Universality in the structure of complex atoms and molecules

Jan Philip Solovej
Department of Mathematical Sciences
University of Copenhagen
Visiting Professor IST Austria

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Outline of Talk

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2. The large Z limit and the Ionization Conjecture
3. A density profile of complex atoms
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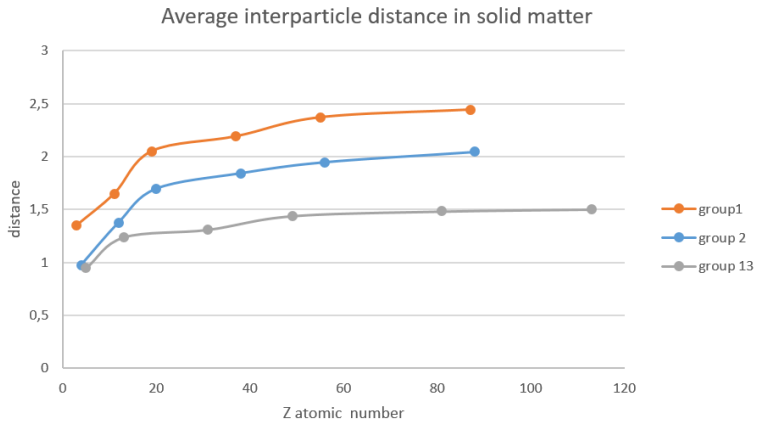
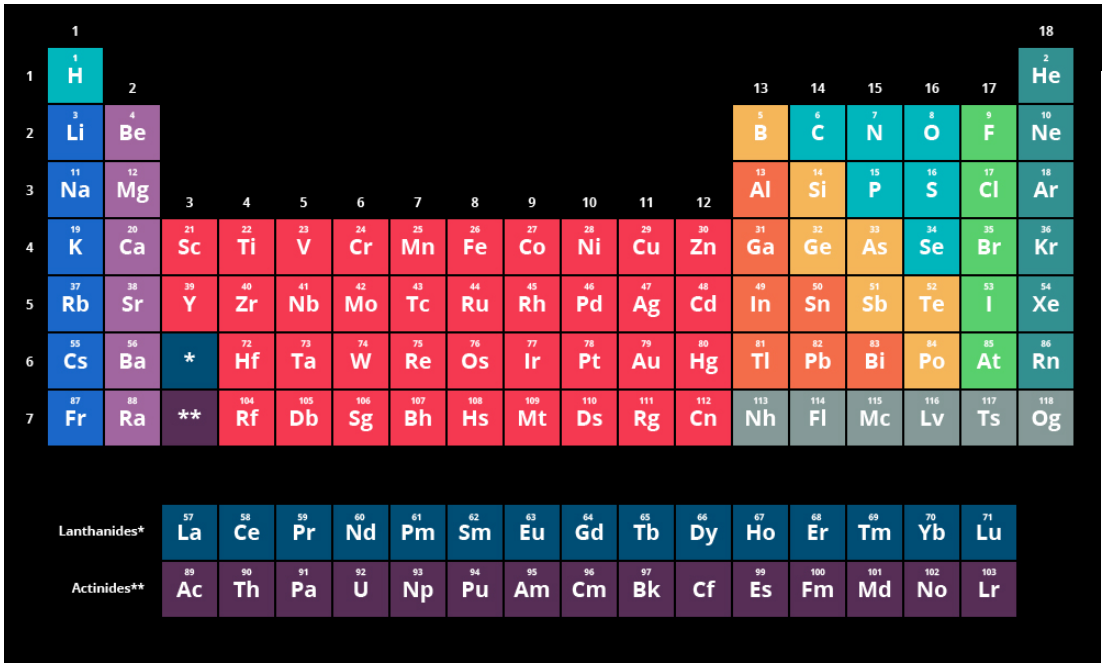
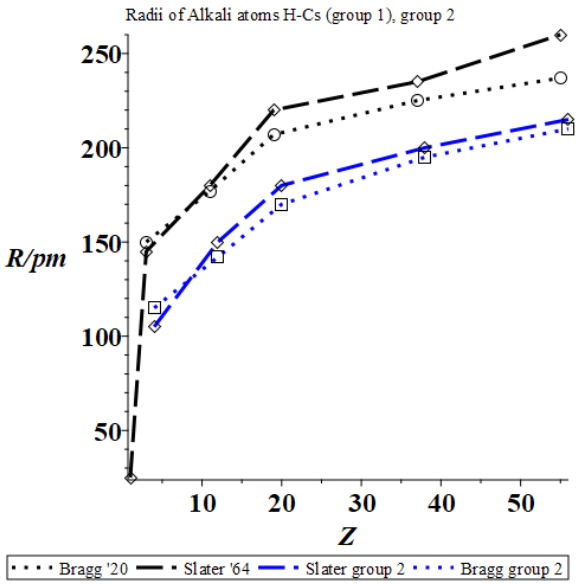
The size of atom

