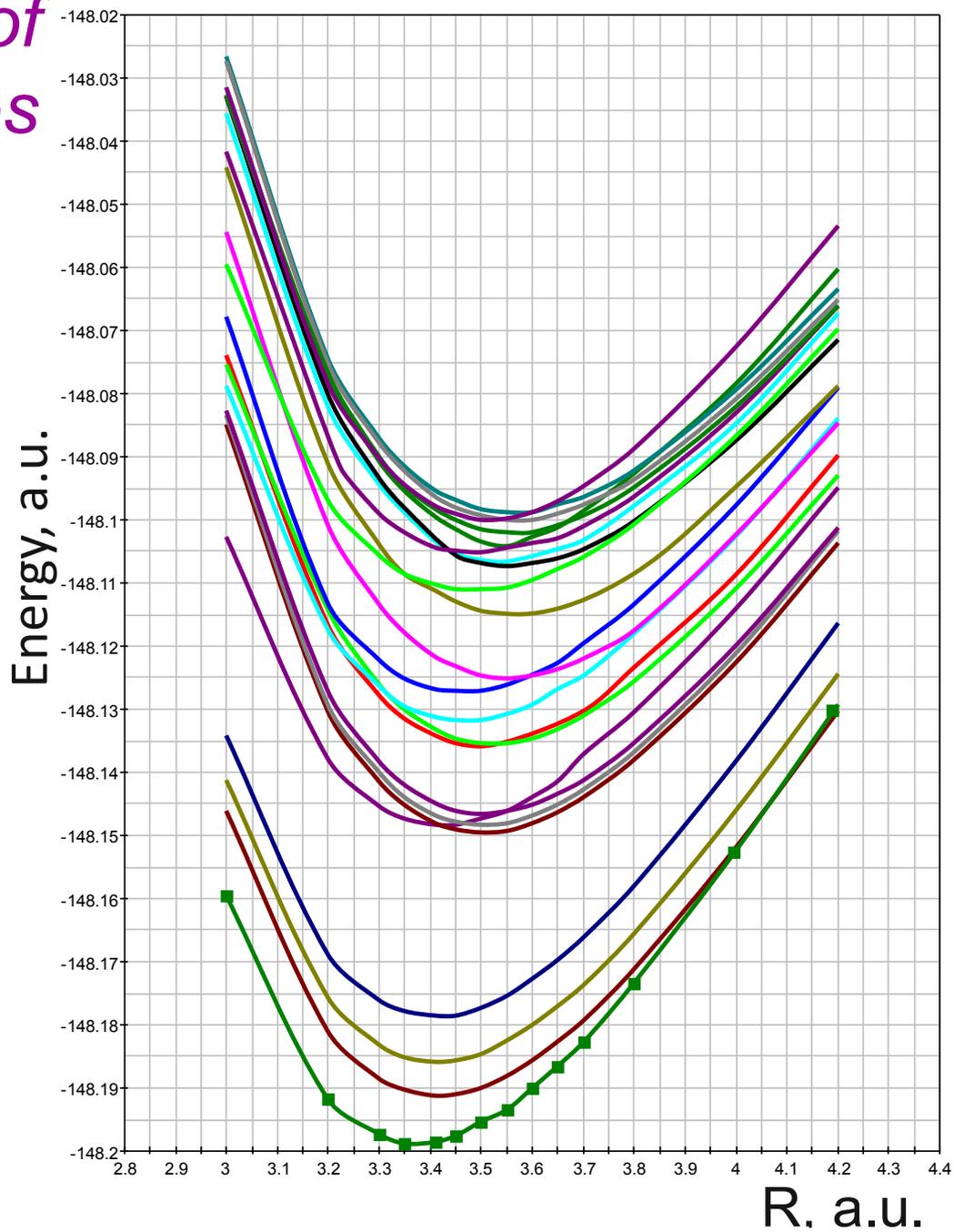
20e-srPP / CCSD(T)

basis set:

Hf: GC

[12,16,16,10,11,4h,2i],

F: ANO [7, 7, 4, 3]



Spectroscopic constants of HfF^+

[K.Cossel et al., *CPL(frontier)* (2012)]

