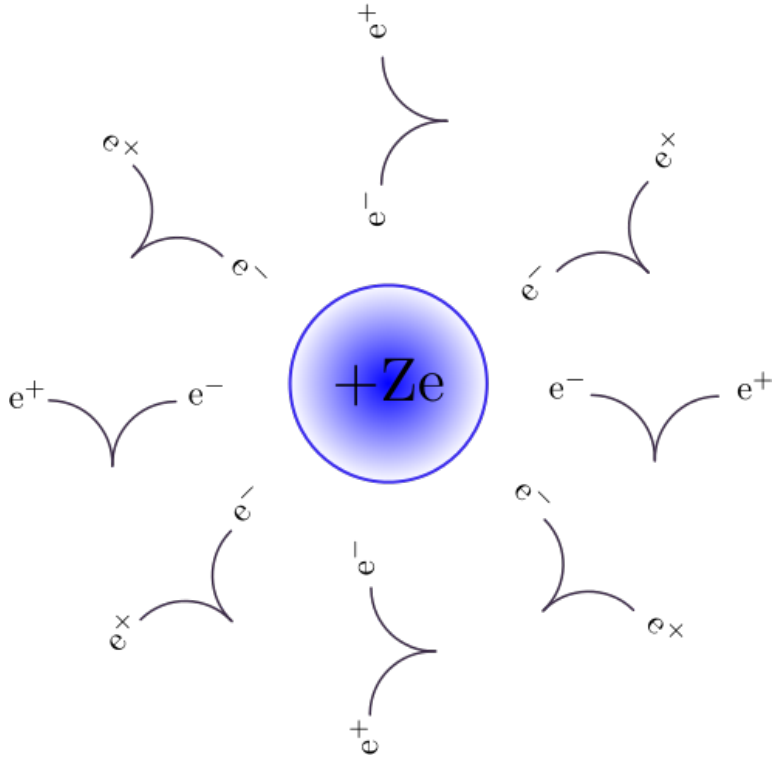

Effective QED-potentials for molecular calculations

Trond Saue

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118 route de Narbonne, 31062 Toulouse, France
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Relativistic molecular calculations

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P	rogram
•	for
A	tomic
•	and
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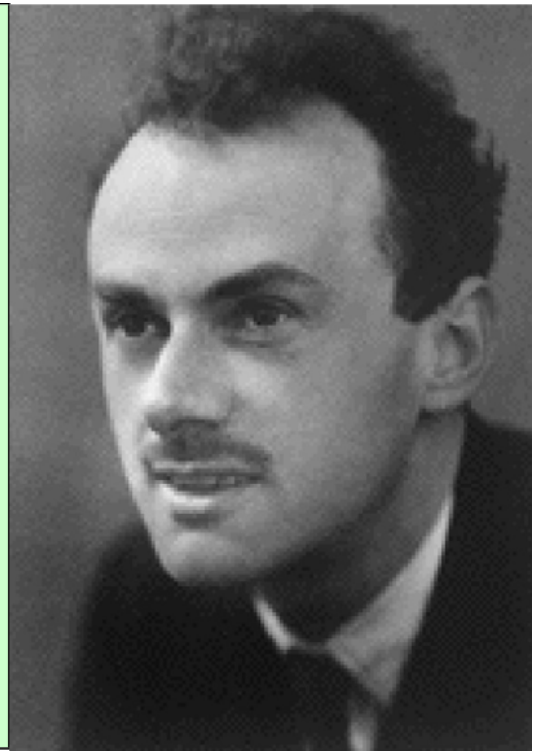
D	irect
I	terative
R	elativistic
A	ll-electron
C	alculations



http://www.diracprogram.org

Trond Saue, Radovan Bast, Andre Severo Pereira Gomes, Hans Jørgen Aagaard Jensen, Lucas Visscher, Ignacio Agustın Aucar, Roberto Di Remigio, Kenneth G. Dyall, Ephraim Eliav, Elke Faßhauer, Timo Fleig, Loıc Halbert, Erik Donovan Hedegård, Benjamin Helmich-Paris, Miroslav Iliaš, Christoph R. Jacob, Stefan Knecht, Jon K Laerdahl, Marta L. Vidal, Malaya K Nayak, Małgorzata Olejniczak, Jógvan Magnus Haugaard Olsen, Markus Pernpointner, Bruno Senjean, Avijit Shee, Ayaki Sunaga, Joost N. P. van Stralen, J. Chem. Phys. **152** (2020) 204104

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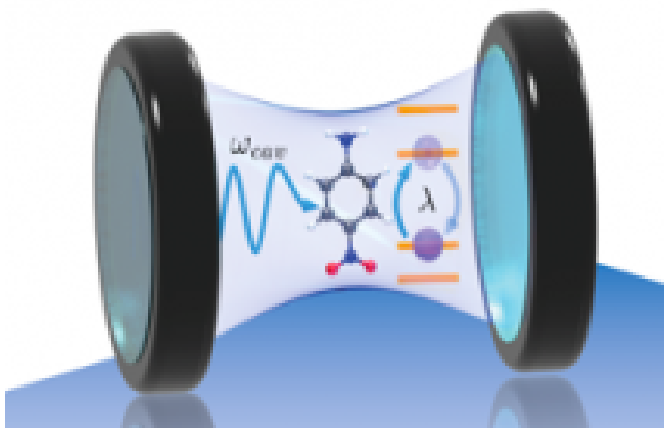

