



HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

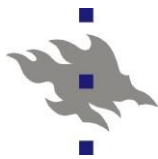
47 Years in Research: Farewell Lecture, 29 October, 2009

Pekka Pyykkö, Department of Chemistry, University of Helsinki.



Muminpappan skriver sina memoarer





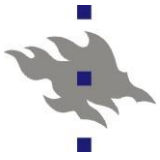
- Family background in Carelia. Two 'Pyykkö' mentioned in Gustav Vasa's tax rolls in 1553-54. Family farm occupied ca. 1740 by Heikki Ristonpoika (Henrik Kristianson) Pyykkö (1678-1754).
- P. P. born at Hinnerjoki in SW Finland 12 October, 1941. Moves to Turku 1945.
- 1951-59 Turku Latin School (Turun klassillinen lyseo).
- Reads Physics, Chemistry and Math at the University of Turku 1959-67. Some teachers V. Hovi and O. V. Lounasmaa in Physics, K. Inkeri and A. Salomaa in Mathematics. Chemistry OK, too. *Teaching at UTu good.*
- Autumn 1962 enters the NMR group of Mauri Luukkala at Wihuri Physical Laboratory. 1965 attends Löwdin's summer school in "Quantum Chemistry" in Sweden. Immediate entry to the international centre of the area.
- Ph. D. genealogy: PP 1967 → V. Hovi 1948 → N. Fontell 1931 → J. A. Wasastjerna 1920 → L. W. Öholm 1907 → S. Arrhenius 1884.
Students of PP 7th generation, since Svante Arrhenius.

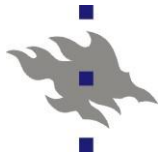


How did the NMR group get started?

- Pekka Jauho writes an article on Nuclear Magnetic Resonance in *Arkhimedes* (1) 30-41 (1955).
- Mauri Luukkala reads the article, knows electronics, contacts Prof. Hovi. Wihuri Foundation pays the magnet. The rest is built locally. After the machine works, Luukkala and Lasse Niemelä visit Leiden and Oxford to see other NMR machines.
- Later group members Matti Punkkinen, PP, Erkki Soini.
- After Ph. D., ML goes to ultrasonics and Applied Physics, Pyykkö to Chemistry. LN and MP stay in NMR. ES moves to Wallac Oy.
- Ammonium and deuterioammonium salts, their phase transitions mentioned to PP by Hovi. Luukkala works on ultrasonically induced nuclear quadrupole transitions. PP starts to work on deuteron quadrupole coupling constants.
- Working style: **Spontaneous activity in self-organizing groups**. Obviously, someone has to pay.

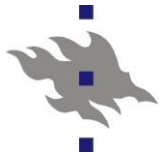
The NMR machine ca. 1963





Prof. Mauri Luukkala, 14 December 2001 (farewell)