I will discuss the structure of complex atoms. A simple example is the variation of the size of atoms which is fairly constant down the groups in the periodic table. **Can this be explained?**





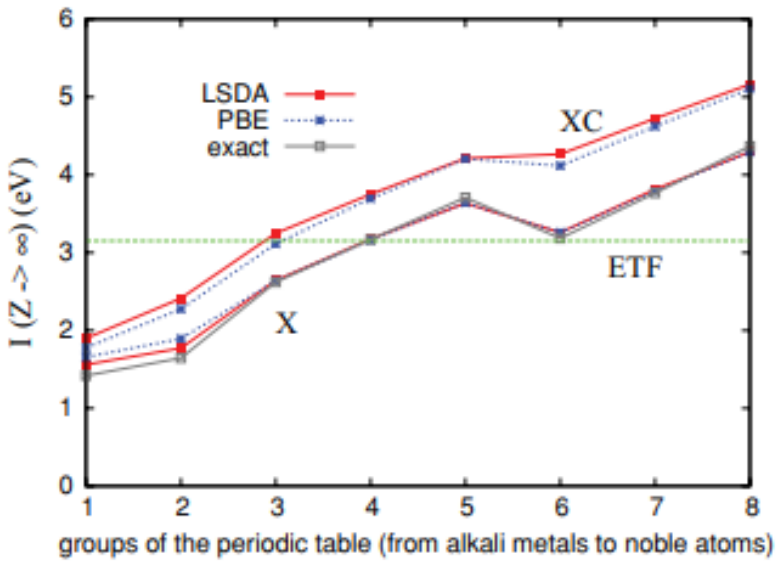


The large Z limit and the Ionization Conjecture

Conjecture (Ionization conjecture)

The **radius**, **maximal negative ionization**, *and* **ionization potential** *of atoms remain bounded as the atomic number* $Z \to \infty$.

There are of course no atoms for very large Z. We can nevertheless still study mathematical models and hope to learn something both **qualitatively** and maybe also **quantitatively** by studying this limit. The plot shows **Density Functional Calculations** of $Z \to \infty$ from:

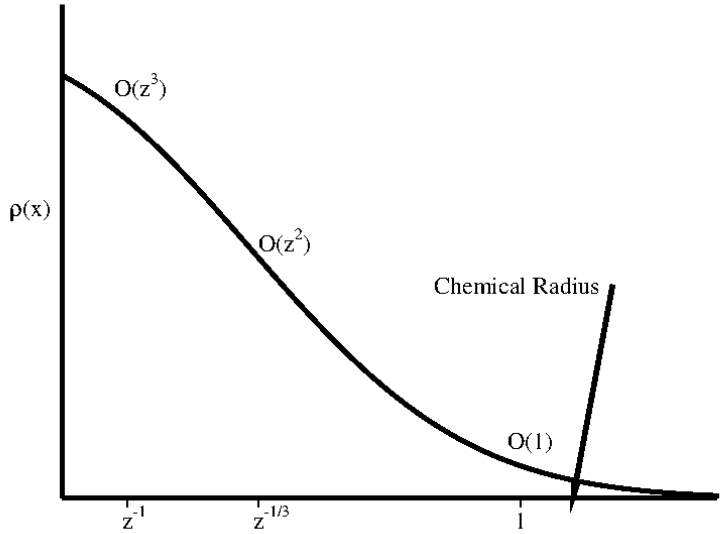


Constantin, Snyder, Perdew, Burke, *Ionization potentials in the limit of large atomic number*, J.Chem.Phys., 2010.