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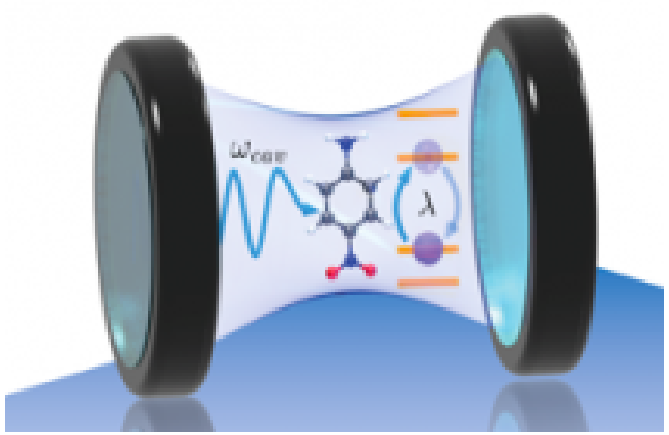
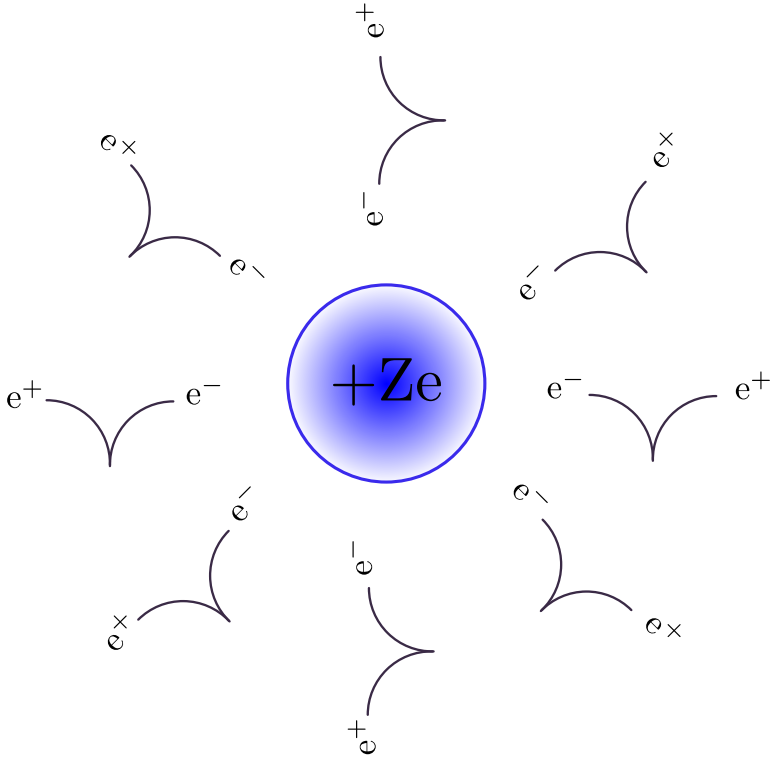


- Coupling to the zero-point vibration of the quantized EM field

Lamb-shift effects



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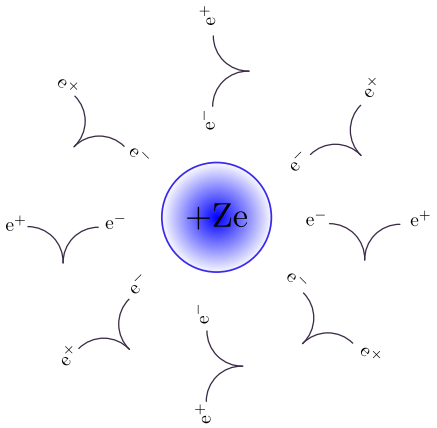

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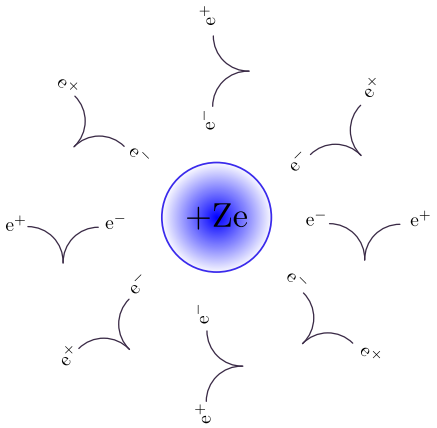

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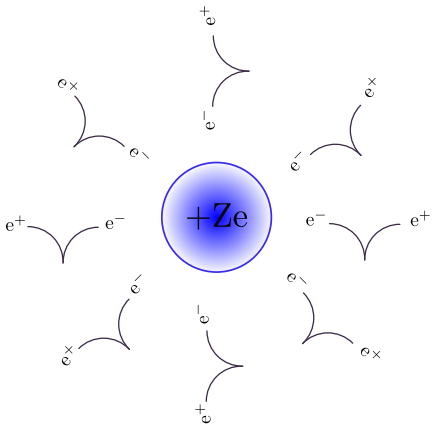

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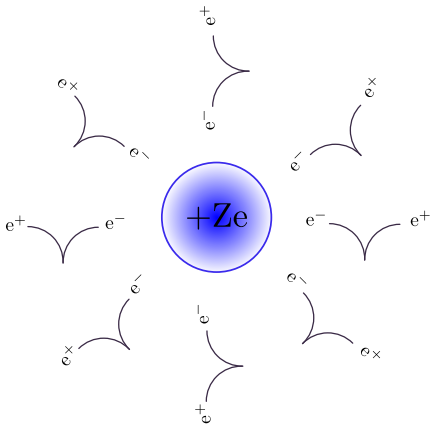

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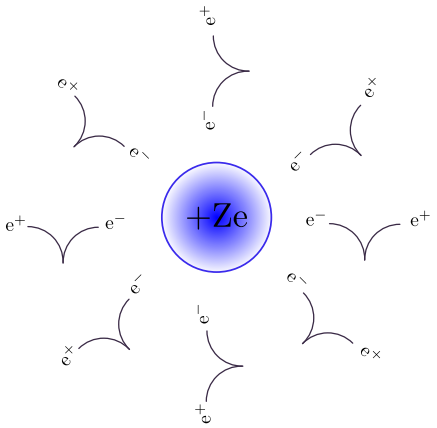

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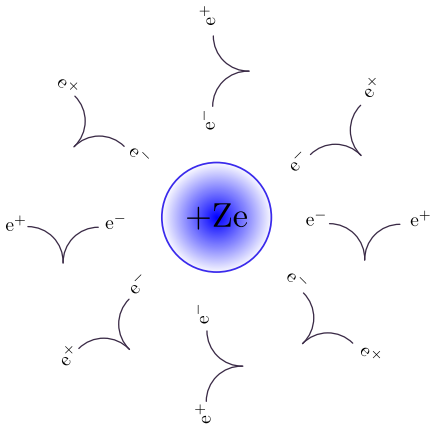

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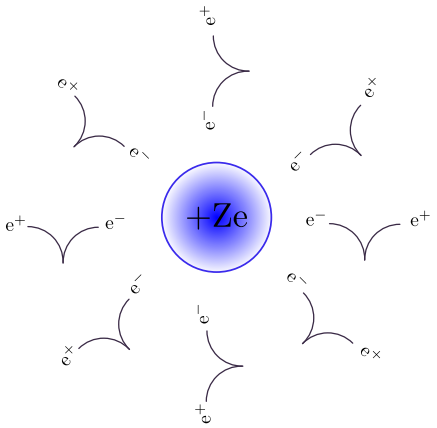