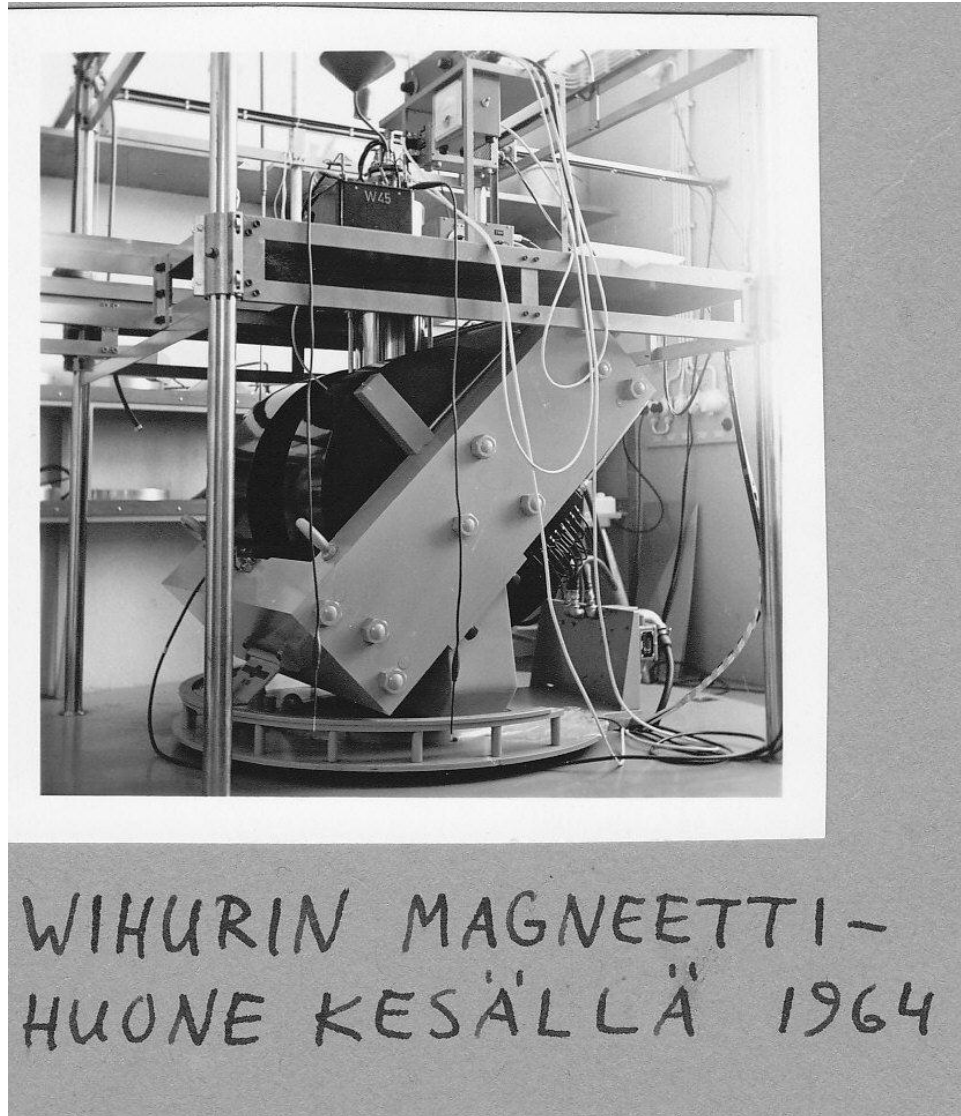




Ph. D. ceremony, 1 June 1967



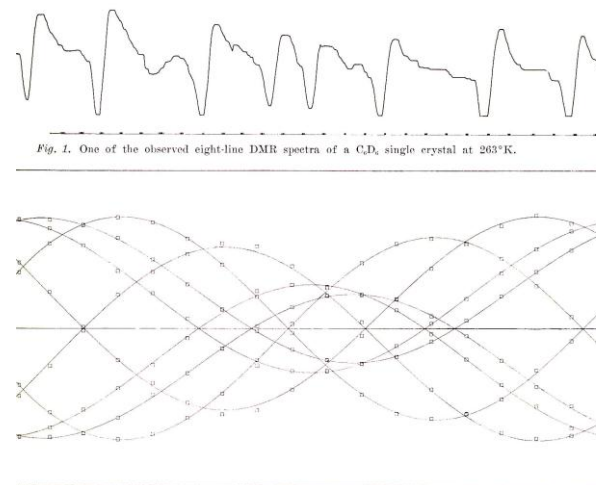
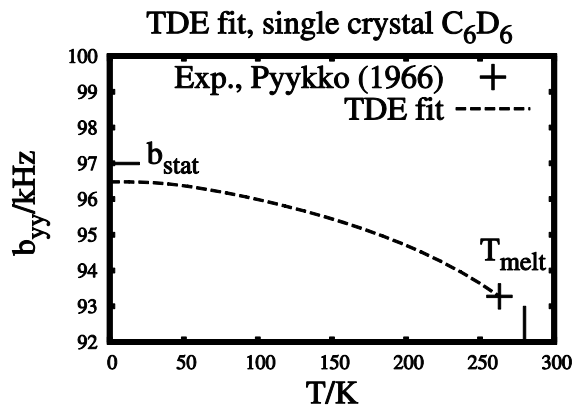
The rotating Varian magnet





The 1966 Measurement on C_6D_6 Single Crystals

- [6] P. Pyykkö, U. Lähteenmäki, Ann. Univ. Turku, Ser. A I , No. 93, (1966). Chem. Abstr. 66, 120609q.
 - This measurement has never been repeated. Other data exist on the DQCC.
 - [270] P. Pyykkö, F. Elmi, PCCP 10 (2008) 3867: A 'temperature-dependent Einstein model' ($\omega = \omega(T)$) for the librations gives true intramolecular DQCC.
 - **Results should be published in best possible journals, not hidden in second- or third-rate journals.** Could have been learned a little earlier.
- Beware of 'open-access'.**





1968-1973: Early work on theory of NMR parameters

- **NORDITA scholar with Jan Linderberg at Theoretical Chemistry, Aarhus 1968-69.**
- **'Nordisk docentstipendiat' at Göteborg 1969-70.**
- **Senior Research Scientist at TFT in Helsinki 1970-71. Attends a course by G. Thomas (former undergraduate student of Feynman) on Relativistic Quantum Mechanics in Fall 1970.**
- **Realizes the importance of relativistic effects on valence-shell magnetic hyperfine effects. Generalizes an earlier expression of Breit (1930) in**
[18] P. Pyykkö, E. Pajanne, Phys. Lett. 35A (1971) 53; Errata 38A, 218.
Effects big and not generally known to NMR spectroscopists.
- **M. Inokuti (Argonne) points out one error [22], informs PP of Jean-Paul Desclaux, CEA, France. 1972 JPD visits Helsinki.**
- **January 1972 – July 1974: Associate Professor at Jyväskylä.**