Density profile of complex atoms

The universal behavior of the size of atoms is a fine balance between **electrostatics** and **Pauli exclusion**

- Pauli no electrostatics: radius$\sim Z^{-1/3}$
- Electrostatics no Pauli: radius$\sim Z^{-1}$



Atom with N electrons described in terms of total binding energy $E_Z(N)$ and density $\rho(\boldsymbol{x})$.

m-th ionization potential: Energy to remove m electrons

$$I_m(Z) = E_Z(N = Z - m) - E_Z(N = Z)$$

Radius to last m electrons: $R_m(Z)$

$$\int_{|\boldsymbol{x}|>R_m(Z)} \rho(\boldsymbol{x}) d^3\boldsymbol{x} = m$$

Full quantum many-body description

Hamiltonian: (in atomic units $\hbar = m_e = e = 1$:

$$H_{N,Z} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{|\boldsymbol{x}_i|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_j|}$$

acting on square integrable functions Ψ antisymmetric $(\boldsymbol{x}_i, \sigma_i) \in \mathbb{R}^3 \times \{\pm 1\}$, $i = 1, \dots, N$.

Energy:

$$E_Z^{\mathrm{Q}}(N) = \inf_{\Psi \neq 0} \frac{\langle \Psi | H_{N,Z} \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

Density: For any minimizing Ψ (may not be unique)

$$\rho^{\mathrm{Q}}(\boldsymbol{x}) = \rho_\Psi(\boldsymbol{x}) = N \int d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_N \sum_{\sigma_1, \dots, \sigma_N} |\Psi(\boldsymbol{x}, \sigma_1, \dots, \boldsymbol{x}_N, \sigma_N)|^2$$

Hartree-Fock theory

Restrict to **Slater determinants** of orbitals $\phi_1, \dots, \phi_N$:

$$\Psi(\boldsymbol{x}_1, \sigma_1, \dots, \boldsymbol{x}_N, \sigma_N) = \det\left[\phi_i(\mathbf{x_j}, \sigma_j)\right]_{ij}.$$

Described by its 1-particle density matrix. A projection operator:

$$\gamma = |\phi_1\rangle\langle\phi_1| + \cdots + |\phi_N\rangle\langle\phi_N|.$$

Its density is $\rho_\gamma(\boldsymbol{x}) = \sum_{i=1}^N \sum_\sigma |\phi_i(\boldsymbol{x}, \sigma)|^2$.

Energy functional:

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \frac{\langle\Psi|H_{N,Z}\Psi\rangle}{\langle\Psi|\Psi\rangle} = \mathrm{Tr}\left[-\nabla^2\gamma\right] - \int \frac{Z}{|\boldsymbol{x}|}\rho(\boldsymbol{x})d\boldsymbol{x} + \frac{1}{2}\iint\left(\frac{\rho(\boldsymbol{x})\rho(\boldsymbol{y}) - \mathrm{Tr}_{\,\mathbb{C}^2}|\gamma(x,y)|^2}{|\boldsymbol{x}-\boldsymbol{y}|}\right)d\boldsymbol{x}d\boldsymbol{y}$$

Energy and density:

$$E_Z^{\mathrm{HF}}(N) = \inf_\gamma \mathcal{E}^{\mathrm{HF}}(\gamma), \qquad \rho^{\mathrm{HF}} = \rho_\gamma \text{ of minimizing } \gamma,$$

Thomas-Fermi theory

The simplest density functional theory **(no exchange)**

$$\mathcal{E}^{\mathrm{TF}}(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3} - \int \frac{Z}{|\boldsymbol{x}|}\rho(\boldsymbol{x})d\boldsymbol{x} + \frac{1}{2}\iint \frac{\rho(\boldsymbol{x})\rho(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|}d\boldsymbol{x}d\boldsymbol{y}$$

First term kinetic energy as free Fermi gas. From semiclassics:

$$\frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} = 2(2\pi)^{-3}\int_{|\boldsymbol{p}|<F}\frac{1}{2}\boldsymbol{p}^2 d\boldsymbol{p}, \quad 2(2\pi)^{-3}\int_{|\boldsymbol{p}|<F} 1 d\boldsymbol{p} = \rho$$

Energy and density: $E_Z^{\mathrm{TF}}(N) = \inf_{\rho,\ \int\rho=N} \mathcal{E}^{\mathrm{TF}}(\rho)$, ρ^{TF} minimizer,

Theorem (Energy and ionization in TF, Lieb-Simon 73, Lieb 81)

$$E_Z^{\mathrm{TF}}(Z) = C_{\mathrm{TF}} Z^{7/3}$$

$$\lim_{Z\to\infty} R_m^{\mathrm{TF}}(Z) = R_1^{\mathrm{TF}} m^{-1/3}, \quad \lim_{Z\to\infty} I_m^{\mathrm{TF}}(Z) = I_1^{\mathrm{TF}} m^{7/3}$$

