QED in finite Gaussian basis sets

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HAMP vQED

European Research Council

Established by the European Commission

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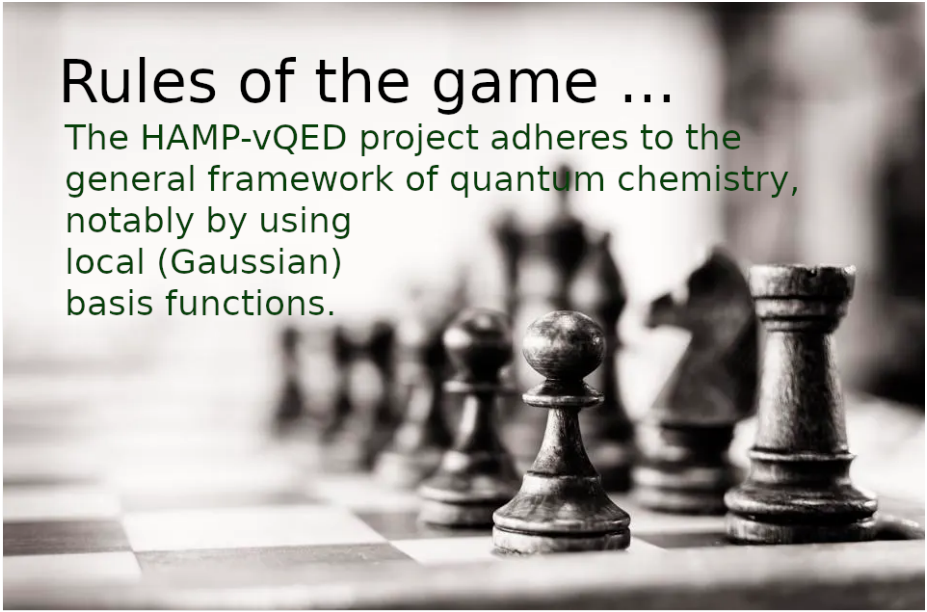
Highly Accurate Molecular Properties

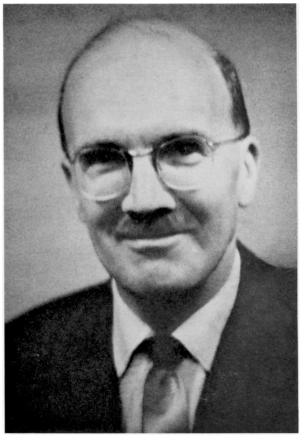
Rules of the game ...

The HAMP-vQED project adheres to the general framework of quantum chemistry, notably by using local (Gaussian) basis functions.



Gaussian-type orbitals (GTOs)

S. F. Boys, Proc. R. Soc. A 200 (1950) 542–554; G. C. Hall, Mol. Phys. 88 (1996) 309-314



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  $$\chi^{GTO} = \mathcal{N} r^{\ell} \exp\left[-\alpha r^2\right] Y_{\ell m}(\theta, \phi)$$

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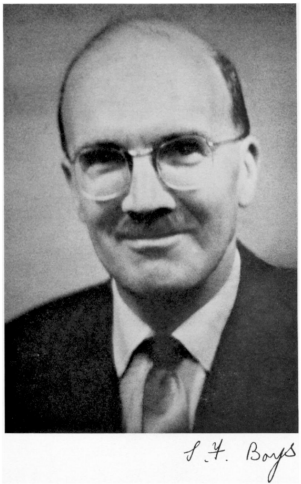

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$$\chi^{GTO} = \mathcal{N} x^i y^j z^k \exp\left[-\alpha r^2\right] \quad i + j + k = \ell$$

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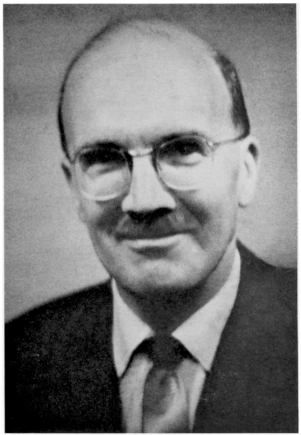

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Boys felt that his approach to quantum chemistry could be extended to other areas of science. [...] He even tried to bring Gaussians into quantum field theory. He knew that the subject was plagued by infinities which were sometimes the result of poor technique and sometimes of poor modelling. His Gaussian-based treatment could get rid of some of these but, when he talked to the local experts about his proposed starting point, they indicated that one infinity remained in the operators which he could not remove, so the entire treatment fell down. Nothing came of it but he was not disheartened.

