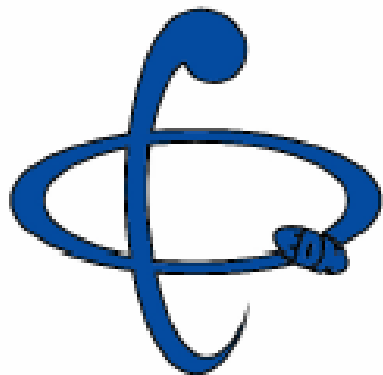


Ab initio study of P,T-parity violation effects in polar heavy-atom molecules

PNPI QChem
Group



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Funding: *RFBR, INTAS, DFG, CRDF, ...*

Outline

- **Historical background**
- **Why measure EDMs?**
- **How to measure an EDM**
- **Computational methods**
 - *GRECP, NOCR, PT2CI, FS-RCC, SODCI*
- **Calculations of YbF, TlF & PbO***

Milestones in studying PNC effects:

1949: Analyzing Einstein's relativity theory, Dirac states that P- and T-invariance is not necessary attribute of the nature laws (i.e. of physical dynamic theories).

1950: Purcell & Ramsey state that the validity of P- or/and T-odd theories must be confirmed experimentally. The search for the neutron EDM is initiated.

1956: Puzzle of τ - θ mesons: $\theta \rightarrow 2\pi(L=0)$; $\tau \rightarrow 3\pi(L=0)$, but $m_\tau \approx m_\theta$; $T_\tau^{1/2} \approx T_\theta^{1/2}$.

Analyzing the decays, Lee and Yang have suggested nonconservation of space parity, P, in decay of $K(J^P=0^-)$ on π -mesons ($J^P=0^-$) / $K_{\pi 3} \equiv \tau$; $K_{\pi 2} \equiv \theta$ /.

They suggest to study spirality (p·S) in decay experiments.

1957: Wu *et al.* discover the P-violation in β decay of ^{60}Co ($n \rightarrow p + e^- + \nu_e$).

To "save" the world from the left-handed asymmetry, Landau, Lee & Yang suggest invariance of the nature laws with respect to the combined CP-parity.

Landau: $d \sim S$, i.e. the proportionality coefficient is P,T-odd, otherwise $d=0$.

1964: Christenson, Cronin, Fitch & Turlay discover nonconservation of the combined inversion, CP, in decay K_L^0 (CP=-1) $\rightarrow 2\pi$ (CP=+1 !).

1967: Sandars suggests to use polar *heavy-atom* molecules for PNC experiments because of relativistic enhancement $\sim \alpha^2 Z^3$ and $E_{\text{mol}}/E_{\text{ext}} \sim 10^5$.

He initiates the search for the P,T-odd effects on ^{205}TlF in Oxford (UK).

1978: Barkov & Zolotarev (Novosibirsk, Russia) found that the atomic Bi vapor rotate the polarization plane of the laser ray (in search for the *neutral weak interaction* of electrons with nuclei). Similar experiments are performed by Sandars *et al.* (Oxford, UK) and Fortson *et al.* (Seattle, USA).

A few months later it was confirmed by Atwood *et al.* (Stanford, USA) in deeply-inelastic scattering of electrons on deuterium & hydrogen.

Labzowsky (St.-Petersburg) has proposed to use the PbF molecule ($^2\Pi$) for studying P-odd effects because of closeness of levels of opposite parity due to Λ -doubling; he initiated study of PNC effects in SPb. Sushkov & Flambaum (Novosibirsk) suggested to use Ω -doubling to search for the electron EDM.

1980: First *ab-initio nonrelativistic* calculations of PNC effects in TlF followed by the relativistic scaling were performed by Hinds & Sandars. First data from the TlF experiment are obtained for the proton EDM etc.

1983: Discovery of W^\pm and then Z^0 bosons by Rubia with coworkers in CERN thus confirming the Standard electroweak Model.

1985: Khriplovich has suggested to use Ω -doubling in diatomic radicals containing heavy elements with the $^2\Sigma_{1/2}$ ground state for the PNC experiments.

The first *semiempirical* calculations on BaF, HgH and HgF (Kozlov) and *ab-initio two-step* calculations on PbF (Titov *et al.*) are performed in SPb.

1987: Flambaum suggest to use $\text{PbO}^*(J=1)$ for PNC search in his DSc thesis.

1991: The last series of the ^{205}TlF experiments is finished at Yale (USA) and the best limitation on the proton EDM $d_p = (-4 \pm 6) \times 10^{-23} e \cdot \text{cm}$ is obtained. Petrov *et al.* (2002) recalculated it as $d_p = (-1.7 \pm 2.8) \times 10^{-23} e \cdot \text{cm}$.

2002: The last series of the ^{205}Tl experiments is finished in Berkeley (USA) and limitation on the electron EDM, $d_e = (-6.9 \pm 7.4) \times 10^{-28} e \cdot \text{cm}$, is obtained.

The first result are obtained by Hinds group on the ^{174}YbF molecular beam experiment at Sussex(UK) for the electron EDM, $d_e = (-0.2 \pm 3.2) \times 10^{-26} e \cdot \text{cm}$.

Now: New series of the electron EDM experiments on YbF, PbF, and on PbO^* are in progress in London (UK), Oklahoma and Yale (USA), correspondingly, and some more candidates, e.g. HgH, HgF, and TeO^* , are discussed.

Calculations of PNC effects in heavy-atom molecules:

- In 1967 Sandars suggested to use polar heavy-atom molecules for PNC experiments because of relativistic enhancement $\sim\alpha^2Z^3$ (1965) and $E_{\text{mol}}/E_{\text{ext}} \sim 10^5$. He initiated the search for the P,T-odd effects on ^{205}TlF in Oxford and estimated the enhancement **semiempirically**.
- First *ab initio* **nonrelativistic** calculations of PNC effects in **TlF** followed by the **relativistic scaling** were performed by Hinds & Sandars in 1980 and by Coveney & Sandars in 1983 (Oxford, UK).
- **Two-step** relativistic calculations at SPbSU & PNPI (SPb): without correlations: on **PbF** & **HgF** (1985-1991); with correlations: on **YbF** (1996,1998), **BaF** (1997), **TlF** (2002), **PbO*** (2004), **Hf*** (2005).
- First **Dirac-Fock** calculations on **TlF** (1997) and **YbF** (1998) are performed by Parpia (USA) and by Quiney et al. (EU).

Status

**Experimental limit
on the electron EDM:**

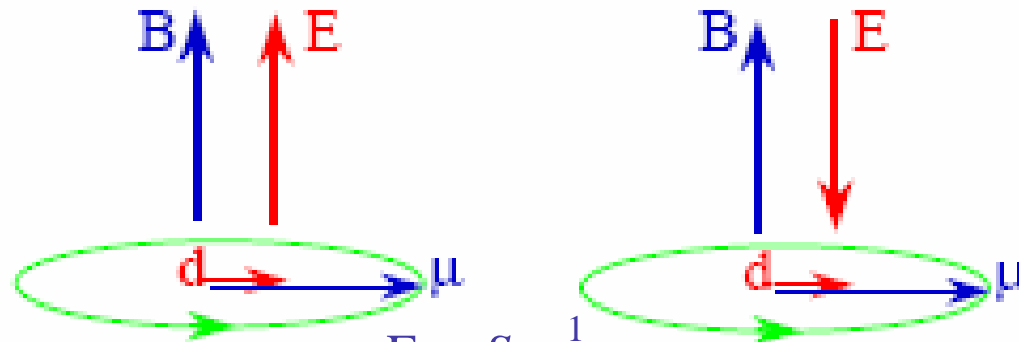
$$|d_e| < 1.6 \times 10^{-27} \text{ e}\cdot\text{cm}$$

B. Regan, E. Commins, C. Schmidt,
D. DeMille, *PRL* **88**, 071805 (2002).

Physics model	$ d_e $
Standard Model	$< 10^{-38} \text{ e}\cdot\text{cm}$
Left-right symmetric	$10^{-26} - 10^{-28} \text{ e}\cdot\text{cm}$
Lepton flavor-changing	$10^{-26} - 10^{-29} \text{ e}\cdot\text{cm}$
Multi-Higgs	$10^{-27} - 10^{-28} \text{ e}\cdot\text{cm}$
Technicolor	$\sim 10^{-29} \text{ e}\cdot\text{cm}$
Supersymmetry	$\sim 10^{-27} \text{ e}\cdot\text{cm}$