The universality in Thomas-Fermi theory

The universality of Thomas-fermi theory can be understood from the Thomas-Fermi equation for the **mean-field Thomas-Fermi potential** $\phi^{\mathrm{TF}}(\boldsymbol{x}) = Z|\boldsymbol{x}|^{-1} - \rho^{\mathrm{TF}} * |\boldsymbol{x}|^{-1}$:

$$\Delta\phi^{\mathrm{TF}}(\boldsymbol{x}) = C\phi^{\mathrm{TF}}(\boldsymbol{x})^{3/2}. \tag{1}$$

This equation has solutions with singularities (as $\boldsymbol{x} \to 0$)

$$\phi_Z^{\mathrm{TF}}(\boldsymbol{x}) = \frac{Z}{|\boldsymbol{x}|} + O(1)$$

and a solution with a strong singularity

$$\phi_\infty^{\mathrm{TF}}(\boldsymbol{x}) = c|\boldsymbol{x}|^{-4}.$$

All solutions of (1) behave like $\phi_\infty^{\mathrm{TF}}$ at infinity and moreover

$$\phi_Z^{\mathrm{TF}}(x) \to \phi_\infty^{\mathrm{TF}}(x), \quad Z \to \infty.$$

Energy asymptotics for full quantum many-body theory

Theorem (Energy asymptotics)

$$E_Z^{\mathrm{Q}}(Z) = E_Z^{\mathrm{HF}}(Z) + o(Z^{5/3}) = C_{\mathrm{TF}} Z^{7/3} + \frac{1}{2} Z^2 + C_{\mathrm{DS}} Z^{5/3} + o(Z^{5/3})$$

DS=Dirac Schwinger. Second term is Scott's term.

- Physics: Thomas, Fermi, Dirac, Scott, Schwinger
- Mathematical physics: Lieb, Simon, Hughes, Siedentop, Weikard, Fefferman and Seco (Fefferman and Seco wrote 7 papers$\sim$1000 pages, 1990–95)

Note the result is not directly useful for the ionization problem, where we aim at $O(1)$ accuracy.

The Ionization Theorem in Hartree-Fock Theory

Theorem (Ionization Theorem for HF, S. *Annals of Math.* 2003)

$$\overline{\lim_{Z\to\infty}} R_m^{\mathrm{HF}}(Z) = R_1^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3}), \quad \text{as } m \to \infty$$

$\overline{\lim} = \limsup$ / $\liminf$ probably no limit: **periodicity of the infinite periodic table?**

Open question: Can we find sequences $Z_n \to \infty$ so that the limits exist?

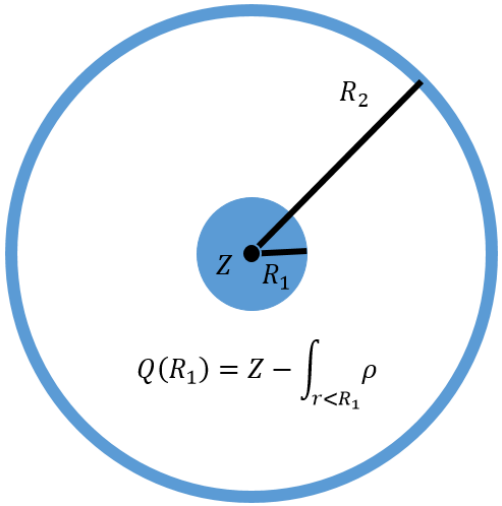
More precisely is this in accordance with the Aufbau principle:

- For fixed $n_\ell + 2\ell$ fill ℓ in increasing order (n_ℓ is ℓ quantum number)
- The groups are $Z_n = \frac{1}{6}n^3 + \ldots$

Proof idea

Iterative semiclassical approximation. Steps:

- Iteration Start. From TF approximation: **Inside charge** $Q(R_0) = \sigma_{\mathrm{TF}} R_0^{-3} + O(R_0^{-3(1-\varepsilon)})$ for $R_0 \sim Z^{-1/3}$.



