Study of the T,P-violating effects in atoms, molecules and solids

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Goals of theoretical treatment

✓ Scheme of energy levels. What is the ground state, etc.?

✓ Transition probabilities.

✓ oscillation frequency, g-factors, etc.

Experiment

$$\text{electron EDM} = \frac{\Delta E}{\mathcal{E}_{\text{eff}}}$$
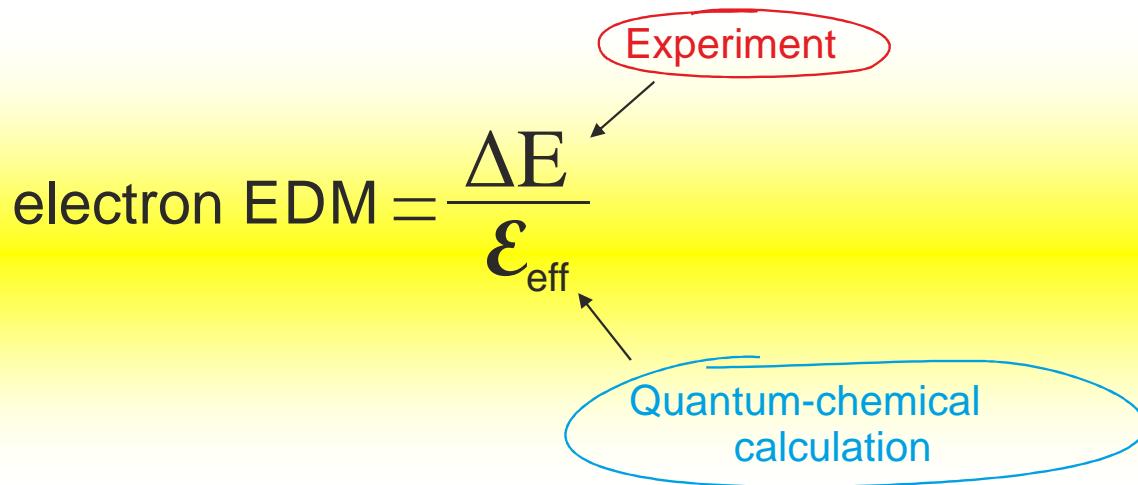
$$\mathbf{H}_d = 2d_{\text{e}} \begin{pmatrix} 0 & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \cdot \vec{E}_{\text{mol}}$$

Quantum-chemical calculation

$$A_{||} = \frac{\mu}{I\Omega} \langle \Psi | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_i}{r_i^3} \right)_z | \Psi \rangle$$

✓ Hyperfine structure constants

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"AiC" properties

"Atoms-in-Compounds" characteristics are determined by the valence wavefunction in the core region of heavy atom
[L.V. Skripnikov, A.V. Titov, Phys. Rev. A 91, 042504 (2015)]

- ➤ **Hyperfine structure**

- ➤ QED corrections

    (in terms of effective QED Hamiltonian)

- ➤ **Chemical shifts of x-ray emission**

- ➤ Parameters of T,P-violating interactions

    (electron EDM enhancement, E_{eff}, etc.)

Can be measured

Methods outline (electronic Hamiltonian):
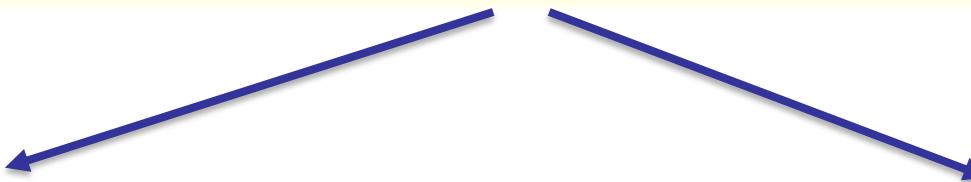
Direct Dirac-Coulomb(-Breit) Hamiltonian

Two-step approach (PNPI):
1. Calculation of the valence and outer-core electron wave function within the generalized relativistic effective core potential
2. Restoration of the core region of the wave function

