Theory of polyvalent atoms

Mikhail Kozlov

ETU "LETI"
SAINT PETERSBURG ELECTROTECHNICAL UNIVERSITY

Solvay Workshop

Brussels, 25 - 27 November 2019

atoms
an Open Access Journal by MDPI

Atoms as probes for *new physics*

- Violation of discrete symmetries
- Violation of the local Lorentz invariance
- Time variation of the fundamental constants
- Exotic long-range interactions
- Interactions with Dark Matter & Dark Energy

Sometimes we study qualitative effects and sometimes we look for quantitative disagreements. In both cases we can not check atomic theory directly.
Here we focus on the qualitative effects.

Symmetry violation & time-dependence of fundamental constants

- We calculate atomic sensitivity to some perturbation.
- Typically a few percent accuracy is sufficient.
- Usually highest sensitivity is found in complex atoms (i.e. heavy, polyvalent, with accidental degeneracies, etc.)

We need universal method and some tools to control the accuracy. Usually we calculate similar properties, which can be measured (spectra, transition rates, g-factors, HFS, polarizabilities).

Non-perturbative methods

- A typical example is configuration interaction (CI) method.
- It works very well for few electron systems.
- The size of CI space scales exponentially with the number of electrons.
- CI becomes ineffective for the number of electrons of the order of 10.

Many-body perturbation theory

Perturbation theory is effective when there is small parameter $\lambda \ll 1$

$$E_i^{\lambda} = E_i^{(0)} + a_i\lambda^2 + b_i\lambda^3 + c_i\lambda^4 + \ldots$$

In atomic theory if we start with some mean-field potential U_0. The residual interaction

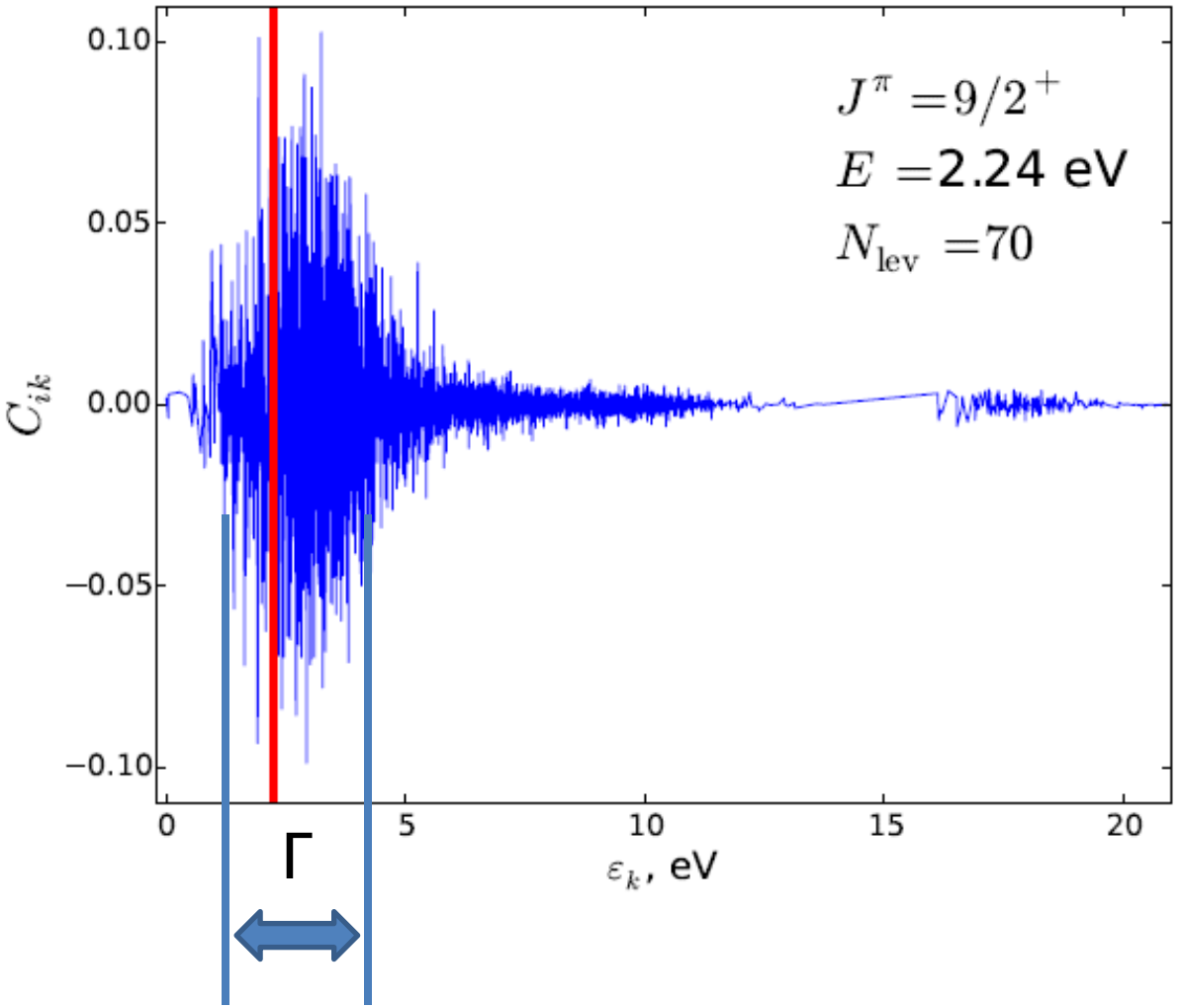
$$V' = V - U_0$$

is usually not small. More precisely, the parameter λ is of the order of unity, $\lambda \approx V'/\Delta \sim 1$. As a result, in general MBPT does not work!

Residual interaction for Pa (Z=91)

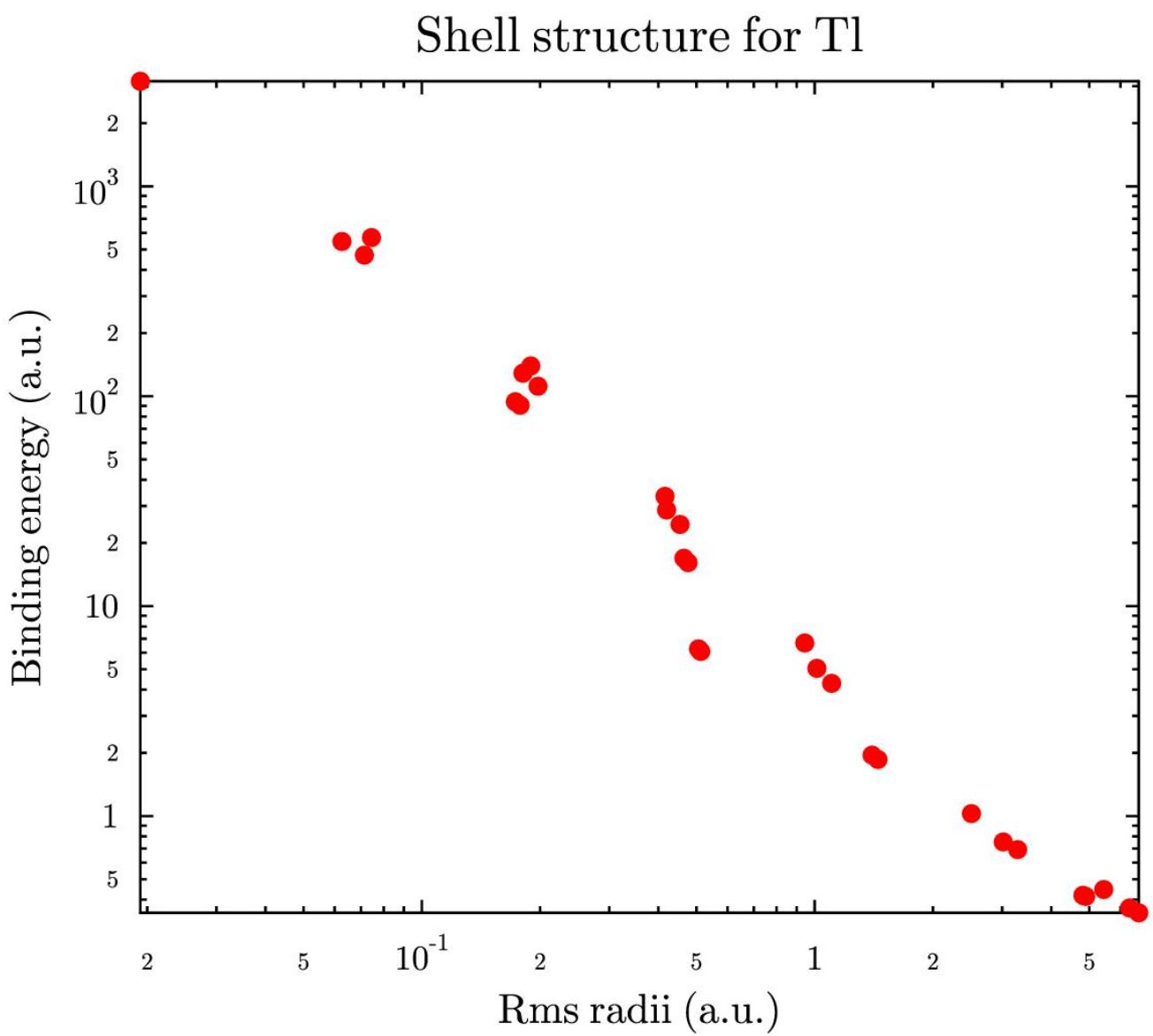
If *V'*≫*D*, where *D* is distance between levels, then *V'* mixes basis states within spreading width