Experimental detection of an EDM

$$H = -\vec{\mu} \cdot \vec{B} - \vec{d} \cdot \vec{E}$$



For $S = \frac{1}{2}$:

$$\omega_1 = \frac{2\mu B + 2dE}{\hbar}$$

$$\omega_2 = \frac{2\mu B - 2dE}{\hbar}$$

$$\omega_1 - \omega_2 = \frac{4dE}{\hbar}$$

Statistical sensitivity:

Single system with coherence time τ : $\delta \omega = \frac{1}{\tau}$

N uncorrelated systems measured for time T τ :

$$\delta d = \frac{\hbar}{2E} \frac{1}{\sqrt{2\tau TN}}$$

Effective relativistic Hamiltonians

The most popular Hamiltonians used in calculations of heavy-atom molecules:

- Dirac-Coulomb(-Breit) Hamiltonian is the most accurate relativistic approximation that is used in practice when calculating many-electron systems.
- Two-component all-electron approaches:
 - Douglas-Kroll transformation (of 2nd & 3rd orders);
 - zero/first-order relativistic approximations (ZORA/FORA).
- Relativistic effective core potentials (RECPs) employing operators of types:
 - radially-local (semi-local) pseudopotentials;
 - Huzinaga-type (*ab initio*) model potentials (using level-shift terms for “freezing” core shells);
 - separable pseudopotentials (applied to many-atomic systems);
 - core polarization potentials (containing one- & two-electron terms).

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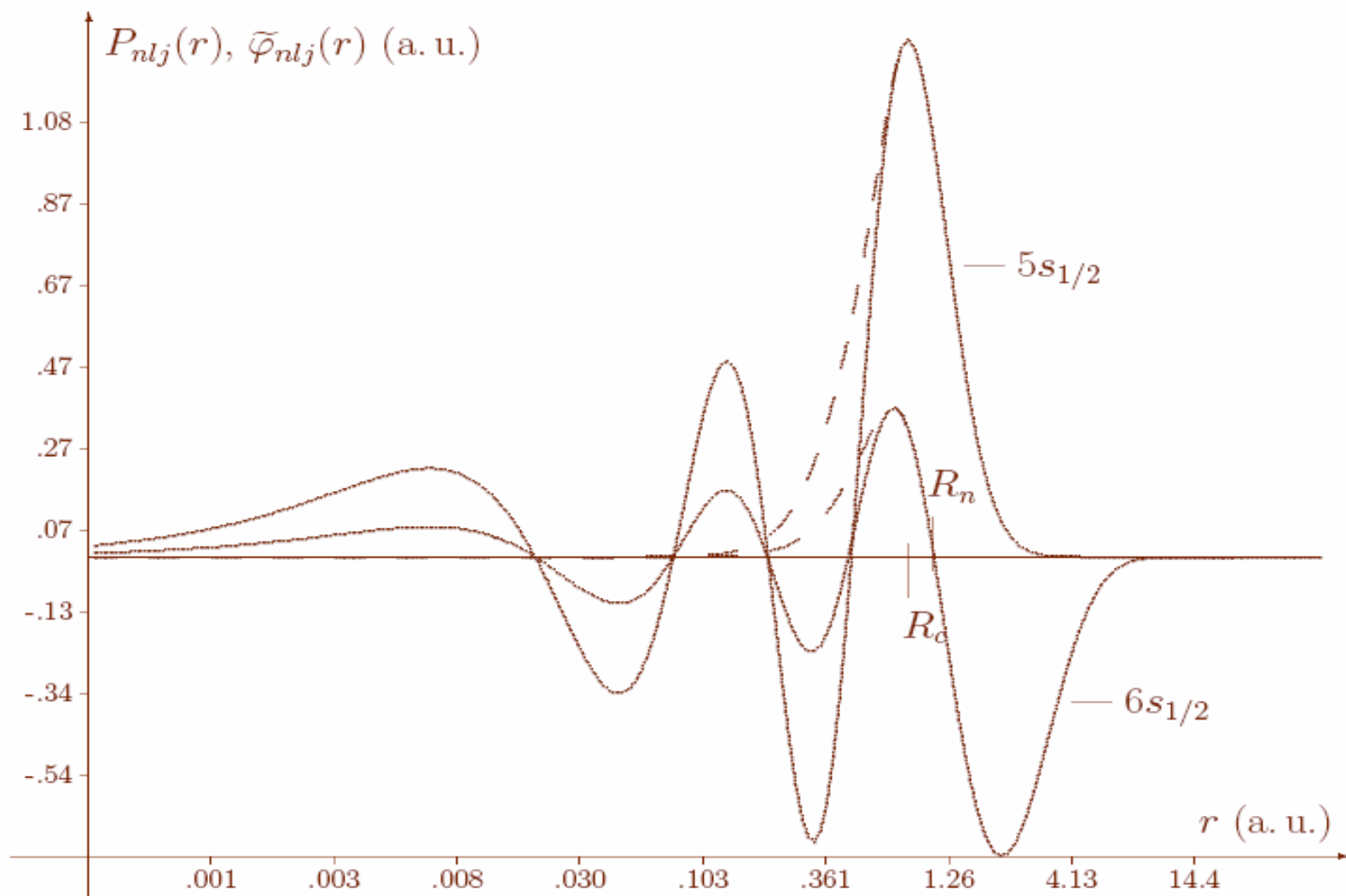
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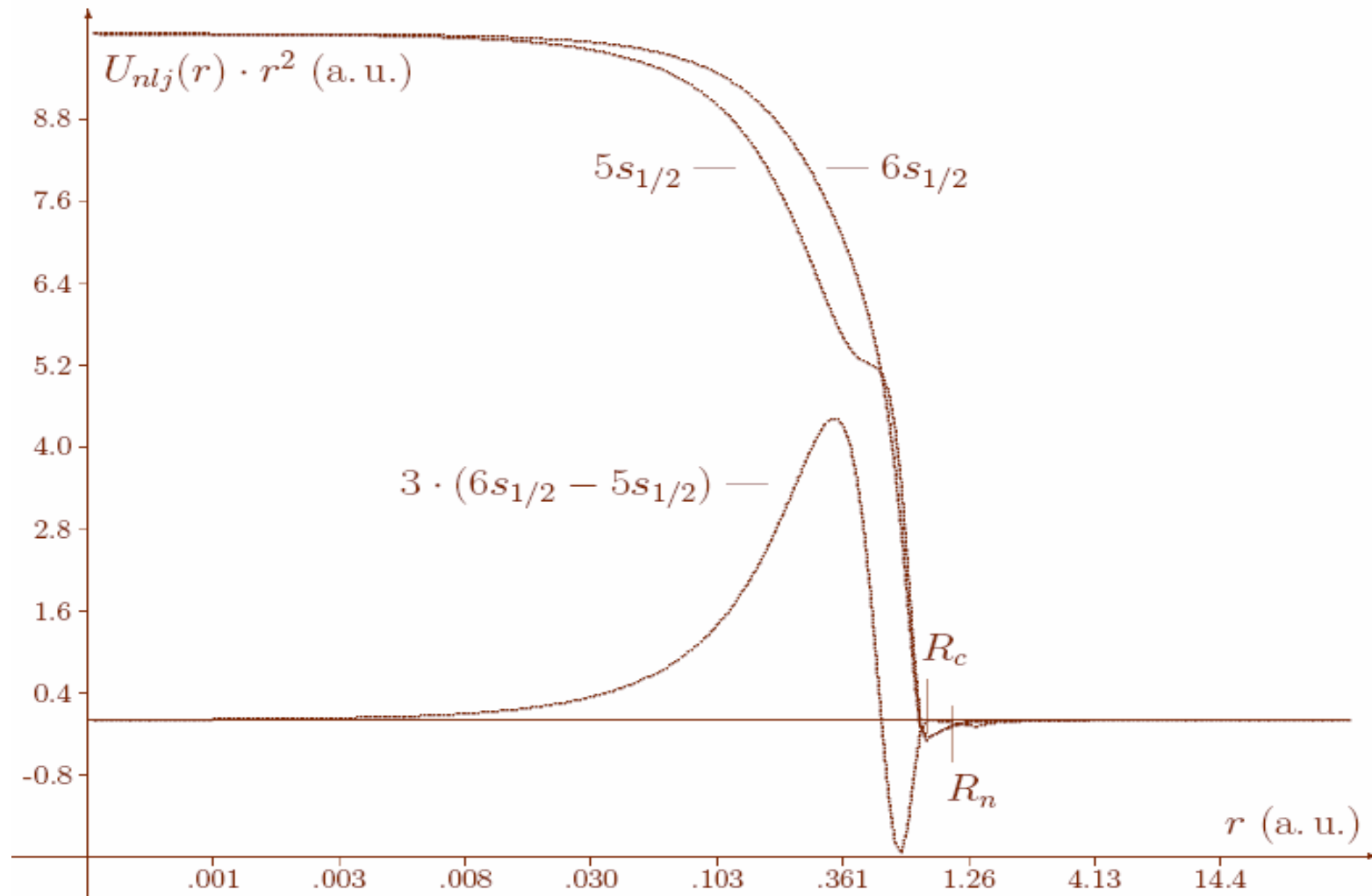
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– core polarization potentials (containing one- & two-electron terms).