Term	Config.	T_e, cm^{-1}		w_e, cm^{-1}		Transitions		
		Calc.	Exp.	Calc.	Exp.	$^1\Sigma^+$	$^3\Delta_1$	$^3\Delta_2$
$^1\Sigma^+$	σ^2	0	0	792	791			
$^3\Delta_1$	$\sigma^1\delta^1$	1229	992	754	761	0.02		
$^3\Delta_2$	$\sigma^1\delta^1$	2394	2149	766	762	-	0.02	
$^3\Delta_3$	$\sigma^1\delta^1$	3995	3951	757	762	-	-	
$^1\Delta_2$	$\sigma^1\delta^1$	10610		747		-	0.04	0.07
$^3\Pi_{0-}$	$\sigma^1\pi^1$	10400	10248	716		0.00	0.27	-
$^3\Pi_{0+}$	$\sigma^1\pi^1$	10658	10437	724		0.15	0.27	-
$^3\Pi_1$	$\sigma^1\pi^1$	11058	10933	712	715	0.25	0.03	0.22
$^3\Pi_2$	$\sigma^1\pi^1$	13452		745		-	0.03	0.01
$^1\Pi_1$	$\sigma^1\pi^1$	13493	13046	699		0.55	0.03	0.18
$^3\Sigma^+$	$\delta^1\delta'^1$	13773	13297	716		0.23	0.08	-
$^3\Sigma_1$	$\delta^1\delta'^1$	14757		711		0.03	0.02	0.07
$^3\Phi_2$	$\delta^1\pi^1$	15284	14963	671		-	0.48	0.10
$^3\Phi_3$	$\delta^1\pi^1$	17457		658		-	-	0.46
$^3\Phi_4$	$\delta^1\pi^1$	20769		740		-	-	-
$^3\Pi_{0-}$	$\delta^1\pi^1$	19167		691		-	0.36	-
$^3\Pi_1$	$\delta^1\pi^1$	19332		698		0.06	0.14	0.39
$^3\Pi_{0+}$	$\delta^1\pi^1$	20074		748		0.12	0.39	-
$^3\Pi_2$	$\delta^1\pi^1$	20338		665		-		0.10
$^1\Gamma_4$	δ^2	18312		641		-		
$^1\Sigma^+$	$\sigma^1\sigma'^1$	20330		610		0.70	0.03	-
$^3\Sigma^-$	$\sigma^1\sigma'^1$	21694		658		-	0.17	-
$^3\Sigma_1$	$\sigma^1\sigma'^1$	21415		665		0.01	0.00	0.03

What should be calculated to interpret the *eEDM* experiments on molecules

- $$H_{P,T\text{-odd}} = W_d d_e (\mathbf{J}_e \cdot \mathbf{n}) \equiv d_e \cdot W_d \Omega$$

where $d_e = |\mathbf{d}_e|$, $(\mathbf{J}_e \cdot \mathbf{n}) = \Omega$ is the projection of the electron momentum on the molecular axis (\mathbf{n}).

- The effective electric field on the electron, $\mathbf{E}_{\text{eff}} \equiv W_d |\Omega|$, is non-zero only due to the relativistic effects (Schiff theorem).
- The strong field is localized near the heavy nuclei, so the one-electron-states with small j_e mainly contribute to \mathbf{E}_{eff} :

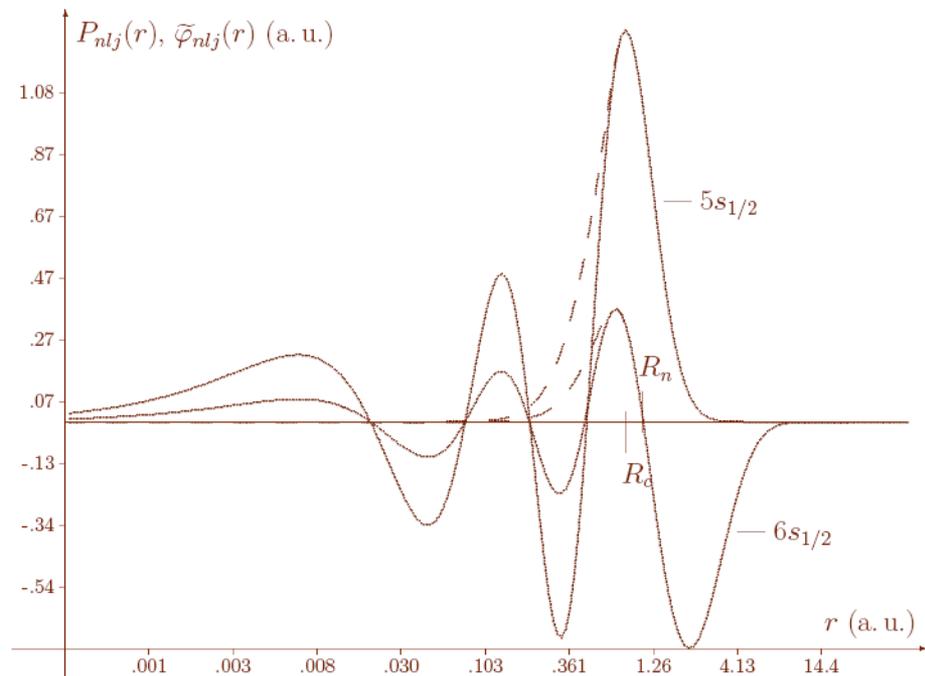
For point nucleus:

$$\psi_{nlj} \sim r^{\gamma_j - 1}, \quad \gamma_j = \sqrt{(j + 1/2)^2 - (\alpha Z)^2}$$

Besides, a lot of other properties (spectroscopic constants, curves, oscillator strengths, half-lives, HFS constants, g-factors) for low-lying states are also required which are not known experimentally.

Smoothing & restoration of spinors in atomic cores:

Radial parts of large components of spinors
 $5s_{1/2}$ and $6s_{1/2}$ and of corresponding
pseudospinors for the Thallium atom.



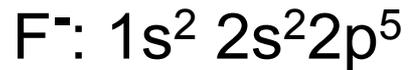
- First, the molecular pseudo-spinors (spin-orbitals) are expanded on the set of *two-component atomic pseudospinors* in some core region to evaluate the MO LCAS expansion coefficients.
- Then, the atomic pseudospinors are replaced by equivalent four-component spinors when forming the molecular spinors (spin-orbitals) with the same MO LCAS expansion coefficients.

YbF: a touchstone for theoretical models

[J. Hudson et al., Nature 473, 493 (2011)]

eEDM experiment on YbF is performed by group of Hinds and new limitation on d_e is obtained $|d_e| < 1.05 \times 10^{-27}$ e·cm

The working (ground) state is $^2\Sigma$ and the leading configuration corresponds to a simple ionic model: **Yb^+F^-**



The first molecule experiment that is now more sensitive to eEDM than the atomic experiments (TI beam, Regan et al. 2002):

Parameters of the spin-rotational Hamiltonian for ^{171}YbF .

(1 GV/cm = 0.242×10^{24} Hz/e·cm)

$$A = (A_{\parallel} + 2A_{\perp})/3; \quad A_d = (A_{\parallel} - A_{\perp})/3$$

Year: **Method** (Author) : Yb: $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2$ A_{\parallel} (MHz) A_d (MHz) E_{eff} (GV/cm)

One-configurational

1996: Generalized PP / SCF (Titov+) ^{a,b}	4974	60	18.8
1997: Semiempirical (Kozlov) ^c	-	-	26.0

1970: **Experiment/matrix** (Knight+) **7821** **102**

2007: **Experiment/beam** (Steimle+) **7424** **82**

Gen.PP: generalized pseudopotential; **PT2**: second order perturbation theory by energy;
(R)CCSD: (relativistic) coupled-cluster with S,D-amplitudes; **CI**: configuration interaction.

Parameters of the spin-rotational Hamiltonian for ^{171}YbF .

(1 GV/cm = 0.242×10^{24} Hz/e·cm)

$$A = (A_{\parallel} + 2A_{\perp})/3; \quad A_d = (A_{\parallel} - A_{\perp})/3$$

Year: Method (Author) : Yb^+ : $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^1$	A_{\parallel} (MHz)	A_d (MHz)	E_{eff} (GV/cm)
<u>One-configurational</u>			
1996: Generalized PP / SCF (Titov+) ^{a,b}	4974	60	18.8
1997: Semiempirical (Kozlov) ^c	-	-	26.0
<u>Core-polarization + pure correlation</u>			
1998: Dirac-Fock + core polarization (PT2) (Quiney+) ^d	7985	60	24.8
1998: Unrestricted Dirac-Fock (Parpia) ^e	-	-	24.9
1998: Gen. PP / effective operator (PT2) (Mosyagin+) ^f	8000	79	24.9
1970: Experiment/matrix (Knight+)	7821	102	
2007: Experiment/beam (Steimle+)	7424	82	

Gen.PP: generalized pseudopotential; **PT2**: second order perturbation theory by energy;
(R)CCSD: (relativistic) coupled-cluster with S,D-amplitudes; **CI**: configuration interaction.

Parameters of the spin-rotational Hamiltonian for ^{171}YbF .

