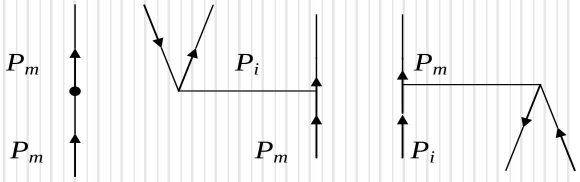
Institute for Nuclear Theory program" Fundamental Physics with Radioactive Molecules" (INT-24-1), INT, Seattle

Benchmark electronic structures calculations and the periodicity law at the edge of Mendeleev's Table

Ephraim Eliav



TEL AVIV UNIVERSITY
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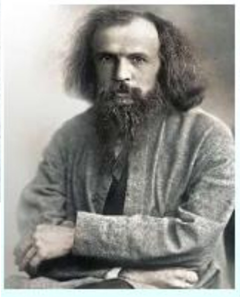


March 28, 2024

Benchmarking. General considerations.

- Benchmark precision for atomic (and molecular) energy spectra and other properties calculations, suitable for modern spectroscopy and "new physics" experiments is less then 0.1% (meVs or less for energy)
- Heavy and super-heavy general open shell (neutral or charged) elements and their compounds could exhibit computational challenges due to:
  1. A very dense (quasi-degenerate) and complicated electronic spectrum.
  2. **Relativistic, QED, nuclear and electron correlation** (dynamic and nondynamic) effects in such systems could be sizeable (non-negligible) , nonadditive and strongly intertwined.
- Benchmark "right for the right reason" treatment of *relativity, QED and correlation*

  1) simultaneously, and on equal footing, by tunable and controllable fashion

  2) efficiently and up to high orders ,"multi-referencely" (in a proper consistent relationship)

  3) size-intensively (proper size-scaling: $E=O(N)$) and

  size-consistently (proper decomposition: $E(A+B)=E(A)+E(B)$; $\Psi(A+B)=\{\Psi(A)\Psi(B)\}$)

Current best framework for relativity treatment

Dirac-Coulomb-Breit Hamiltonian and “no-virtual-pairs approximation” (NVPA)

NO Retardation and NO virtual pairs. Not covariant, correct to α^2; “Mini-Max” SCF; Sucher 1980

$$H^{+}_{DCB}(N)=\sum_{i}^{N} h_D(\mathrm{i}) + \sum_{i<j}^{N} \Lambda_i^{+}\Lambda_j^{+}\left(1/r_{ij}+B_{ij}\right)\Lambda_j^{+}\Lambda_i^{+} - \sum_{i}^{N} U_i$$

where h_d – single electronic Dirac Hamiltonian

$$h_D = c\vec{\alpha}\cdot\vec{p} + (\beta - \mathbf{1}) + V(\vec{r}) + V^{ext}(\vec{r}) + U(\vec{r})$$

Λ_i – projection onto the positive energy-spectrum of h_d

U – SCF ; V – a finite size nuclear potential; V^{ext} - external fields (including QED and nuclear corrections by using model potentials (MP)).

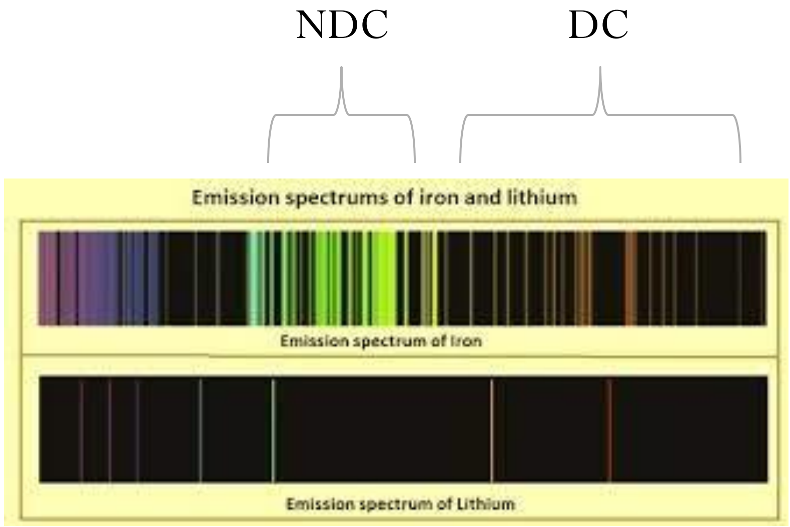
Energy independent Breit interaction, 1932-33

$$B_{12} = -\frac{1}{2r_{12}}\left[\vec{\alpha}_1\bullet\vec{\alpha}_2 + \left(\vec{\alpha}_1\bullet\vec{r}_{12}\right)\left(\vec{\alpha}_2\bullet\vec{r}_{12}\right)/r_{12}^2\right]$$

Nuclear corrections: finite volume, hyper-fine and weak interactions effects by MPs; recoil and nuclear polarization effects by perturbation theory.

Benchmark electronic structure method for heavy open shell systems: the cutting-edge approach

Relativistic size-extensive all order method for dynamic correlation (DC) +
“size-consistently dressed” valence (CAS) CI for non-dynamic correlation (NDC), in particular:
Multi-state multireference coupled cluster (MRCC) approach, based on:
Dirac-Coulomb-Breit Hamiltonian + nuclear and QED corrections
by model potentials (corrected “no-virtual-pairs-approximation”(CNVPA))



Method of choice: multi-state multi-reference approach

- Multi-state approach: $H\Psi^a = E^a \Psi^a$; $a=1,..,d$. d-dimensional target space

  Here: $H = H_0 + V$, where $H_0|\mu\rangle = E^0_\mu|\mu\rangle$

- Multi-reference method: $P^\mu = |\mu\rangle\langle\mu|$; $P = \sum_\mu P^\mu$ - model space ($D \geq d$- dimensional)

  $P=P_m+P_i$ (P_m –main (d-dim); P_i –intermediate); $Q=1-P$ – reciprocal space

- Effective Hamiltonian: $H_{eff}\Psi^a_0 = E^a\Psi^a_0$; $\Psi^a_0 = \sum_\mu C^a_\mu|\mu\rangle$, $a = 1, 2, ..., d$; $|\mu\rangle \in P$

- Wave operator: $\Omega\Psi_0{}^a = \Psi^a$ BLOCH EQUATION (BE): $\boxed{H\Omega = \Omega H_{eff}}$

- Normalization condition
  - Intermediate normalization (INN) $P=P\Omega P \Rightarrow$

    Effective Hamiltonian: $H_{eff}=PH\Omega P$;

    Bloch Equation : $QH\Omega P=Q\Omega PH\Omega P$
  - Isometric normalization (ISN) $P=P\Omega^+\Omega P \Rightarrow$

    Effective Hamiltonian: $H_{eff}=P\,\Omega^+ H\Omega P$ *(suitable for quantum algorithms)*

    Bloch Equation : $QH\Omega P=Q\Omega\, P\Omega^+\, H\Omega P$

Multi-state (Effective or Intermediate Hamiltonian) multi-reference relativistic coupled cluster approaches

1. **Fock-space (FS**) (Lindgren ansatz) : $\Omega=\sum exp\{S_l^{(m,n)}\}P$

   EE, Kaldor (1992); Visscher, EE (2001); Mukherjee, Das et al (2005);

   Approximations to Relativistic "Valence Universal" or FS Coupled Cluster*:*

   - *Relativistic EOM-CC : Sahoo et al (2014); Shee at al (2018)*
   - *Relativistic "all-order-CI" : Safronova, Kozlov, Johnson (2009)*
   - *Relativistic Linear Response CC : Chaudhuri at al(2013)*

2. **Hilbert-space (HS)** (Jeziorski-Monkhorst): $\Omega=\sum\{exp(S_l^{(\mu)})P^{(\mu)}\}$

   EE, Borshevsky, Shamasundar, Pal, Kaldor (2009).

   Approximations to Relativistic "State Universal" or HS Coupled Cluster*:*

   - State selective MRCC: Fleig, Sorensen, Olsen (2007)

   - State specific MRCC: Ghosh, Chaudhuri, Chattopadhyay (2016)

3. **Mixed-sector (MS):** Ω – like in FS, H_{eff} – like in HS

   Landau, EE, Kaldor (2004)

Advantages of Fock-space and Mixed-sectors MRCC

$$\Omega = \exp\{\sum_{n,m}\sum_{l} S_l^{(n,m)}\}P$$

common Fermi vacuum (P – *closed shell single reference state);* and a unique set of excitation operators $S_l^{(n,m)}$ *(n,m) – Fock-space sector with n – holes, m - particles*)

$$H\Omega = \Omega H_{eff} \;\Rightarrow\; \text{CCE: } Q\left[S_l^{(n,m)}, H_0\right]P = Q\left\{V\Omega - \Omega P H_{eff}\right\}_{l,conn}^{(n,m)} P;\;\; H_{eff} = P^{(n,m)}\Omega H P^{(n,m)}$$

- ***FSCC:*** Solved using subsystem embedding condition (SEC) : “sector-by-sector”
- ***Mixed sectors CC (MSCC):*** *solved simultaneously for the (m,n), (m+1,n+1), … (m+k,n+k) sectors (no SEC !) ⇒ RELAXATION in low lying sectors.*

  H_{eff} is non-diagonal relative to FS sectors: $H_{eff}=P^{(k,m)}(H\Omega)_{conn}P^{(k+i,m+i)}$: few sectors, belonging to the same Hilbert-space are coupled and diagonalized simultaneously ⇒ efficient inclusion of non-dynamic correlation

  Quasi-closed configurations ($\mathbf{p}_{1/2}^{2}, \mathbf{d}_{3/2}^{4}, \mathbf{f}_{5/2}^{6}$) could be used as reference **P**.
- *Both Methods: - Symmetry adaptation (JJ or LS) is automatic;*

  - Size-extensivity: is supported separately for core and valence electrons.

  - Intermediate Hamiltonian: Efficient solution of the intruder states problem.

  - Easy implementable on a base of existing single reference CC codes.