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



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



Generalized relativistic ECP

- The inner core (IC), outer core (OC) and valence (V) electrons are **first** treated employing different approximations for each (including relaxation of IC shells).
- GRECP involves both radially-local, separable and Huzinaga-type potentials (shifting the core energies) as its components.
- The GRECP operator includes terms of other types (self-consistent and term-splitting) for economical treatment of *transition metals, lanthanides and actinides*.
- The **outermost core** pseudoorbitals (*nodeless*) together with **valence** pseudoorbitals (*nodal*) are used for constructing the GRECP components.
- Quantum electrodynamics effects (Breit etc.) and **correlations with the IC shells** *can be efficiently treated within GRECPs*.

Generalized RECP operator with separable correction:

$$\begin{aligned}
 U_{\text{GS}}^{\text{Ef}} = & U_{n_v L J}(r) + \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} [U_{n_v l j}(r) - U_{n_v L J}(r)] \sum_{m=-j}^j |l j m\rangle \langle l j m| \\
 & + \sum_{n_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} \{ [U_{n_c l j}(r) - U_{n_v l j}(r)] \tilde{\mathbf{P}}_{n_c l j} + \tilde{\mathbf{P}}_{n_c l j} [U_{n_c l j}(r) - U_{n_v l j}(r)] \} \\
 & - \sum_{n_c, n'_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{l+1/2} \tilde{\mathbf{P}}_{n_c l j} \left[\frac{U_{n_c l j}(r) + U_{n'_c l j}(r)}{2} - U_{n_v l j}(r) \right] \tilde{\mathbf{P}}_{n'_c l j} , \quad (1)
 \end{aligned}$$

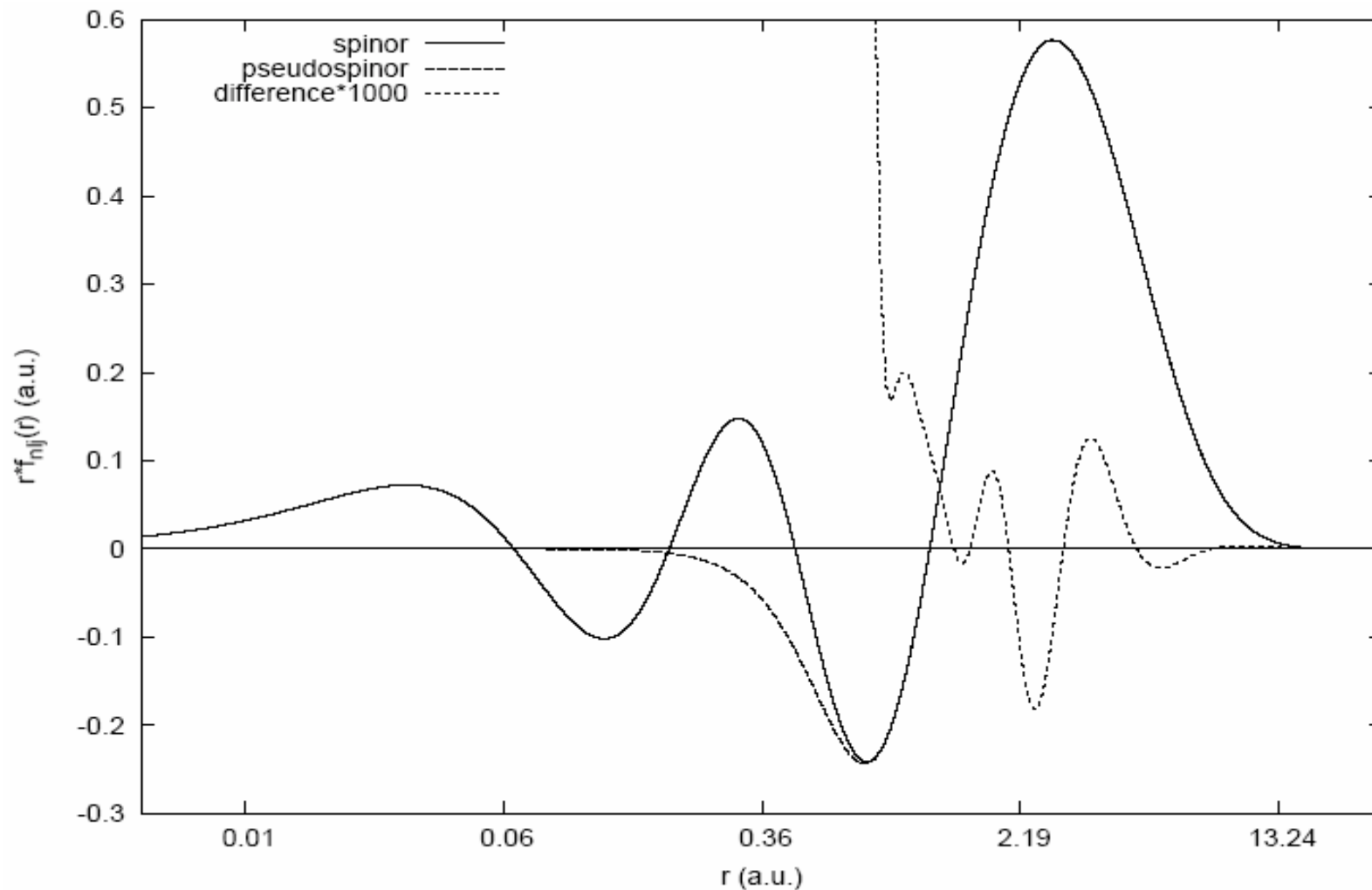
$$\tilde{\mathbf{P}}_{n_c l j} = \sum_{m=-j}^j |n_c \bar{l} j m\rangle \langle n_c \bar{l} j m| .$$

- *The separable terms* (the second and third lines in Eq.(1)) are added to *the conventional radially-local RECP operator*.
- These terms take into account the difference between the potentials acting on the outercore and valence electrons with the same l & j .