(1 GV/cm = 0.242×10^{24} Hz/e·cm)

$$A = (A_{\parallel} + 2A_{\perp})/3; \quad A_d = (A_{\parallel} - A_{\perp})/3$$

Year: Method (Author) : Yb: $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2$	A_{\parallel} (MHz)	A_d (MHz)	E_{eff} (GV/cm)
<u>One-configurational</u>			
1996: Generalized PP / SCF (Titov+) ^{a,b}	4974	60	18.8
1997: Semiempirical (Kozlov) ^c	-	-	26.0
<u>Core-polarization + pure correlation</u>			
1998: Dirac-Fock + core polarization (PT2) (Quiney+) ^d	7985	60	24.8
1998: Unrestricted Dirac-Fock (Parpia) ^e	-	-	24.9
1998: Gen. PP / effective operator (PT2) (Mosyagin+) ^f	8000	79	24.9
<u>Improving correlation</u>			
2002: Generalized PP / 31e-RCCSD (4f corr., unpubl.)	7710	109	24.0
2009: Dirac-Fock / 31e-CI (Nayak & Chaudhuri)	-	-	24.0
2012: 51e-Gen.PP/CCSD+T+SO+large basis (Skr.+)	(7308)	-	22.0
1970: Experiment/matrix (Knight+)	7821	102	
2007: Experiment/beam (Steimle+)	7424	82	

Gen.PP: generalized pseudopotential; **PT2**: second order perturbation theory by energy;
(R)CCSD: (relativistic) coupled-cluster with S,D-amplitudes; **CI**: configuration interaction.

Scheme of evaluation of E_{eff} and A in YbF

51e-scalar-relativistic calculation by CCSD in a large basis set

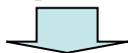
$$\text{Yb: } 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 6s^2 \quad \text{F: } 1s^2 2s^2 2p^5$$
$$\Psi = e^{\hat{T}} \Phi_0 \quad \hat{T} \equiv \hat{T}_1 + \hat{T}_2 \rightarrow \text{CCSD}; \quad \text{Complexity(CCSD)} \sim N_{\text{occ}}^2 N_{\text{virt}}^4$$



Optimizing the basis set for the high correlation treatment of the $^2\Sigma$ state of YbF

500 basis functions \rightarrow 100 basis functions (compact basis)

Yb [24s 22p 14d 13f 9g 9h 3i]; F [14s 9p 4d 3f] \rightarrow Yb [7s 7p 4d 3f 2g]; F [3s 2p]



Correction on 3-body amplitudes with CCSDT in the compact basis set

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \rightarrow \text{CCSDT} \quad \sim 1.000.000.000 \text{ independent cluster amplitudes}$$
$$\text{Complexity(CCSDT)} \sim N_{\text{occ}}^3 N_{\text{virt}}^5$$



Spin-orbit correction with SODCI in a compact basis set

$$\text{SO-correction} = \left(H_{\text{sr}} + H_{\text{SO}} \right) - \left(H_{\text{sr}} \right)$$

WC molecule studies for eEDM experiment

Leanhardt group

W: [Xe] 4f¹⁴ 5s² 5p⁶ 5d⁴ 6s² 6p⁰

C: [He] 2s² 2p²

Estimates for electronic spectrum:

(about 100 relativistic terms within 30' 000 cm⁻¹ !)

State	Our "Te"	Exp [*]	Exp [**]
³ Δ ₁	0	0	0
³ Δ ₂	1120	1194	1189
³ Δ ₃	4344	4355 " ¹ Σ ⁺ "	
¹ Δ ₂	4721	4864 " ³ Δ ₁ (II)"	4753 "???"
¹ Σ ₊	3131	???	2775 " ¹ Δ ₂ "
³ Δ ₁ (II)	~5570	5307 " ¹ Δ ₂ "	
.....			
	~17071 (μ=2.7D)		17584 " ³ Φ ₂ " (μ=2.57D ^{***})
³ Φ ₂ (II)	~21500 ???		

(*) Photoelectron spectra by Rothgeb, D., Hossain E., Jarrold C., JCP 129, 114304 (2008);

(**) Optical spectra by Sickafoose S.M., Smith A.W., Morse M.D., JCP 116, 993 (2002).

eEDM experiment on ³Δ₁ ground state:

WC: [6s(W)+d_{zz}(W)+6p_z(W)]¹ [d_{xy}(W)]¹

Our theoretical prediction (2011):

A_{||} = -1191 MHz

E_{eff} = -36.0 GV/cm

μ = 4.1 D (molecule-frame dipole moment)

(***) F. Wang and T.C. Steimle, JCP 134, 201106 (2011):