- Jan Linderberg's three first postdocs, 40 years later in
- December 2008. Theoretical Chemistry at Aarhus.
-

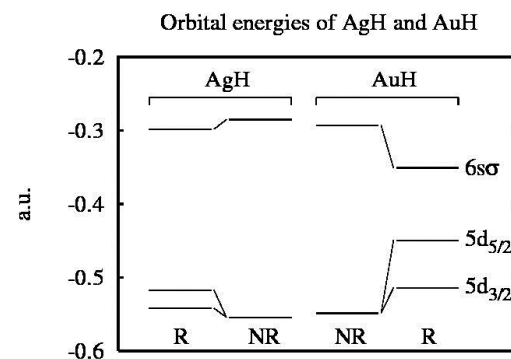
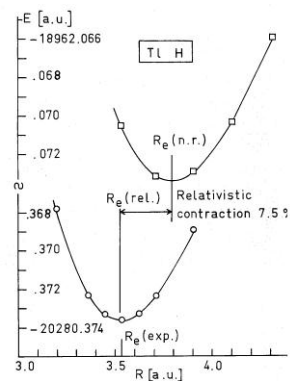


Mark Ratner, (Mary Jo Ondrechen), JL, Josef Michl, PP



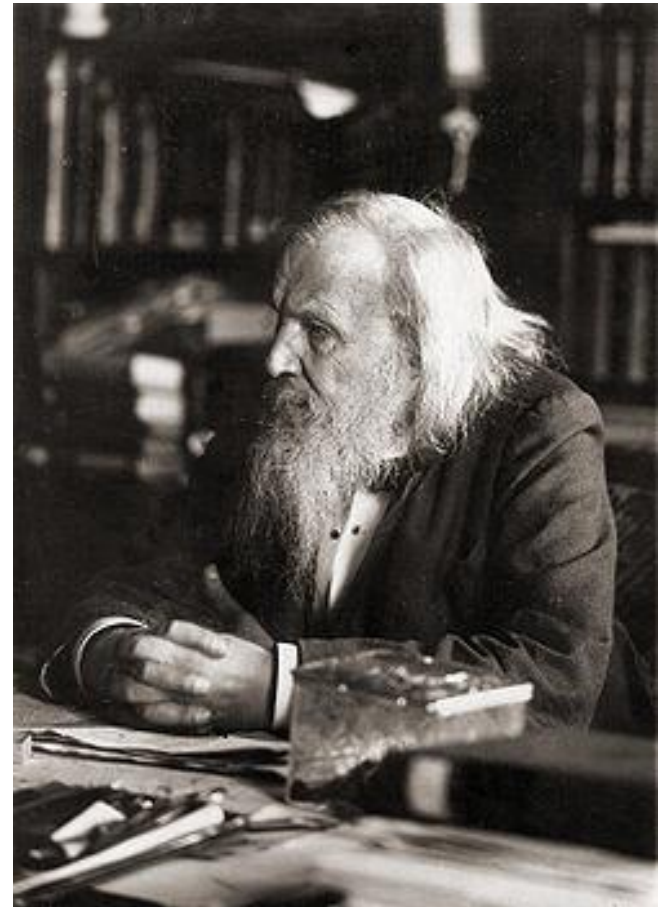
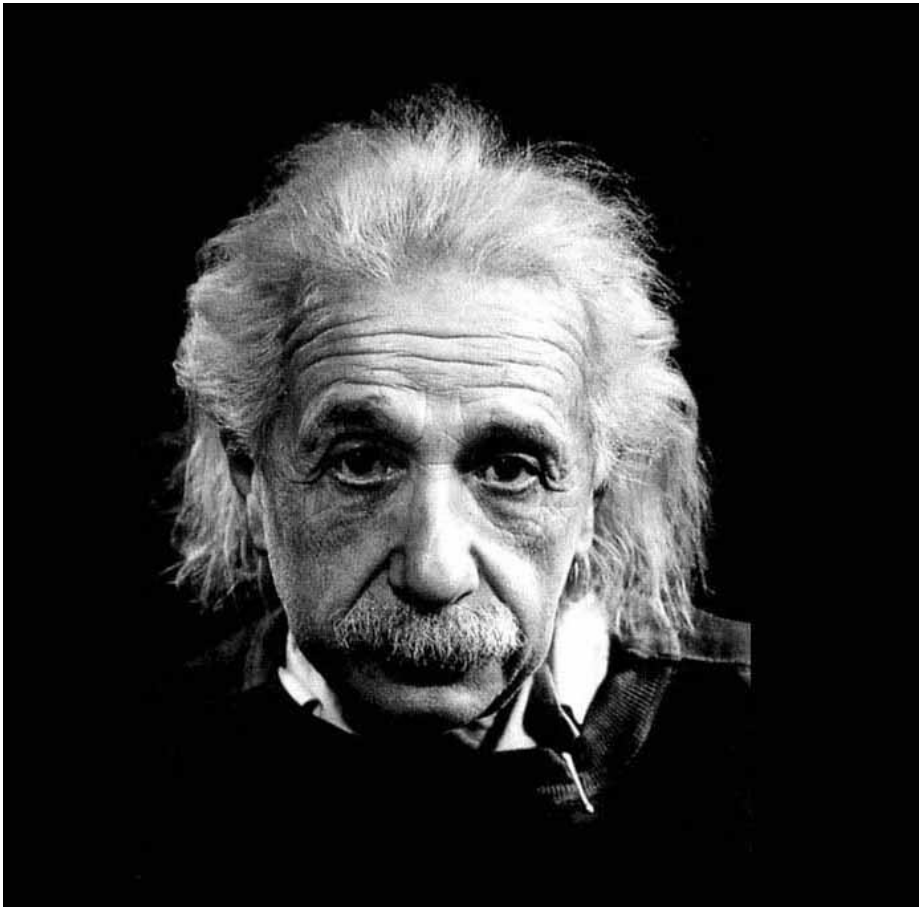
1973-81: Collaboration with Jean-Paul Desclaux