+ the most accurate electronic Hamiltonian

+ very flexible, very compact basis set can be used for considering high-order correlation effects & huge basis sets for basis set corrections

- Complicated calculation => limited basis set & high order correlation effects

- some uncertainty due restoration using approximated version of the GRECP

✓ **One can combine two-step and 4-component approaches => all uncertainties are minimized**

Methods outline (correlation treatment): the coupled cluster method

$$\Psi_{cc} = e^{\hat{T}} \Phi_0 \qquad\qquad \Psi_{ci} = (1 + \hat{T})\Phi_0$$

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad \rightarrow \boldsymbol{CCSD}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \quad \rightarrow \boldsymbol{CCSDT}$$

$$\hat{T}_1 = \sum_i \hat{t}_i = \sum_{i,a} t_i^a \, a_a^+ a_i$$

$$\hat{T}_2 = \frac{1}{2} \sum_{ij} \hat{t}_{ij} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \, a_a^+ a_b^+ a_j a_i$$

- more efficient than CI: t(CISD) ~ t(CCSD)
- size extensive

E_{eff} in ThO

eEDM-experiment on ThO:
D.DeMille et al.:Yale Uni.;
J.Doyle & G.Gabrielse at al.: Harvard

Progress in E_{eff}:

- [J. Chem. Phys. (Communications) 139, 221103 (2013)]:
38e-CCSD(T)/two-step   **Eeff=84 GV/cm, uncertainty ~ 15%**

ACME: $|d_e| < 8.7 \times 10^{-29}\ e \cdot cm$ (2014)

- [J. Chem. Phys. 142, 024301 (2015)]:
38e-CCSD(T)/two-step + **CCSDT(Q)**+analysis   **Eeff=81.5 GV/cm, uncertainty ~ 7%**

- [J. Chem. Phys., 145, 214301 (2016)]:
Combined (Dirac-Coulomb(-Breit) and two-step) approach:
98e-CCSD(T)/**4c** + CCSDT(Q)+corrections+analysis   **Eeff=79.9 GV/cm, < uncertainty < 4%**

Contributions to E_{eff}(ThO) within 4c-CCSD(T)

18 valence els.
[6s6p7s6d(Th)+2s2p(O)]

~74 GV/cm

18 outer-core els.
[5s5p5d(Th)]

~4 GV/cm

62 inner-core els.
[1s..4f(Th)+1s(O)]

~4 GV/cm

Contribution to E_{eff} from the CORE electrons ~ 9 %

(1s..3d below)