Energy shifts

Gell–Mann-Low-Sucher formula

Dávid Ferenc
Thursday 17h

- Electron self-energy:

$$\Delta E_a^{\mathrm{SE}} = 2\mathrm{i}\alpha\varepsilon_0 c^2 \int_{C_F} \mathrm{d}z \int \mathrm{d}^3\mathbf{r}_1 \int \mathrm{d}^3\mathbf{r}_2 \underbrace{D(z,\mathbf{r}_{12})}_{\substack{\text{photon}\\ \text{propagator}}} \psi_a^\dagger(\mathbf{r}_2)\alpha^\mu \underbrace{G\left(\epsilon_a - z, \mathbf{r}_2, \mathbf{r}_1\right)}_{\substack{\text{bound-electron}\\ \text{Green function}}} \alpha_\mu \psi_a(\mathbf{r}_1)$$

$$\underbrace{-\delta m \int \mathrm{d}^3\mathbf{r}\, \psi_a^\dagger(\mathbf{r})\beta\psi_a(\mathbf{r})}_{\text{mass counter-term}}$$

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$$\Delta E_a^{\mathrm{VP}} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \underbrace{\left\{-e\psi_a^\dagger\left(\mathbf{r}_1\right)\psi_a\left(\mathbf{r}_1\right)\right\}}_{\rho_a} \frac{1}{4\pi\epsilon_0\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \underbrace{\left\{-\frac{e}{2\pi i}\int_{C_F} dz \mathrm{Tr}\left[G\left(\mathbf{r}_2, \mathbf{r}_2; z\right)\right]\right\}}_{\rho^{\mathrm{VP}}}$$

VP energy shifts: non-linear contribution

VK Ivanov, SS Baturin, DA Glazov, and AV Volotka, Physical Review A 110 (2024) 032815; shell nucleus; in eV

- Energy shift of orbital φ_{1s}:

$$\Delta E_{1s}^{\mathrm{VP}} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \underbrace{\left\{-e\psi_{1s}^{\dagger}\left(\mathbf{r}_1\right)\psi_{1s}\left(\mathbf{r}_1\right)\right\}}_{\rho_{1s}} \frac{1}{4\pi\epsilon_0\left|\mathbf{r}_1-\mathbf{r}_2\right|}\rho^{VP[n\geq 3]}\left(\mathbf{r}_2\right)$$

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TABLE II. Contributions from different κ to the Wichmann-Kroll correction and their sum for the $1s$ electron in hydrogen-like uranium for different calculation methods. In parentheses, the difference between the corrections calculated by FBS (B-spline and Gaussian bases) and Green's function integration methods is shown.

	$\Delta E_{\mathrm{WK}}\left(\Delta E_{\mathrm{WK}}^{\mathrm{FBS}}-\Delta E_{\mathrm{WK}}^{\mathrm{Green}}\right)$, eV				
$\lvert\kappa\rvert$	Green's integr.	B spline $n=126$	Gaussian $n=30$	Gaussian $n=100$	Gaussian $n=120$
1	4.473	6.153 (1.680)	4.508 (0.035)	4.489 (0.016)	4.479 (0.006)
2	0.394	2.131 (1.737)	0.426 (0.032)	0.405 (0.011)	0.396 (0.002)
3	0.081	1.485 (1.404)	0.117 (0.036)	0.089 (0.008)	0.085 (0.004)
4	0.024	1.104 (1.080)	0.069 (0.045)	0.032 (0.008)	0.029 (0.005)
5	0.009	0.844 (0.835)	0.045 (0.036)	0.018 (0.009)	0.014 (0.005)
Sum	4.981	11.787 (6.806)	5.165 (0.184)	5.033 (0.052)	5.003 (0.022)

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- Convergence is challenging !