- 1973 (Jan-Aug): PP in Paris (Orsay), initiates collaboration with JPD. Aim: Generalize the Desclaux atomic code to molecules using one-centre expansions. Full Dirac equation, full exchange potential used. High-level numerical methods for radial functions.
- Fall 1973, Spring 1974, Summer 1974: Work continued in Oulu, Jyväskylä and Åbo Akademi. August 1974: Method works!
- First paper discovers the relativistic contraction of bond lengths: [28] J. P. Desclaux, P. Pyykkö, Chem. Phys. Lett. 29 (1974) 534.
- Second paper finds that the chemical difference between silver and gold comes from relativity: [36] J. P. Desclaux, P. Pyykkö, Chem. Phys. Lett. 39 (1976) 300.





Albert Einstein's special relativity coupled to Dmitrii Mendeleev's Periodic System !





■ 1974-84: Associate Professor of QC at ÅA

- Department of Physical Chemistry, established by Per Ekwall; current Professor was Ingvar Danielsson. ÅA has excellent reputation in Chemistry. First position in Quantum Chemistry in Finland. Instant adaption.
- Some students Matti Hotokka, Leif Laaksonen, Dage Sundholm (TkL), Hannu T. Toivonen (M.Sc., Techn.).
- Desclaux collaboration continues. Review [51] 'Relativity and the Periodic System', Acc. Chem. Res. 12 (1979) 276. **Sells relativity to the chemists.**
- The Relativistic Extended Hückel (REX) model created with Lawrence L. Lohr (U Mich), [49]... Applied on NMR with Laurent Wiesenfeld [64], Notker Rösch [95, 102] and others. A. Görling's first paper [102]. München.
- Double group tables. Relativistic theories for NMR J , σ sketched.
- Symposium REQC-82 (satellite to ICQC in Uppsala).
- The fully numerical '2D' code for diatomics developed with Leif Laaksonen and Dage Sundholm [77] (1983)... Back to nuclear quadrupole effects [88] (1984) ... [284] (2009). **International standard values of Q.**



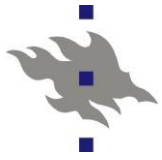
'My' computers

- 1965: Wegematic 1000 (Alwac III-E). First commercially manufactured university computer in Finland. Obtained to TY/ÅA by K. V. Laurikainen.
- IBM 1620 at Turku.
- IBM 1130 at Turku.
- CDC at Uppsala.
- ...
- 1973- : **UNIVAC 1108 at 'CSC'** .
- Later supercomputers at CSC. Latest 'Louhi' (Cray XT4/XT5) and 'Murska' (HP CP4000).



Dr. and Mrs. Desclaux, Ruissalo 1974





Ian Grant at Tavastgatan 30





Per Stenius, Ingvar Danielsson etc.