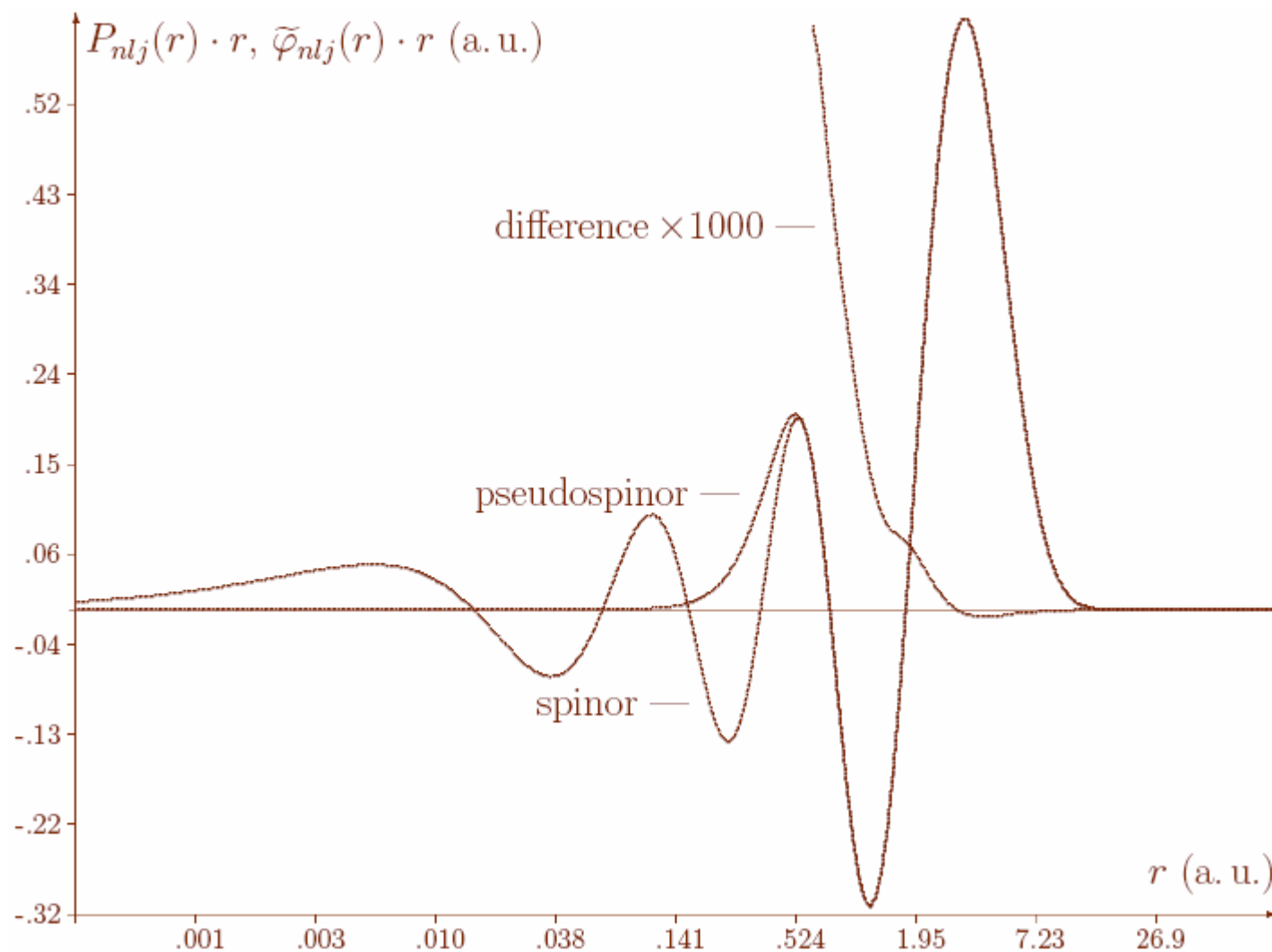
GRECP accuracy

- The GRECPs provides the level of “chemical accuracy” (1 kcal/mol or 350 cm⁻¹) for valence energies.
- The GRECP accuracy can be even higher than the accuracy of the *frozen core approximation* when accounting for the inner core relaxation terms.
- The cumulative computational precision is *limited by current possibilities of correlation methods* and codes.
- The expenses of correlation treatment can be seriously reduced as compared to Dirac-Coulomb-Breit methods when using basis of *spin-orbitals* instead of *spinors*.

The radial parts of the large component of the $6p_{1/2}$ bispinor and the corresponding pseudospinor obtained in equivalent Dirac-Fock and 21-electron GRECP/SCF calculations for the state averaged over the relativistic $6s^2_{1/2}6p^1_{1/2}$ configuration of *Thallium*. Their difference is multiplied by 1000. The GRECP is generated for the nonrelativistically averaged $6s^16p^16d^1$ configuration.



Radial parts of the $7s_{1/2}$ spinor (all-electron Dirac-Fock) and pseudospinor 32-electron GRECP/SCF) of Uranium for the state averaged over the nonrelativistic $5f^26d^17s^2$ configuration and their difference multiplied by 1000.



Nonvariational One-Center Restoration (NOCR) of electronic structure in cores of heavy-atoms in a molecule:

- Generation of *equivalent* basis sets of one-center four-component spinors $\begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{2j-l,jm} \end{pmatrix}$ and smoothed two-component pseudospinors $\tilde{f}_{nlj}(r)\chi_{ljm}$ in finite-difference DF(B) and GRECP/SCF calculations of *the same* atomic configurations.

- The molecular *pseudospinorbitals* are then expanded in the basis set of one-center two-component atomic *pseudospinors*

$$\tilde{\phi}_i(\mathbf{x}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{|l+1/2|} \sum_{n,m} c_{nljm}^i \tilde{f}_{nlj}(r)\chi_{ljm}, \quad (2)$$

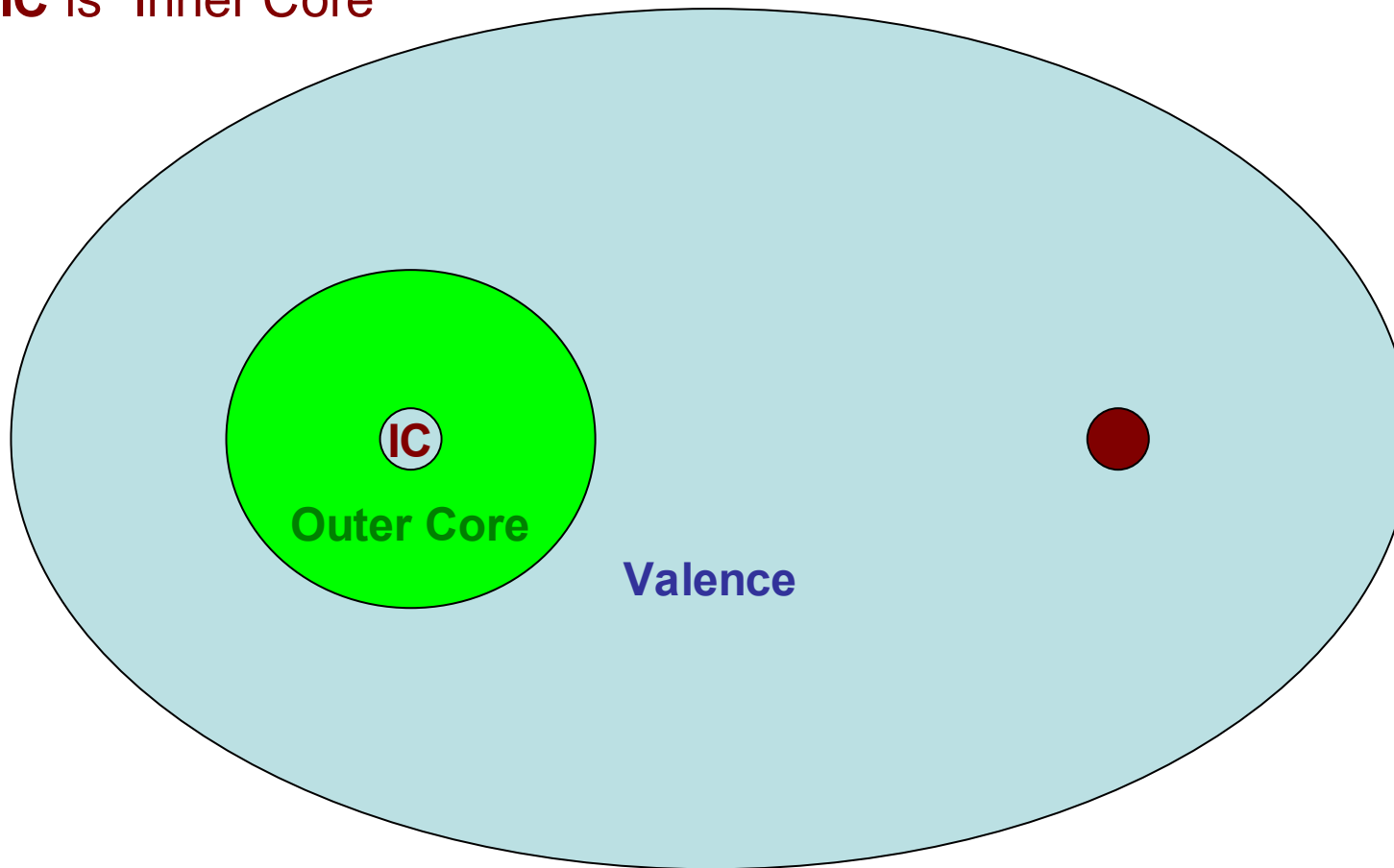
where \mathbf{x} denotes spatial and spin variables, $r \leq R_c^{\text{rest}}$, $R_c^{\text{rest}} \geq R_c$.