Vacuum polarization: atomic case

Ryan Benazzouk,Maen Salman and Trond Saue, Phys. Rev. A 113 (2026) 032813

Ryan Benazzouk

- VP density

$$\rho^{VP}(r,Z) = \sum_{\kappa=\pm1,\pm2,\ldots} \rho^{VP}_{\kappa}(r,Z)$$

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$$\rho_{\kappa}^{VP}(r,Z) = \frac{e\,|\kappa|}{4\pi r^2} \sum_{n} \mathrm{sgn}\left(\epsilon_{n,\kappa} - mc^2\right) \varphi_{n,\kappa}^{\dagger}\varphi_{n,\kappa}; \quad \varphi_{n,\kappa} = \begin{bmatrix} P_{n,\kappa} \\ Q_{n,\kappa} \end{bmatrix}$$

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- We focus on the non-linear part (Wichmann–Kroll)

$$\rho_\kappa^{VP[n\geq 3]}(r,Z) = \rho_\kappa^{VP}(r,Z) - \rho_\kappa^{VP[1]}(r,Z)$$

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- with the linear part calculated analytically using free-particle solutions $\left\{\varphi_{\ell\kappa}^0\right\}$

$$\rho_\kappa^{VP[1]}(r,Z) = \frac{-e\,|\kappa|}{4\pi r^2} \sum_{\substack{\epsilon_{n\kappa}^0 > mc^2 \\ \epsilon_{\ell\kappa}^0 \leq mc^2}} 4 \frac{\langle\varphi_{n\kappa}^0|V|\varphi_{\ell\kappa}^0\rangle}{\epsilon_{n\kappa}^0 - \epsilon_{\ell\kappa}^0} \varphi_{n\kappa}^{0\dagger}(r)\,\varphi_{\ell\kappa}^0(r)$$

Basis set construction

Maen Salman and Trond Saue. Symmetry 12 (2020) 1121

- Restricted kinetic balance (RKB):

$$\varphi^{KB}_{n,\kappa} = \sum_{i=1}^{n_\kappa} c^L_{n,\kappa,i} \begin{bmatrix} \pi^+_{\kappa,i} \\ 0 \end{bmatrix} + \sum_{i=1}^{n_\kappa} c^S_{n,\kappa,i} \begin{bmatrix} 0 \\ \frac{\hbar}{2mc}\left[\frac{d}{dr} + \frac{\kappa}{r}\right]\pi^+_{\kappa,i} \end{bmatrix}$$

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V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. Lett. **93** (2004) 130405

$$\varphi^{DKB}_{n,\kappa} = \sum_{i=1}^{n_\kappa} c^{+}_{n,\kappa,i} \begin{bmatrix} \pi^{+}_{\kappa,i} \\ \frac{\hbar}{2mc}\left[\frac{d}{dr} + \frac{\kappa}{r}\right]\pi^{+}_{\kappa,i} \end{bmatrix} + \sum_{i=1}^{n_\kappa} c^{-}_{n,\kappa,i} \begin{bmatrix} \frac{\hbar}{2mc}\left[\frac{d}{dr} - \frac{\kappa}{r}\right]\pi^{-}_{\kappa,i} \\ \pi^{-}_{\kappa,i} \end{bmatrix}$$

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- Recent DKB-like scheme: $\frac{\hbar}{2mc} \rightarrow \frac{\hbar c}{mc^2 \pm E^{\pm}_{\kappa,i}}$; $\quad E^{\pm}_{\kappa,i} = \pm\sqrt{m^2c^4 + c^2\langle p^2_{\kappa,i}\rangle}$

I. Grant and H. Quiney, Atoms **10** (2022) 108

Vacuum polarization density in a Gaussian basis

Maen Salman and Trond Saue, Phys. Rev. A 108 (2023) 012808

Maen Salman

- DKB with radial Gaussian basis functions:

$$\pi^{\pm}_{\kappa,i}(r) = r^{\ell_{\pm\kappa}+1} e^{-\zeta^{\pm}_{\kappa,i} r^2}; \quad \ell_\kappa = |\kappa| + \frac{1}{2}(\mathrm{sgn}(\kappa) - 1)$$