A_{||} = 1363±17 MHz

μ = 3.90 ± 0.04 D

J. Lee, J. Chen, L. Skripnikov, ...

A. Leanhardt (PRA 2013, in press):

A_{||} = -1177±43 MHz

Calculations of PNC effects in heavy-atom molecules (continued):

PHYSICAL REVIEW A 78, 010502(R) (2008)

Edmund R. Meyer* and John L. Bohn

TABLE I. Comparisons of published values of F_{eff} to old results from Ref. [14] and new results in the present work. All values are given in GV/cm. (1 GV/cm = 0.242×10^{24} Hz/e·cm)

Molecule	Published	Old (2006)	New (2008)
BaF	7.4 [9]	5.1	6.1
YbF	22 (2012)	43	32
HgF	99 [8]	68	95
PbF	-33 (2010)	-36.6	-31
$\sigma(1)$ PbO	26.2 [11]	3.2 [22]	23
HI ⁺	0.34 [13]	0.57	0.34
HfF ⁺	24 [15]	18	30
ThO	60 (2010)	N/A	104
ThF ⁺	N/A	N/A	90
PtH ⁺	28 (2009)	73	
WC	36 (2011)		54 (2009)

P, T-odd interactions and the Schiff moment

In diatomics, the effective interaction between electrons and the Schiff moment of heavy nucleus can be written as:

$$H_{eff} = -6SX \vec{\sigma}_N \cdot \vec{\lambda}, \quad X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_\psi(\vec{r}) \right]_{x,y,z=0}$$

According to [1]:

$$S(Ra) \approx 200 * S(Tl)$$

$$X(Ra) \approx 2.2X(Tl)$$

Our results:

	$X(Tl)$ [2]	$X(RaO)$ [3]
SCF	8967	-9609
RCC-SD	7635	-7696

[1] V.V. Flambaum, PRA **77**, 024501 (2008).

[2] , A. N. Petrov *et al.*, PRL **88**, 073001 (2002).

[3] A.D. Kudashov, A.N. Petrov, L.V. Skripnikov *et al.*, PRA **87**, 020102(R) (2013).

SCF approximation: RaO and TlF comparison

Shell: main contribution	$X(\text{RaO})$	$X(\text{TlF})$	Shell: main contribution
$1\sigma^2: 1s^2(\text{O})$	-50	3	$1\sigma^2: 1s^2(\text{F})$
$2\sigma^2: 6s^2(\text{Ra})$	3862	-1114	$2\sigma^2: 5s^2(\text{Tl})$
$3\sigma^2: 2s^2(\text{O})$	9936	1897	$3\sigma^2: 5p_z^2(\text{Tl})$
$4\sigma^2: 6p_z^2(\text{Ra})$	-14426	-358	$4\sigma^2: 2s^2(\text{F})$
$5\sigma^2: 2p_z^2(\text{O})$	-9036	-2	$5\sigma^2: 5d_{zz}^2(\text{Tl})$
$1\pi^4: 6p_x^2 6p_y^2(\text{Ra})$	50	-4414	$6\sigma^2: (6s(\text{Tl})+2 p_z(\text{F}))^2$
$2\pi^4: 2p_x^2 2p_y^2(\text{O})$	54	12954	$7\sigma^2: (6s(\text{Tl})-2 p_z(\text{F}))^2$
Total SCF(spin-averaged)	-9609	8967	Total SCF(spin-averaged)

Analysis based on contributions from canonical molecular orbitals is inconclusive in the case of RaO.

RaO: one-particle density matrix analysis

Decomposing all original basis functions (centered either on Ra or O) into atomic orbitals of Ra (obtained using the Dirac-Fock method for a single Ra atom) the mean value for X can be rewritten in the form

$$\langle \widetilde{X} \rangle = \sum_{ij} \widetilde{D}_{ij} X_{ji}$$

Applying this scheme the following contributions can be obtained:

- Polarization of outer-core **6p_z** orbital of Ra into **7s, 8s ...** contributes more than **50%** to the mean value of **X**.
- Other contributions are due to mixing of **7s, 8s, 9s ...** orbitals of Ra with different **p_z** orbitals.