Covariant MRCC: Double Fock-space CC

FS: natural framework for development of the correlation methods based on Lagrangians with variable number of particles (QED: ē & ɣ | QCD: N & π); (appropriate tool – covariant-evolution-operator (CEO) method of Lindgren leads to "double" Fock-space approach: $^{[k]}S_l^{(n,m)}$ k- number of uncontracted exchange transverse photons; theory: EE & Uzi Kaldor (2010))

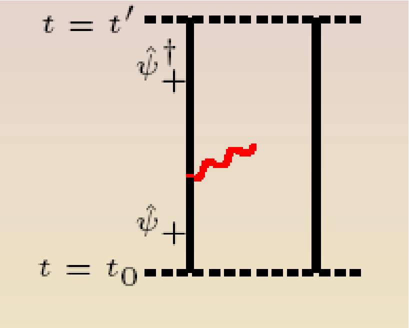
$$^{(0)}S = {}^{(0)}G_Q({}^{(0)}V\,{}^{(0)}\Omega + \overline{{}^{(1)}V\,{}^{(1)}\Omega} + \overline{\overline{{}^{(2)}V\,{}^{(2)}\Omega}} - {}^{(0)}\Omega\,{}^{(0)}H_{eff} - \overline{{}^{(1)}\Omega\ {}^{(1)}H_{eff}} - \overline{\overline{{}^{(2)}\Omega\ {}^{(2)}H_{eff}}})_{conn}P$$

$$^{(1)}S = {}^{(1)}G_Q({}^{(1)}V\,{}^{(0)}\Omega + {}^{(0)}V\,{}^{(1)}\Omega + \overline{{}^{(1)}V\,{}^{(2)}\Omega} + \overline{{}^{(2)}V\,{}^{(1)}\Omega} - {}^{(1)}\Omega\,{}^{(0)}H_{eff} - {}^{(0)}\Omega\ {}^{(1)}H_{eff} - \overline{{}^{(1)}\Omega\ {}^{(2)}H_{eff}} - \overline{{}^{(2)}\Omega\ {}^{(1)}H_{eff}})_{conn}P$$

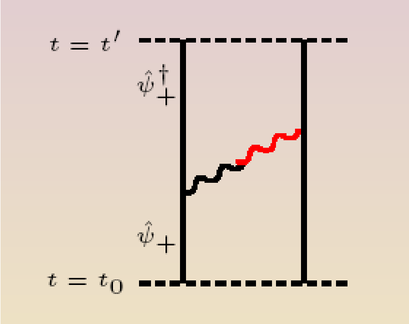
$$^{(2)}S = {}^{(2)}G_Q({}^{(2)}V\,{}^{(0)}\Omega + {}^{(1)}V\,{}^{(1)}\Omega + {}^{(0)}V\,{}^{(2)}\Omega - {}^{(2)}\Omega\,{}^{(0)}H_{eff} - {}^{(1)}\Omega\,{}^{(1)}H_{eff} - {}^{(0)}\Omega\,{}^{(2)}H_{eff})_{conn}P$$

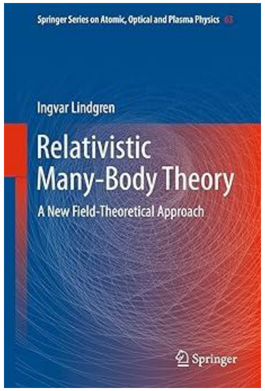
The hook represents integration over the photon momentum ***k*** and summation over the angular momentum ***l***, according to the single- and the double- photon expressions derived from CEO method.

Fock Space:



Hilbert space:





retarded uncontracted virtual photon

The hierarchy of approximations:

- *Using different approximation schemes for the excitation amplitudes calculations (like CCSD(T), popular in the single-reference CC case).*
- *Using **approximate** subsystem embedding condition.*
- *Solution of the Fock-space sectors, belonging only to the particular Hilbert-space (amplitudes from low lying sectors are not iterated; similar to the Hilbert-space CC).*
- *Using the intermediate Hamiltonian (IH) method for solution of the intruder states problem inside different blocks of* H_{eff} *and for the appropriate and balanced approximations of the less important blocks of the* H_{eff}

$P=P_m+P_i \quad Q=Q_m+P_i \qquad P_i \cap Q_i \neq 0$

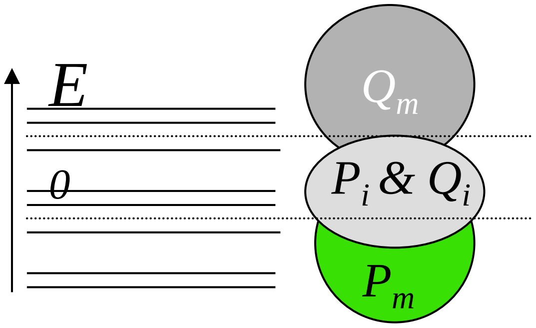
IH: H_I - successful modeling of Q_iSP_i

PIH: $Q_i\,\Omega P_m H\Omega\, P_i = Q_i\, H\Omega\, P_i$

IH-n: PT-n order –based; 0- order: $Q_iSP_i=0$

XIH: $Q_i\,[S,H_0+P_i\Delta]\,P_i = Q_i(H\Omega - \Omega H\Omega)P_i$

a-posteriori extrapolation: $\Delta\to 0$; then $H_I \to H_{eff}$



The recent IH-FSCC developments:

(in collaboration with A. Zaitsevskii)

- **Using incomplete main model space P_m**

  A. Zaitsevskii, N. Mosyagin, A. Oleynichenko, E. Eliav, ArXiv:2208.12296v1 (2022)
- **Particular determinant's (instead of orbital energies) shifts**

  A. Oleynichenko, A. Zaitsevskii, L. Scripnikov, E. Eliav, Symmetry, 12, 1101 (2020)
- **Complex shifts' values**

  A. Zaitsevskii, N. Mosyagin, A. Stolyarov, E. Eliav, PRA, 96,022516 (2017)
- **Pade extrapolation procedure towards zero shift value**

  A. Zaitsevskii, E. Eliav, IJQC, 118(23):e25772 (2018)
- **New form of the Mixed-sector approach for the non-diagonal properties**

  A. Zaitsevskii, A. Oleynichenko, E. Eliav, Symmetry, 12(11):1845, (2020)

Software for low sectors ((k,n), where {k,n}≤2) FS CC

- **Atomic:** FSCCSD, Mix-sectors CCSD(T)
  TRAFS-3C, Tel Aviv atomic computational package
  Tel-Aviv Relativistic Atomic Fock-Space coupled cluster code, written by E.Eliav and U.Kaldor, with contributions from Y. Ishikawa, A. Landau, A. Borschevsky
- **Molecular:** FSCCSD
  DIRAC, a relativistic *ab initio* electronic structure program, release 2024 , written by L. Visscher, H. J. Aa. Jensen, R. Bast, A. S. P. Gomes and T. Saue, with contributions from I. A. Aucar, V. Bakken, J. Brandejs, C. Chibueze, J. Creutzberg, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, T. Helgaker, B. Helmich-Paris, J. Henriksson, M. van Horn, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, N. H. List, H. S. Nataraj, M. K. Nayak, P. Norman, A. Nyvang, M. Olejniczak, J. Olsen, J. M. H. Olsen, A. Papadopoulos, Y. C. Park, J. K. Pedersen, M. Pernpointner, J. V. Pototschnig, R. Di Remigio, M. Repisky, K. Ruud, P. Sałek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. Sunaga, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, S. Yamamoto and X. Yuan (available at http://dx.doi.org/10.5281/zenodo.6010450, see also http://www.diracprogram.org).

High FS sectors: the novel EXP-T program

A. Oleynichenko, A. Zaitsevskii, E. Eliav,
Program Package Communications in Computer and Information Science 1331:375-386 (2020) [http://qchem.pnpi.spb.ru/expt]

Models:

- ✓ CCSD
- ✓ CCSD+T(3)
- ✓ CCSDT-1,2,3
- ✓ CCSDT

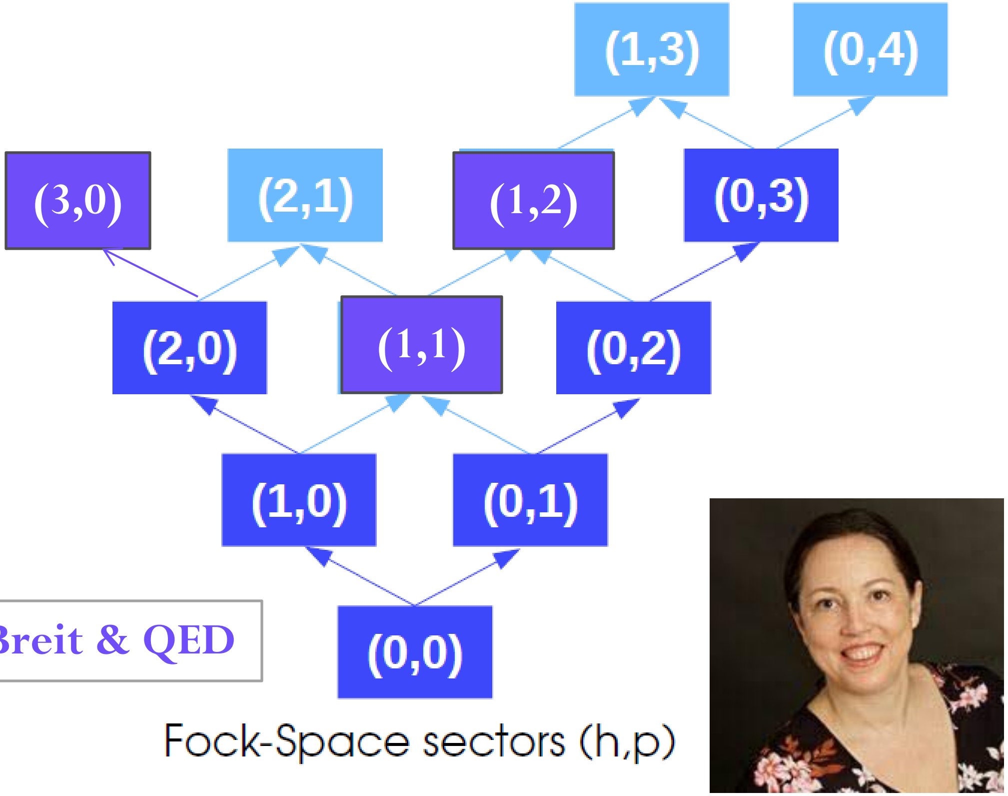
Molecular integrals:

- ✓ DIRAC, OneProp
- ✓ any symmetries and Hamiltonians

GRPP (Titov -Mosyagin) + Breit & QED

Parallelization:

- ✓ OpenMP
- ✓ CUDA



Fock-Space sectors (h,p)

Atomic (radial) version of the EXP-T code is under construction in collaboration with A. Borschevsky

being used

planned

First tests of the FS RCCSDT model

Ionization potentials and excitation energies of Tl and Pb atoms

A. Oleynichenko, A. Zaitsevskii, L. V. Skripnikov, E. Eliav, *Symmetry*, 12(7), 1101 (2020)

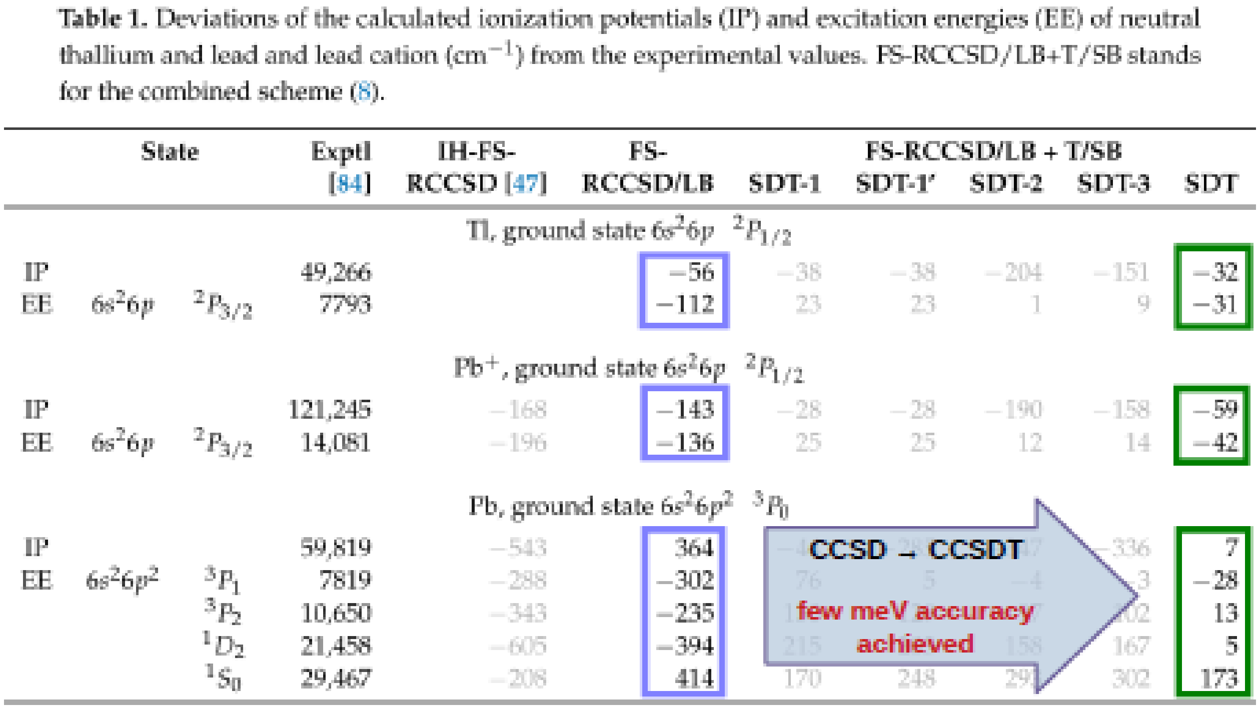


Table 1. Deviations of the calculated ionization potentials (IP) and excitation energies (EE) of neutral thallium and lead and lead cation (cm^{-1}) from the experimental values. FS-RCCSD/LB+T/SB stands for the combined scheme (8).

State			Exptl [84]	IH-FS-RCCSD [47]	FS-RCCSD/LB	FS-RCCSD/LB + T/SB SDT-1	SDT-1′	SDT-2	SDT-3	SDT
Tl, ground state $6s^2 6p$ $^2P_{1/2}$										
IP			49,266		−56	−38	−38	−204	−151	−32
EE	$6s^2 6p$	$^2P_{3/2}$	7793		−112	23	23	1	9	−31
Pb$^+$, ground state $6s^2 6p$ $^2P_{1/2}$										
IP			121,245	−168	−143	−28	−28	−190	−158	−59
EE	$6s^2 6p$	$^2P_{3/2}$	14,081	−196	−136	25	25	12	14	−42
Pb, ground state $6s^2 6p^2$ $^3P_0$										
IP			59,819	−543	364	[illegible]	[illegible]	[illegible]	−336	7
EE	$6s^2 6p^2$	$^3P_1$	7819	−288	−302	76	5	−4	−3	−28
		$^3P_2$	10,650	−343	−235	[illegible]	[illegible]	[illegible]	[illegible]	13
		$^1D_2$	21,458	−605	−394	215	[illegible]	158	167	5
		$^1S_0$	29,467	−208	414	170	248	[illegible]	302	173

CCSD → CCSDT

few meV accuracy achieved

the most precise calculations of non-alkali atoms?

A. Landau, E. Eliav, Y. Ishikawa, U. Kaldor, J. Chem. Phys. 114, 2977 (2001)
J. E. Sansonetti, W. C. Martin, J. Phys. Chem. Ref. Data, 34, 1559 (2005)

Courtesy of A. Oleynichenko, PNPI

Pilot application of the sector (0,3) FSCCSDT

- *Scripnikov, et al, PRC, 104, 034316 (2021)*: **Bi atom *p^3* states**

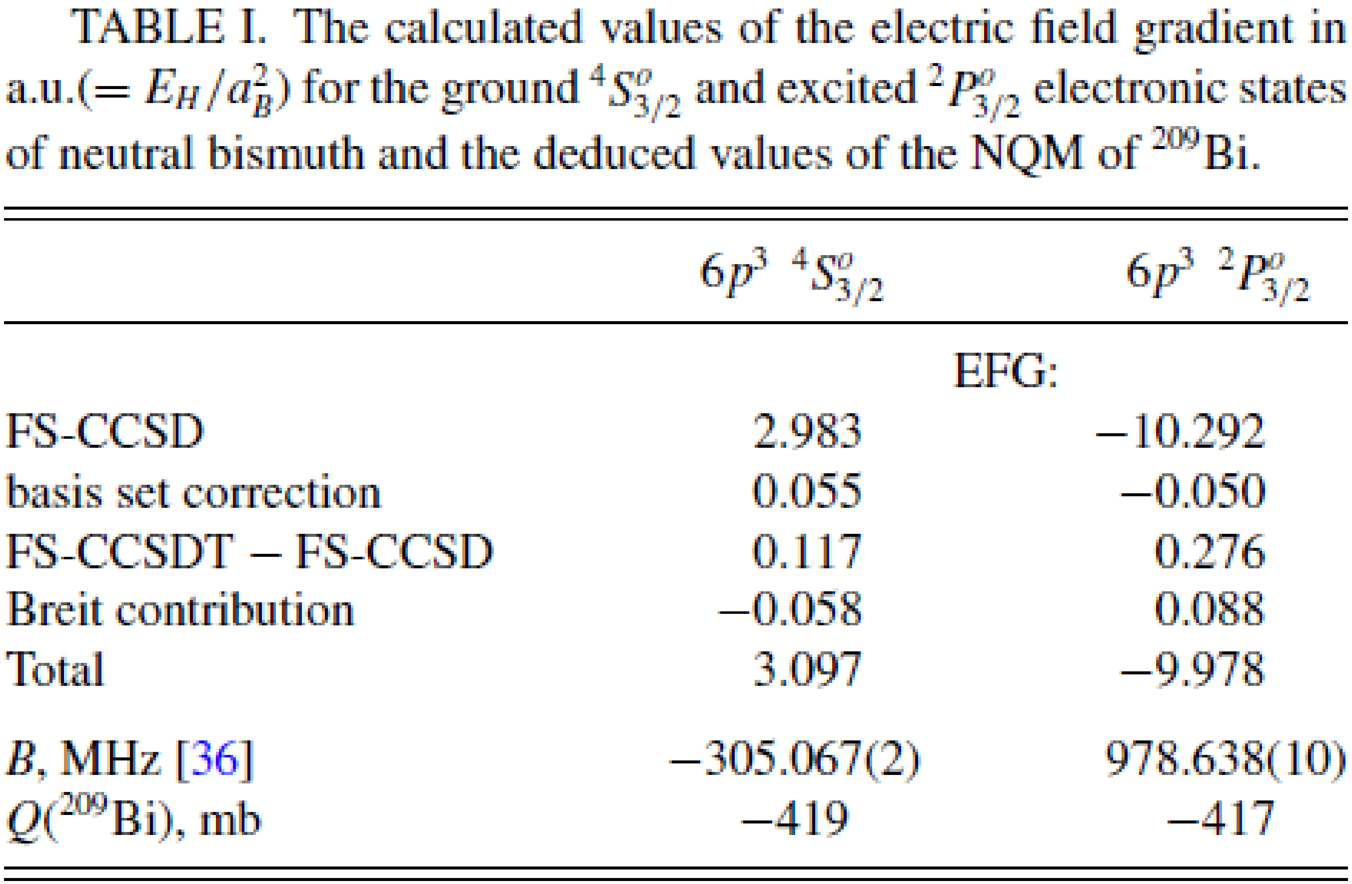


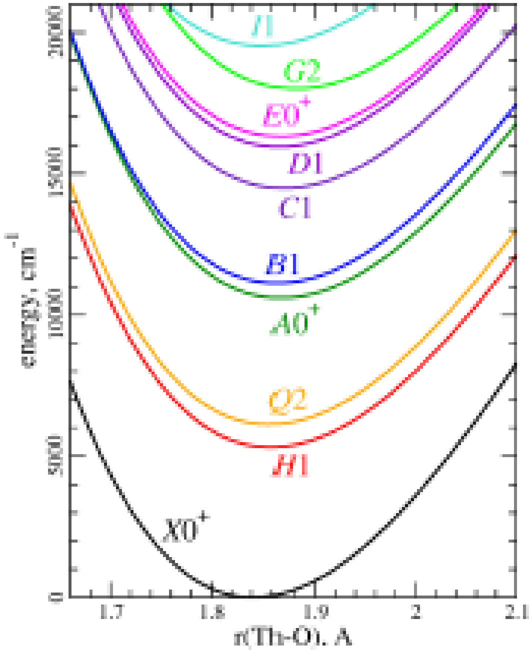
TABLE I. The calculated values of the electric field gradient in a.u.(= E_H/a_B^2) for the ground $^4S^o_{3/2}$ and excited $^2P^o_{3/2}$ electronic states of neutral bismuth and the deduced values of the NQM of ^{209}Bi.