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- Charge-conjugation symmetry can be realized in DKB provided $\zeta^{\pm}_{\kappa,i} = \zeta^{\mp}_{-\kappa,i}$

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  - $\rho^{VP[n\geq 3]}(\mathbf{r})$: **even-tempered basis** $\left\{\zeta_i = \zeta_1 \beta^{i-1}\right\}_{i=1}^{N}$

Even-tempered basis

K Ruedenberg, RC Raffenetti, and RD Bardo, in Energy, structure, and reactivity, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1972) pp. 164–169,
Proceedings of the 1972 Boulder Seminar Research Conference on Theoretical Chemistry.

- Overlap of normalized Gaussians only depends on exponent ratio
  C. M. Reeves, J. Chem. Phys. **39** (1963) 1

$$\langle \chi(r,\zeta_1)\,|\chi(r,\zeta_2)\rangle_r = \left(\frac{2\sqrt{\zeta_1\zeta_2}}{\zeta_1+\zeta_2}\right)^{l+\frac{3}{2}} = \left(\frac{2\sqrt{(\zeta_1/\zeta_2)}}{1+(\zeta_1/\zeta_2)}\right)^{l+\frac{3}{2}}; \quad \chi(r,\zeta) = \mathcal{N}_\zeta r^\ell \exp\left[-\zeta r^2\right]$$

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  - suggests selection of exponents according to geometric progression
- Writing a radial orbital as an integral transform

$$R(r) = \int_0^\infty d\zeta\, \chi(r,\zeta)\, f(\zeta) = \int_{-\infty}^{+\infty} d(\ln\zeta)\, \chi(r,\zeta)\, \tilde{f}(\zeta)$$

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$$\langle \chi(r,\zeta_1) | \chi(r,\zeta_2) \rangle_r = \left(\frac{2\sqrt{\zeta_1\zeta_2}}{\zeta_1+\zeta_2} \right)^{l+\frac{3}{2}} = \left(\frac{2\sqrt{(\zeta_1/\zeta_2)}}{1+(\zeta_1/\zeta_2)} \right)^{l+\frac{3}{2}} ; \quad \chi(r,\zeta) = \mathcal{N}_\zeta r^\ell \exp\left[-\zeta r^2\right]$$

  - suggests selection of exponents according to geometric progression
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Even-tempered basis

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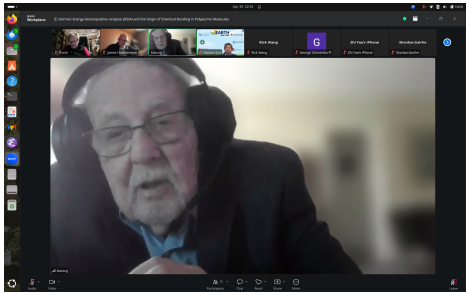
  - suggests complete basis obtained in the limit $N\to\infty$, $\beta\to 1$, $\zeta_1\to 0$.

Klaus Ruedenberg

Born August 25, 1920 in Bielefeld, Germany



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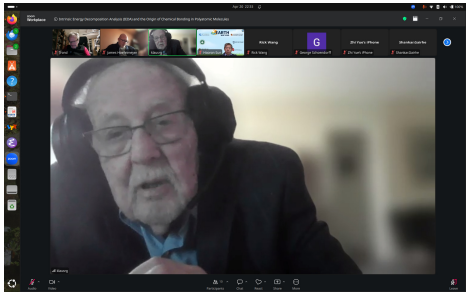

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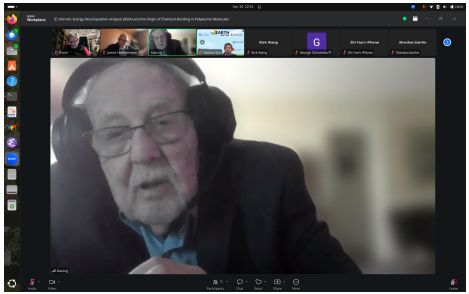