Outline of P,T-violation search in solids

1968: Shapiro proposed to search EDMs in solids

[Usp. Fiz. Nauk., 95 145 (1968)]

1978: Ni-Zn ferrite: $d_e < (0.81 \pm 1.16) \times 10^{-22}$ e-cm

[B.V. Vasil'ev, E.V. Kolycheva, JETP, 47(2) 243 (1978)]

2002: Gd-Ga / Gd-Iron Garnet: eEDM search

[S. Lamoreaux, PRA 66 022109 (2002)]

2005: PbTiO₃: proposal to search the Schiff moment of ²⁰⁷Pb

[T. N. Mukhamedjanov, O. P. Sushkov, PRA 72, 034501 (2005)]

2010: Eu_{0.5}Ba_{0.5}TiO₃: proposal of the eEDM search

[A.O. Sushkov et. al. Rhys. Rev. A 81, 022104 (2010)]

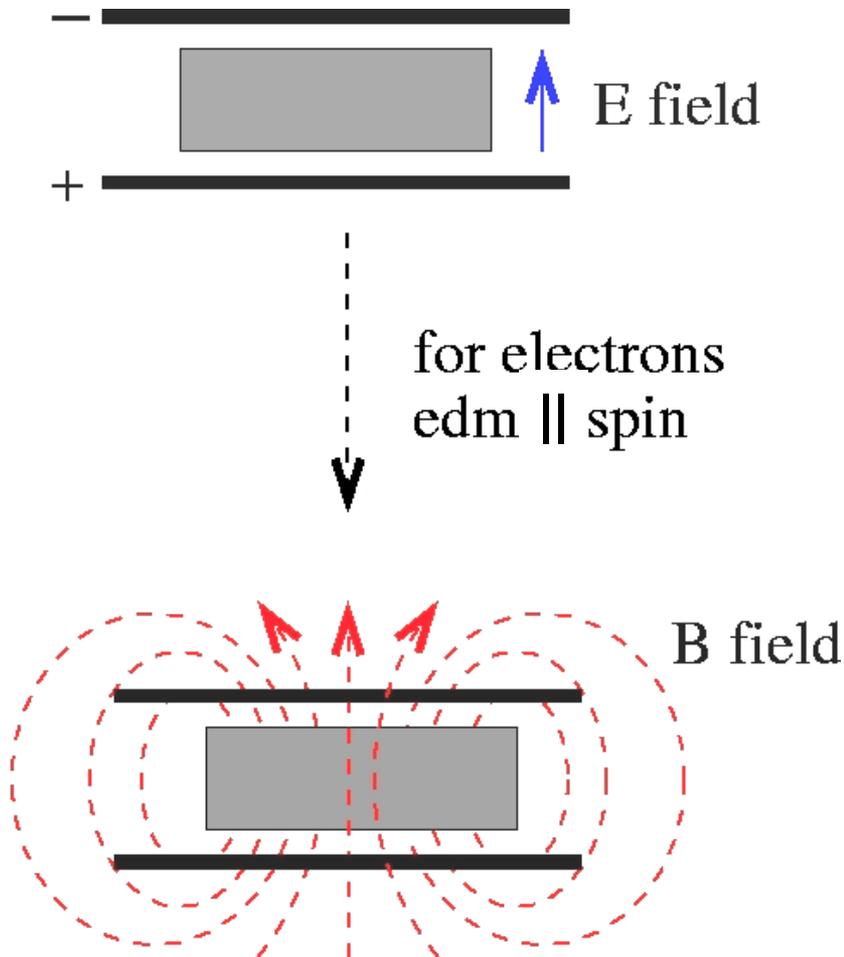
2012: Eu_{0.5}Ba_{0.5}TiO₃: the best eEDM limitation in solids:

$d_e < 6.05 \times 10^{-25}$ e-cm

[S. Eckel, A.O. Sushkov, S.K. Lamoreaux PRL 109, 193003 (2012)]

Shapiro's proposal -- using a solid state system to measure eEDM

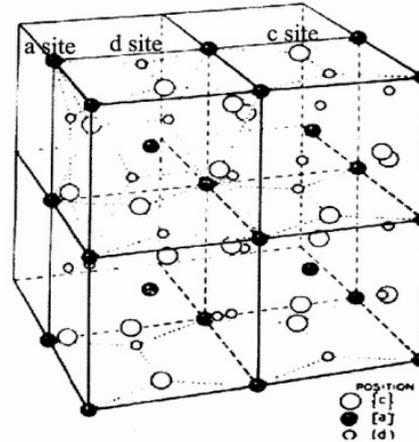
Usp. Fiz. Nauk., 95 145 (1968)



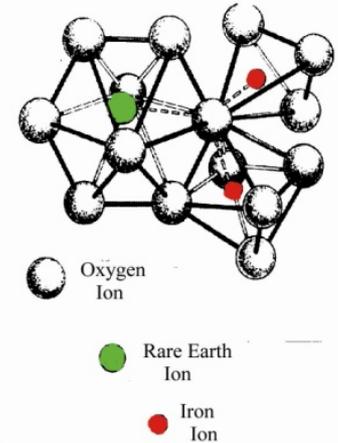
B.V. Vasil'ev and E.V.
Kolycheva, Sov. Phys. JETP, 47
[2] 243 (1978) /Ni-Zn ferrite/
 $d_e = (0.81 \pm 1.16) \times 10^{-22}$ e-cm