	$6p^3\ ^4S^o_{3/2}$	$6p^3\ ^2P^o_{3/2}$
	EFG:	
FS-CCSD	2.983	−10.292
basis set correction	0.055	−0.050
FS-CCSDT − FS-CCSD	0.117	0.276
Breit contribution	−0.058	0.088
Total	3.097	−9.978
B, MHz [36]	−305.067(2)	978.638(10)
$Q(^{209}\text{Bi})$, mb	−419	−417

- Molecular results : ***-420(8)*** *[Teodoro et al(2013)],* ***-415*** *[Shee et al(2016)]*
- Muonic atoms : ***-320(26)*** *[Lee et al(1972)],* ***-500(80)*** *[Raghavan (1989]*

Electronic states of the diatomic ThO molecule

Potential energy curves and excitation energies



	deviation from experimental T_e, cm^{-1}		
	RPP/IH-IMMS[1]	DC/IH-CMMS[2]	
	0h2p	0h2p	1h1p
H(i)1	104	700	-149
Q(i)2	97	738	-62
A(ii)0+	242	691	1098
B(ii)1	302	927	–
C(iii)1	424	1698	-39
D(iv)1	440	1698	–
E(iii)0+	312	960	-1950
G(iv)2	165	–	–
F(iv)0+	431	–	–
I(vi)1	367	–	–

- Relativistic Hamiltonian: GRPP accounting for Breit and QED
- Ground state calculations: single-reference coupled cluster CCSD(T)
- Excited states: Fock space coupled cluster FS-CCSD

[1] A. Zaitsevskii, A. V. Oleynichenko, E. Eliav, *Mol. Phys.*, e2236246 (2023);

[2] P. Tecmer, C. E. González-Espinoza, *Phys. Chem. Chem. Phys.* 20, 23424 (2018)

Courtesy of A. Oleynichenko, PNPI

GRPP: summary

- Deviation from the 4-component Dirac-Coulomb-Gaunt model:

		GRPP	semilocal	DC	Ret.+QED
ThO	max abs	46	335	802	212
	rms	29	181	341	151
UO_2	max abs	110	345	767	142
	rms	51	128	316	112

- the error of GRPP is balanced for all electronic states
- the Dirac-Coulomb Hamiltonian is inherently less accurate than even a semi-local potential
- contributions of retardation and QED effects are greater than the error of GRPP
- our future: pseudopotentials accounting for QED

GRPP seems to be the most precise Hamiltonian for real-life molecular calculations?

Applications to SHEs (Z > 100) with experimentally known properties (“atom-at-time” technique)

nature

THE INTERNATIONAL WEEKLY JOURNAL OF SCIENCE

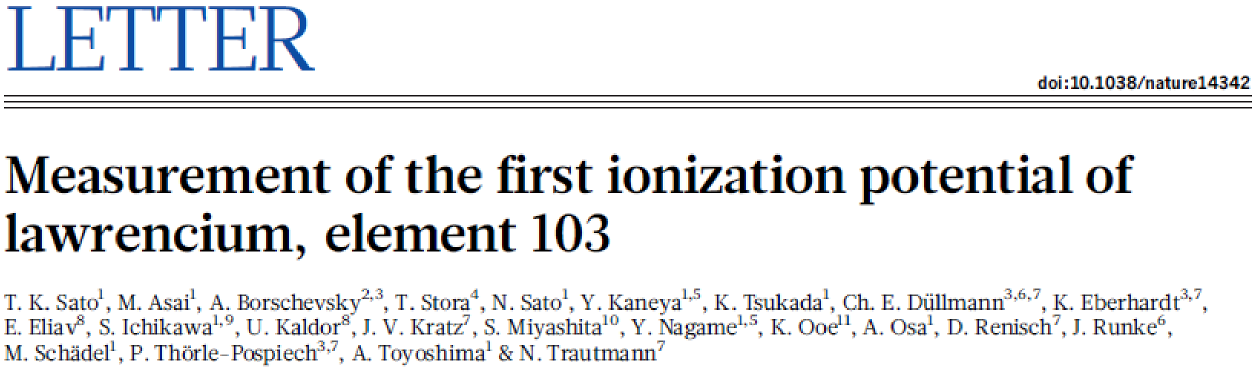
EXTREME CHEMISTRY

Experiments on rare lawrencium atoms illuminate a relativistic region of the periodic table PAGES 166 & 209

POSTDOC OF THE FUTURE
Why permadocs must become superdocs

BIOLOGY BY THE NUMBERS
Data analysis is undervalued in the life sciences

COLD COMFORT
Green-house gas release may be slow but prolonged



LETTER

doi:10.1038/nature14342

Measurement of the first ionization potential of lawrencium, element 103

T. K. Sato[1], M. Asai[1], A. Borschevsky[2,3], T. Stora[4], N. Sato[1], Y. Kaneya[1,5], K. Tsukada[1], Ch. E. Düllmann[3,6,7], K. Eberhardt[3,7], E. Eliav[8], S. Ichikawa[1,9], U. Kaldor[8], J. V. Kratz[7], S. Miyashita[10], Y. Nagame[1,5], K. Ooe[11], A. Osa[1], D. Renisch[7], J. Runke[6], M. Schädel[1], P. Thörle-Pospiech[3,7], A. Toyoshima[1] & N. Trautmann[7]

The first ever measured IP for superheavy (Z> 100) element, produced by "atom-at-time" technology. The GS of Lr has been confirmed to be $7s^2p_{1/2}$

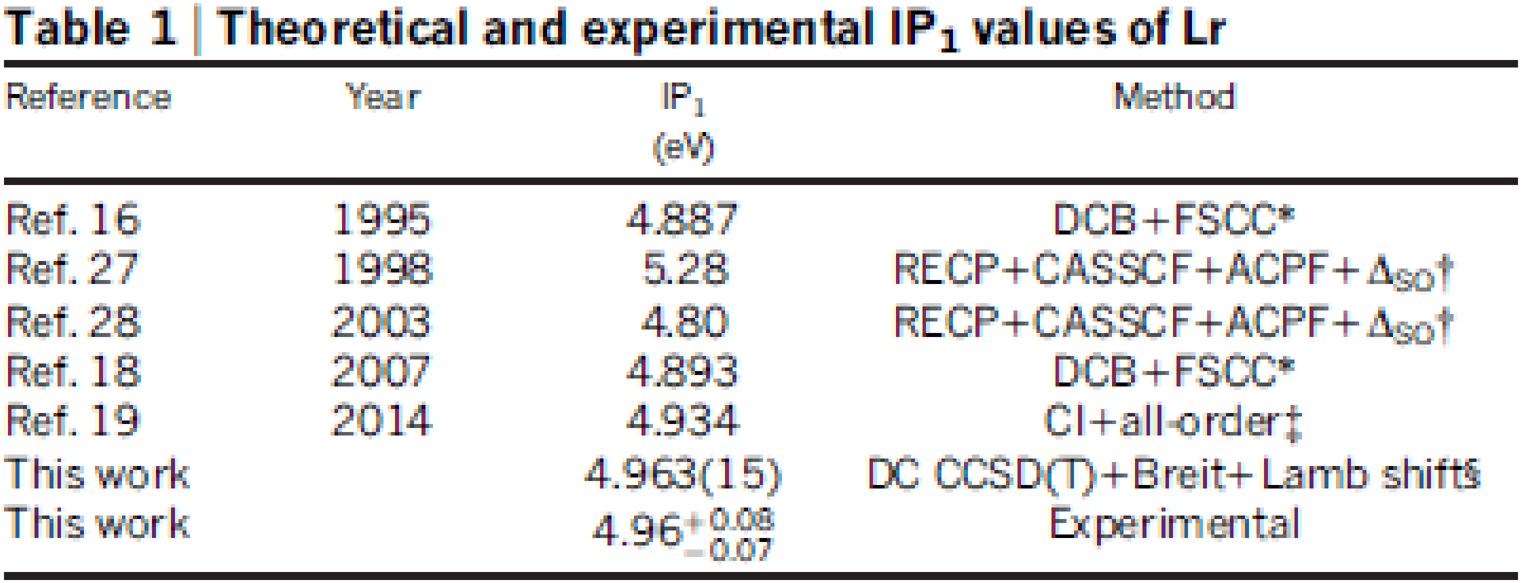


Table 1 | Theoretical and experimental IP_1 values of Lr

Reference	Year	IP_1 (eV)	Method
Ref. 16	1995	4.887	DCB+FSCC*
Ref. 27	1998	5.28	RECP+CASSCF+ACPF+Δ_{SO}†
Ref. 28	2003	4.80	RECP+CASSCF+ACPF+Δ_{SO}†
Ref. 18	2007	4.893	DCB+FSCC*
Ref. 19	2014	4.934	CI+all-order‡
This work		4.963(15)	DC CCSD(T)+Breit+Lamb shift§
This work		$4.96^{+0.08}_{-0.07}$	Experimental