- PhD-advisor: Gregor Wentzel (ETH Zürich)

- First publication:
  - K. Ruedenberg, *On the Theory of Strong Coupling between Nucleons and Pseudovector Mesons*, Helv. Phys. Acta, **24** (1951) 89

Numerical linear dependence

- Solving the Dirac equation in a finite basis leads to a generalized eigenvalue problem

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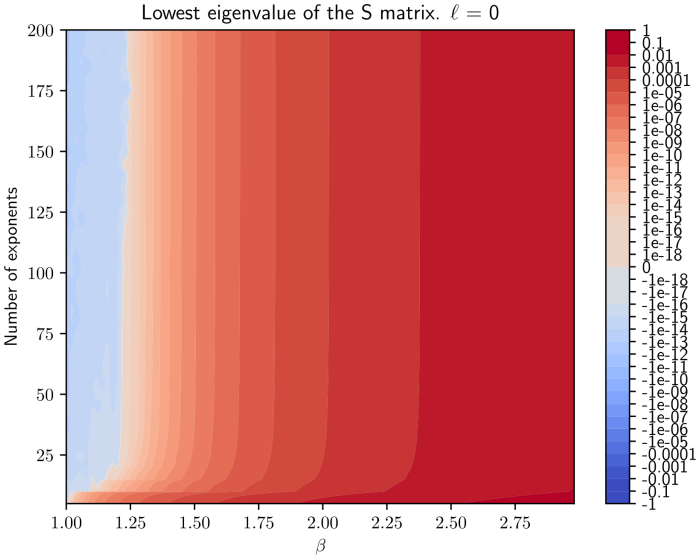
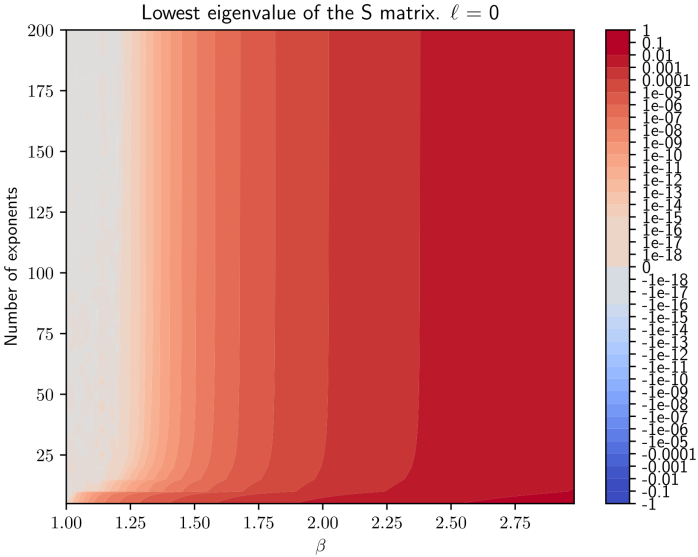
- Recall: In an even-tempered basis $\left\{\zeta_i = \zeta_1\beta^{i-1}\right\}_{i=1}^{N}$ the overlap matrix depends only on β

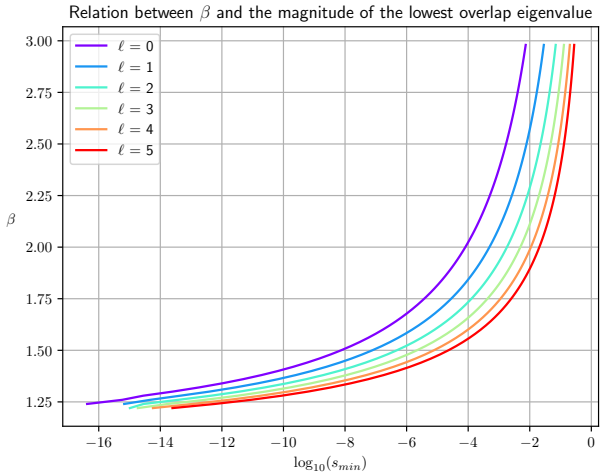
Heatmap of min $\sigma(S)$: regular diagonalization (dsyev)