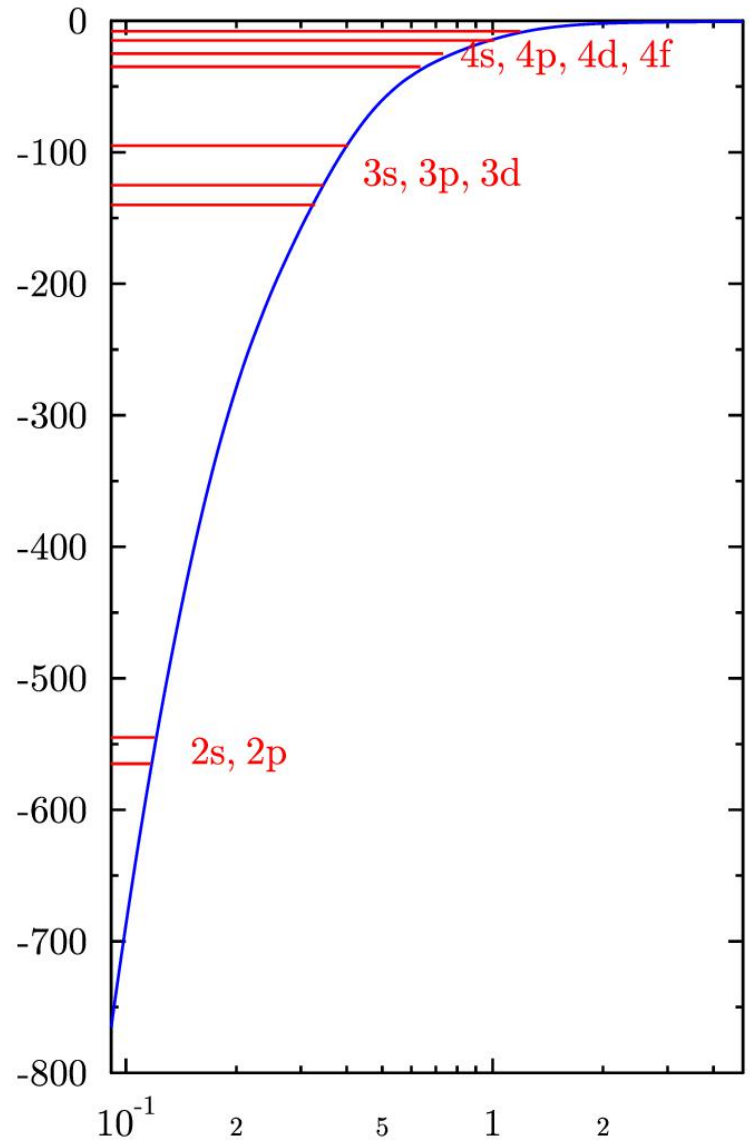
$$\Gamma = 2\pi\langle V'\rangle^2 / D$$

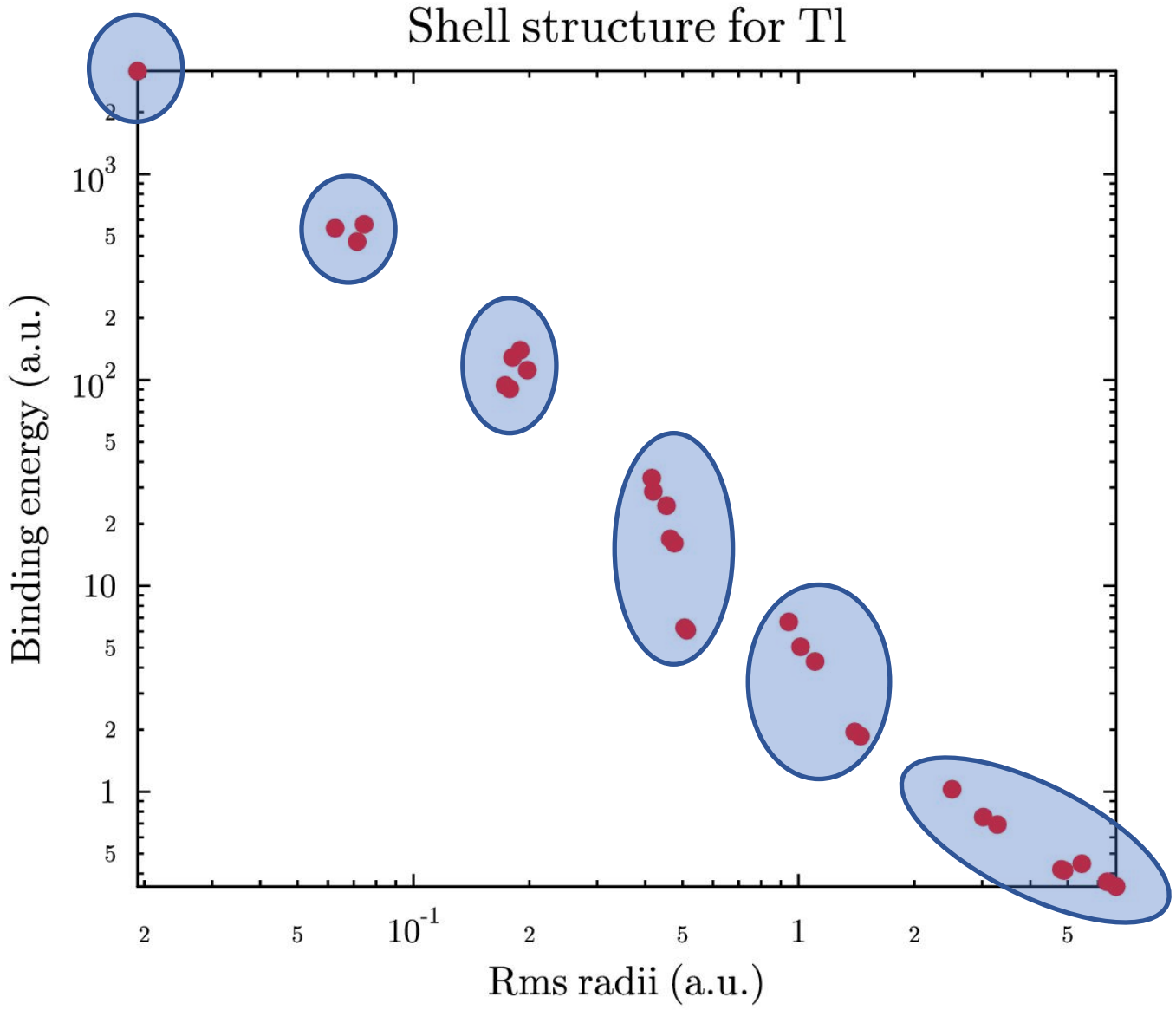


Structure of the eigenstate of Protactinium atom ([Rn]5f² 6d 7s²). $\Gamma \approx 2$ eV.