Gadolinium Gallium Garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$)

- Gd^{3+} in GGG - $4f^7 5d^0 6s^0$
(7 unpaired electrons)
- Atomic enhancement factor = -4.9 ± 1.6
- Langevin paramagnet
- Dielectric constant ~ 12
- Low electrical conductivity and high dielectric strength
- Volume resistivity = $10^{16} \Omega\text{-cm}$
- Dielectric strength = 10 MV/cm for amorphous sample



The unit cell of GdIG. The cell contains 16 Fe^{3+} ions at octahedral sites (a), 24 Fe^{3+} ions at tetrahedral sites (d), and 24 Gd^{3+} ions at dodecahedral sites (c). The oxygen ions are not shown.



Garnet Structure:



–A {dodecahedron}: M^{3+}

•Ca, Mn, Fe, R (La,..Gd,..Lu)

–B [octahedron], C (tetrahedron):

•Fe, Ga, ...

What should be calculated?

Effective field – connects experimental datum with eEDM / Schiff moment

Schiff moment S: $H_{\text{eff}} = -6SX\vec{\sigma}_N \cdot \vec{\lambda}$ **where** $X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_\psi(\vec{r}) \right]_{x,y,z=0}$

Electron EDM d_e : $H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma \mathbf{E} \end{pmatrix}$

The mean values are determined by valence electrons in the core region



Both relativistic and correlation effects should be treated

Calculation of core properties in solids

Considerably more complex problem than that in atoms and molecules

Methods:

- 1. Scalar-relativistic calculation of solid state using DFT;
Core electrons are treated by the relativistic PP**
- 2. Calculation of one electron density matrix in a direct lattice**
- 3. Non-variational restoration of core region**
- 4. Calculation of core properties**

Results: $^{207}\text{PbTiO}_3$

Lattice parameters (Space group P4mm, 99)

parameter	Calc.	Experiment*
a, Å	3.89	3.90
c, Å	4.11	4.16
z(Pb), Å	-0.42	-0.46

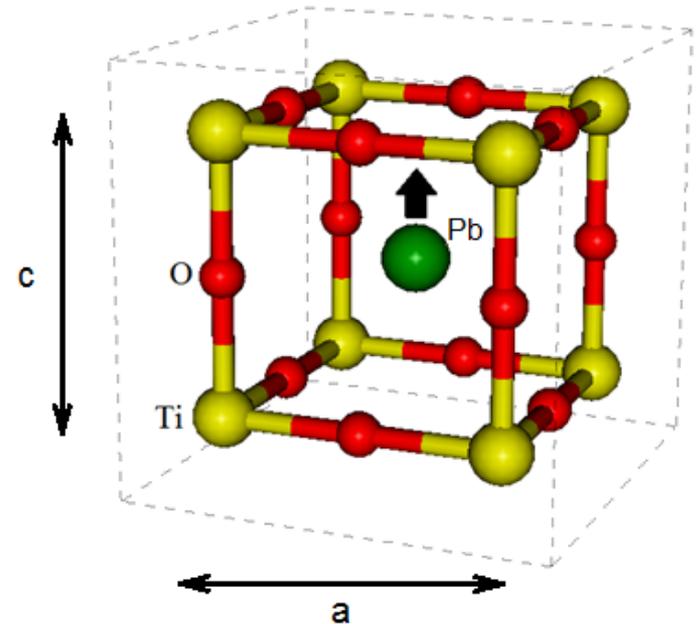
* [R.J.Nelmes, W.F. Kuhs, Solid State Comm. 54(8) 721 (1985)]

$$\Delta E \sim A \cdot (z \cdot S(^{207}\text{Pb}))$$

since $A = 6X/z = 43000$ a.u. (PBE0) is almost constant

Cluster model calculation:

[J.A. Ludlow, O.P. Sushkov, arXiv:1210.2117 (2012)]: $6X/z = 22000$



Proposal: $S(^{225}\text{Ra})$ in RaTiO_3

- [V.V. Flambaum, PRA 77, 024501 (2008)]: $S(^{225}\text{Ra}) / S(^{205}\text{Tl}) \sim 200$
and refs