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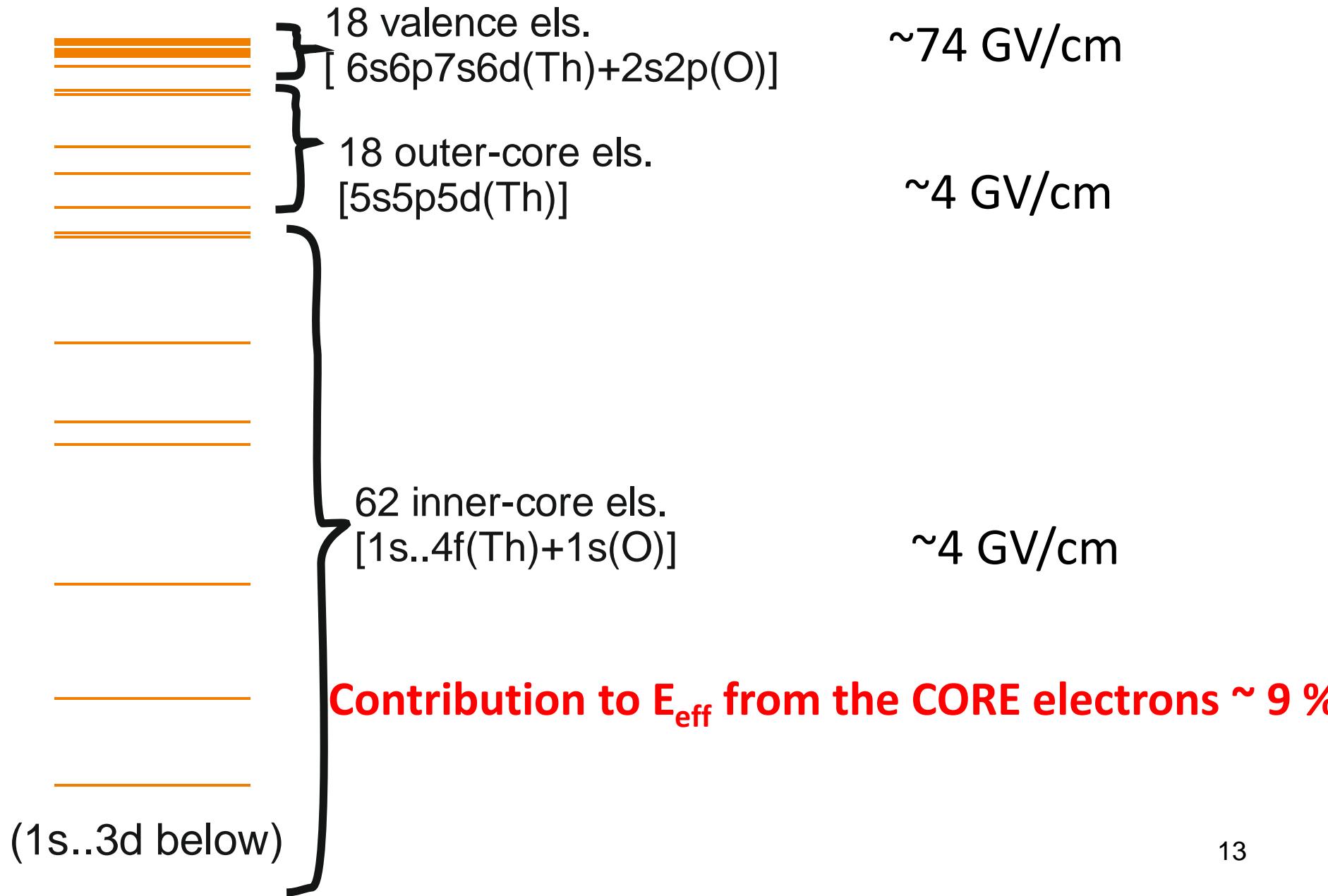
CC vs CI for E_{eff}(ThO)

Correlation contributions to E_{eff} in 18-electron CI and CC relative to 2e-CISD, (scalar-relativistic treatment, small basis set)

Method	Correlation energy (Hartree)	E_{eff} (GV/cm)
CCSD	−0.247	18.3
CCSD(T)	−0.258	15.7
CCSDT	−0.257	15.7
CCSDTQ	−0.258	15.6
CISD	−0.227	16.5
CISDT	−0.235	18.3
CISDTQ	−0.256	16.5
CISDTQP	−0.257	15.8

➢ Very slow convergence of the CI series

➢ High order excitations should be included explicitly in the CI case, part of them can be included in practice MR-CISD treatment

➢ **Even CCSD(T) method gives converged value of E_{eff}**

Ab initio calculation of the $H^3\Delta_1$ state of ThO

L.V. Skripnikov, J. Chem. Phys. 145(21) 214301 (2016):

Method	T_e, cm^{-1}	Dipole, D	E_{eff}, GV/cm
CVTZ/36e-4c-CCSD(T)/4c	5604	4.17	78.6
			Correlation
CCSDT(Q)-CCSD(T)/2-step	100	0.08	0.0
Inner core, 4c (1s..4f)	-5	0.01	3.6
			Basis
Basis set correction/2-step	-277	-0.03	-0.6
			Hamiltonian
Gaunt/4c	-94	-0.03	-1.5
Vibrational contribution/2-step	---	0.04	-0.1
Final	**5327**	**4.24**	**79.9 (<4%)**
		4.24(0.1);	
Experiment	**5337**	**4.098(3)**	**-**