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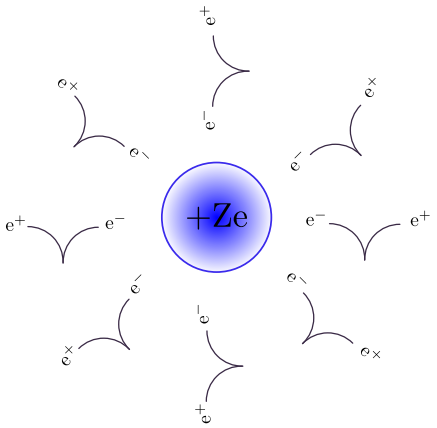

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- **Can QED-effects play a role in the chemistry of heavy elements ?**

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- **Main challenge:** Regularization/renormalization

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- Perturbation expansion $\hat{\mathcal{S}} = \hat{U}(+\infty, -\infty) = \sum_{n=0}^{\infty} \hat{\mathcal{S}}^{(n)}$

$$\hat{\mathcal{S}}^{(n)} = \frac{1}{n!\,(i\hbar c)^n} \int d^4x_1 \ldots \int d^4x_n \mathrm{T}\left[\hat{\mathcal{H}}_I(x_1)\ldots\hat{\mathcal{H}}_I(x_n)\right] e^{-\epsilon(|t_1|+|t_2|+\ldots|t_n|)/\hbar}$$

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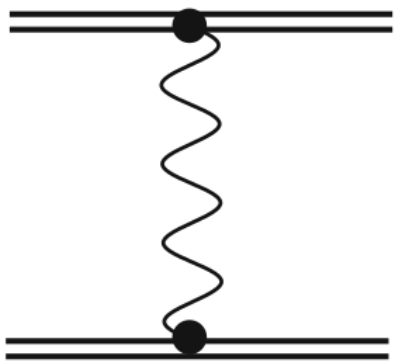

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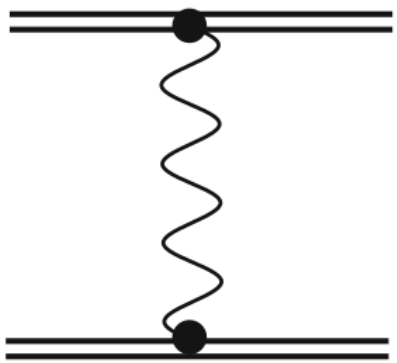

Classical electrodynamics ...teaches us that the idea of an interaction energy between particles is only an approximation and should be replaced by the idea of each particles emitting waves, which travel outward with a finite velocity and influence the other particles in passing over them.

P. A. M. Dirac, *Relativistic Quantum Mechanics*, Proc. Roy. Soc. A **136** (1932) 453

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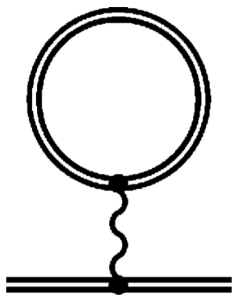

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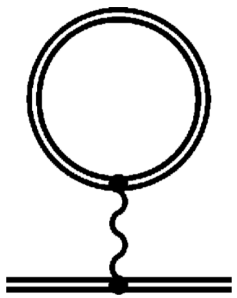

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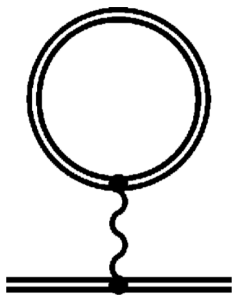

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Self-energy tends to dominate vacuum polarization

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  - P. Pyykkö and U. B. Zhao, J. Phys. B: At. Mol. Opt. Phys. **36** (2003) 1469
  - V. V. Flambaum and J. S. M. Ginges, Phys. Rev. A **72** (2005) 052115
  - V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin, Phys. Rev. A **88** (2013) 012513

Effective QED-potentials for molecular calculations

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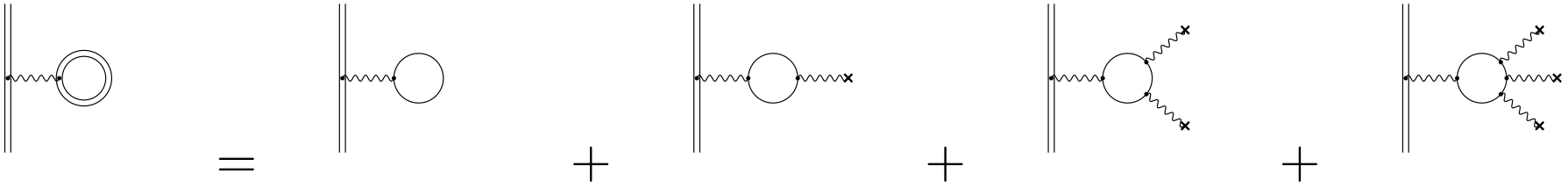
- See recent complementary work:
  L. V. Skripnikov, The Journal of Chemical Physics **154** (2021) 201101

Vacuum polarization

E. A. Uehling, Phys. Rev. 48, 55 (1935);
E. H. Wichmann and N. M. Kroll, Phys. Rev. 101, 843 (1956)



α	$\alpha(Z\alpha)^0$	$\alpha(Z\alpha)^1$	$\alpha(Z\alpha)^2$	$\alpha(Z\alpha)^3$
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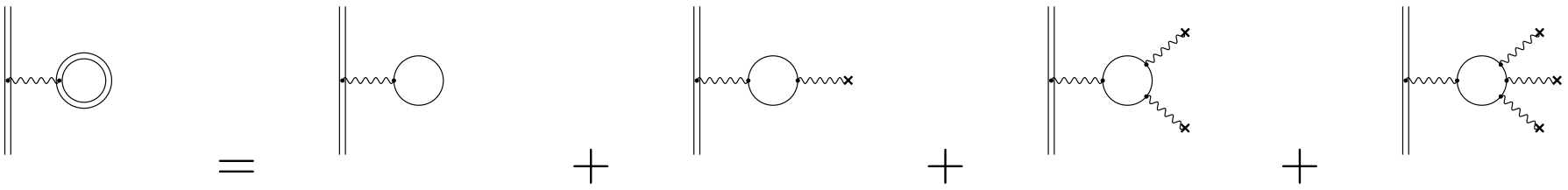

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- We use the Uehling potential in the present work