- Finally, the atomic two-component pseudospinors in the molecular basis are replaced by equivalent four-component spinors and the expansion coefficients from Eq. (2) are preserved:

$$\phi_i(\mathbf{x}) \approx \sum_{l=0}^{L_{\max}} \sum_{j=|l-1/2|}^{|l+1/2|} \sum_{n,m} c_{nljm}^i \begin{pmatrix} f_{nlj}(r)\chi_{ljm} \\ g_{nlj}(r)\chi_{l'jm} \end{pmatrix}. \quad (3)$$

Variational one-center restoration

IC is “Inner Core”



A.V. Titov, IJQC (1996)

Spin-rotational Hamiltonian for YbF, HgF etc.

For the ^{171}Yb isotope with the nuclear spin $I=\frac{1}{2}$, the molecular spin-rotational degrees of freedom are described by the Hamiltonian:

$$\mathbf{H}_{\text{sr}} = B\vec{\mathbf{N}}^2 + \gamma\vec{\mathbf{S}}\vec{\mathbf{N}} - D_e\vec{\lambda}\vec{E} + \vec{\mathbf{S}}\hat{\mathbf{A}}\vec{\mathbf{I}} + \mathbf{H}_{\text{sr}}^{\text{P,T}} \quad (9)$$

- $\vec{\mathbf{N}}$ is the *rotational angular momentum*;
- B is the *rotational constant*;
- $\vec{\mathbf{S}}, \vec{\mathbf{I}}$ are the *effective spins of the electron and the Yb nucleus*;
- $\vec{\lambda}$ is the *unit vector from Yb to F*;
- γ is the *spin-doubling constant for spin-rotational interaction*;
- D_e is the *molecular dipole moment*;
- \vec{E} is the *external electric field*;
- $\hat{\mathbf{A}}$ is the axial tensor describing *magnetic HFS* on the Yb nucleus:

$$\mathbf{H}_{\text{sr}}^{\text{hfs}} = \frac{\mu_N \vec{\mathbf{I}} \cdot \vec{\alpha} \times \vec{r}}{I r^3}, \quad \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad (10)$$

that can be described by *isotropic* and *differential* HFS constants:

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

P- and P,T-odd terms in H_{sr} for YbF, HgF etc.

$$\mathbf{H}_{sr}^{P,T} = W_A k_A \vec{\lambda} \times \vec{S} \cdot \vec{I} + (W_S k_S + W_d d_e) \vec{S} \vec{\lambda} . \quad (11)$$

- the *first* of them is interaction of the electron spin with the *anapole moment* of the nucleus k_A ;
- the *second* one corresponds to the scalar *P, T-odd* electron-nucleon interaction, k_S is its dimensionless constant;
- the *third* one describes interaction of the electron EDM d_e with the internal molecular field \vec{E}_{mol} :

$$\mathbf{H}_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \cdot \vec{E}_{mol} , \quad (12)$$

$$W_d d_e = 2 \langle {}^2\Sigma_{1/2} | \mathbf{H}_d | {}^2\Sigma_{1/2} \rangle . \quad (13)$$

$E_{eff} = \frac{1}{2} W_d$ is an *effective electric field* on the unpaired electron.

$W_A, W_S,$ & W_d depend on the *electron spin-density* in a vicinity of nuclei like A and A_d .

First two-step calculations of ^{199}HgF and ^{207}PbF

		A_{\parallel} (MHz)	A_{\perp} (MHz)	G_{\parallel}	G_{\perp}	W_d ($10^{24} \frac{\text{Hz}}{\text{e cm}}$)	W_S (kHz)
HgF	(a)	22621	21880	1.993	1.961		
	(b)					-48	-191
	(c)	24150	23310	1.996	1.960	-48	-185
PbF	(d)	8690	-7460	0.034	-0.269	10	51
	(e)	9550	-8240	0.114	-0.438	18	99
	(c)	10990	-8990	0.040	-0.326	14	55

- (a) experimental data [L.B.Knight, Jr. *et al.*, *JCP* **74**, 6009 (1981)];
 (b) semiempirical results [M.G.Kozlov, *Sov.Phys.-JETP* **62**, 1114 (1985)];
 (c) *ab initio* calculations [Yu.Yu.Dmitriev *et al.*, *PLA* **167**, 280 (1992)];
 (d),(e) *ab initio* calculations with semiempirical accounting for the spin-orbit mixing models [M.G.Kozlov *et al.*, **20**, 4939 (1987)].

Why is accurate accounting for correlation important?

As an illustrative example, let us consider an electronic state of a many-electron system which is described by the CI expansion of a normalized WF:

$$\Psi = \Psi_S + \Psi_U \equiv \sum_{s=1}^{N_S \sim (10^2 \div 10^6)} C_s \Phi_s + \sum_{u=1}^{N_U \gg N_S} C_u \Phi_u, \quad (4)$$

$$\left(1 - \sum_{s=1}^{N_S} |C_s|^2\right) = \sum_{u=1}^{N_U} |C_u|^2 \equiv w_U \ll 1. \quad (5)$$

where S stands for *selected*, and U for *unselected* (or rest) configurations. Estimates for $\{|C_u|\}$ from (5) is as $|C_u| \sim \sqrt{\frac{w_U}{N_U}}$ and for mean value of a property described by operator \mathbf{X} are as (putting below $\langle \mathbf{X} \rangle \equiv X_{SS} + 2\Re[X_{SU}] + X_{UU}$):

$$X_{SS} = \langle \Psi_S | X | \Psi_S \rangle \sim N_S \cdot (1 - w_S) \cdot \overline{\langle s' | \mathbf{X} | s \rangle}, \quad (6)$$

$$X_{SU} = \langle \Psi_S | X | \Psi_U \rangle \sim \sqrt{N_U} \cdot \sqrt{N_S w_U (1 - w_U)} \cdot \overline{\langle s | \mathbf{X} | u \rangle}, \quad (7)$$

$$X_{UU} = \langle \Psi_U | X | \Psi_U \rangle \sim N_U \cdot w_U \cdot \overline{\langle u' | \mathbf{X} | u \rangle}, \quad (8)$$

where $|s, u\rangle$ stands for $|\Phi_{s,u}\rangle$. The problem is that $\langle \mathbf{X} \rangle$ can be changed dramatically with increasing N_U if the criteria of configuration selection for $\{\Phi_s\}$ do not reflect appropriately the structure of contributions to the property determined by the speed of convergence of $\overline{\langle s, u' | \mathbf{X} | u \rangle} \rightarrow 0$ when $N_U \rightarrow \infty$.

The *PT2/CI* method

The Hilbert space, where the many-electron equation

$$\mathbf{H}|\Psi\rangle = E|\Psi\rangle \quad (14)$$

is defined, is partitioned into subspaces \mathcal{P} & \mathcal{Q} . The corresponding projection operators, \mathbf{P} & \mathbf{Q} , satisfy the relation $\mathbf{P}+\mathbf{Q}=\mathbf{1}$. \mathbf{P} is defined as the projector on the states of an atom having completely occupied core shells. Write

$$\begin{aligned} \mathbf{H} &= \mathbf{P}\mathbf{H}\mathbf{P} + \mathbf{P}\mathbf{H}\mathbf{Q} + \mathbf{Q}\mathbf{H}\mathbf{P} + \mathbf{Q}\mathbf{H}\mathbf{Q} , \\ |\Psi\rangle &= \mathbf{P}|\Psi\rangle + \mathbf{Q}|\Psi\rangle \equiv |\phi\rangle + |\chi\rangle . \end{aligned} \quad (15)$$

Accounting for \mathcal{Q} leads to the CI equation on the model space \mathcal{P}

$$(\mathbf{P}\mathbf{H}\mathbf{P} + \Sigma(E))|\phi\rangle = E|\phi\rangle , \quad (16)$$

where

$$\Sigma(E) = (\mathbf{P}\mathbf{H}\mathbf{Q}) \frac{1}{E - \mathbf{Q}\mathbf{H}\mathbf{Q}} (\mathbf{Q}\mathbf{H}\mathbf{P}) . \quad (17)$$

The PT2/CI method (cont.)

The $\Sigma(E)$ operator is calculated by diagrammatic techniques within PT2 with some approximation for E , then Eq. (16) is solved by the CI method. The basis sets used for calculating $\Sigma(E)$ and solving Eq. (16) need not be identical.