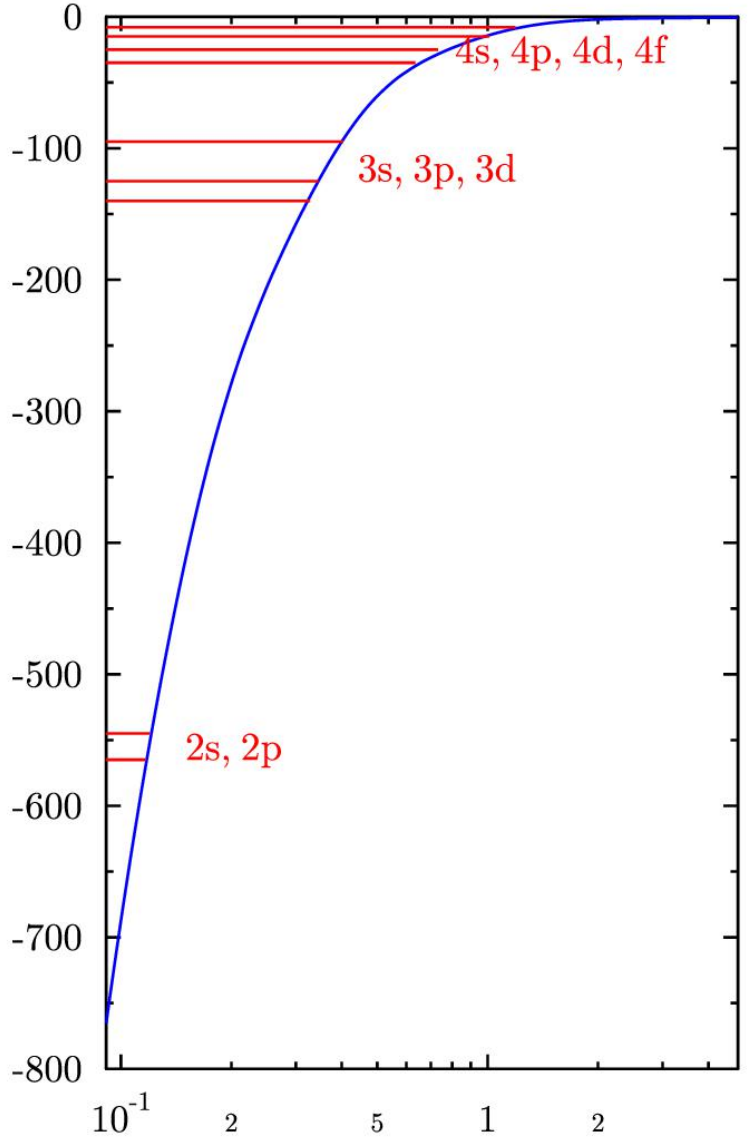
[A.Viatkina, MK, V Flambaum, PRA **95**, 022503 (2017)]

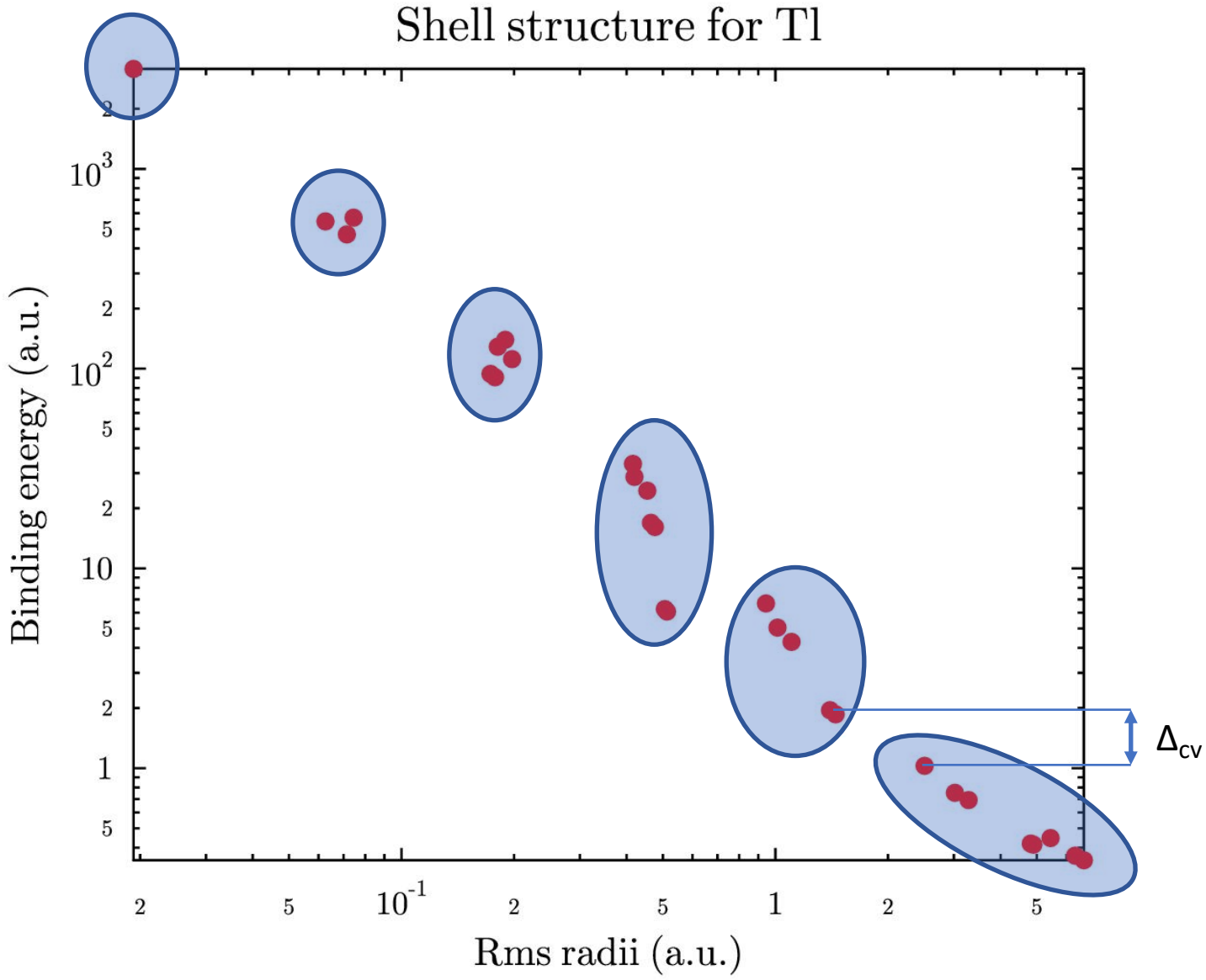

Shell structure for Tl
Binding energy (a.u.)
Rms radii (a.u.)
2
5
10^3
10^2
10
1
10^{-1}