Predicted spectrum of atomic No

Borschevsky, A., EE, Kaldor U., *et al*, *Phys. Rev. A* 75 (2007), 042514

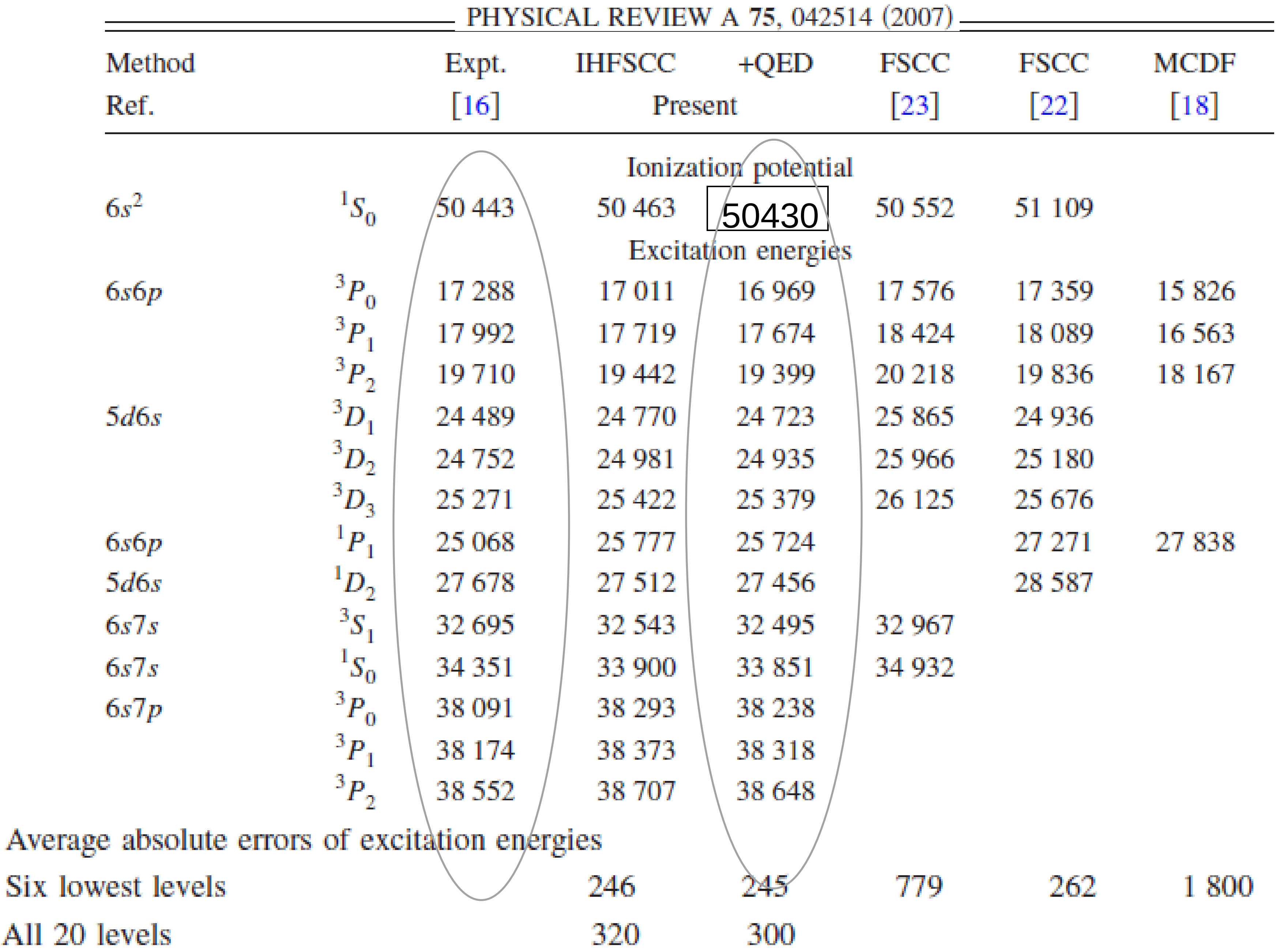
State	**IHFSCC**	**+QED**	**Experiment**
$5f^{14}7s^2$ $^1S_0$ (IP), ev	6.646	6.635	6.63±0.08⁽¹⁾, 6.635 ±0.030⁽²⁾
$5f^{14}7s7p$ $^3P_0$ (EE), cm^{-1}	19028	18879	
$5f^{14}7s7p$ $^3P_1$	20605	20454	
$5f^{14}7s7p$ $^3P_2$	25527	25374	
$5f^{14}7s7p$ $^1P_1$	30224	30056	29961⁽²⁾
$5f^{14}7s6d$ $^3D_1$	28496	28338	
$5f^{14}7s6d$ $^3D_2$	28935	28778	
$5f^{14}7s6d$ $^3D_3$	30040	29897	
$5f^{14}7s6d$ $^1D_2$	33071	32892	

Experiments on atomic No spectra measurements (“atom-at-time” technology)

(1) JAEA labs; [an efficient surface ion-source and a radioisotope detection system coupled to amass separator], T.Sato et al., JACS, 140, 14609, 2018

(2) GSI, [Laser resonance ionization spectr.], M. Laatiaoui, et al, Nature 538, 495, 2016

Calculated spectra of Yb atom (cm^{-1})



PHYSICAL REVIEW A 75, 042514 (2007)

Method		Expt.	IHFSCC	+QED	FSCC	FSCC	MCDF
Ref.		[16]	Present		[23]	[22]	[18]
			Ionization potential				
$6s^2$	$^1S_0$	50 443	50 463	50430	50 552	51 109	
			Excitation energies				
$6s6p$	$^3P_0$	17 288	17 011	16 969	17 576	17 359	15 826
	$^3P_1$	17 992	17 719	17 674	18 424	18 089	16 563
	$^3P_2$	19 710	19 442	19 399	20 218	19 836	18 167
$5d6s$	$^3D_1$	24 489	24 770	24 723	25 865	24 936	
	$^3D_2$	24 752	24 981	24 935	25 966	25 180	
	$^3D_3$	25 271	25 422	25 379	26 125	25 676	
$6s6p$	$^1P_1$	25 068	25 777	25 724		27 271	27 838
$5d6s$	$^1D_2$	27 678	27 512	27 456		28 587	
$6s7s$	$^3S_1$	32 695	32 543	32 495	32 967		
$6s7s$	$^1S_0$	34 351	33 900	33 851	34 932		
$6s7p$	$^3P_0$	38 091	38 293	38 238			
	$^3P_1$	38 174	38 373	38 318			
	$^3P_2$	38 552	38 707	38 648			
Average absolute errors of excitation energies							
Six lowest levels			246	245	779	262	1 800
All 20 levels			320	300			

Applications to SHEs with experimentally unknown properties.

Theoretical predictions of extended Periodic Table.

Ea of Oganesson: recent developments

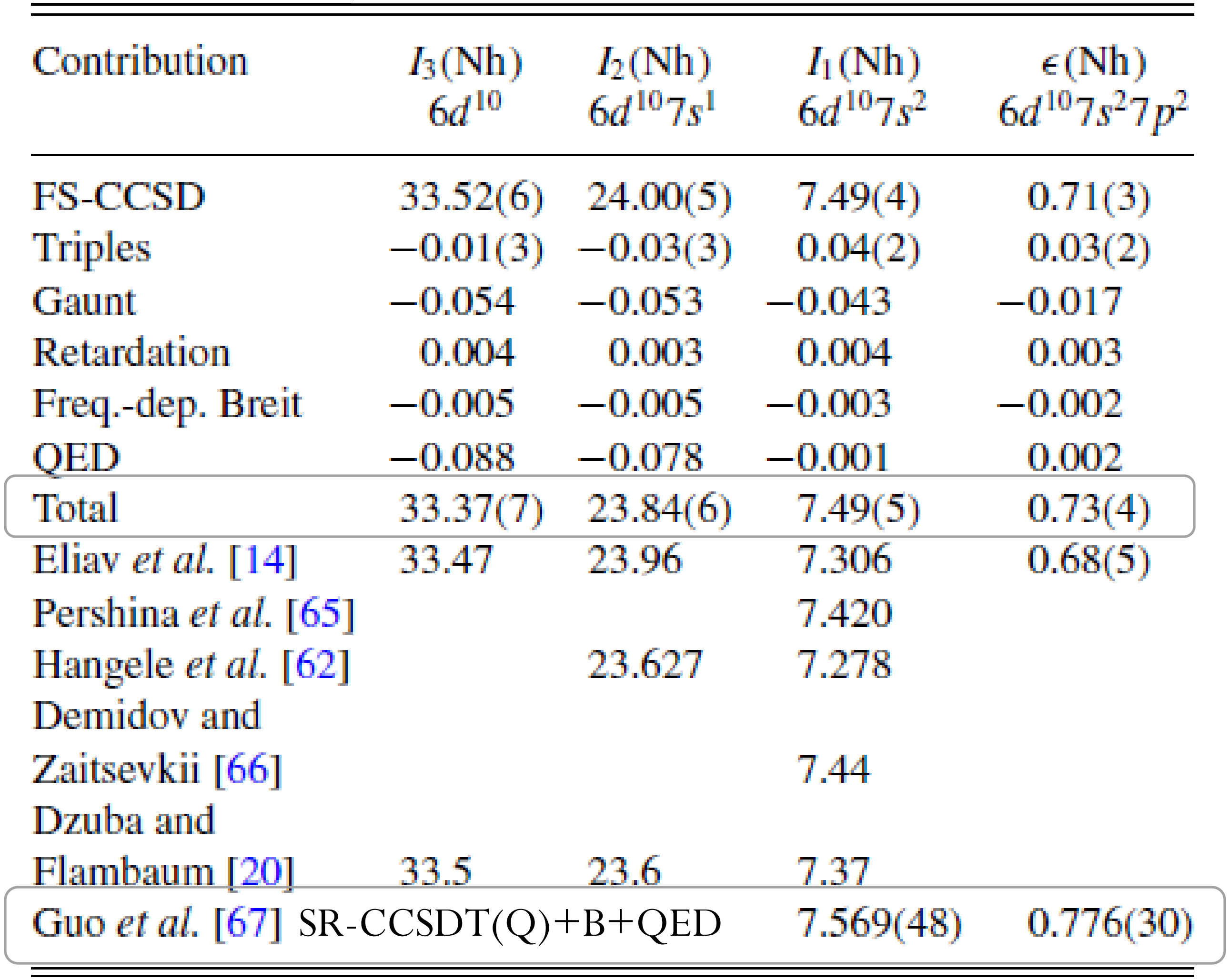
EA is the consequence of a tiny interplay between relativity and electron correlation. Nonrelativistic or uncorrelated calculations give no electron affinity for Oganesson. QED contribution large (about 3-5%)