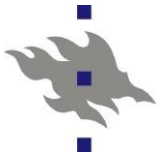




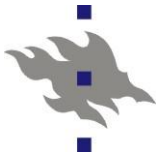
Den finlandssvenska sångkulturen



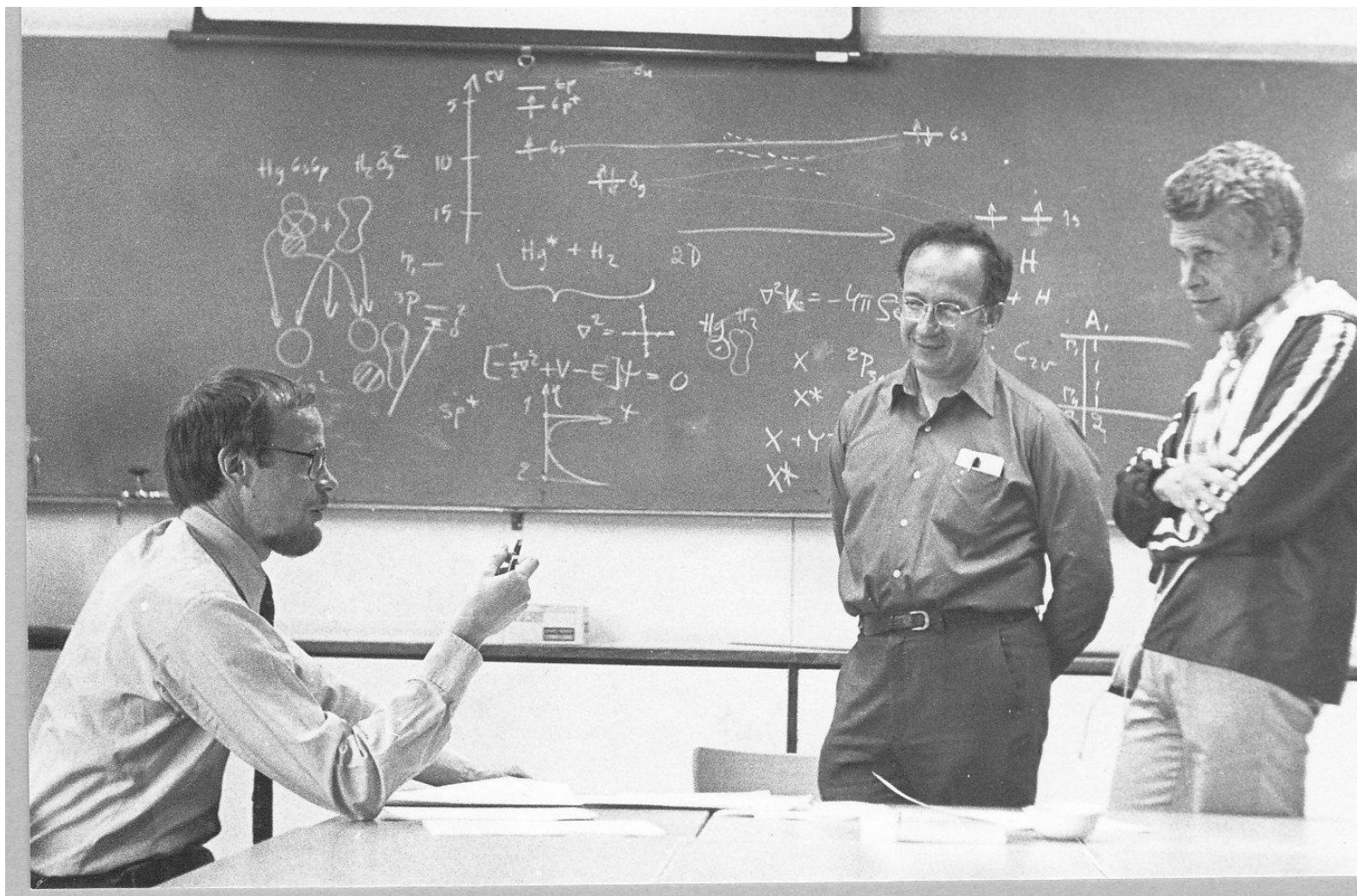
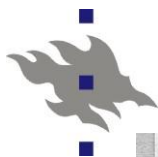
The ÅA QC group 1979



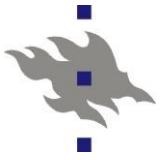
The ÅA QC group 1981



1982 Roald Hoffmann at ÅA



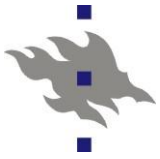
1983 John Pople at ÅA





- **When necessary, 'jump ship'!**
- **Fall term 1982- : Acting Professor in Helsinki.**
- **Nominated 1 February 1984- to 'Swedish Chair of Chemistry' at the University of Helsinki.**
- **2nd-oldest Chair of Chemistry in Finland, established in 1908 as the "Parallel Chair of Chemistry". (Komppa's chair at HUT also established 1908).**
- **Earlier holders:**
 - Lars William Öholm (1915-1939). Physical Chemist.**
 - Kurt Buch (1942-1949). Analytical Chemist. CO₂ in the World oceans!**
 - Terje Enkvist (1951-1971). Organic Chemist. Speciality wood chemistry.**
 - Jacobus Sundman (1973-1980). Organic Chemist. Medical substances.**

'Installation' 1984





Södra Hesperiaagatan 4, 'Svenska Kemen' 1963-95

My office ►



Arkitekt Walter Jungs prisbelönta förslag till Centrallaboratoriets nybygge vid Södra Hesperiaagatan 4, 1923. Centrallaboratoriet verkade i byggnaden 1925—1962. Sedan år 1963 ägs huset av Helsingfors universitet och inhyser kemiska institutionens svenskspråkiga avdelning och institutet för seismologi.