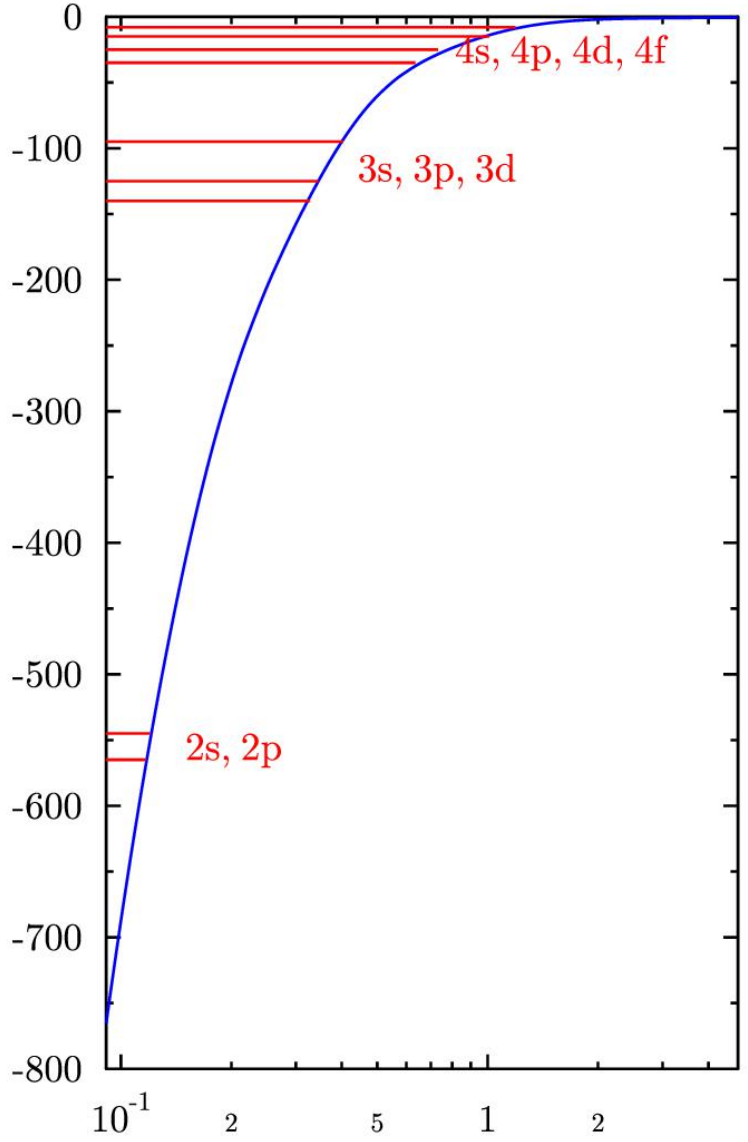

0
-100
-200
-300
-400
-500
-600
-700
-800
4s, 4p, 4d, 4f
3s, 3p, 3d
2s, 2p
10^{-1}
2
5
1

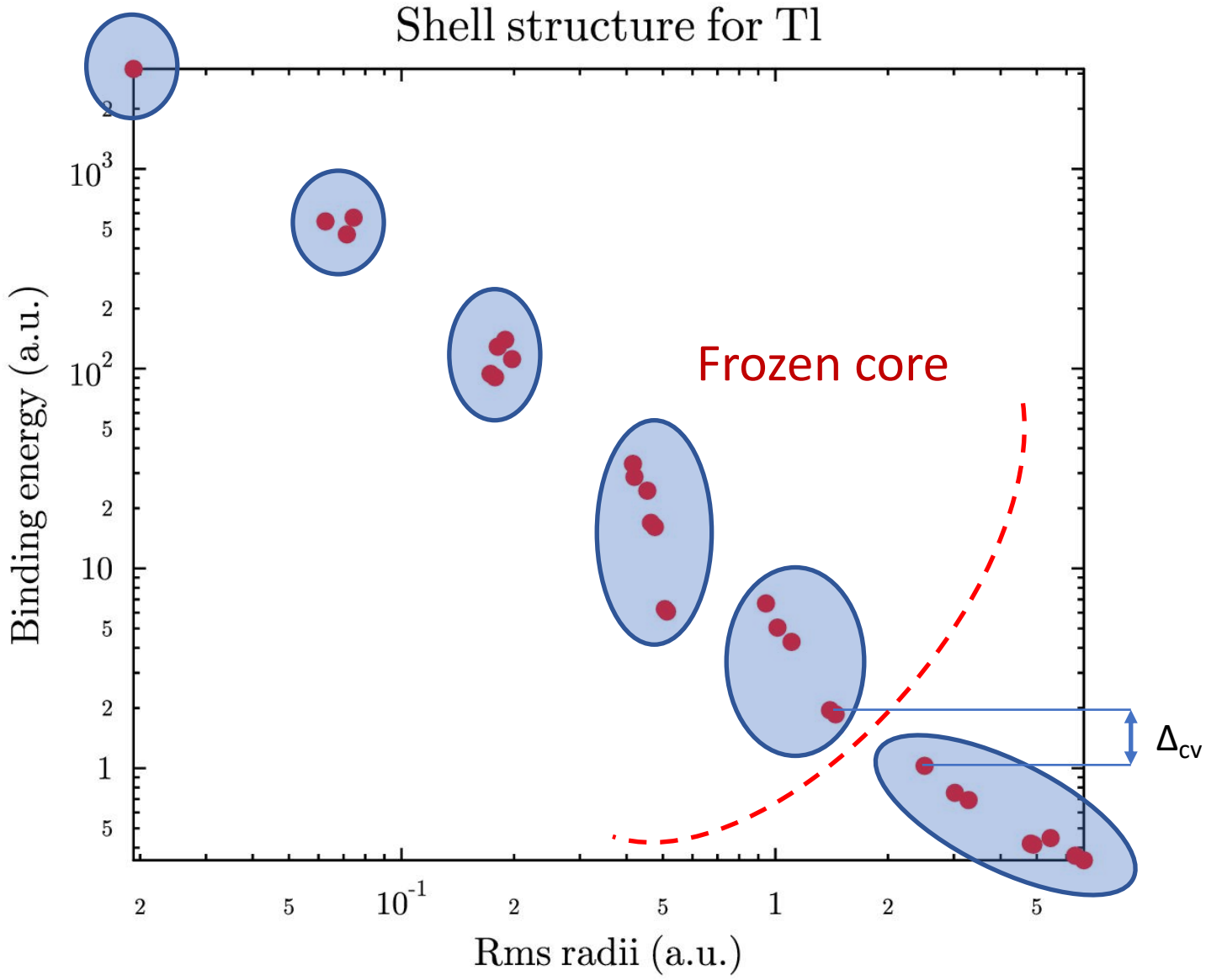

Shell structure for Tl
Binding energy (a.u.)
Rms radii (a.u.)