Reference	Method	EA, eV
Eliav, et al, PRL, 77,5350 (**1996**)	FSCCSD+Breit	0.056(10)
Goidenko, et al, PRA,67,020102 (**2003**)	FSCCSD+Breit+QED	0.058(3)
Lackenby, et al,PRA, 98, 042512 (**2018**)	CI+MBPT (+Breit?+QED?)	0.096
Guo, et al, ACQ,83,107(**2021**)	SR-CCSDT(Q)+Breit+QED	0.080(5)
Kaygorodov, et al,PRA,104,012819(**2021**)	FSCCSDT+Breit(ω)+QED	0.076(4)

IPs and EA of Nh: *Kaygorodov, et al, PRA,105,062805 (2022)*

- FSCC scheme:

$$\mathrm{Nh}^{3+}(2h0p) \leftarrow \mathrm{Nh}^{2+}(1h0p) \leftarrow \mathrm{Nh}^{+}(0h0p) \rightarrow \\ \rightarrow \mathrm{Nh}(0h1p) \rightarrow \mathrm{Nh}^{-}(0h2p),$$



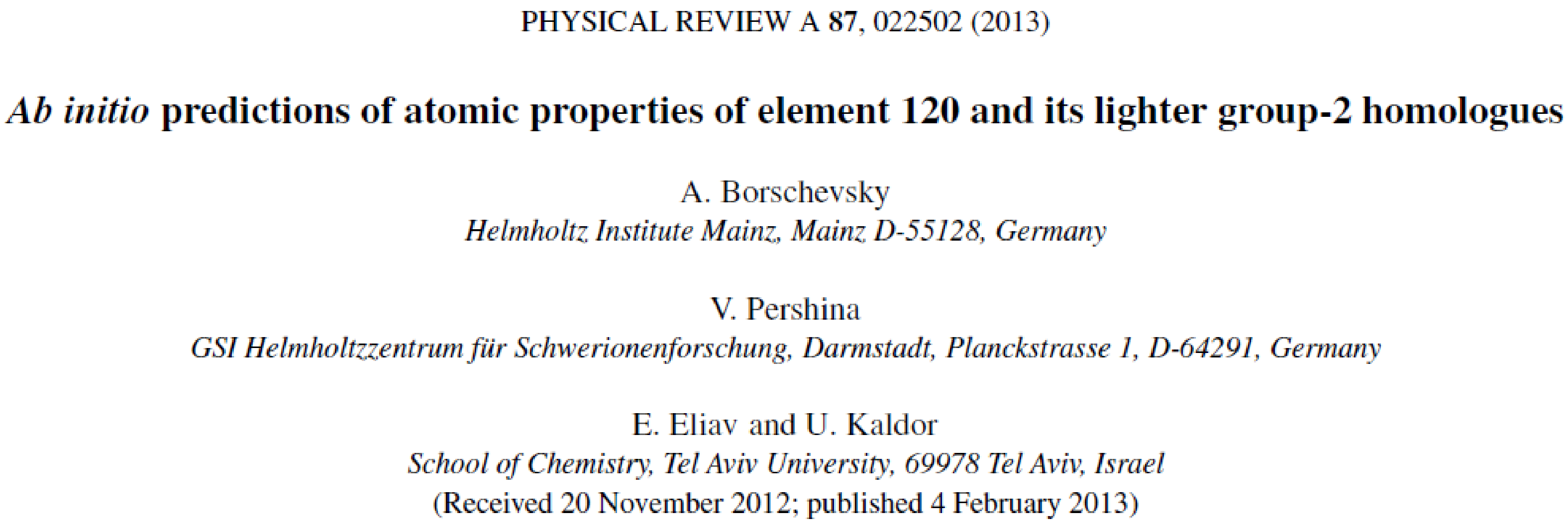
Contribution	I_3(Nh) $6d^{10}$	I_2(Nh) $6d^{10}7s^1$	I_1(Nh) $6d^{10}7s^2$	ϵ(Nh) $6d^{10}7s^27p^2$
FS-CCSD	33.52(6)	24.00(5)	7.49(4)	0.71(3)
Triples	−0.01(3)	−0.03(3)	0.04(2)	0.03(2)
Gaunt	−0.054	−0.053	−0.043	−0.017
Retardation	0.004	0.003	0.004	0.003
Freq.-dep. Breit	−0.005	−0.005	−0.003	−0.002
QED	−0.088	−0.078	−0.001	0.002
Total	33.37(7)	23.84(6)	7.49(5)	0.73(4)
Eliav *et al.* [14]	33.47	23.96	7.306	0.68(5)
Pershina *et al.* [65]			7.420	
Hangele *et al.* [62]		23.627	7.278	
Demidov and Zaitsevkii [66]			7.44	
Dzuba and Flambaum [20]	33.5	23.6	7.37	
Guo *et al.* [67] SR-CCSDT(Q)+B+QED			7.569(48)	0.776(30)

Spectra of Ra and element E120

cm^{-1}		Ra		E120 [cm^{-1}]
		IHFSCC	**Exp.**	**IHFSCC**
IP		42608	42573	47191
nsnp	$^3P_0$	13093	13078	15648
	$^3P_1$	14017	13999	17587
	$^3P_2$	16675	16689	25192
	$^1P_1$	20792	20716	27513
(*n*-1)*dns*	$^3D_1$	13827	13716	22903
	$^3D_2$	14021	13994	23034
	$^3D_3$	14839	14707	23782
	$^1D_2$	17159	17081	27247
ns*(*n*+1)*s	$^3S_1$	26762	26754	30862
ΔE		**139**		

Spectra of Ra and element E120

cm^{-1}		Ra		E120 [cm^{-1}]
		IHFSCC	**Exp.**	**IHFSCC**
IP		42608	42573	47191
nsnp	$^3P_0$	13093	13078	15648
	$^3P_1$	14017	13999	17587
	$^3P_2$	16675	16689	25192



PHYSICAL REVIEW A **87**, 022502 (2013)

Ab initio predictions of atomic properties of element 120 and its lighter group-2 homologues

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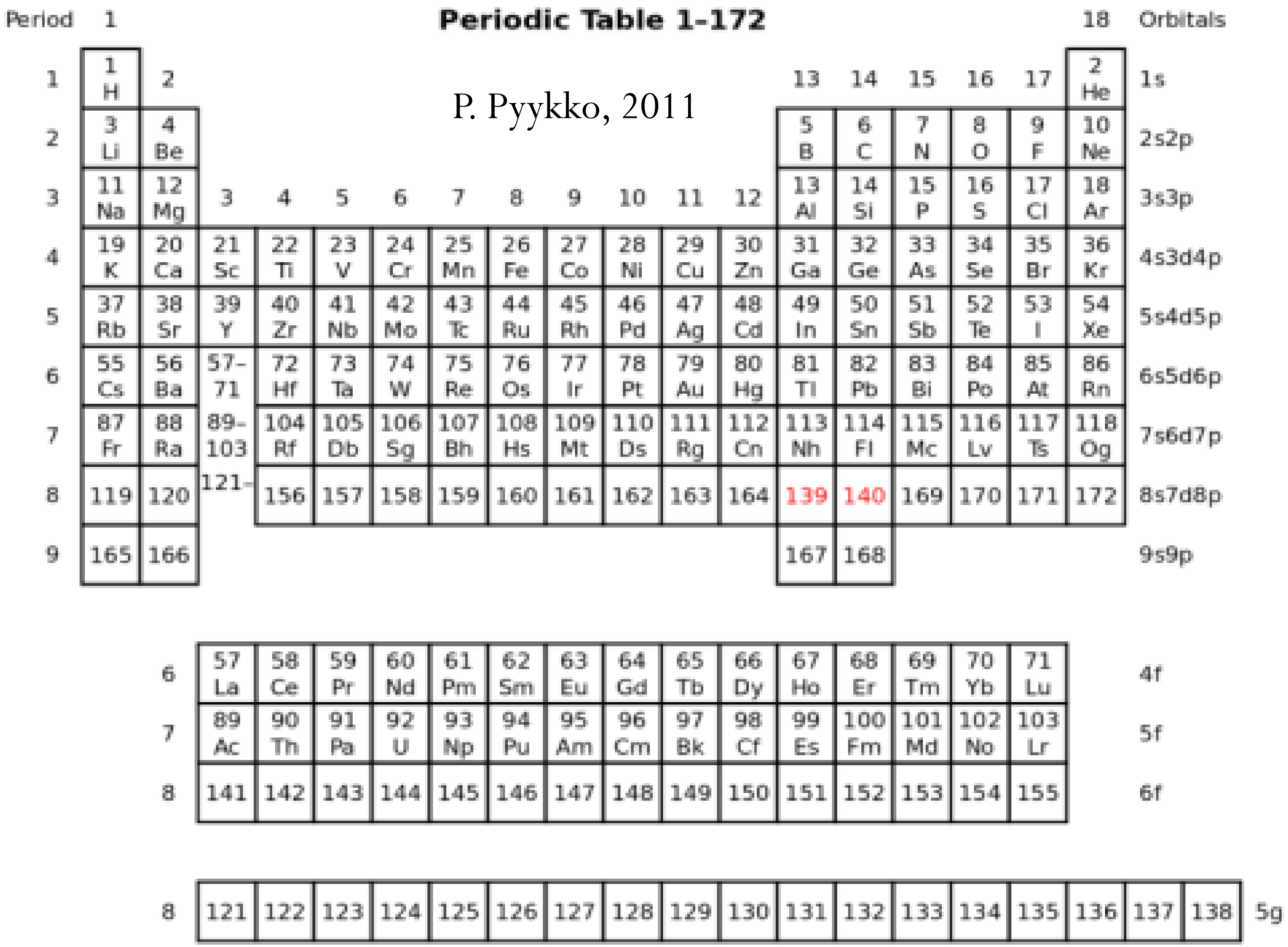
(Received 20 November 2012; published 4 February 2013)