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

Method	$A=(A_{\parallel}+2A_{\perp})/3;$		$A_d=(A_{\parallel}-A_{\perp})/3$		
	A (MHz)	A_d (MHz)	W_d ($10^{24} \frac{\text{Hz}}{\text{e}\cdot\text{cm}}$)	W_A (Hz)	W_S (kHz)
GRECP/RASSCF ^{a,b}	4854	60	-9.1	486	-33
Semiemp. ^c (with $4f$ -hole correction)			-12.6		-43
DF+CP ^a (Quiney <i>et al.</i>) ^d	7865	60	-12.0	620	-42
Unrestricted DF (Parpia) ^e			-12.03		-44
GRECP/RASSCF/EO ^f	7842	79	-12.06	634	
(with $4f$ -hole correction)	(7839)	(94)			
GRECP/RCC-SD ^g ($4f$ correlated)	7492	109	-11.61		
Experiment ^h	7617	102			

^a **RASSCF** is the Restricted Active Space SCF; **DF** stands for the Dirac-Fock;
EO stands for the Effective Operator technique; **CP** is Core Polarization;

^b A.V.Titov, N.S.Mosyagin, & V.F.Ezhov, *PRL* **77**, 5346 (1996).

^c M.G.Kozlov, *JPB* **30**, L607 (1997).

^d H.M.Quiney, H.Skaane, & I.P.Grant, *JPB* **31**, L85 (1998).

^e F.A.Parpia, *JPB* **31**, 1409 (1998).

^f N.S.Mosyagin, M.G.Kozlov, & A.V.Titov, *JPB* **31**, L763 (1998).

^g N.S.Mosyagin *et al.*, unpublished data with small basis set (2002).

^h L.B.Knight, Jr. & W.Weltner, Jr., *JCP* **53**, 4111 (1970).

The PT2/CI method (cont.)

Advantages:

- ★ relative simplicity of the method, good convergence;
- ★ economical treatment of core-valence correlations and good description of valence correlations for a group of states.

Disadvantages:

- fast growth of computational expenses with enlarging one-electron basis set for valence electrons;
- lost of accuracy when describing core-valence correlations with small gap between core and valence shells.

The Coupled-Cluster Approaches

According to decomposition $\mathbf{H} = \mathbf{H}^{[0]} + \mathbf{V}$; $\mathbf{H}^{[0]}|\Phi_m\rangle = E_m^{[0]}|\Phi_m\rangle$;
 $\mathbf{V} \equiv \mathbf{V}^{\text{corr}} + \mathbf{H}^{\text{SO}}$, the complete space of $\{\Phi_m\}$ is divided into two subspaces:

\mathcal{M}_0 , model space, consists of small number of the most important configurations $\{\Phi_m\}_{m=1}^{N_M}$ to describe *static* and other *nondynamic* correlations, which are taken into account exactly on \mathcal{M}_0 ;

\mathcal{M}_0^\perp , rest of space (usually very large), is included approximately to account for *dynamic correlations*.

The eigenstates of interest are presented as

$$|\Psi_n\rangle = \sum_{m=1}^{N_M} C_{mn} \exp(\mathbf{S}^{\{m\}}) |\Phi_m\rangle, \quad (25)$$

where $\mathbf{S}^{\{m\}} \equiv \mathbf{S}_1^{\{m\}} + \mathbf{S}_2^{\{m\}} + \dots$ is the *cluster operator* for the Φ_m state:

$$\begin{cases} \mathbf{S}_1^{\{m\}} = \sum_{a,b} s_{a,b}^{\{m\}} \mathbf{a}_a^+ \mathbf{a}_b, \\ \mathbf{S}_2^{\{m\}} = \frac{1}{2} \sum_{ab,cd} s_{ab,cd}^{\{m\}} \mathbf{a}_a^+ \mathbf{a}_b^+ \mathbf{a}_d \mathbf{a}_c, \\ \dots \end{cases} \quad (26)$$

Solution of Coupled-Cluster equations:

The *cluster amplitudes* $\{s_{a,b}^{\{m\}}, s_{ab,cd}^{\{m\}}, \dots\}$ are evaluated solving Bloch equations:

$$\mathbf{U}\mathbf{H}\mathbf{U} = \mathbf{H}\mathbf{U}, \quad \mathbf{U} \equiv \sum_{m=1}^{N_M} \exp(\mathbf{S}^{\{m\}}) |\Phi_m\rangle \langle \Phi_m|. \quad (27)$$

The coefficients C_{mn} and final energies E_n are obtained from diagonalization of the effective Hamiltonian \mathbf{H}^{eff} on the model space:

$$\mathbf{H}^{\text{eff}} \sum_{m=1}^{N_M} C_{mn} |\Phi_m\rangle = E_n \sum_{m=1}^{N_M} C_{mn} |\Phi_m\rangle, \quad (28)$$

$$\mathbf{H}_{nm}^{\text{eff}} \equiv \langle \Phi_n | [\mathbf{H}_{\mathcal{N}} \exp(\mathbf{S}^{\{m\}})]_{\mathcal{C}} | \Phi_m \rangle. \quad (29)$$

Three basic Coupled Cluster categories:

- One-state or state-selective ($N_M=1$);
- ★ Fock-space or valence universal methods ($\mathbf{S}_l^{\{m\}} \equiv \mathbf{S}_l^{\{1\}}$, $m=2, \dots, N_M$);
- Hilbert-space or state-universal approaches ($N_M \geq 2$).

The Coupled-Cluster Approaches (cont.)

Advantages:

- ★ It is the size-extensive method, i.e. the energy of the system is scaled properly with increase in the number of electrons (whereas the CI method is not size-extensive in general).
- ★ The CC-SD method takes into account the contributions not only from the determinants obtained from the model space by applying the $(1+T_1^{(m)}+T_2^{(m)})$ operator but also approximately from all the rest determinants (whereas the CI method with the same number of unknown coefficients does not).
- ★ The CC method is one of the best methods for accounting the dynamic correlation (that is the most serious drawback of linear CI approaches).

The Coupled-Cluster Approaches (cont.)

Disadvantages:

- The model space is usually small by size. Otherwise, intruder states (i.e. such states from the \mathcal{M}_0^\perp subspace which are lying within the \mathcal{M}_0 subspace energy span) destroy the convergence of the CC iterations. Serious effort is yet required to overcome this problem in general.
- The effective Hamiltonian is usually non-Hermitian and the CC equations are nonlinear that seriously complicate their solution. This is a nonvariational method, i.e. the CC energy is not an upper bound to the exact energy of the system (whereas the CI energy is).
- Calculation of reduced density matrices (and, therefore, properties other than spectroscopic) is a complicated problem for the exponential WF ansatz.

P,T-odd interactions in TIF:

The effective Hamiltonian with the Tl nucleus EDM in TIF is

$$H^{\text{eff}} = (d^V + d^M)\vec{\sigma}_N \cdot \vec{\lambda}, \quad (18)$$

where $\vec{\sigma}_N$ is a unit vector parallel to the spin of the Tl nucleus \vec{I} ,
 $\vec{\lambda}$ is the unit vector along z (from Tl to F),
 d^V & d^M are volume and magnetic constants [Schiff 1963].

Volume effect:

$$d^V = 6SX = (-d_p R + Q)X , \quad (19)$$

S is the nuclear Schiff moment, d_p is the proton EDM,

$$X = \frac{2\pi}{3} \left[\frac{\partial}{\partial z} \rho_\psi(\vec{r}) \right]_{x,y,z=0} , \quad (20)$$

$\rho_\psi(\vec{r})$ is the electronic density calculated from the WF ψ ;

R and Q are factors determined by the *nuclear* structure of ^{205}Tl :

$$R = \langle \psi_N(\mathbf{r}_n) | \sum_n (q_n/Z - \delta_{n,3s}) r_n^2 | \psi_N(\mathbf{r}_n) \rangle ,$$

$$Q = [3/5 \langle \psi_N(\mathbf{r}_n) | \sum_n (q_n \mathbf{r}_n) | \psi_N(\mathbf{r}_n) \rangle - \\ 1/Z \langle \psi_N(\mathbf{r}_n) | \sum_n (q_n r_n^2) | \psi_N(\mathbf{r}_n) \rangle \times \\ \langle \psi_N(\mathbf{r}_n) | \sum_n (q_n \mathbf{r}_n) / r_n^2 | \psi_N(\mathbf{r}_n) \rangle] \bar{I} ,$$

where $\psi_N(\mathbf{r}_n)$ is nuclear WF.

Magnetic effect:

$$d^M = 2\sqrt{2}(d_p + d_N) \left(\frac{\mu}{Z} + \frac{1}{2mc} \right) M , \quad (23)$$

where d_N is the nuclear EDM arising due to P,T-odd nuclear forces; μ , m & Z are the magnetic moment, mass & charge of Tl nucleus,

$$M = \frac{1}{\sqrt{2}} \langle \psi | \sum_i \left(\frac{\vec{\alpha}_i \times \vec{\mathbf{l}}_i}{r_i^3} \right)_z | \psi \rangle , \quad (24)$$

$\vec{\mathbf{l}}_i$ is the orbital momentum for electron i ; $\vec{\alpha}_i$ are its Dirac matrices.