1984-: Professor of Chemistry at Helsinki

- Relativistic Quantum Chemistry consolidated: Books 'Relativistic Theory of Atoms and Molecules' I-III, Springer-Verlag (1985, 1993, 2000) [100, 150, 200]. The RTAM data base *rtam.csc.fi*.
- The 1988 review [106] 'Relativistic Effects in Structural Chemistry' (cited 1304 times on 13 October 2009).
- The 1993-98 REHE programme of the ESF ('Relativistic Effects in Heavy-Element Chemistry and Physics'). PP Chair, Bernd A. Hess Vice-Chair. The REHE symposia still continue. Until 2006 Europe, 2010 Beijing.
- Some Ph. D. students Ingegerd Forsskåhl, Henrik Konschin, Dage Sundholm (1985), Bertel Westermarck (1988), Nino Runeberg (1996), Michaela Ekholm and Michal Straka (2001), Michael Patzschke (2006), Patryk Zaleski-Ejgierd (2009).

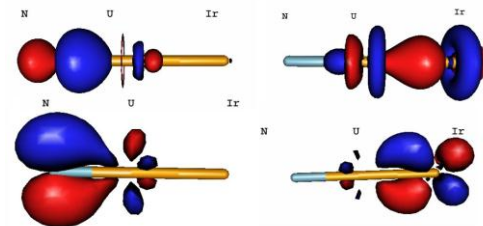
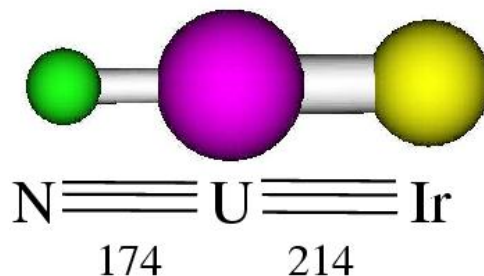
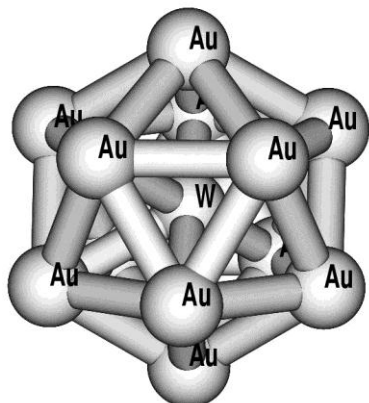


1984-: Professor of Chemistry at Helsinki (cont.)

- The 1997 review 'Strong Closed-Shell Interactions in Inorganic Chemistry' [160] (cited 1036 times on 14 September 2009).
- Explains (and names) the 'metallophilic attraction' between closed-shell metal ions as a strong dispersion effect.
- Problem mentioned to PP by Prof. Dr. Hubert Schmidbaur (TU München) ca. 1986. First paper [131] (1991) with Yongfang Zhao. Later co-workers Jian Li, Nino Runeberg, Fernando Mendizabal, Michal Straka, Toomas Tamm, Patryk Zaleski-Ejgierd, Jesús Muñiz, Cong Wang, ...
- From TU München 14 'alemanitos' 1994-2002.
- **'Secret of success in science':**
 - a) Do some decent work.**
 - b) Write the first, leading review in Chemical Reviews.**

1977-: Predicting New Chemical Species

- With Desclaux [43], predict new metal hydrides MH_n ; $M = Ti, Zr, Hf$. Made much later by Lester Andrews using matrix spectroscopy.
- 1989-91: Multiply-bonded (mainly chain) species AB to ABCDE [115-126]. Lead to experimental syntheses of $OCNCO^+$, N_5^+ and others. The only new 'nitrogen' of the 20th century. Synthesized as $[(N_5^+)(AsF_6^-)]$ by Karl Christe in 1999.
- $C\equiv Au^+$ with Maria Barysz in 1998 [170].
- WAu_{12} predicted with Nino Runeberg in 2002 [221]. Made immediately by Lai-Sheng Wang's group at PNL.
- $OUIr^+$ predicted with Laura Gagliardi in 2004 [239]. Made by a Portuguese-American collaboration (Santos, 2006).
- Gold-glued sheets, stripes and rings [259, 264, 267].





Simple Understanding of Chemical Bonding

- The covalent radii for single, double and triple bonds redone (with M. Patzschke, S. Riedel, M. Atsumi) [279, 288, 249]. Fitting program written by PP.
- A new chemical analogy: $O \leftrightarrow Pt$ etc. $CO \leftrightarrow CPt$. Used to predict $OUIr^+$ etc. and to find new species for the triple-bond data set.
- After 8, 18, a new 'magic number' 32 hunted, and found (with Jean-Pierre Dognon and Carine Clavaguéra): $Pu@Pb_{12}$ [261], AnC_{28} [280].
- Transition-metal atoms in vacancies in graphene [285].
- 'Coulomb pays for Heitler-London' in reversible H_2 splitting and storage [276, 287, 290].
- Low-energy path from uranyl (UO_2^{2+}) compounds to 'antiuranyl' (UO_4^{2-}) compounds [135, 146]. 'Frozen soft mode'.