The recent decade most referenced extended PTE

P. Pyykko, 2011



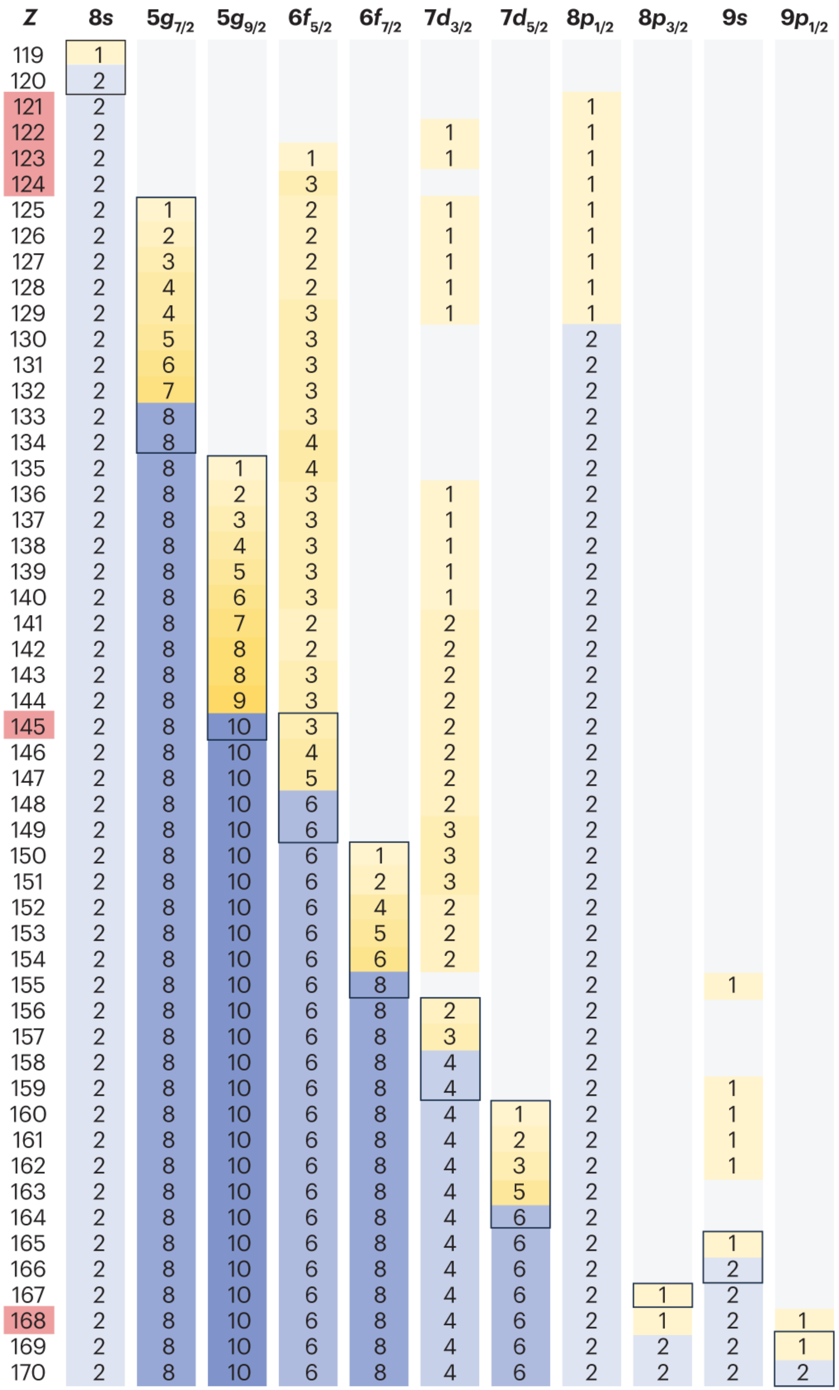
Periodic Table 1-172

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Orbitals
1	1 H																	2 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p
6	55 Cs	56 Ba	57– 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p
7	87 Fr	88 Ra	89– 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	7s6d7p
8	119	120	121–	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p
9	165	166											167	168					9s9p

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g

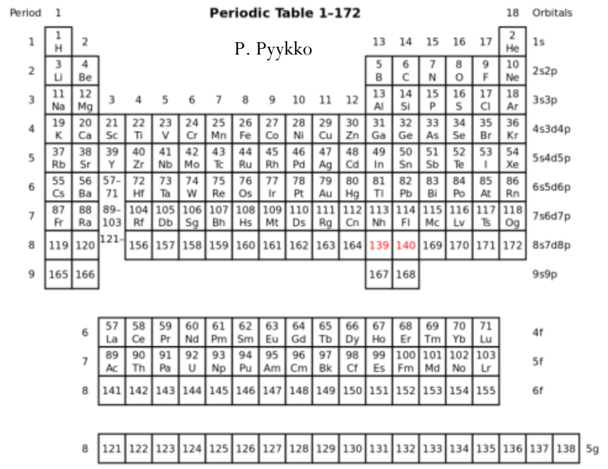
Ground state configuration of SHEs (Z>119): systematic study of the electron-correlation (DC &NDC), Breit, and QED effects.



Z	8s	$5g_{7/2}$	$5g_{9/2}$	$6f_{5/2}$	$6f_{7/2}$	$7d_{3/2}$	$7d_{5/2}$	$8p_{1/2}$	$8p_{3/2}$	9s	$9p_{1/2}$
119	1										
120	2										
121	2							1			
122	2					1		1			
123	2			1		1		1			
124	2			3				1			
125	2	1		2		1		1			
126	2	2		2		1		1			
127	2	3		2		1		1			
128	2	4		2		1		1			
129	2	4		3		1		1			
130	2	5		3				2			
131	2	6		3				2			
132	2	7		3				2			
133	2	8		3				2			
134	2	8		4				2			
135	2	8	1	4				2			
136	2	8	2	3		1		2			
137	2	8	3	3		1		2			
138	2	8	4	3		1		2			
139	2	8	5	3		1		2			
140	2	8	6	3		1		2			
141	2	8	7	2		2		2			
142	2	8	8	2		2		2			
143	2	8	8	3		2		2			
144	2	8	9	3		2		2			
145	2	8	10	3		2		2			
146	2	8	10	4		2		2			
147	2	8	10	5		2		2			
148	2	8	10	6		2		2			
149	2	8	10	6		3		2			
150	2	8	10	6	1	3		2			
151	2	8	10	6	2	3		2			
152	2	8	10	6	4	2		2			
153	2	8	10	6	5	2		2			
154	2	8	10	6	6	2		2			
155	2	8	10	6	8			2		1	
156	2	8	10	6	8	2		2			
157	2	8	10	6	8	3		2			
158	2	8	10	6	8	4		2			
159	2	8	10	6	8	4		2		1	
160	2	8	10	6	8	4	1	2		1	
161	2	8	10	6	8	4	2	2		1	
162	2	8	10	6	8	4	3	2		1	
163	2	8	10	6	8	4	5	2			
164	2	8	10	6	8	4	6	2			
165	2	8	10	6	8	4	6	2		1	
166	2	8	10	6	8	4	6	2		2	
167	2	8	10	6	8	4	6	2	1	2	
168	2	8	10	6	8	4	6	2	1	2	1
169	2	8	10	6	8	4	6	2	2	2	1
170	2	8	10	6	8	4	6	2	2	2	2

- DCBQ – CI approach: NDC – good, but DC – relatively poor; non-size-extensive *Savelyev I.M. Kaygorodov M.Y., Kozhedub Y.S., Malyshev A.V., Tupitsyn, I.I., Shabaev V.M, PRA, 107, 042803, 2023*
- Occupied shells – by blue; partially filled – by yellow; bold borders – around symmetry blocks. The red boxes - elements, which cannot be placed unambiguously in the PTE (based on DCBQ-CI2 from *Smits, O.R., Düllmann, C.E., Indelicato, P. Nazarewicz W, Schwerdtfeger P., The quest for superheavy elements and the limit of the periodic table. Nature Rev Phys (2023)*)

Breakdown of periodicity in the PTE (Smith, et. Al.) , based on DCBQ-CI2 (Savelyev, et. Al.)