Experiment: [Vutha et al., PRA 84, 034502 (2011)]

Theoretical study of $^3\Delta_1$ state of HfF$^+$

	E_{eff}, GV/cm	$W_{T,P}$, kHz	$A_{\parallel}$, MHz	Dip., a.u.	$G_{\parallel}$
Theory	22.5	20.1	-1429	-1.53	0.0115
Experiment	-	-	-	-1.54(1)	0.0118

- **$W_S = W_{T,P}*(Z+N)/Z$ = 50.3 kHz**

- **Gaunt contribution is about -3%**

- **^{177}HfF$^+$ can also be used to measure nuclear magnetic quadrupole moment:**
[L.V. Skripnikov, A.V. Titov, V.V. Flambaum, Phys. Rev. A 95, 022512 (2017)]

Theory: arXiv:1704.06631 (2017); arXiv:1704.07318 (2017)
Experiment: H. Loh, Ph.D. thesis, Massachusetts Institute of Technology (2006);
        H. Loh, et al., Science 342, 1220 (2013)

Fr results: scalar-pseudoscalar interaction

$$\hat{H}_{T,P} = k_{T,P}\, i\, \frac{G_F}{\sqrt{2}} Z \sum_p \gamma_p^0 \gamma_p^5 \rho_N(\mathbf{r}_p) = k_{T,P}\, \hat{h}_{T,P}$$

$$d_{\text{Atom}} = \sum_{j>0} \frac{\langle \Psi_0 | \sum_p e\hat{z}_p | \Psi_j \rangle \langle \Psi_j | \hat{H}_{T,P} | \Psi_0 \rangle}{E_0 - E_j} + \text{H.c.} \qquad R_s = \frac{\partial^2 \Delta E}{\partial E_{\text{ext}} \partial k_{T,P}} (E_{\text{ext}} = 0)$$

$$= k_{T,P}\, R_s,$$

Contribution	R_s, 10^{-18} |e|*cm	IP, meV
87e-4c-CCSD(T)/CVTZ/4c	-4.51	4056.5
Extended basis, 59e-4c-CCSD(T)/4c	-0.09	11.1
Increased cutoff/4c	-0.01	−0.5
Gaunt/4c	0.03	−0.5
27e-CCSDT(Q)-CCSD(T)/2-step	**0.08**	**−2.7**
High harmonics/59e-CCSD(T)/2-step	0	7.2
Total	**-4.50**	**4071.2**

This work: L.V. Skripnikov, D.E. Maison, N.S. Mosyagin, Phys. Rev. A 95, 022507 (2017)

R_s is in a good agreement with [V.A. Dzuba, V.V. Flambaum, C. Harabati, PRA 84, 052108 (2011)]

Fr ionization potential, meV

Method	IP(QM)	IP(QM+QED)
Correlation potential [1]	4082.9	4077.9
FS-CCSD [2]	4071.5	4066.4
This work	4071.2	4066.1
Experiment [3]		4072.7

QED: -5.07 meV, I. Tupitsyn et al (private communication) (2017)

[1] T.H. Dinh, V.A. Dzuba, V.V. Flambaum, J.S.M. Ginges, Phys. Rev. A 78, 022507 (2008).
[2] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A 50, 1121 (1994).
[3] J. E. Sansonetti, J. Phys. Chem. Ref. Data 36, 497 (2007).

This work: L.V. Skripnikov, D.E. Maison, N.S. Mosyagin, Phys. Rev. A 95, 022507 (2017)

Other recent results for diatomics

Molecule	Dipole, D	HFS, MHz	$G_{||}$
TaN$_{theory}$ [a]	4.74	-3132	
PbF$_{theory}$ [b]	3.87	9942	0.081 (e)
PbF$_{\textbf{experiment}}$	3.5(3) [c]	10147 [c,d]	0.081(5) [e]
			0.12(1) [c]