The parameters X and M (in a.u.) for the ground state of ^{205}TlF in Dirac-Fock (DF)^{1,2} and GRECP/RCC³ calculations.

	$R_e = 2.0844 \text{ \AA}$		$R = 2.1 \text{ \AA}$			
Expansion	s, p	s, p, d, f	s, p	s, p	s, p, d, f	s, p
Shells : main contr.	M		X	M		X
DF ¹ Tl:(28,28,12,8)	15.61		7743			
DF ² Tl:(28,28,14,8)					13.62 ^a	8089
Tl:(34,34,16,9)					13.63 ^a	8747
GRECP/RCC-S	16.12	13.84	9813	16.02	13.82	9726
GRECP/RCC-SD		11.50	7635			

^a M is calculated in [2] with using two-center molecular spinors corresponding to infinite value of L_{max} .

¹F.A.Parpia, *JPB* 30, 3983 (1997).

²H.M.Quiney, J.K.Laerdahl, K.Faegri Jr., T.Saue, *PRA* 57, 920 (1998).

³A.N.Petrov, N.S.Mosyagin, T.A.Isaev *et al.*, *PRL* 88, 073001 (2002).

PbO* is a Novel System for Measuring Electron EDM $|d_e|$

- $a(1)$ has very small Ω -doublet splitting
 - \Rightarrow complete polarization with small fields (>15 V/cm)
 - equivalent to $E \sim >10^{10}$ V/cm on an atom!
- PbO is thermodynamically stable
 - $a(1)$ populated via laser excitation
 - \Rightarrow **can work in *vapor cell*.**

MUCH larger density than beam:

PbO Cell (Yale):

$$N = nV \sim 10^{16}$$

TI Beam (Berkeley):

$$N = nV \sim 10^8$$

Errors in all-electron transition energies of the Pb atom obtained by the RCC-SD and PT2/CI methods for states with the 6s²6p² configuration.

Term	Exper. transition energies (in cm ⁻¹)	Errors ^a in transition energies (in cm ⁻¹)							
		RCC-SD				CI			
		Number of correlated electrons							
		4	14	22	36	4	14	22	36
³ P ₀	0	0	0	0	0	0	0	0	0
³ P ₁	7819	-1161	-630	-450	-414	-807	-535	-393	-365
³ P ₂	10650	-1229	-539	-364	-320	-752	-428	-294	-282
¹ D ₂	21457	-2263	-963	-618	-530	-1707	-849	-573	-402
¹ S ₀	29466	-1362	-70	199	291	-1553	-270	-33	90
Max. error		2263	963	817	821	1707	849	573	492
Av. error		945	497	417	411	843	392	301	270

^a Errors are taken as differences between calculated and experimental values.

Contributions from triple and quadruple CC amplitudes to total energies of the *Pb* terms and errors for the VCIC-corrected transition energies.

Term (Leading configuration)	Basis set			Errors in transition energies ^c		
	[3,5]	[3,5,3]	[3,5,3,2]	(All values in cm^{-1})		
	Δ^a	Δ^a	Δ^a			
Number of correlated electrons						
	4	4	4	14	22	36
3P_0 ($6s_{1/2}^2 6p_{1/2}^2$)	-334	-690	-586	0	0	0
3P_1 ($6s_{1/2}^2 6p_{1/2}^1 6p_{3/2}^1$)	-120	-389	-232	-276	-96	-60
3P_2 ($6s_{1/2}^2 6p_{1/2}^1 6p_{3/2}^1$)	-104	-242	-109	-62	113	157
1D_2 ($6s_{1/2}^2 6p_{3/2}^2$)	-11	47	-30	-407	-62	26
1S_0 ($6s_{1/2}^2 6p_{3/2}^2$)	-412	-680	-777	-261	8	100
Max. error	412	737	777	407	209	217
Aver. error	196^b	410^b	347^b	206	88	106

^a $\Delta_i = E_i^{CI} - E_i^{RCC}$.

^b $\Delta_{av} = \frac{1}{5} \sum_{i=1}^5 |E_i^{CI} - E_i^{RCC}|$.

^c Differences between calculated (RCC-SD + VCIC) and experimental data.

Spin-Orbit Conguration Interaction

Write a Hamiltonian \mathbf{H} for a molecule as

$$\mathbf{H} = \mathbf{H}^{[0]} + \mathbf{V}^{\text{corr}} + \mathbf{H}^{\text{SO}}, \quad (30)$$

where $\mathbf{H}^{[0]}$ is an unperturbed spin-independent Hamiltonian, \mathbf{V}^{corr} is a two-electron correlation operator, and \mathbf{H}^{SO} is a one-electron spin-orbit operator.

$$\mathbf{H}^{[0]}\Phi_I^{(n)\Lambda S} = E_I^{(n)\Lambda S}\Phi_I^{(n)\Lambda S}, \quad (31)$$

where $n=1, 2, \dots$ numerates groups of states by the excitation level with respect to a set of the most important (*reference or main*) configurations, $\{\Phi_I^{(0)\Lambda S}\}$.

Two main approaches: “Conventional CI” ($\langle\Phi_I^{(n)\Lambda S}|\mathbf{H}|\Phi_J^{(n)\Lambda'S'}\rangle$ are saved in memory) and “Direct CI” (the above matrix elements are calculated only as required).

The singly- and doubly-excited configurations, $\{\Phi_I^{(1,2)\Lambda S}\}$, can be *completely* included to the final CI calculations or *selected* (“Table CI”) due to some criteria.

The SO-CI computational scheme:

The Spin-Orbit MultiReference single- and Double-excitation CI method employing the point double-group symmetry consists of the following stages:

1. SCF (MCSCF) calculation with the spin-Averaged RECP part, $\mathbf{U}^{\text{AREP}} \subset \mathbf{H}^{[0]}$ is performed; the obtained spin-orbitals are used for generating the Spin- and space-symmetry adapted many-electron Functions (SAFs) $\{\Phi_J^{(0,1,2)\Lambda S}\}$;
2. selection of the reference configurations (Mains) $\{\Phi_J^{(0)\Lambda S}\}$ and diagonalization of $\mathbf{H} \equiv \mathbf{H}^{[0]} + \mathbf{V}^{\text{corr}} + \mathbf{H}^{\text{SO}}$ on them for constructing the starting approximations for required states, $\Psi_I^{(0)} = \sum_{\Lambda S, J} C_{IJ}^{(0)\Lambda S} \Phi_J^{(0)\Lambda S}$, $E_I^{(0)} = \langle \Psi_I^{(0)} | \mathbf{H} | \Psi_I^{(0)} \rangle$;
3. singly- ($n=1$) and doubly-excited ($n=2$) SAFs $\Phi_J^{(n)\Lambda S}$ (with respect to Mains) are selected by PT2 with thresholds T_1 & T_2 ($\langle \mathbf{H}^{[0]} | \Phi_J^{(n)\Lambda S} \rangle = E_J^{(n)\Lambda S} | \Phi_J^{(n)\Lambda S} \rangle$):

$$\delta E_J^{(n)\Lambda S}(I) = \frac{|\langle \Phi_J^{(n)\Lambda S} | \mathbf{V}^{\text{corr}} + \mathbf{H}^{\text{SO}} | \Psi_I^{(0)} \rangle|^2}{E_J^{(n)\Lambda S} - E_I^{(0)}} \geq T_{1,2}, \quad (32)$$

Perturbative corrections to CI:

4. a required set of low-lying solutions, $\Psi_I^{T_k}$, of Hamiltonian \mathbf{H} on the space of the selected SAFs is obtained using iterative Davidson procedure;

5. accounting for the linear correction on zero threshold, $T=0$, for I -th root:

$$E_I^{T=0} = E_I^{T_k} + \lambda P_I^{T_k} \quad \Rightarrow \quad \lambda = -(P_I^{T_1} - P_I^{T_2}) / (E_I^{T_1} - E_I^{T_2}), \quad (33)$$

where $k = 1, 2$ and

$$E_I^{T_k} = \langle \Psi_I^{T_k} | \mathbf{H} | \Psi_I^{T_k} \rangle, \quad P_I^{T_k} = \sum_{(\mathbf{n}, \Lambda S, J): \delta E_J^{(\mathbf{n})\Lambda S}(I) < T_k} \delta E_J^{(\mathbf{n})\Lambda S}(I),$$

i.e. multiindex $(\mathbf{n}, \Lambda S, J)$ runs only over *unselected* SAFs with respect to T_k ;

6. accounting for triple and quadruple excitations (generalized Davidson or Full-CI correction) for approximate calculating the Full-CI energies:

$$\Delta E_I^{TQ} \approx \Delta E_I^{SD} (1 - |c_I^{(0)}|^2), \quad \Delta E_I^{SD} = E_I^{T=0} - E_I^{(0)}, \quad (34)$$

where $|c_I^{(0)}|^2$ is the weight of $\Psi_I^{(0)}$ in $\Psi_I^{T_{\min}}$.