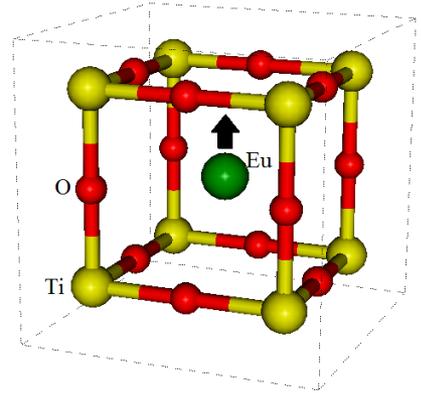
Lattice parameters (Space group P4mm, 99) [preliminary]:

parameter	Calc	Experiment
a, Å	3.98	-
c, Å	4.32	-
z(Ra), Å	0.28	-

$$6X/z = -6000 \text{ a.u.}$$

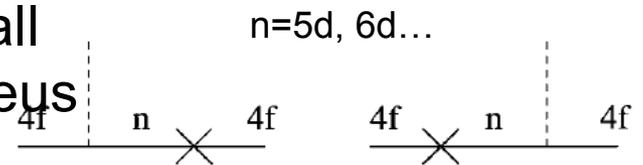
Electronic structure of Eu^{++}

The goal is to evaluate the enhancement coefficient: $K = \frac{E_{\text{eff}}}{E_{\text{ext}}}$

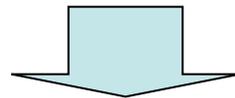
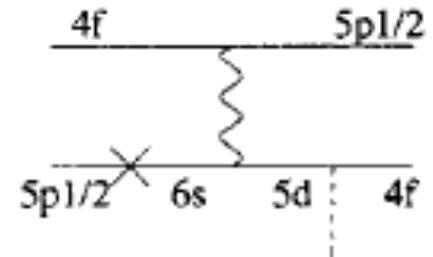


➤ Configuration of Eu^{++} ground state: $4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^7 5d^0$

➤ “Direct” contribution to $K \sim \langle d | H_{P,T} | f \rangle$ is small since $|d\rangle$ and $|f\rangle$ are small close to the nucleus



➤ $\langle s | H_{P,T} | p \rangle \gg \langle d | H_{P,T} | f \rangle$, but $|s\rangle$ and $|p\rangle$ are doubly occupied and contributions from s, p are suppressed at the SCF level:



The value of K is mainly due to the correlation effects!

Calculations of E_u^{++}

[Skripnikov et al. Phys. Rev. A 84, 022505 (2011)]

✓ Enhancement coefficient K :

	K	
method reference:	UHF [$\langle S^2 \rangle$]	ROHF
CCSD	-4.1 [15.75033]	-4.6 [15.75026]
CCSDT	-4.6 [15.75000]	-4.6 [15.75000]
MP2	-4.4	-3.6
MP3	-2.5	-2.7
MP4	-5.5	—

✓ Contributions to K from matrix elements s-p, p-d, d-f:

$K = -4.6$

	s	p	d	f
s	-	-3.3	0	0
p		-	0.3	0
d			-	-1.6 *
f				-

$$\mathbf{H}_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \cdot \vec{E}_{\text{mol}}$$

✓ Screening by 1s-3d decreases the f-d contribution on 25%

Concluding remarks

- computational accuracy can be higher than experimental; the properties which cannot be obtained experimentally to-date can be evaluated with good accuracy, that is important for many (fundamental) experiments;
- good prospects for further improvement of accuracy with accounting for correlation and relativistic effects, the application field can be extended on more complicated systems, other properties and processes;
- the pseudopotential method (+ electronic structure restoration in atomic cores for studying core properties) is a very efficient, prospective and universal approach for calculating not only polyatomic systems but even for diatomics when relativistic effects are important;
- though there is no universal scheme to uniquely select a method for correlation treatment, reasonable recommendations can be formulated;
- pseudopotentials and basis sets are accessible by internet.

Our thanks to:

- *L. Labzowskii, M. Kozlov, Yu. Dmitriev & A. Mitrushchenkov (St.Petersburg, Russia)*
- *E. Eliav & U. Kaldor (Tel-Aviv, Israel)*
- *R. Buenker & A. Alekseyev (Wuppertal, Germany)*
- *D. DeMille (Yale, USA)*
- *E. Cornell (Boulder) & A. Leanhardt (Michigan, USA)*
- *I. Khriplovich (Novosibirsk, Russia)*
- *O. Sushkov & V. Flambaum (Sydney, Australia)*
- *A. Zaitsevskii (Moscow, Russia)*

Thank you for your attention!

The end.