Electron self-energy

P. Pyykkö and L.-B. Zhao, J. Phys. B 36, 1469 (2003;
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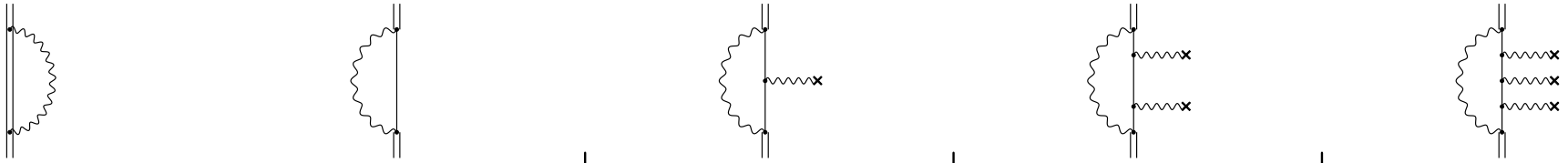

α	$=$	$\alpha(Z\alpha)^0$	$+$	$\alpha(Z\alpha)^1$	$+$	$\alpha(Z\alpha)^2$	$+$	$\alpha(Z\alpha)^3$
		logarithmic divergent		logarithmic divergent		convergent		convergent
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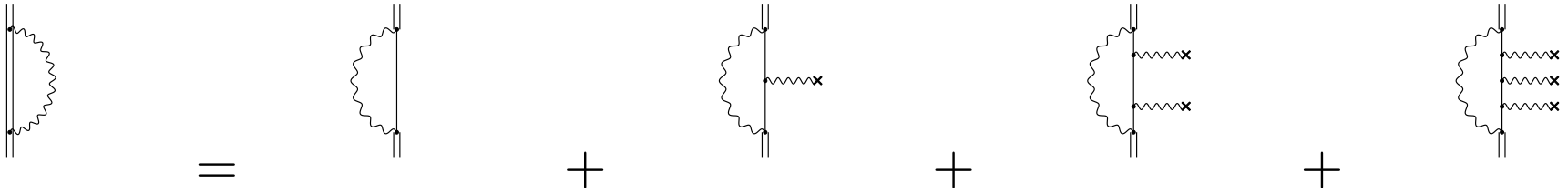

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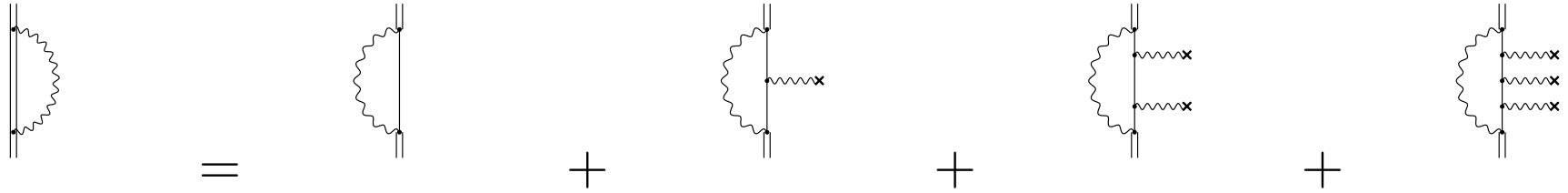

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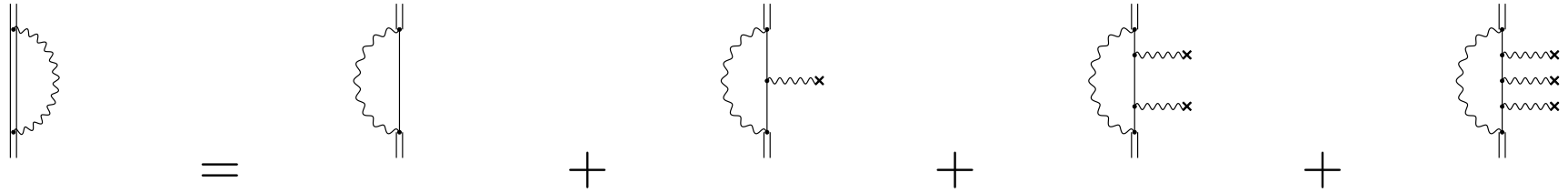

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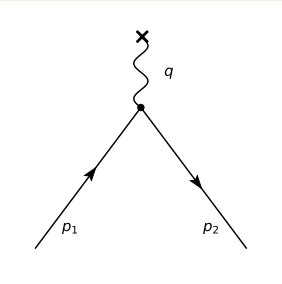
- Pyykkö/Zhao: $\varphi_{SE}(\mathbf{r}) = B(Z)\, e^{-\beta(Z) r^2}$
- Flambaum/Ginges starts from the vertex-correction term
  - further modelling, including parameter fitting, is introduced such that their effective SE potential can account for full SE to all orders in $(Z\alpha)$

Vertex correction

V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, Quantum Electrodynamics (1982)

Scattering of a free electron in an external potential



$$\mathcal{S}^{(1)} = -\frac{e}{i\hbar}\int\frac{d^4p_2}{(2\pi\hbar)^4}\int\frac{d^4p_1}{(2\pi\hbar)^4} : \hat{\bar{\psi}}\left(p_2\right)\gamma^\mu A^e\left(p_2-p_1\right)\hat{\psi}\left(p_1\right) :$$

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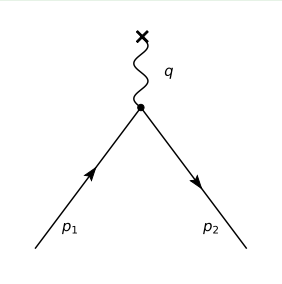

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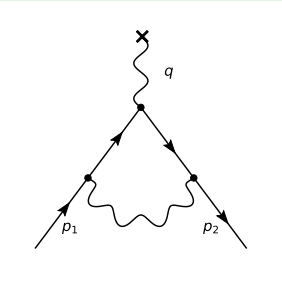
One of four lowest-order radiative corrections



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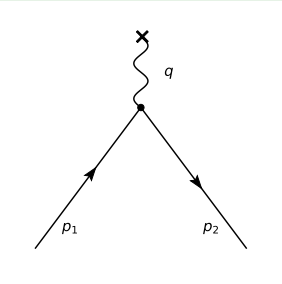

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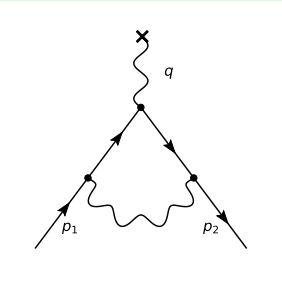

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Electric and magnetic form factors