[a] L.V. Skripnikov, A.N. Petrov, N.S. Mosyagin, A.V. Titov, V.V. Flambaum, PRA 92, 012521 (2015).
[b] L.V. Skripnikov, A.D. Kudashov, et al, PRA **90**, 064501(2014)
[c] R.J. Mawhorter et al., PRA **84**, 022508 (2011)
[d] A.N. Petrov, L.V. Skripnikov, A.V. Titov, R. J. Mawhorter, PRA **88**, 10501 (2013)
[e] L.V. Skripnikov, A.N. Petrov, A.V. Titov, R.J. Mawhorter, et al., PRA 92, 032508 (2015)

New fit of (e) for g-factor

Other T,P-violating experiments

Atoms: $|d_e| < 1.6 \times 10^{-27}$ *e·cm*

[Regan et. al. *PRL* **88,** 071805 (2002)]

Molecules: $|d_e| < 9 \times 10^{-29}$ *e·cm*

[ACME Collaboration, Science. **343** 269. (2014)]

Crystals: $|d_e| < 6.05 \times 10^{-25}$ *e·cm*

Molecules:

➢ ThO* beam (ACME collaboration: D.DeMille:Yale Uni.; J.Doyle & G.Gabrielse: Harvard);

$|d_e| < 9 \times 10^{-29}$ e·cm (2014)

➢ YbF-radical beam (E.Hinds: Imperial college, London,UK);

$|d_e| < 1.0 \times 10^{-27}$ e·cm (2011)

➢ HfF$^+$ (& ThF$^+$, PtH$^+$ ...) trapped cations (E.Cornell: JILA, Boulder);

➢ WC ($^3\Delta_1$ – ground state) molecular beam (A.E.Leanhard: Michigan U.)

➢ PbO ($^3\Sigma^+$) (Eckel, DeMille et al Yale Uni)

$|d_e| < 1.7 \times 10^{-26}$ e·cm (2013)

Solids:

➢ $Eu_{0.5}Ba_{0.5}TiO_3$ (ferroelectric structure) (S. Eckel, A.O.Sushkov, S. Lamoreaux: Yale Uni).

$|d_e| < 6.05 \times 10^{-25}$ e·cm (2011)

➢ Gd-Ga Garnet (S. Lamoreaux: LANL ; C.-Y. Liu: Indiana)

➢ Gd-Iron Garnet (L. Hunter: Amherst),

➢ **$PbTiO_3$,** **(Sushkov et al.)**

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Search of T,P-violating effects in solids

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

E field

for electrons
edm | spin

B field
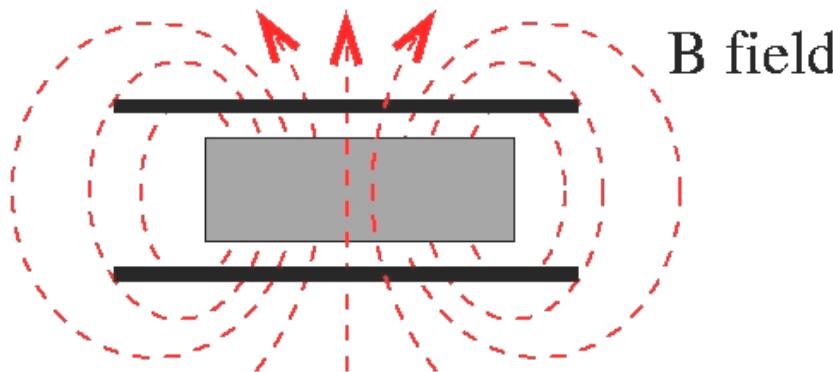
B.V. Vasil'ev and E.V. Kolycheva, Sov. Phys. JETP, 47 [2] 243 (1978) **/Ni-Zn ferrite/**

$$d_e = (0.81 \pm 1.16) \times 10^{-22} \text{ e-cm}$$

Problem

T,P odd interaction of electrons with the Schiff moment in PbTiO$_3$,
proposed by T.N. Mukhamedjanov and O.P. Sushkov, PRA 72, 034501 (2005):