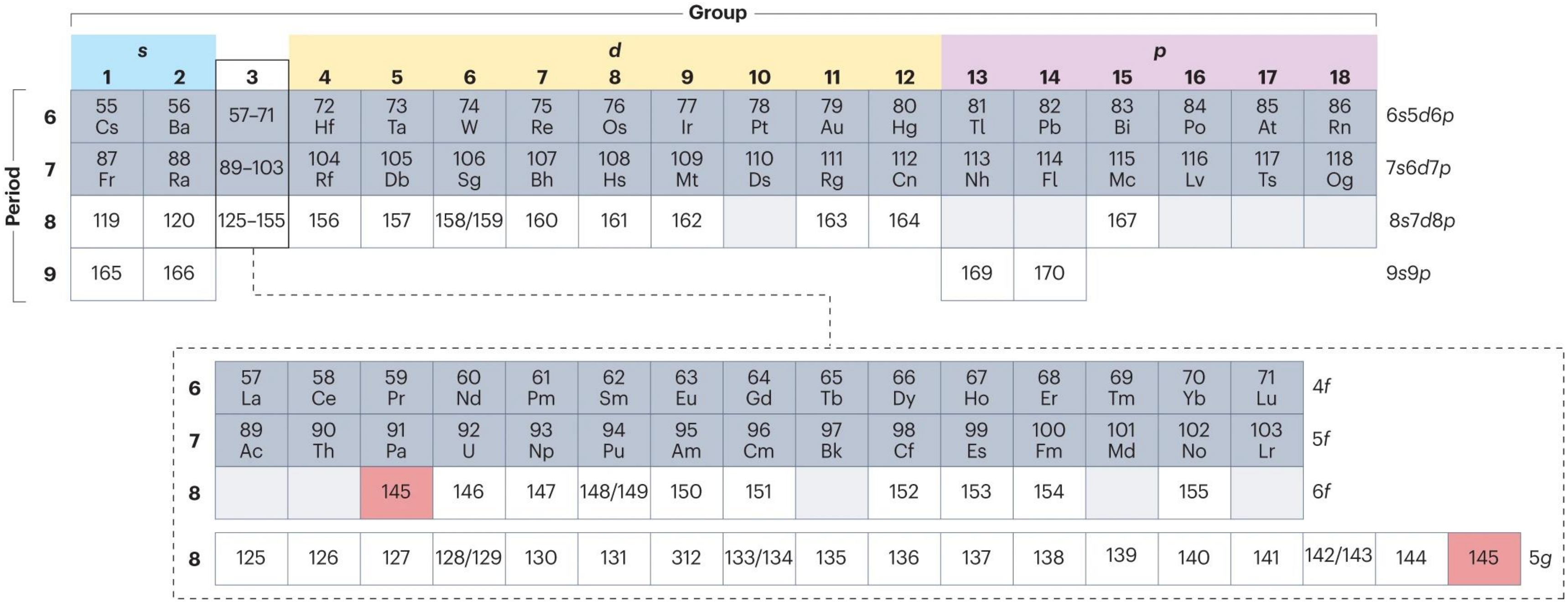
Periodic Table 1-172

P. Pyykko

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Orbitals
1	1 H																	2 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p
6	55 Cs	56 Ba	57- 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p
7	87 Fr	88 Ra	89- 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	7s6d7p
8	119	120	121-	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p
9	165	166											167	168					9s9p

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g



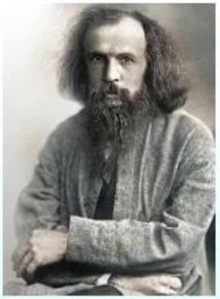
		Group																	
	s			d									p						
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
6	55 Cs	56 Ba	57–71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p
7	87 Fr	88 Ra	89–103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	7s6d7p
8	119	120	125–155	156	157	158/159	160	161	162		163	164			167				8s7d8p
9	165	166											169	170					9s9p

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8			145	146	147	148/149	150	151		152	153	154		155		6f

8	125	126	127	128/129	130	131	312	133/134	135	136	137	138	139	140	141	142/143	144	145	5g

- Z = 145 is placed twice.
- Z = 121, 122, 123, 124 and 168 cannot be placed unambiguously.
- 8th period: a few entries are doubly occupied, whereas others remain vacant.

Extended Periodic Table of Elements & the 8th *p* – block structure

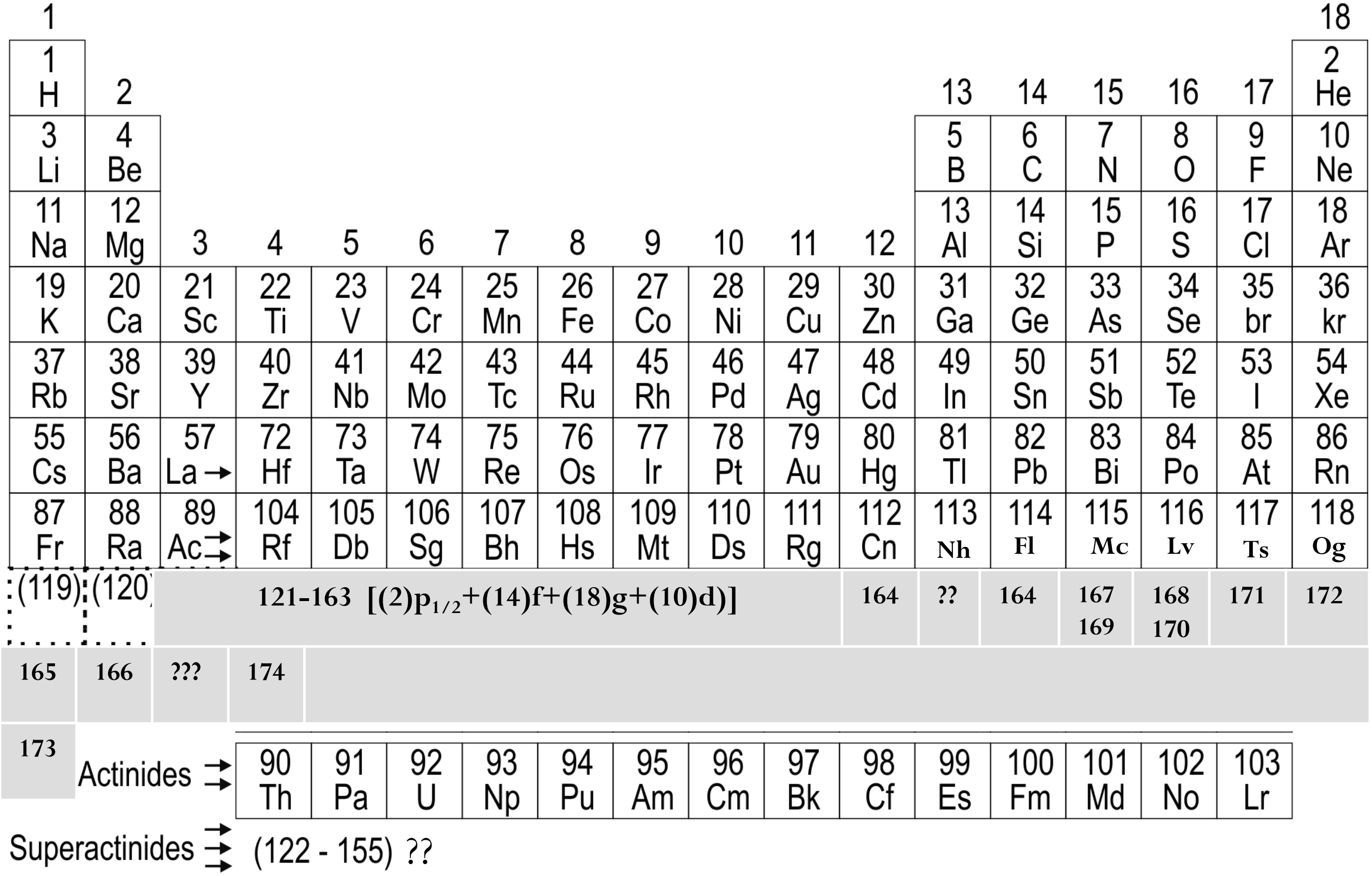


H	2											13	14	15	16	17	He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 br	36 kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La →	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac ⇉	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**
Fricke		156 ...									164	167	168	169	170	171	172
Seaborg		154 ...									162	163	164	165	166	167	168
Pyykkö		156 ...									164	**139** **167**	**140** **168**	**169** **- 9th period**	**170**	**171**	**172**
Smith		156 …									164	**???** **169**	**???** **170**	**167** **- 9th period**	**???**	**???**	**???**

IH-FSCC electronic configurations and properties of SHE with 164 ≤ Z ≤ 174 (unpublished)

Z	Configuration	Possible group	Period	Properties (eV)	
				IP	EA
164	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2$	12, 14	8	7.513	0.071
165	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s$	1	9	5.652	0.987
166	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2$	2	9	7.345	0.518
167	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2 8p_{3/2}$	15	8	6.639	1.290
168	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2 8p_{3/2}^2$	16	8	8.055	
169	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2 9p_{1/2}^2 8p_{3/2}$	15	8	8.968	2.518
170	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2 9p_{1/2}^2 8p_{3/2}^2$	16	8	9.975	
171	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p_{1/2}^2 9s^2 9p_{1/2}^2 8p_{3/2}^3$	17	8	10.917	3.922
172	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p^6\ 9s^2 9p_{1/2}^2$	18	8	11.967	<0
173	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p^6 9s^2 9p_{1/2}^2 10s$	1	10	3.070	0.478
174	$[\mathrm{Og}]8s^2 5g^{18} 6f^{14} 7d^{10} 8p^6 9s^2 9p_{1/2}^2 10s 8d$	4	9	3.614	

Possible variant of 8th p-block of EPT (unpublished)



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 br	36 kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La →	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac ⇉	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
(119)	(120)	121-163 [(2)$p_{1/2}$+(14)f+(18)g+(10)d)]									164	??	164	167 169	168 170	171	172
165	166	???	174														
173	Actinides ⇉		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
Superactinides ⇉			(122 - 155) ??														

Closed shell GS configurations:

E164, E165^{+}, E166^{2+} ([Og]$8s^{2}5g^{18}6f^{14}7d^{10}8p_{1/2}^{2}$)

E166, E167^{+}, E168^{2+} ([Og]$8s^{2}5g^{18}6f^{14}7d^{10}8p_{1/2}^{2}9s^{2}$)

E172, E171^{-}, E173^{+}, E174^{2+} ([Og]$8s^{2}5g^{18}6f^{14}7d^{10}8p^{6}9p_{1/2}^{2}9s^{2}$)

Closed shell lower lying ES configurations:

E168 ([Og]$8s^{2}5g^{18}6f^{14}7d^{10}8p^{6}$)

E170 ([Og]$8s^{2}5g^{18}6f^{14}7d^{10}8p^{6}9s^{2}$)

Conclusions

- FS-RCC is powerful and flexible computational approaches suitable for precise calculation of properties of heavy and SHE open shell systems.
- Excellent agreement with experiment where data are available and reliable predictions of spectra and other properties.
- Successful collaborations with experiment
- The periodic Table concept on it's SHE edge should be changed and reformulated:
  - Simple Madelung rules do not work!
  - JJ coupling instead of LS should be used. Many super-actinides SHEs will have combinations of multiple LS-configurations with compatible weighs.
  - The "one-to-one" relationship: single LS configuration shell corresponds to single cell of Periodic Table does not work! (multiply filled and empty cells could exist).
  - Jumps to the next period and back could happen.
  - End of Periodic Table:
    - ***Nuclear stability perspective:*** minimal time of isotope survival 10^{-14} sec needed for element formation could limit $Z<170$
    - Atomic structure stability perspective: elements with $Z > 173$ (supercritical atoms) will be still stable