- $\Lambda_R^\mu\left(q\right) = \gamma^\mu F_1\left(q^2\right) + \frac{i}{2m_e c}\sigma^{\mu\nu}q_\nu F_2\left(q^2\right)$

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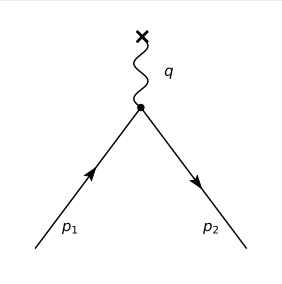

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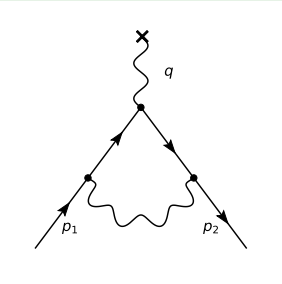

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Electron Affinity and Ionization Potential of Gold

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- QED effects **reduce** relativistic effects by about 1%.
  P. Pyykkö, M. Tokman, and L. Labzowsky,Physical Review A **57** (1998) R689

What about molecules ?

Pekka Pyykkö, Davidson lecture, UNT, Oct 25 2013
[http://www.chem.helsinki.fi/~pyykko/Videos/UNT.mp4]

Accurate structures for molecular MCN, M=Cu,Ag,Au

- Microwave molecular structures exist for Cu [1], Ag, Au [2].
- Carry out large-basis relativistic pseudopotential CCSD(T) calculations, correlating the 5s5p semicore and adding BSSE and spin-orbit corrections. cc-pVQZ basis. 19-VE Figgen pseudopotential.
- Final **M-C bond-lengths** agree with experiment within 0.7 pm.

1. D.B. Grotjahn, M.A. Brewster, L.M. Ziurys, JACS 124 (2001) 5895.
2. T. Okabayashi, E. Y. Okabayashi, F. Koto, T. Ishida, M. Tanimoto, JACS 131 (2009) 11712.
3. P. Zaleski-Ejgierd, M. Patzschke, P. Pyykkö, J. Chem. Phys.128 (2008) 224303.
4. J. G. Hill, A.O. Mitrushchenkov,K.A. Peterson, J. Chem. Phys. 138 (2013) 134314.

	CuCN	AgCN	AuCN
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Calc.[3]	182.36 (r_e)	202.42 (r_e)	191.05 (r_e)
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32

Orbital sizes $\left\langle r^2 \right\rangle^{1/2}$ of the neutral gold atom

B3LYP/dyall.3zp/QED:VP(Uehling)+SE(FG)

- The effect of relativity (in pm):

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	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	$6s_{1/2}$
NR	81.617	89.327	89.327	128.787	128.787	196.070
+R	73.863	80.303	88.203	128.418	135.406	167.538
Δ_{rel}	-9.50%	-10.10%	-1.26%	-0.29%	5.14%	-14.55%

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+QED	73.929	80.306	88.214	128.379	135.382	167.791
Δ_{QED}	0.09%	0.00%	0.01%	-0.03%	-0.02%	0.15%
$\Delta_{QED/R}$	-0.85%	-0.03%	-0.98%	10.57%	-0.36%	-0.89%

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$\Delta_{QED/R}$	-0.85%	-0.03%	-0.98%	10.57%	-0.36%	-0.89%

- Does the $\Delta_{QED} = +0.25$ pm for the valence $6s_{1/2}$ orbital translate into a corresponding bond extension ?

Effects of relativity and QED on AuCN bond lengths

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Au-C(pm)	B3LYP/dyall.3zp/QED:VP(Uehling)+SE(FG)				
Hamiltonian	NR	SF	DC	DCG	+QED
	218.54	193.23	192.94	193.16	193.35
				Δ_R=-11.64%	Δ_{QED} =+0.10%
					$\Delta_{QED/R} = -0.75\%$

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	CCSD(T)-dyall.ae∞z+ΔT+ΔQ	
Hamiltonian	^{2}DCG^M	+QED
Au-C(pm)	190.75	190.94

Effects of relativity and QED on AuCN bond lengths

	CuCN	AgCN	AuCN
Exp	182.962(4)(r_m)	203.1197(23)(r_m)	191.22519(84)(r_s)
Calc.[3]	182.36 (r_e)	202.42 (r_e)	191.05 (r_e)
Calc.[4]	182.65 (r_e)	202.99 (r_e)	190.71 (r_e)

3. PP-CCSD(T)/cc-pVQZ with SO correction
   P. Zaleski-Ejgierd, M. Patzschke, and P. Pyykkö, JCP **128** (2008) 224303
4. PP-CCSD(T)-F12/cc-pV5Z with high-order corrections

   J. Grant Hill, A. O. Mitrushchenkov, and K. A. Peterson, JCP **138** (2013) 134314

	CCSD(T)-dyall.ae∞z+ΔT+ΔQ	
Hamiltonian	^{2}DCG^M	+QED
Au-C(pm)	190.75	190.94

Definition of bond lengths

J. Demaison, J. E. Boggs, A. G. Császár, Equilibrium Molecular Structure, CRC Press 2011

- Microwave spectroscopy:

T. Okabayashi, E. Y. Okabayashi, F. Koto, T. Ishida, and M. Tanimoto, JACS **131** (2009) 11712

r_0	191.251(16)	pm
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Isotopomer	B_0(MHz)
$^{197}Au^{12}C^{14}N$	3230.21115(18)
$^{197}Au^{13}C^{14}N$	3177.20793(13)
$^{197}Au^{12}C^{15}N$	3079.73540(12)

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  - the effective structure r_0 is obtained by least-square fitting from moments of inertia
  - the substitution structure r_s is obtained by consideration of change of center-of-mass upon single isotope substitution
  - General observation: $r_0 \geq r_s \geq r_e$

Calculating rotational constants

- General formula

$$B_\nu^\xi = B_e^\xi - \sum_i \alpha_i^\xi \left(\nu_i + \frac{d_i}{2}\right) + \frac{1}{2}\sum_{i.j} \gamma_{i,j}^\xi \left(\nu_i + \frac{d_i}{2}\right)\left(\nu_j + \frac{d_j}{2}\right) + \dots$$

  - $\alpha_i^\xi, \gamma_{i,j}^\xi$: vibration-rotation interaction constants

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- For AuCN we use

$$B_0 \approx B_e - \frac{1}{2}\left[\underbrace{\alpha_{100}}_{\text{C-N stretch}} + \underbrace{\alpha_{001}}_{\text{Au-C stretch}} + \underbrace{2\alpha_{01^10}}_{\text{bending}}\right]$$