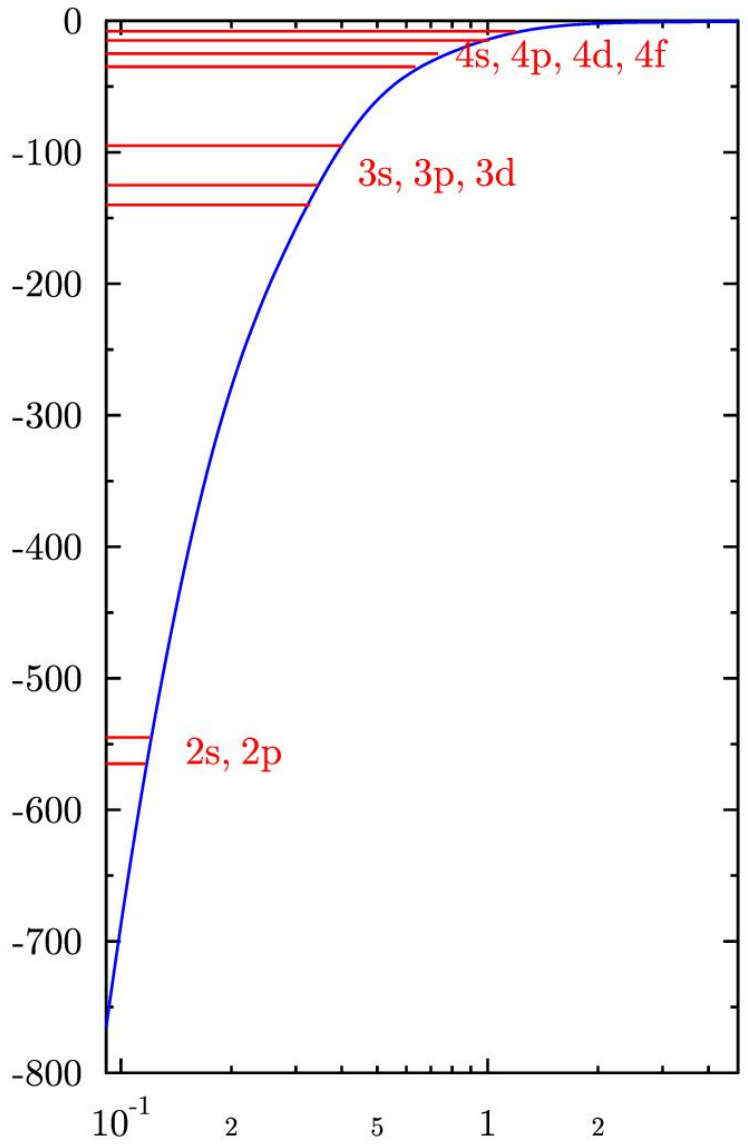
Δ_{cv}


4s, 4p, 4d, 4f
3s, 3p, 3d
2s, 2p


Shell structure for Tl
Binding energy (a.u.)
Rms radii (a.u.)
Δ_{cv}


4s, 4p, 4d, 4f
3s, 3p, 3d
2s, 2p


Shell structure for Tl
Binding energy (a.u.)
Rms radii (a.u.)
Frozen core
Δ_{cv}


4s, 4p, 4d, 4f
3s, 3p, 3d
2s, 2p

Effective small parameter for core-valence correlation corrections

Let us single out the core with excitation energy Δ_{cv} ~1. Then for the core-valence correlations we can introduce

$$\lambda_{\text{eff}} = \frac{\langle V' \rangle}{\Delta_{cv}}$$

Comparing this to the correlation correction:

$$\delta E_{cv} = \frac{\langle V' \rangle^2}{\Delta_{cv}}$$

we can write:

$$\lambda_{\text{eff}} = \sqrt{\frac{\delta E_{cv}}{\Delta_{cv}}}$$

And now λ_{eff} can be small.

CI+MBPT and CI+AO methods

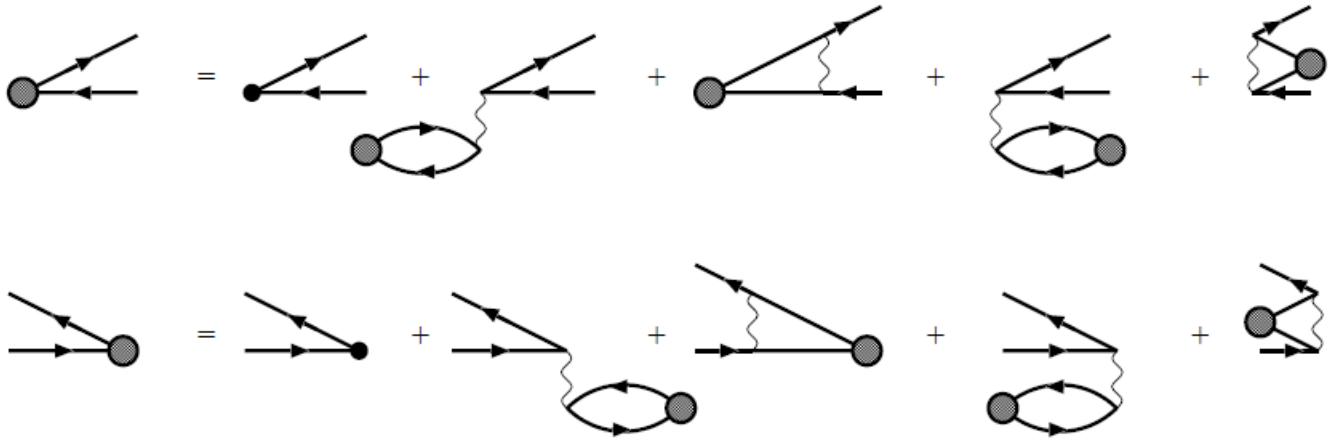
- Valence correlations are treated within configuration interaction (CI) method.
- Core-valence & core-core correlations are accounted for by many-body perturbation theory (MBPT), or by all-order (AO) coupled cluster (CC) method.
- MBPT, or CC method is used to form effective Hamiltonian in the valence CI space.
- Effective operators are also formed for all valence observables.

Effective Hamiltonian for valence electrons

- We define valence space so that all core electrons are frozen.
- We use MBPT, or CC to form H_{eff} in the valence space.
- Zero order Hamiltonian is the valence Hamiltonian in the frozen core approximation.
- We diagonalize effective Hamiltonian using configuration interaction method.