Ionic and Covalent Radii: 1938 and 2005-09

SOCIETAS SCIENTIARUM FENNICA
ÅRSBOK — VUOSIKIRJA
XVI: B no 7

OM ATOMERNAS STORLEK

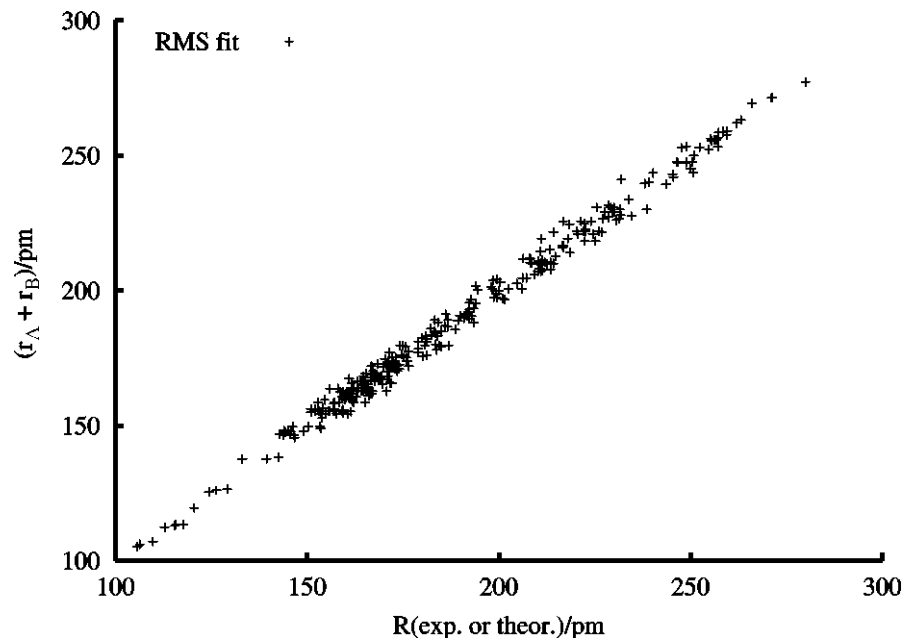
FÖREDRAG HÅLLET VID FINSKA VETENSKAPS-SOCIETETENS
100-ÅRS JUBILEUM 28-29 APRIL 1938

AV

JARL A. WASASTJERNA



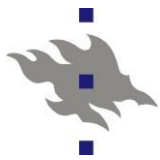
HELSINGFORS 1938



Triple-bond covalent radii for $Z = 4 - 112$ [249].

1998 Sir John Pople at UH





1985: H. Konschin disputerar. Vinterskolan.





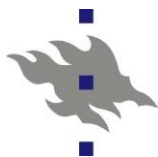
1985 Dage Sundholm disputerar



Dage Sundholms
disputation den 14. 9. 1985

Fakultetsopponent:
dr Jean-Paul Desclaux
(Grenoble)