PHYSICAL REVIEW A 72, 034501 (2005)

Suggested search for ^{207}Pb nuclear Schiff moment in PbTiO$_3$ ferroelectric

T. N. Mukhamedjanov and O. P. Sushkov

" tures. For a 10-day averaging, statistics allows to reach a "
sensitivity of ten orders of magnitude better than the present
result (2). Another possibility would be an NMR experiment

$$S(^{199}\text{Hg}) < 0.75 \times 10^{-50} \ e \ \text{cm}^3 = 0.5 \times 10^{-25} \ e \ a_B^3 \quad (2)$$

$$\Delta\varepsilon = 6SX\vec{\sigma}_N \cdot \vec{\lambda}$$

$$X = \frac{2\pi}{3}\left[\frac{\partial}{\partial z}\rho_\psi\left(\vec{r}\right)\right]_{x,y,z=0}$$

- X connects experimental energy shift with the nuclear Schiff moment S
- X is the AIC property

Relativistic solid state correlation calculation

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Calculation of AiC properties in solids

Our approach (generalization of the two-step approach):

[L.V. Skripnikov, A.V. Titov, J. Chem. Phys., 145, 054115 (2016)]:

1. Calculation of valence electronic structure of a crystal using the generalized relativistic effective core potential

2. Calculation of reduced density matrix in the direct lattice

$$P_{\mu\nu}^{\mathbf{g}-\mathbf{g}'} = \sum_{\mathbf{k}} P_{\mu\nu}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{g}-\mathbf{g}')}$$

3. Restoration of 4-component structure in the core region

$$P_{\mu\nu}^{\mathbf{g}} \longrightarrow \tilde{D}_{pq} = D_{pq}$$

4. Calculation of required AIC properties

$$\langle A \rangle = \sum_{pq} D_{pq} A_{pq}$$

Results: $^{207}PbTiO_3$

Lattice parameters (group P4mm, 99)

	Calc	Exp.*
a, Å	3.82	3.90
c/a	1.15	1.07
Shift z(Pb), Å	-0.42	-0.46

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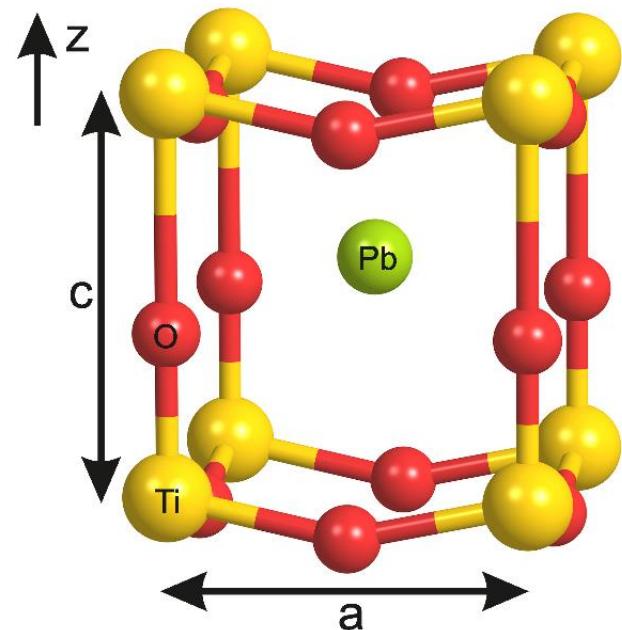


Band gap: **2.7 eV**
Experiment [Phys. Status Solidi B 124, 625 (1984)]:   **3.4 eV**