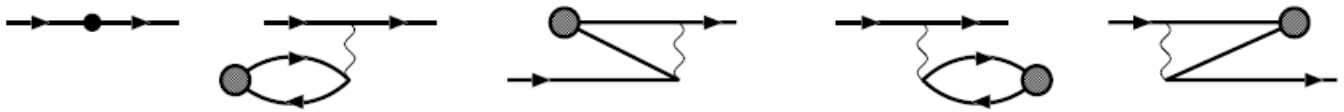
Effective operators for observables

RPA for core

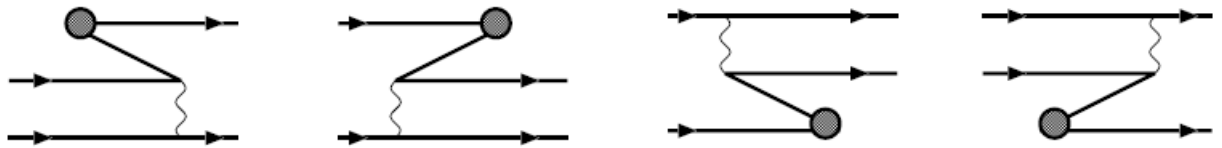


Valence amplitudes

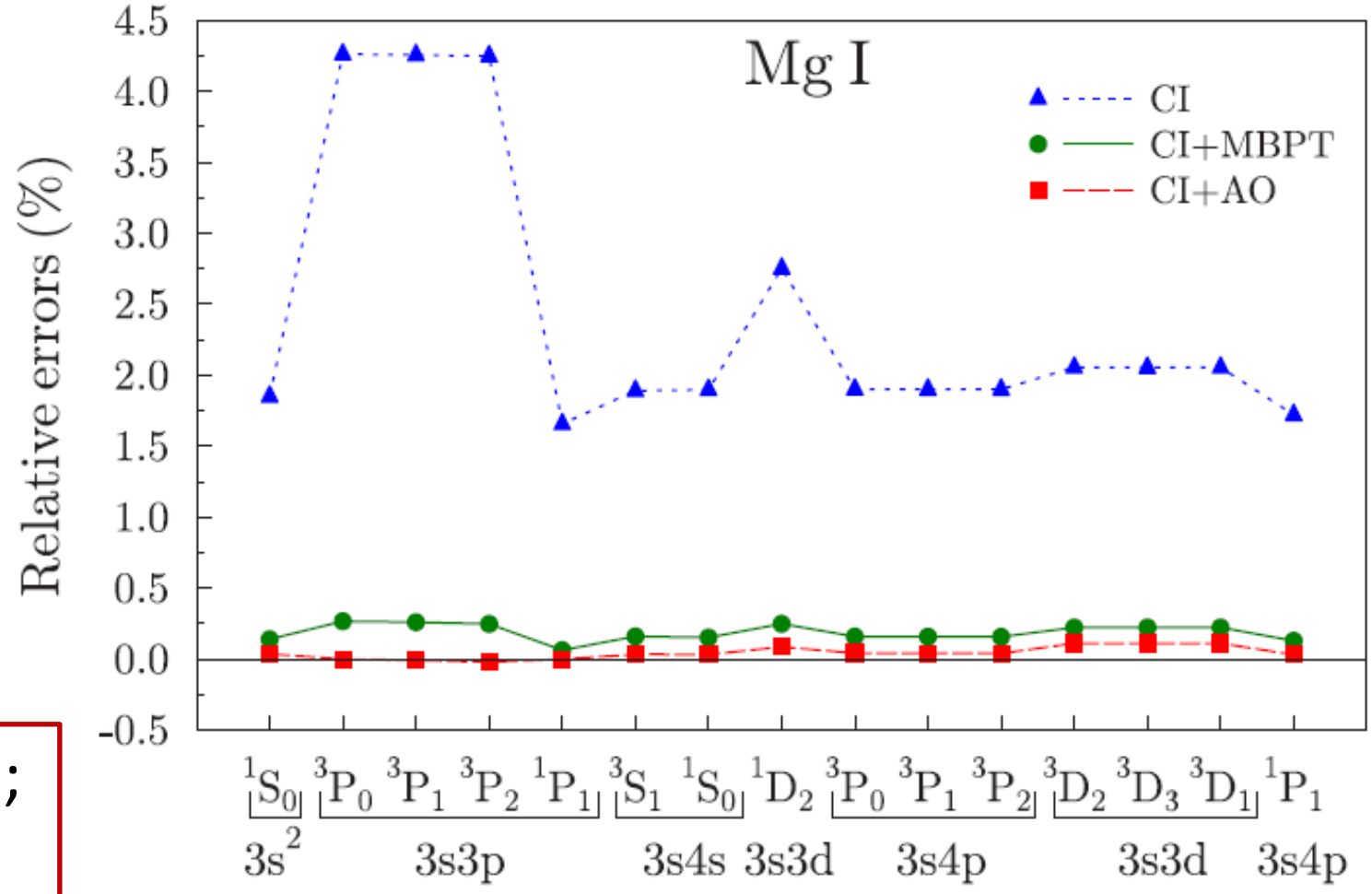
1-e



2-e



Accuracy of CI, CI+MBPT, & CI+AO for Mg I



δE_{cv}=0.015 a.u.;
Δ_{cv}=2.46 a.u.;
→ λ_{eff}=0.08

[E Konovalova & MK, PRA, **92**, 042508 (2015)]

HFS of ^{205}Tl (MHz)

	$A_{6p_{1/2}}$	$A_{6p_{3/2}}$	$A_{7s_{1/2}}$	$A_{7p_{1/2}}$	$A_{7p_{3/2}}$	$A_{6d_{3/2}}$	$A_{6d_{5/2}}$
DF	17339	1291	7579	1940	187	21	9
CI	924	−1369	3799	−102	112	−185	391
H_{eff}	3428	−45	765	331	−56	114	−226
A_{RPA}	959	359	1031	103	73	5	15
A_{σ}	−1071	−31	−269	−92	−9	3	−5
A_{sbt}	−1389	−161	−75	−113	−19	−19	−8
A_{tp}	1731	120	−22	133	4	21	7
A_{SR}	209	88	−29	14	6	−1	0
Norm.	−467	−4	−113	−20	−3	0	0
Total	21663	248	12666	2193	295	−41	183
Theor. [a]	21760	−1919	12470	2070	195		
Theor. [b]	21300	339	12760				
Theor. [c]	21623	264	12307	2157	315	−35	184
Expt.	21311	265	12297	2155	309	−43	229

[MK, S G Porsev, & W R Johnson, 2001]

Polarizabilities of $^1S_0$ & $^3P_0$ clock states in B^+, Al^+, & In^+ ions

Ion		CI	CI + MBPT	CI + all
B^+	$\alpha_0(2s^2\,{}^1S_0)$	9.575	9.613	9.624
	$\alpha_0(2s2p\,{}^3P_0^o)$	7.779	7.769	7.772
	$\Delta\alpha_0$	−1.796	−1.844	−1.851
Al^+	$\alpha_0(3s^2\,{}^1S_0)$	24.405	24.030	24.048
	$\alpha_0(3s3p\,{}^3P_0^o)$	24.874	24.523	24.543
	$\Delta\alpha_0$	0.469	0.493	0.495
In^+	$\alpha_0(5s^2\,{}^1S_0)$	26.27	23.83	24.01
	$\alpha_0(5s5p\,{}^3P_0^o)$	28.60	25.87	26.02
	$\Delta\alpha_0$	2.33	2.04	2.01

[M Safronova , MK, C Clark, PRL, **107**, 143006 (2011)]

Hyperfine-induced quadrupole transitions $^1S_0 - {}^3D_1$ in Yb

MK, V Dzuba, & V Flambaum, PRA 99, 012516 (2019)

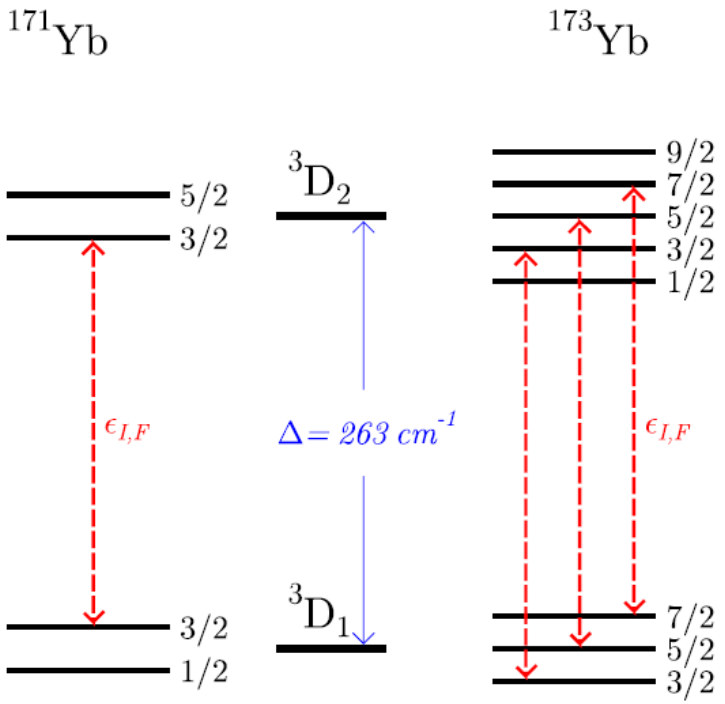


FIG. 1. Hyperfine mixings $\varepsilon_{I,F}$ of the $5d6s\,{}^3D_1$ and $5d6s\,{}^3D_2$ levels in odd isotopes ^{171}Yb ($I = 1/2$) and ^{173}Yb ($I = 5/2$).

TABLE IV. Reduced matrix elements of the transitions $6s^2\,{}^1S_0, I, F' = I \to 5d6s\,{}^3D_1, I, F$ for the isotopes ^{171}Yb ($I = 1/2$) and ^{173}Yb ($I = 5/2$). The HFI quadrupole transition amplitudes (17) are in ea_0^2. Subscripts A, B, and tot correspond to the contributions from the magnetic dipole and electric quadrupole mixings and the sum of the two. Equation (19) defines the PV $E1$ transitions in terms of the amplitude A_P, which was calculated in Refs. [11–13].