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- Using calculated vibration-rotation interaction constants we obtain

B_0(MHz)	w/o QED	with QED	Exp.
$^{197}Au^{12}C^{14}N$	3235.1		
$^{197}Au^{13}C^{14}N$	3182.1		
$^{197}Au^{12}C^{15}N$	3084.3		

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B_0(MHz)	w/o QED	with QED	Exp.
$^{197}Au^{12}C^{14}N$	3235.1	3230.4	
$^{197}Au^{13}C^{14}N$	3182.1	3177.5	
$^{197}Au^{12}C^{15}N$	3084.3	3079.9	

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r_s(Au−C)	190.991	191.184	191.22519(84)

QED effects on a chemical reaction

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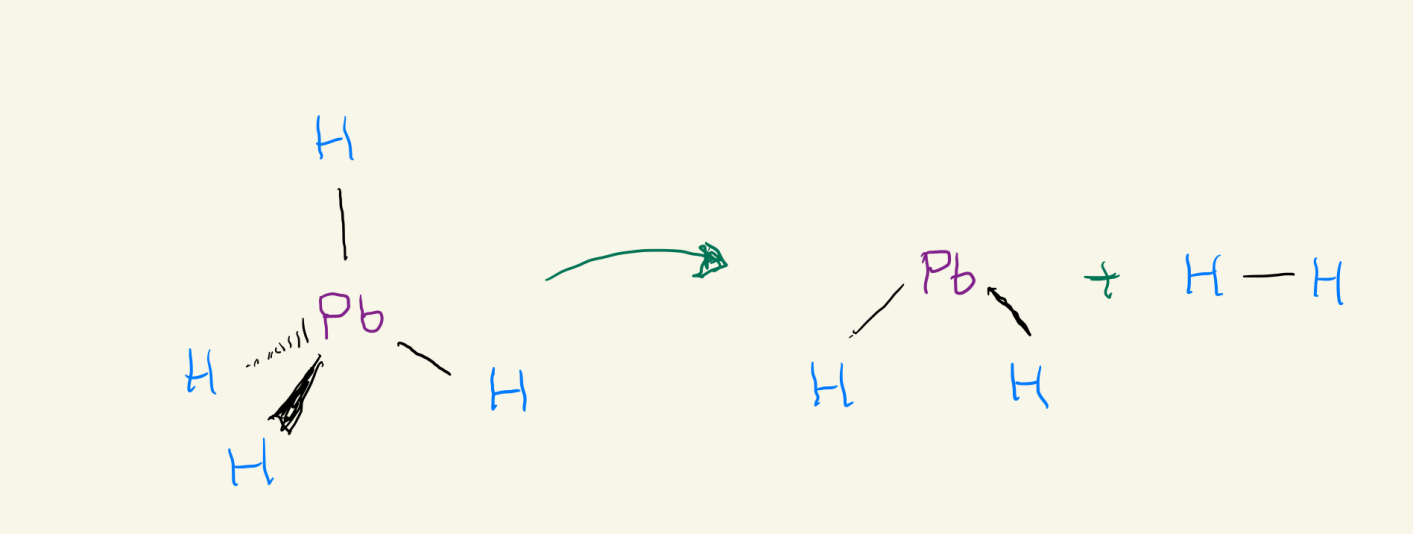

- large change in Pb 6s-population: 1.41 $\rightarrow$ 1.86 $=$ 0.45

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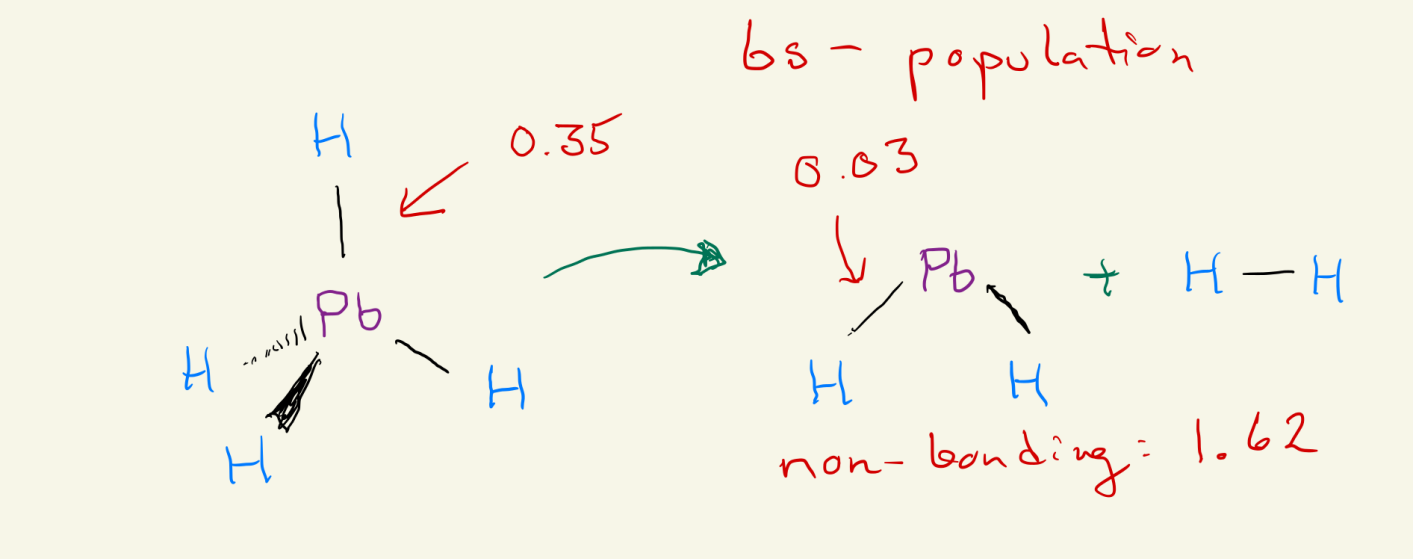