Results: ^{207}PbTiO$_3$
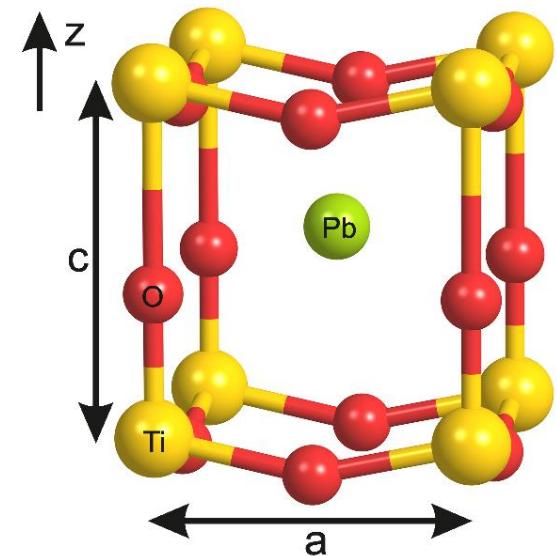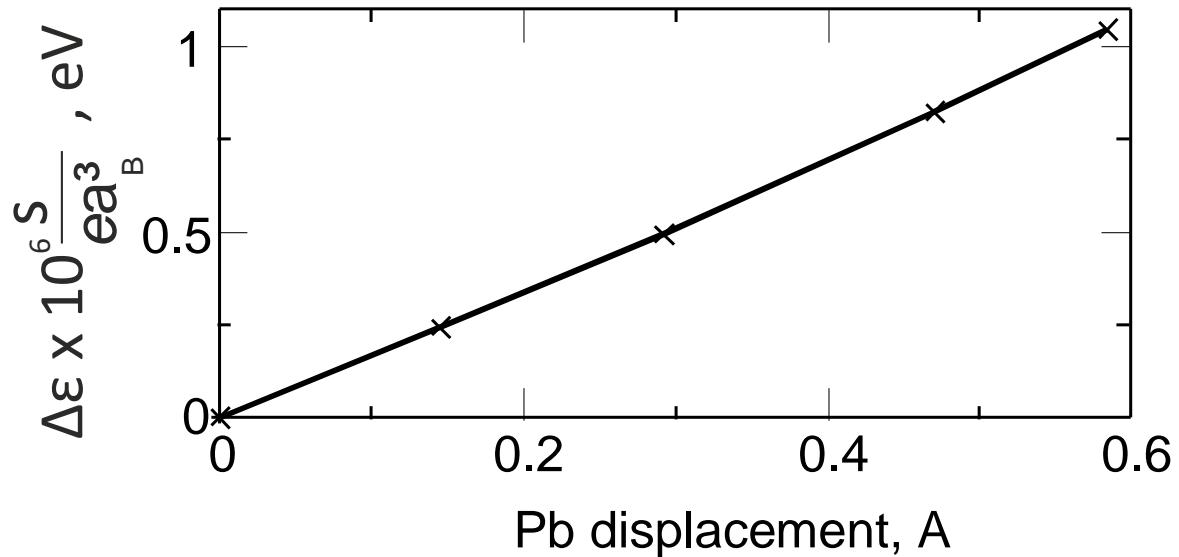
Interaction energy = 0.82×10^6 S(^{207}Pb)/e·a$_B^3$ eV

Electric field gradients

$$V_{ij} = \lim_{r \to 0}\left(\frac{\partial^2 V(\mathbf{r})}{\partial r_i \partial r_j} - \frac{1}{3}\delta_{ij}\nabla^2 V(\mathbf{r})\right)$$ - another AIC property

V_{zz}(Pb) in PbO molecule (at the HF level):
- Two-step approach: -19.5 V/m^2
- 4-component Dirac-Coulomb: -19.4 V/m^2

V_{zz}(Pb) in PbTiO$_3$:
- Two-step approach: 0.43 V/m^2

Features of 2-step in solids

- ✓ The finite nuclear size model

- ✓ Effective and efficient treatment of the Breit interaction

- ✓ **Unified treatment of atoms, molecules, and crystals**

- ✓ High order correlation corrections on clusters

- ✓ Extension to the embedding approaches

- ✓ Very accurate four-component wavefunction in the vicinity of a heavy atom (polynomial decomposition with correct asymptotic behavior)

- ✓ Almost any solid state code can be used

This is critically important in the case of electronic density gradient due to the strong cancellation of contributions from large and small components[33]

Thank you!