I, F	1/2, 1/2	1/2, 3/2	5/2, 3/2	5/2, 5/2	5/2, 7/2
$E2_A \times 10^3$	0.0	+0.643	−0.363	+0.634	−0.752
$E2_B \times 10^3$	0.0	0.0	−0.039	+0.021	+0.028
$E2_{\rm tot} \times 10^3$	0.0	+0.64(10)	−0.40(6)	+0.66(10)	−0.72(12)
$E1_{\rm PV}^{\rm NSD}/A_P$	+0.667	+0.471	−0.660	+0.231	+0.667

CI+AO results for E1 transition amplitudes and polarizability of Pb

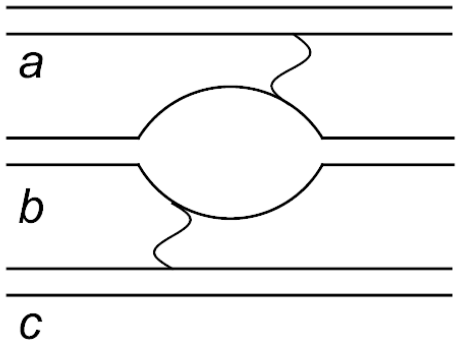
S Porsev, MK, M Safronova, & I Typitsyn, PRA 93, 012501 (2016)

TABLE III. V^{N-2} approximation. The reduced MEs $|\langle f||d||i\rangle|$ (in a.u.) for the electric-dipole transitions, obtained in the CI+all-order approximation and including RPA, Sbt, σ, SR, and normalization corrections. In last column the MEs extracted from the experimental transition probabilities are presented. The value of the ground-state static polarizability is given in the last line.

Transition	This work	Experiment
$6p^2\ ^3P_1$ -$6p7s\ ^3P_0^o$	1.89	2.04(7)[a]
		2.05(10)[b]
$6p^2\ ^3P_0$ -$6p7s\ ^3P_1^o$	1.32	1.37(4)[a]
		1.20(5)[c]
$6p^2\ ^3P_0$ -$6p6d\ ^3D_1^o$	2.01	1.62(4)[a]
		1.67(8)[b]
$\alpha(6p^2\ ^3P_0)$	46.5	47(7)[d]

Effective three-particle interactions

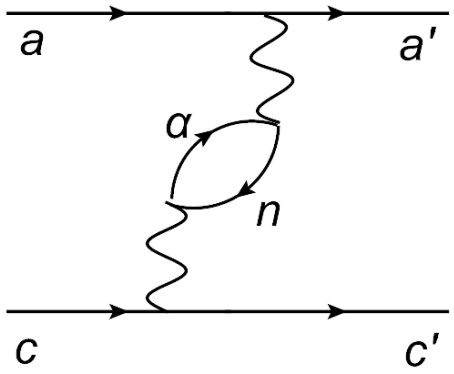
In nuclear physics:



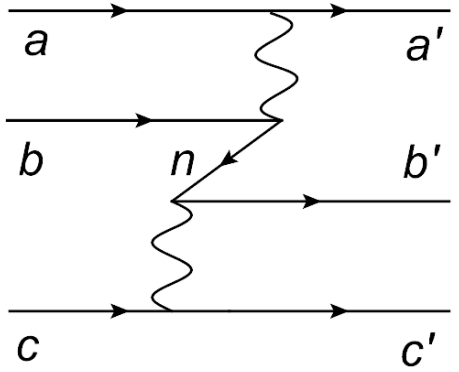
Nucleon can be polarized by its neighbor and then it can interact with another neighbor.

This effect is caused by the internal structure of the nucleon.

Three electron interactions between valence electrons in an atom:

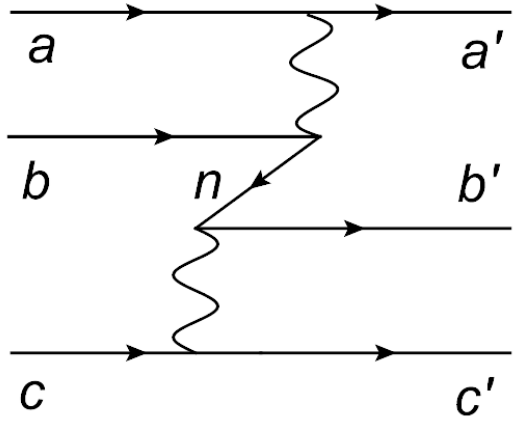


Two-particle interaction screened by the core



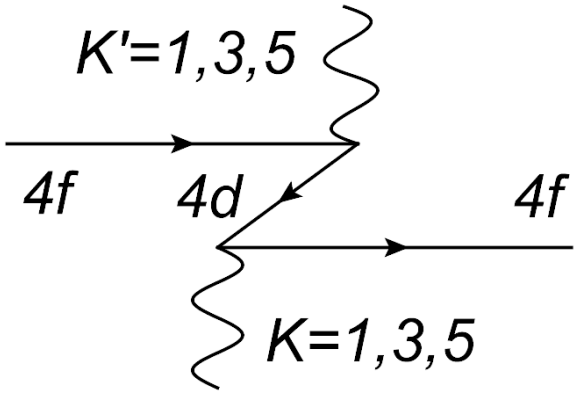
Correction due to the presence of the particle *b*

Typical scale for TPI

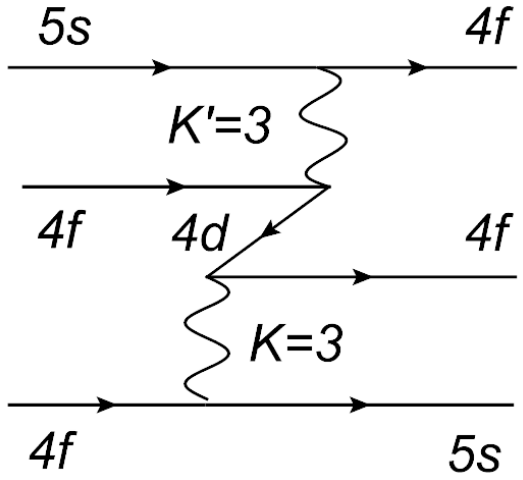


- Atoms with valence electrons ***ns & np***: **~10 cm^{-1}**
- Transition metals with ***nd*** valence electrons: **~100 cm^{-1}**
- Lanthanides & actinides (***4f & 5f***): **~1000 cm^{-1}**

TPI in atoms with filling *4f* shell



Allowed multipoles for *d-f* interaction



TPI diagram for $4f^2 5s$ configuration

…TPI in atoms with filling *4f* shell

Configurations with "large" TPI corrections for last core shell *4d*:

- $4f^2 5s$
- $4f5s5p$

Configurations with "small" TPI corrections:

- $4f^3$
- $4f^2 5p$
- $4f5s^2$

Examples:

Ce^{9+},Pr^{10+},Nd^{11+}:

$5s^2 5p$; $4f5s^2$

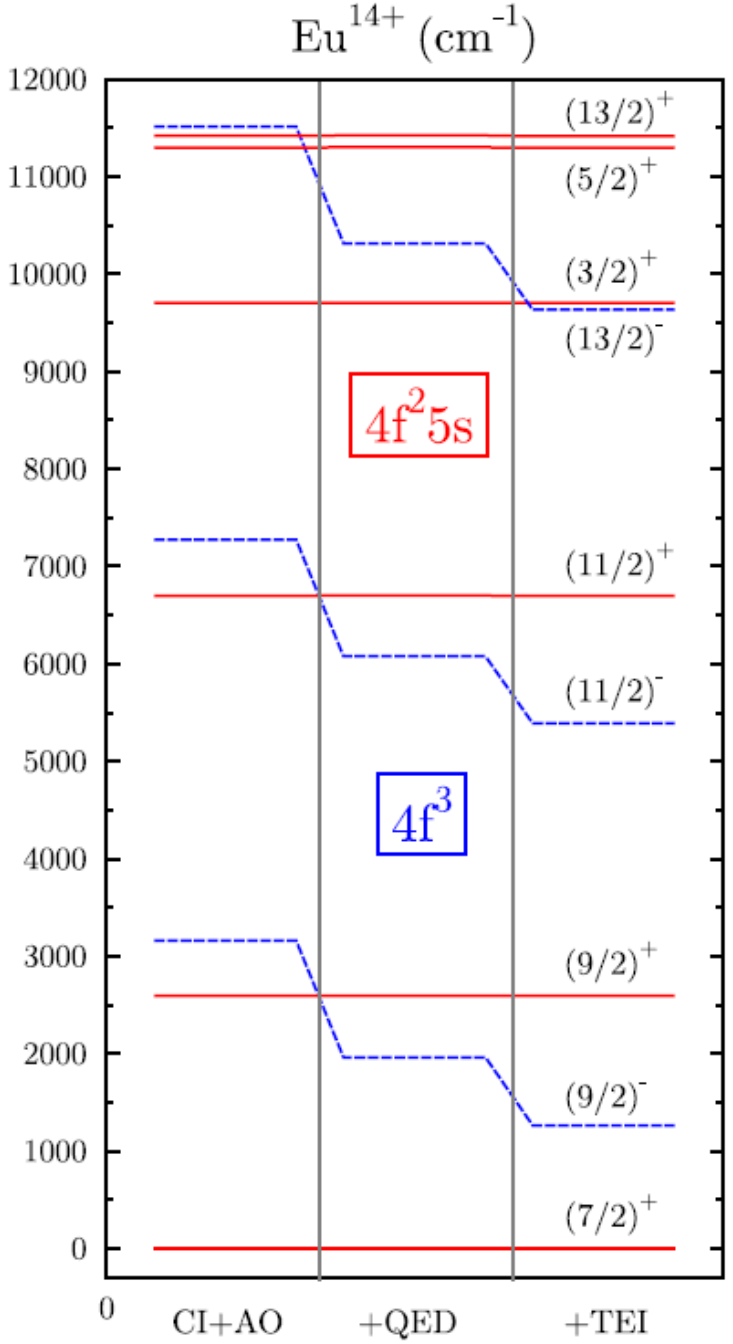
Eu^{14+}:

$4f^2 5s$; $4f^3$; $4f5s^2$

TPI and QED corrections to the spectrum of Eu^{14+}

Ground configuration:

$[1s^2 \ldots\ldots 4d^{10}]\ 4f^2 5s$



Summary A: Advantages

- Applicable to atoms and ions with arbitrary number of closed shells including superheavy elements.
- Applicable to polyvalent atoms.
- Computationally relatively inexpensive.
- Allows to calculate large variety of properties, which depends mainly on valence electrons.
- Some high-order MBPT corrections can be included within CI+all-order (CI+AO).

Summary B: Limitations

- Difficult to include high-order MBPT corrections consistently:
  - energy-dependence of the effective Hamiltonian;
  - effective many particle interactions.
- Difficult to use for atoms with too many electrons in the open shells:
  - CI space grows too fast;
  - choice of the mean field
  - The role and the number of the effective many particle interactions grows with N_v.

Conclusions

- CI+MBPT and CI+AO methods are typically an order of magnitude more accurate than valence CI.
- We can calculate different atomic properties and estimate the accuracy of the results. This makes our predictions sufficiently reliable.
- These methods are efficient for atoms and ions with up to 4-5 valence electrons.
- Generally, they can not be used for quantitative tests of fundamental physics.

Collaborators

- Vladimir Dzuba
- Julian Berengut
- Victor Flambaum
- Walter Johnson
- Sergey Porsev
- Marianna Safronova
- Ilya Tupitsyn

- Yurii Demidov, Rayhan Imanbaeva, Elena Konovalova

atoms

an Open Access Journal by MDPI

2020 TRAVEL AWARDS

FOR POSTDOCS AND PHD STUDENTS

Subject Areas

- atomic and molecular properties
- atomic, molecular, and nuclear spectroscopy and collisions
- nuclear energy (fusion and fission), radioactive decay
- quantum theory, applications and foundations
- experimental and theoretical atomic, molecular, and nuclear physics, chemical physics
- the study of atoms, molecules, nuclei and their interactions and constituents (protons, neutrons, and electrons)

Journal Statistics and indexing:

•Founded: 2013 (Volumes: 7)

•(**ESCI** - Web of Science), Scopus (Elsevier), ADS and INSPEC (IET)

EiC: Dr. James F. Babb Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics

Associate Editor: Dr. Hyun-Kyung Chung Department of Physics and Photon Science, Gwangju Institute of Science and Technology

37 EBMs

Travel Award 2020
(500 CHF for Each Person)
Application deadline: 30 November 2019

The editorial team of *Atoms* is inviting applications for a Travel Award for two young investigators to support participation at a conference in 2019. The nominations and applications will be assessed by an Evaluation Committee organized by the *Atoms* Editorial Board.

For more details, please contact atoms@mdpi.com

Atoms (ISSN 2218-2004; CODEN: ATOMC5) is an international, peer-reviewed and cross-disciplinary scholarly journal of scientific studies related to all aspects of the atom published quarterly online by MDPI.
https://www.mdpi.com/journal/atoms

MDPI

Search:

Journals / Atoms

atoms

COVERED BY EMERGING SOURCES CITATION INDEX CLARIVATE ANALYTICS

CITESCORE 1.20 SCOPUS

SJR Scimago Journal & Country Rank

Atoms

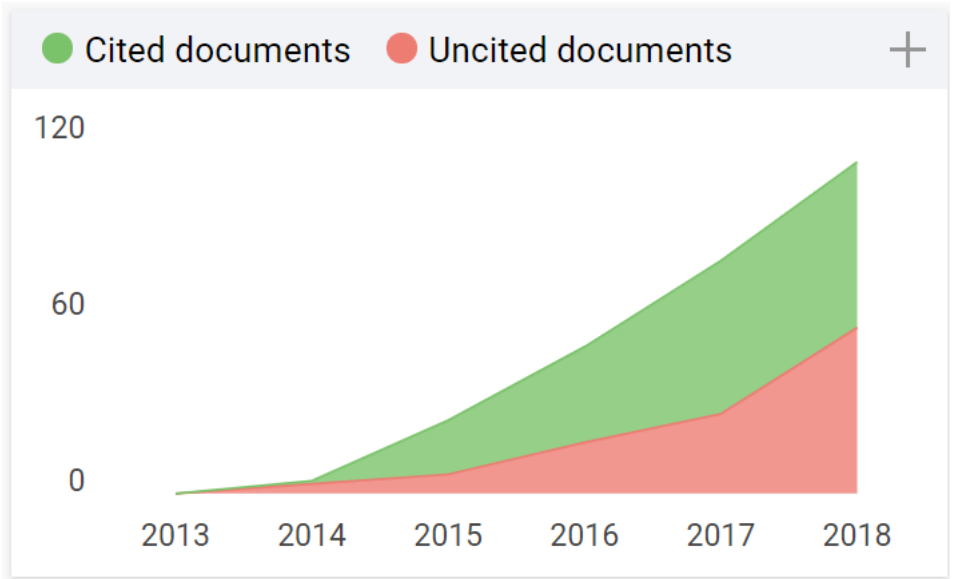
Q3 Atomic and Molecular Physics, and Optics

best quartile

SJR 2018

0.39

powered by scimagojr.com



symmetry

an Open Access Journal by MDPI

IMPACT FACTOR 2.143

Development of New Methods in Atomic and Molecular Theory

Guest Editor

Prof. Mikhail Kozlov

Deadline

31 May 2020

Special Issue

mdpi.com/si/35589

Invitation to submit

Thank you!