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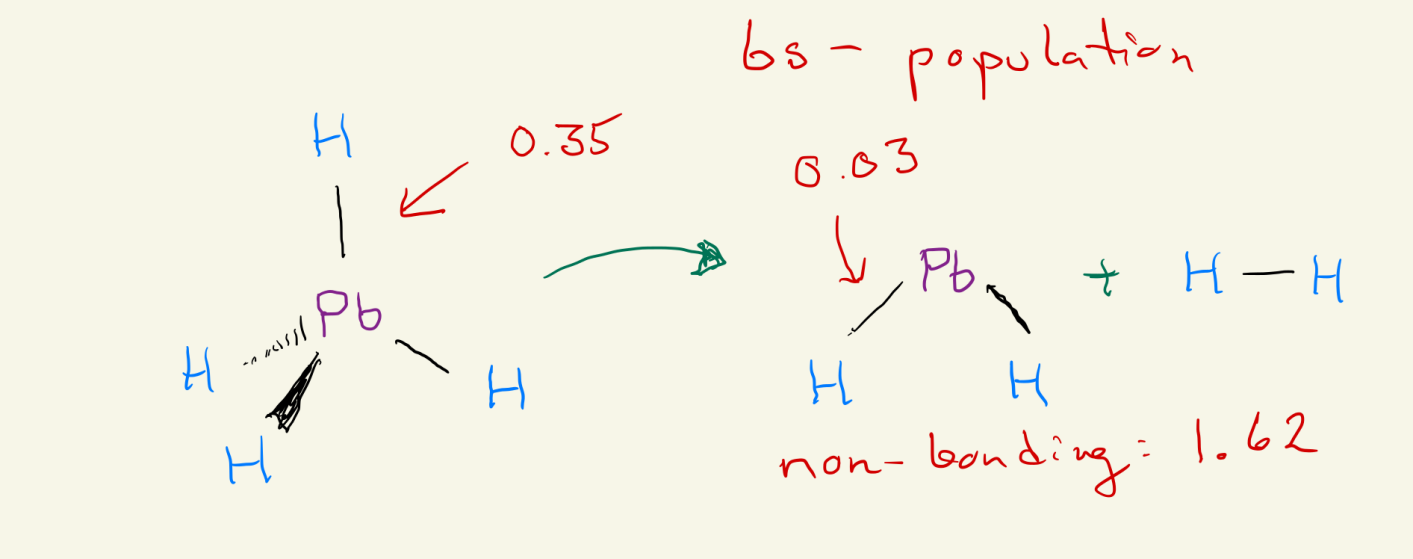

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$PbH_4 \longrightarrow PbH_2 + H_2$

Reaction energy		Δ(kcal/mol)	Δ(%)
NR	16.47		
DCG	-8.99	-25.46	
DCG+QED	-8.66	0.32	-1.27

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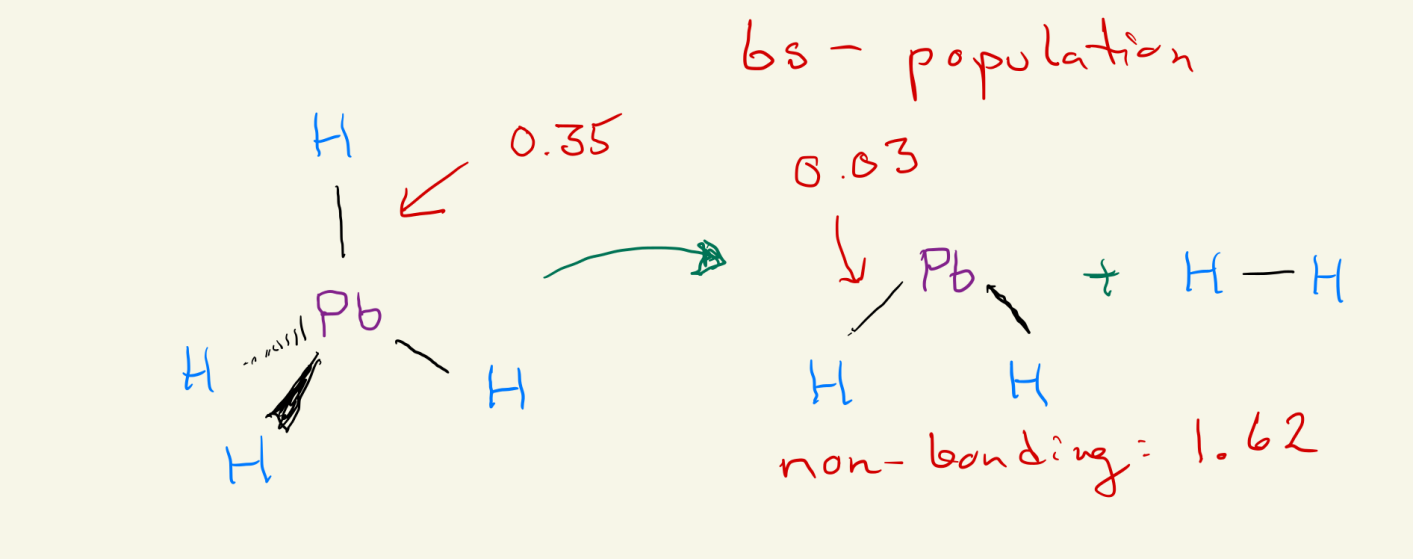

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Reaction energy		Δ(kcal/mol)	Δ(%)
NR	16.47		
DCG	-8.99	-25.46	
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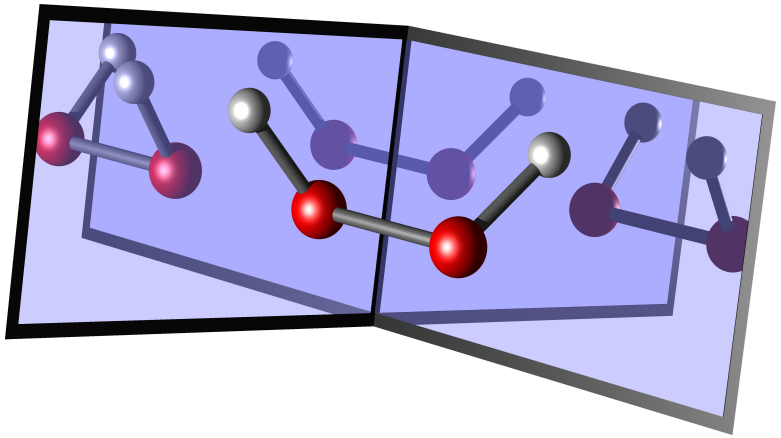
$FlH_4 \longrightarrow FlH_2 + H_2$

Reaction energy		Δ(kcal/mol)	Δ(%)
NR	9.52		
DCG	-60.02	-69.54	
DCG+QED	-59.67	0.35	-0.50

QED effects on parity violation energies of chiral molecules
Ayaki Sunaga and Trond Saue, Molecular Physics (2021) e1974592