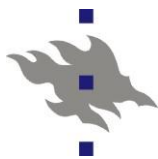
1996 Nino Runeberg disputerar



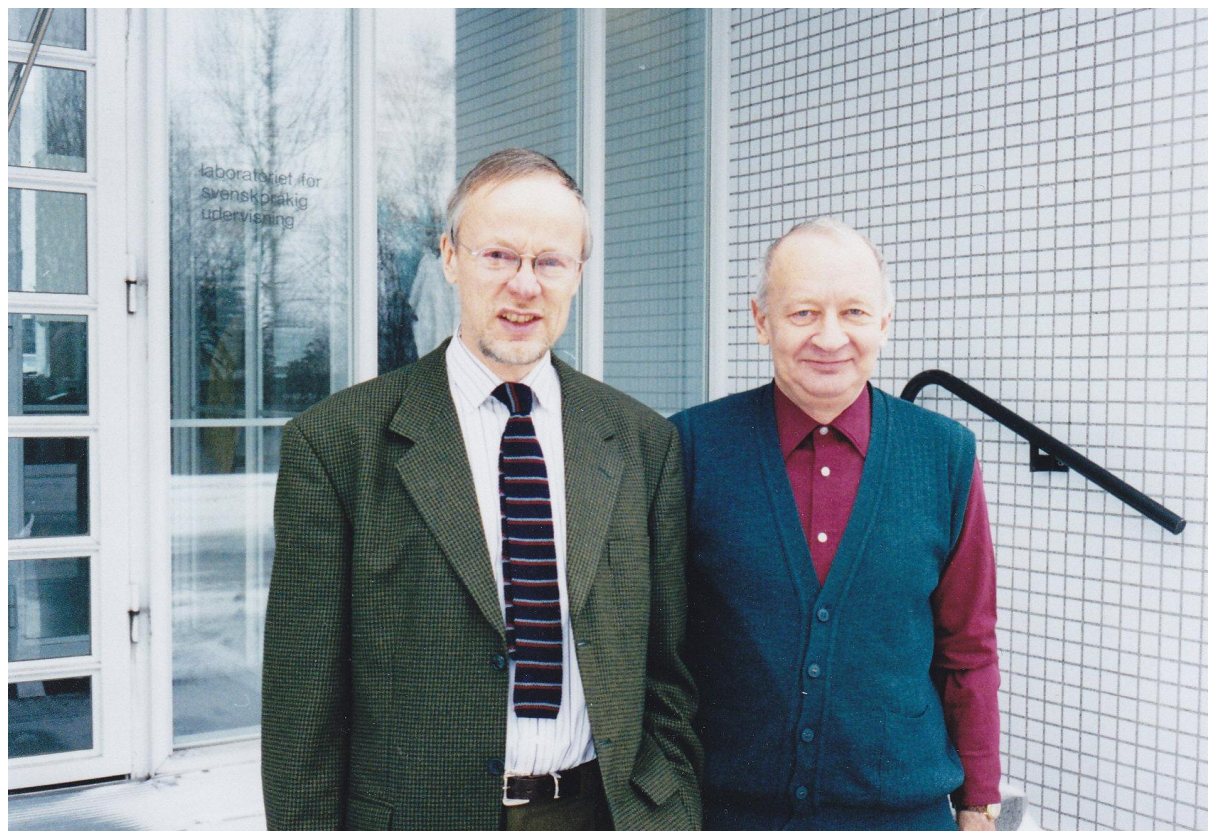
2009: Patryk Zaleski-Ejgierd disputerar



Quantum Electrodynamics in Chemistry 1998-

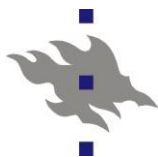


**Leonti N. Labzowsky, SPb State U.
QED effects about -1% of Dirac ones**



1972

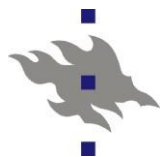
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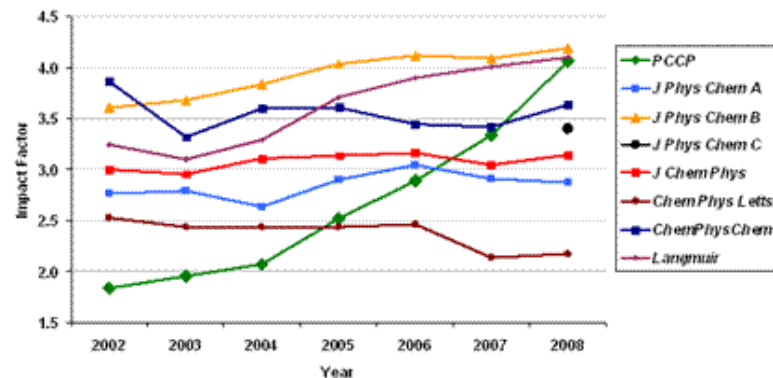
1997 Hubert Schmidbaur in Chile



Some Other Tasks



Impact Factor Trends of General Physical Chemistry Journals



- **Teaching: Hopefully normal.**
- **University administration: Chairman for Department of Chemistry when financing for Kumpula granted by the Parliament. (Chairmen Koskikallio and Saarinen did more for the effort).**
- **Academy of Finland: Research Council for Natural Sciences 1986-91.**
- **Finnish CoE in Computational Molecular Science (CMS) (Chair 2006-08).**
- **13-ICQC, Helsinki, 22-27 June, 2009 (671 participants from 54 countries).**
- **COST D9, D23.**
- **Chemical societies, FKS and SKKS.**
- **Ca. 70 referee reports, 7 conference talks/year, lately.**
- **Academies: IAQMS (President July 2009-), FVS and others.**
- **Journals: *Physical Chemistry Chemical Physics* (Editorial Board Chair 2009-), *Chem. Eur. J.* (1995-) and others.**

Jubiläer idag

Svenska kemen mår bra

— Får jag föreslå en rubrik: Svenska kemen mår bra, säger dagens jubilar, **Pekka Pyykkö**, 50. Han bör veta vad han talar om eftersom han under 17 år innehaft svenskspråkiga kemi-professorer i Finland, varav de senaste sju-åtta åren i Helsingfors. Sedan han disputerade vid 25 års ålder vid Turun yliopisto har han gjort en stadig karriär uppåt med forskning bl.a. i Sverige och Danmark, professorer i Jyväskylä och Åbo akademi, blivit internationellt uppmärksammas för sina insatser inom kvantkemin, har ett 140-tal vetenskapliga publikationer bakom sig, medarbetarskap i ett halvtdussin internationella vetenskapliga tidskrifter. O.s.v.

Så inte har han behov av PR för egen del, men han vill slå ett slag både för den svenska kemiundervisningen och hela den svenska studiesektorn vid Helsingfors universitet som han tycker att massmedierna borde uppmärksamma betydligt mera.



□ Svenska kemiprofessorn Pekka Pyykkö mot en bakgrund av ritningarna till Gumtäktsprojektet som, om allt går enligt planerna, borde stå färdigbyggt 1994.