Heatmap of min $\sigma(S)$: singular value decomposition (dgesvd)



Choosing β



Designing VP even-tempered basis $\left\{\zeta_i = \zeta_1 \beta^{i-1}\right\}_{i=1}^{N}$

- Start from "safe" ζ_1 and β and add exponents until convergence on energy shift. This fixes an exponent interval $\{\zeta'_{\mathsf{min}}, \zeta_{\mathsf{max}}\}$.

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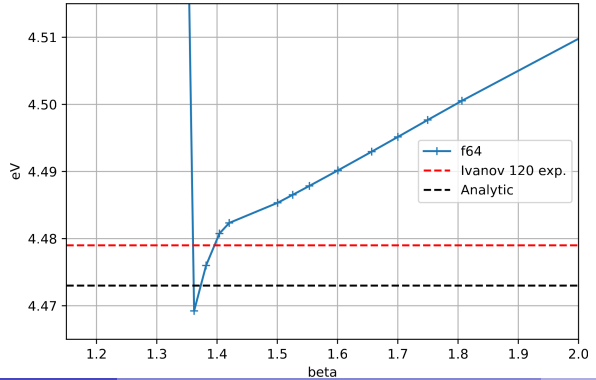
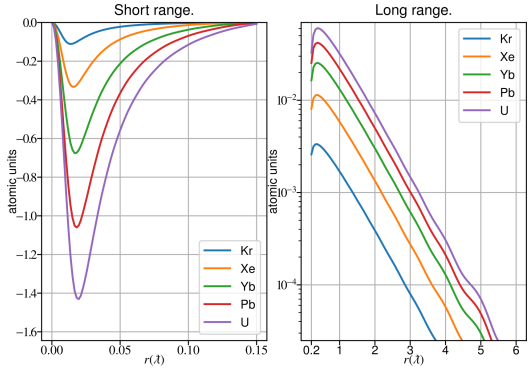


Non-linear VP-density $r^2 \rho_\kappa^{VP[n\geq 3]}(r, Z)$, $|\kappa| = 1$

$\zeta_{\mathsf{min}} = 201$, $\zeta_{\mathsf{max}} = 195883180777$, $N = 50$



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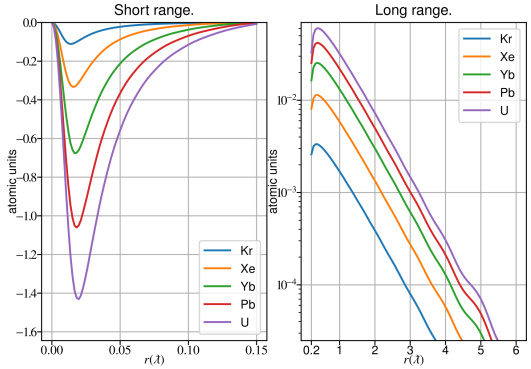

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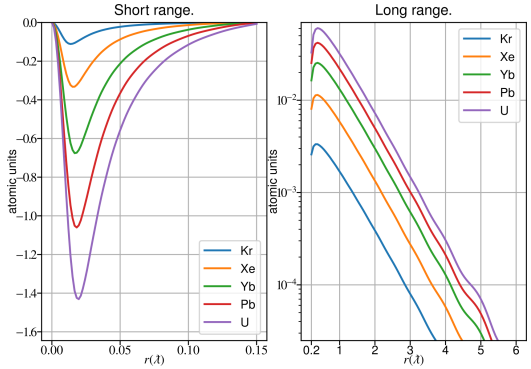

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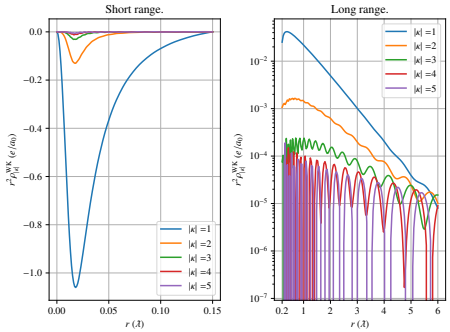