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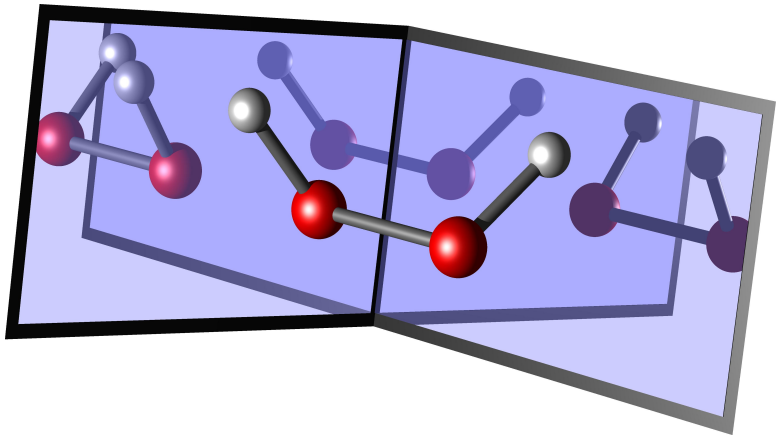

$$E^{PV} = \frac{G_F}{2\sqrt{2}} \sum_A Q_W^A \sum_i^{N_e} \langle \Psi | \gamma_i^5 \rho_A(\mathbf{r}_i) | \Psi \rangle$$

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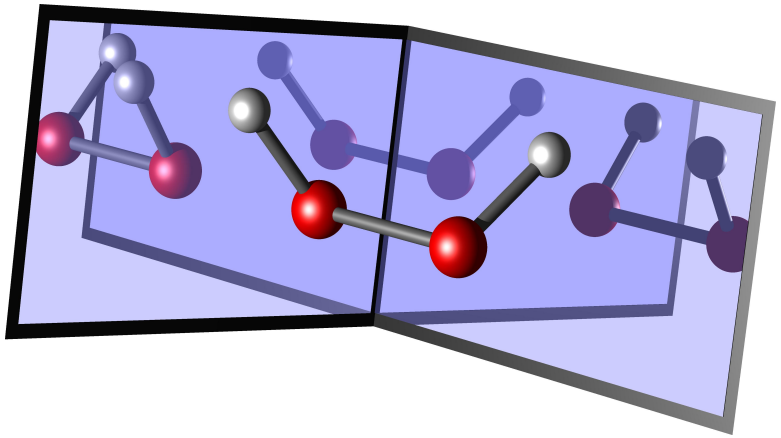

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CCSD	E^{PV} (E_h)	Δ (U+PZ) (%)	Δ (U+FG) (%)
H_2Se_2	-2.463E-15	-0.19	-1.18
H_2Te_2	-3.536E-14	-0.33	-1.89
H_2Po_2	-1.337E-12	-0.51	-2.38

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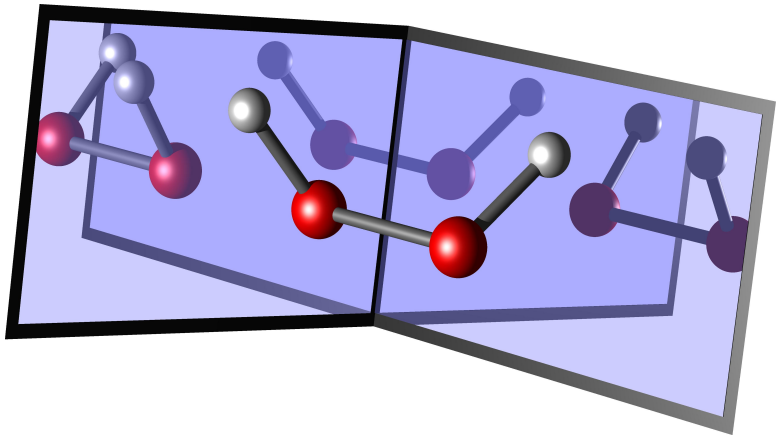

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Are the effective QED-potentials outside their domain of validity ?

Core-ionization energies (in eV) of the xenon atom

T. Mooney, E. Lindroth, P. Indelicato, E. G. Kessler, and R. D. Deslattes, Phys. Rev. A, 45 (1992) 1531

Level	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
Dirac-Fock (Coulomb)	34 755.77	5509.33	5161.43	4835.57
Relaxation	−70.00	−37.80	−41.66	−40.58
Dirac-Fock (Breit)	−80.71	−7.64	−13.05	−8.81
Breit relaxation	−1.46	−0.08	−0.07	−0.11
Higher-order retardation	0.78	−0.08	0.00	0.34
Correlation	1.80	1.99	3.05	3.02
Breit correlation	0.95	0.21	0.31	0.24
Core-core	−0.32	−8.29	−3.18	−2.75
Higher-order core-core	0.02	0.96	0.15	0.11
Auger shift	0.35	−0.06	0.23	0.53
Self-energy	−50.98	−7.73	−0.09	−0.75
Self-energy screening	2.91	1.69	0.47	0.57
Vacuum polarization $\alpha(Z\alpha)$	6.95	0.81	−0.02	−0.04
Vacuum polarization $\alpha(Z\alpha)^3$	−0.16	−0.02	0.00	0.00
Vacuum polarization $\alpha^2(Z\alpha)$	0.06	0.01	0.00	0.00
Total ionization energy	34 565.95	5453.30	5107.57	4787.34

Calculated SE shifts of 1s orbital energies (E_h)

Z	element	FG [1]	n-FG [2]	Welton [3]
30	Zn	0.277	0.248	0.247
36	Kr	0.520	0.461	0.459
48	Cd	1.409	1.226	1.221
54	Xe	2.123	1.833	1.827
80	Hg	8.534	7.402	7.408
86	Rn	11.126	9.741	9.760
112	Cn	31.497	29.751	30.575
118	Og	39.520	38.415	39.783

1. V. V. Flambaum and J. S. M. Ginges, Phys. Rev. A **72** (2005) 052115
2. C. Thierfelder and P. Schwerdtfeger, Phys. Rev. A **82** (2010) 062503
3. K. Kozioł and G. A. Aucar, J. Chem. Phys. **148** (2018) 134101

Conclusions and perspectives

- Effective QED potentials have been implemented in the DIRAC code for relativistic molecular calculations

Ayaki Sunaga, Maen Salman and Trond Saue,
J. Chem. Phys. **157** (2022)164101

https://tinyurl.com/molqed22

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- Are **core properties** within the domain of validity of the effective QED potentials ?

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