Spin-Orbit Conguration Interaction (cont.)

Advantages:

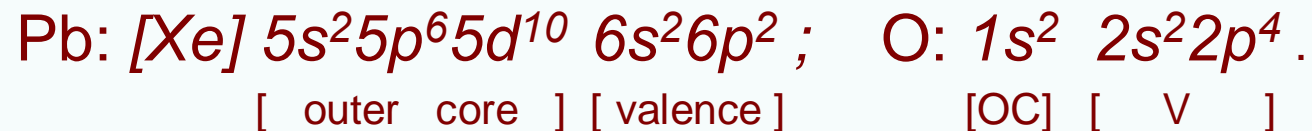
- ★ simplicity of the method, there are no problems with the convergence *independently* of the numbers of roots and open shells;
- ★ well describes “static” and other “nondynamic” (valence) correlations.

Disadvantages:

- it is badly working for large number of correlated electrons when (semiempirical) linear $T=0$ and/or generalized Davidson (Full CI or FCI) correction on unselected configurations are usually large;
- “thrill of points” on the potential curves as a result of the configuration selection by some thresholds;
- though, in principle, the corrections of $T=0$ and FCI types can be used when calculating properties other than spectroscopic; their justification is not as straightforward as in calculating energies.

Calculation of PbO^* : Starting point

- PbO* crude model of $a(1)$: two valence electrons, one is excited both nominally in π -orbitals: *no s-wave component*



⇒ any admixture of *s-wave* due to relativistic & correlation effects can dramatically influence on the calculated HFS and PNC values.

⇒ Accurate calculation of electronic structure both in the valence and core regions of PbO is required:

⇒ Combination of SO-CI (*nondynamic* or V correlations) & RCC-SD (*dynamic* or OC-V correlations) is applied:

$$W = W [30\text{-el. RCC-SD}] - W [10\text{-el. RCC-SD}] + W [10\text{-el. SO-CI}]$$

Pb:[4s7p5d3f] + O:[4s3p2d1f] :<Basis sets>: Pb:[5s7p4d2f] + O:[4s3p2d1f]

Calculated parameters A (in MHz) and W_d (in 10^{24} Hz/($e \cdot \text{cm}$))

Experiment: $A = -4113$ MHz for a(1); $A = 5000 \pm 200$ MHz for B(1)

State	$a(1) \ ^3\Sigma^+ \ \sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_1^3 \pi_2^1$	$B(1) \ ^3\Pi \ \sigma_1^2 \sigma_2^2 \sigma_3^1 \pi_1^4 \pi_2^1$		
Parameters	$A \quad W_d$	$A \quad W_d$		
Internuclear distance R = 3.8 a.u.				
10e-RCC-SD	-2635	-3.05	3878	-10.10
30e-RCC-SD	-2698	-4.10	4081	-9.70
<i>Outecore</i>	-63	-1.05	203	0.40
10e-CI	-3446	-4.13	4582	-10.64
FINAL	-3509	-5.18	4785	-10.24
Internuclear distance R = 4.0 a.u.				
<u>10e-CI</u>	-3689	-4.81	4762	-7.18
FINAL	-3752	-5.86	4965	-6.78

A (in MHz) and W_d (in 10^{24} Hz/($e \cdot \text{cm}$))

calculated by CI & RCC with different thresholds (T).

State Parameters	$a(1) \ ^3\Sigma^+ \ \sigma_1^2 \sigma_2^2 \sigma_3^2 \pi_1^3 \pi_2^1$ A	W_d	$B(1) \ ^3\Pi \ \sigma_1^2 \sigma_2^2 \sigma_3^1 \pi_1^4 \pi_2^1$ A	W_d
T (number of SAFs)	Internuclear distance R=4.0 a.u.			
Reference (2 500)	-2025	-0.72	4150	-6.22
T=0.1 (120 000)	-3124	-2.44	4357	-7.35
T=0.01 (500 000)	-3458	-3.61	4590	-6.94
T=0.0025 (1 100 000)	-3536	-4.08	4662	-7.02
T=0.001 (2 000 000)	-3571	-4.31	4692	-7.07
T=0 (175 000 000)	-3625	-4.65	4739	-7.15
<u>T=0 + FCI</u>	-3689	-4.81	4762	-7.18

Calculation of E_{int} in PbO^* : Results

- *Semi-empirical* model of wave functions using experimental data to constrain partial waves near Pb
[M.Kozlov and D.DeMille, PRL **89**, 133001 (2002)]

⇒ $E_{int} > 5 \times 10^{10}$ V/cm!

- *Ab initio* RCCSD + SODCI calculations of QChem PNPI
RCCSD: [T.Isaev *et al.*, PRA **69**, 030501(R) (2004)]
SODCI: [A.Petrov *et al.*, arXiv: physics/0409045; PRA (2005)]

⇒ $E_{int} \sim 2.5 \times 10^{10}$ V/cm.

HI^+ : Calculated $E_{\text{eff}} \equiv W_d |\Omega|$ (in 10^{24} Hz/($e \cdot \text{cm}$)), $|\Omega|=3/2$, A_{\parallel} and quadrupole HFS constant eQq_0 (in MHz) for the ground state $X^2\Pi_{3/2}$ of $H^{127}I^+$. $A_{\parallel}^{\text{expt}} = 1021$ MHz; $eQq_0^{\text{expt}} = -712.6$ MHz ($Q = -710(10)$ mbarn). “SAFs” are spin-adapted functions.

Method		A_{\parallel}	eQq_0	$W_d \Omega $
“ionic” DHF approx. ¹				-0.09
“covalent” CI approx. ¹				-0.49
RCC-S	<i>7 electrons</i> ²	863	-719	0.206
RCC-SD		881	-708	0.347
SODCI	1 911 282 SAFs	892	-709	0.336
RCC-S	<i>25 electrons</i> ²	906	-807	0.226
RCC-SD		962	-752	0.345
SODCI	12 678 133 SAFs	968	-745	0.336

¹B.Ravaine, S.G.Porsev, & A.Derevianko, *PRL* **94**, 013001 (2005).

²T.A.Isaev, N.S.Mosyagin, A.N.Petrov, & A.V.Titov, arXiv: physics/0412177.

Concluding remarks (core properties):

- ⇒ *High-accuracy calculations of heavy-atom systems are of primary interest for modern (planned) experiments to search for PNC effects.*
- ⇒ *Up to now, all the most precise calculations of polar heavy-atom diatomics of interest are performed by the GRECP / NOCR approach.*
- ⇒ *Accuracy is limited by current possibilities of correlation methods and not by the finite basis set, GRECP and NOCR approximations.*
- ⇒ *The two-step method has better flexibility than the four-component approaches and good prospects for further improvement of accuracy.*
- ⇒ *Extension of the method to study more complicated systems (liquids etc.) is planned; simulation of environment by GRECPs is possible. Applicability to a multitude of other properties is straightforward.*
- ⇒ *Further development of accurate effective Hamiltonians, correlation methods and new schemes of the basis set generation is required:*
- ⇒ *Correlated GRECPs and schemes of correlated restoration can dramatically reduce the computational efforts in prospect.*

Concluding remarks (valence properties):

- Calculations with “chemical accuracy” are now accessible for variety of properties in heavy-atom molecules by different ways.
- Computational accuracy can be higher than experimental one; the properties not attainable to experimental research can be reliably calculated.
- There are good prospects for further improvement of accuracy. Studying more complicated systems (molecules and clusters) and new phenomena is possible. As a result, new areas can be a subject of further both theoretical and experimental research.
- RECPs provide best flexibility in such calculations and sufficient accuracy.

Thank you!