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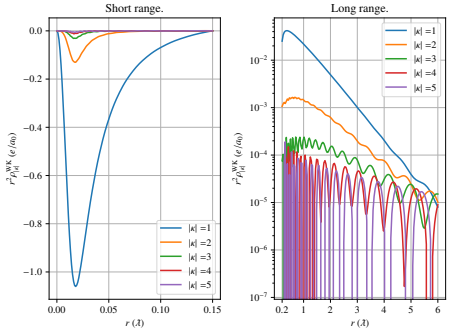

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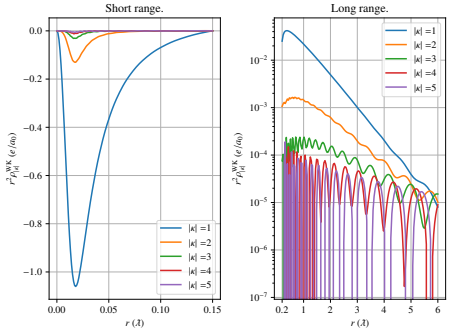

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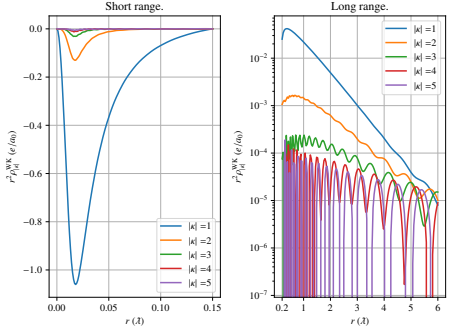

- Suggests that the same VP basis can be used for all κ
- Increasing oscillations;
  - basis set effect; can be damped
    Zoia A. Mandrykina, Zewen Sun, Natalia S. Oreshkina, arXiv:2601.22979 (2026)

Non-linear VP energy shifts (in eV) for $1s_{1/2}$ in U^{91+} (shell nucleus)

$\lvert\kappa\rvert$	Green	Ivanov
1	4.473	4.479
2	0.394	0.396
3	0.081	0.085
4	0.024	0.029
5	0.009	0.014
Total	4.981	5.003

Non-linear VP energy shifts (in eV) for $1s_{1/2}$ in U^{91+} (shell nucleus)

$\lvert\kappa\rvert$	Green	Ivanov	Us
1	4.473	4.479	4.482
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3	0.081	0.085	0.099
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Total	4.981	5.003	5.054

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Katsuhisa Ozaki, Takeshi Ogita, Shin'ichi Oishi, and Siegfried M Rump, Numerical Algorithms **59** (2012) 95

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2	0.394	0.396	0.405	0.399
3	0.081	0.085	0.099	0.089
4	0.024	0.029	0.042	0.032
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Densification of basis

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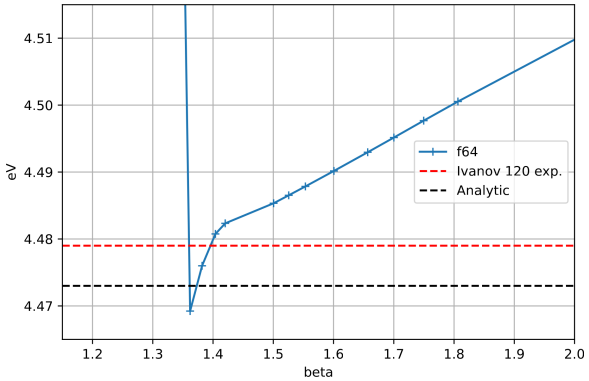

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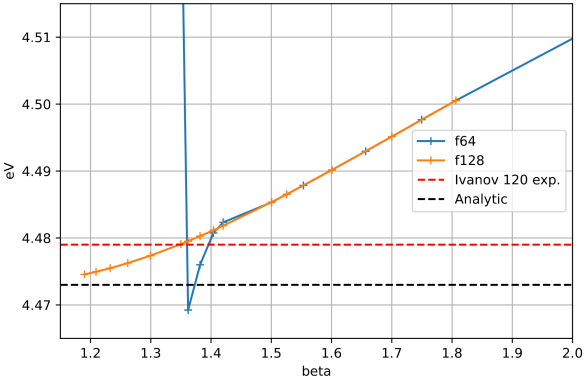

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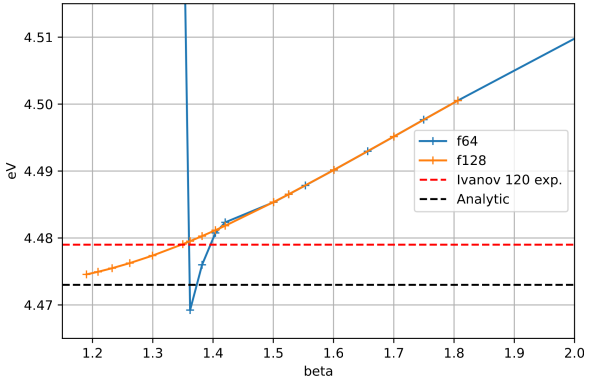

- Suggests extrapolation $\beta \to 1$.

Non-linear VP energy shifts (in eV) for $1s_{1/2}$ in U^{91+} (shell nucleus)

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- Cubic extrapolation

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2	0.394	0.396	0.405	0.399	0.393	0.385
3	0.081	0.085	0.099	0.089	0.081	0.071
4	0.024	0.029	0.042	0.032	0.024	0.011
5	0.009	0.014	0.025	0.015	0.009	-0.005
Total	4.981	5.003	5.054	5.009	4.981	4.941

- Cubic extrapolation
- So far less successful in double precision

More non-linear VP energy shifts (in eV) for $1s_{1/2}$

H. Persson, I. Lindgren, S. Salomonson, and P. Sunnergren, Phys. Rev. A 48, 2772 (1993)

			Persson	Us	
		$\langle r_n^2 \rangle^{1/2}$ (fm)		$N(\beta)$	f128
Kr	uniform	4.230	0.0155	120 (1.19)	0.0152
Xe	uniform	4.826	0.1695	120 (1.19)	0.1703
Yb	uniform	5.273	0.8283	130 (1.17)	0.8248
Pb	uniform	5.505	2.2900	130 (1.17)	2.2890
U	uniform	5.860	4.9863	120 (1.19)	4.9943
U	shell	5.751	4.9815	100 (1.23)	5.0135

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Pb	uniform	5.505	2.2900	130 (1.17)	2.2890	2.2809
U	uniform	5.860	4.9863	120 (1.19)	4.9943	4.9787
U	shell	5.751	4.9815	100 (1.23)	5.0135	4.9811

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		$\langle r_n^2 \rangle^{1/2}$ (fm)		$N(\beta)$	f128	f128+ep
Kr	uniform	4.230	0.0155	120 (1.19)	0.0152	0.0149
Xe	uniform	4.826	0.1695	120 (1.19)	0.1703	0.1686
Yb	uniform	5.273	0.8283	130 (1.17)	0.8248	0.8207
Pb	uniform	5.505	2.2900	130 (1.17)	2.2890	2.2809
U	uniform	5.860	4.9863	120 (1.19)	4.9943	4.9787
U	shell	5.751	4.9815	100 (1.23)	5.0135	4.9811

- Persson: $|\kappa| \in [1,5]$ +extrapolation in $|\kappa|^{-4}$.

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Xe	uniform	4.826	0.1695	120 (1.19)	0.1703	0.1686	0.1695
Yb	uniform	5.273	0.8283	130 (1.17)	0.8248	0.8207	0.8287
Pb	uniform	5.505	2.2900	130 (1.17)	2.2890	2.2809	2.2880
U	uniform	5.860	4.9863	120 (1.19)	4.9943	4.9787	4.9847
U	shell	5.751	4.9815	100 (1.23)	5.0135	4.9811	

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