- Assumption: For some $R_1 \geq R_0$ **inside charge** $Q(R_1) = \sigma_{\mathrm{TF}} R_1^{-3} + O(R_1^{-3(1-\varepsilon)})$
- Perform semiclassical approximation of **"Outside Energy"**

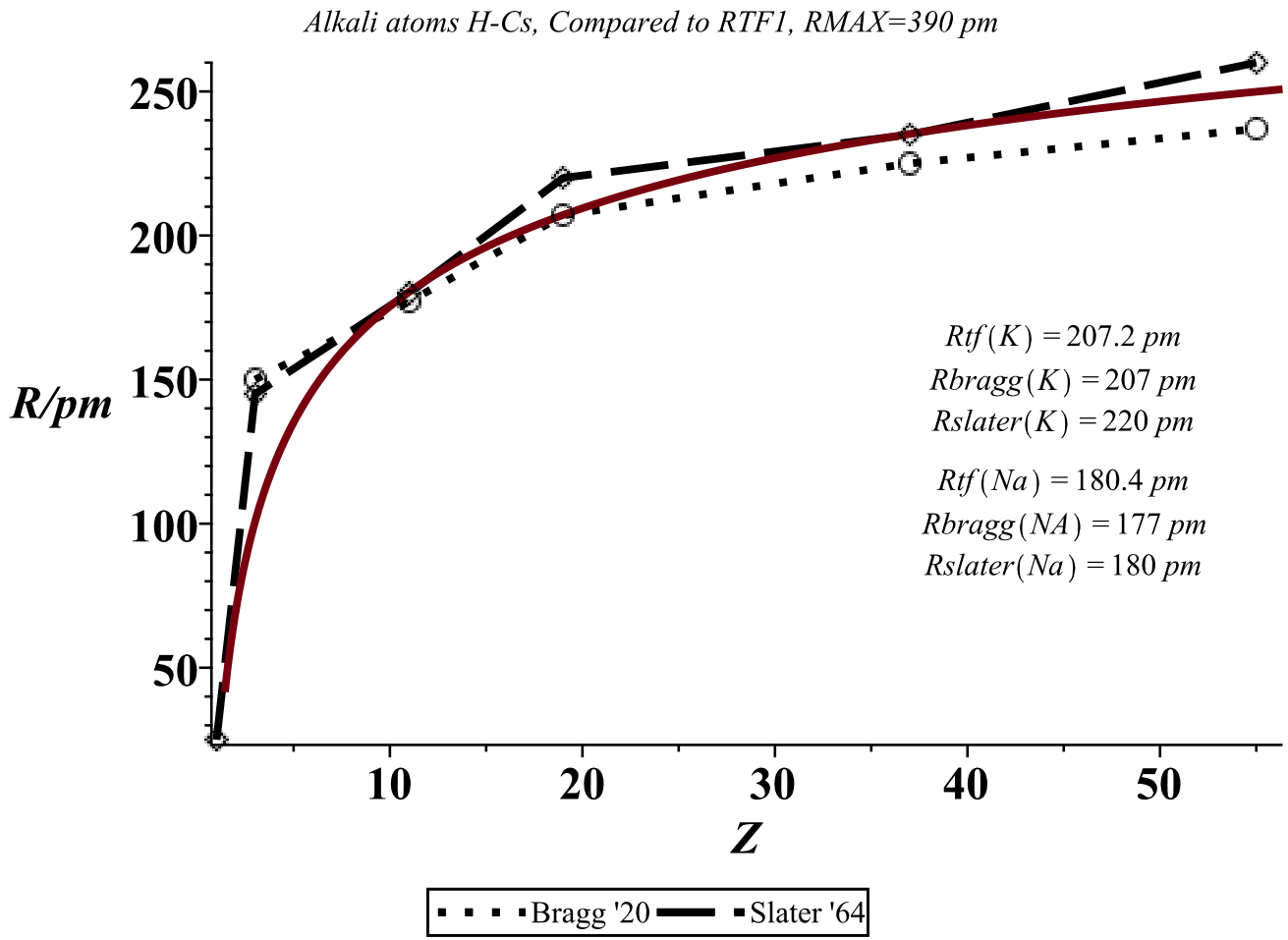
$$E(R_1) = C_{\mathrm{TF}} Q(R_1)^{7/3} + O(Q(R_1))^{7/3(1-\delta)}$$

- For $R_2 = R_1^{(1-\varepsilon')}$ TF universality $\Rightarrow$ $Q(R_2) = \sigma_{\mathrm{TF}} R_2^{-3} + O(R_2^{-3(1-\varepsilon)})$.

Note: Error is in terms of R_2 *not* R_1.

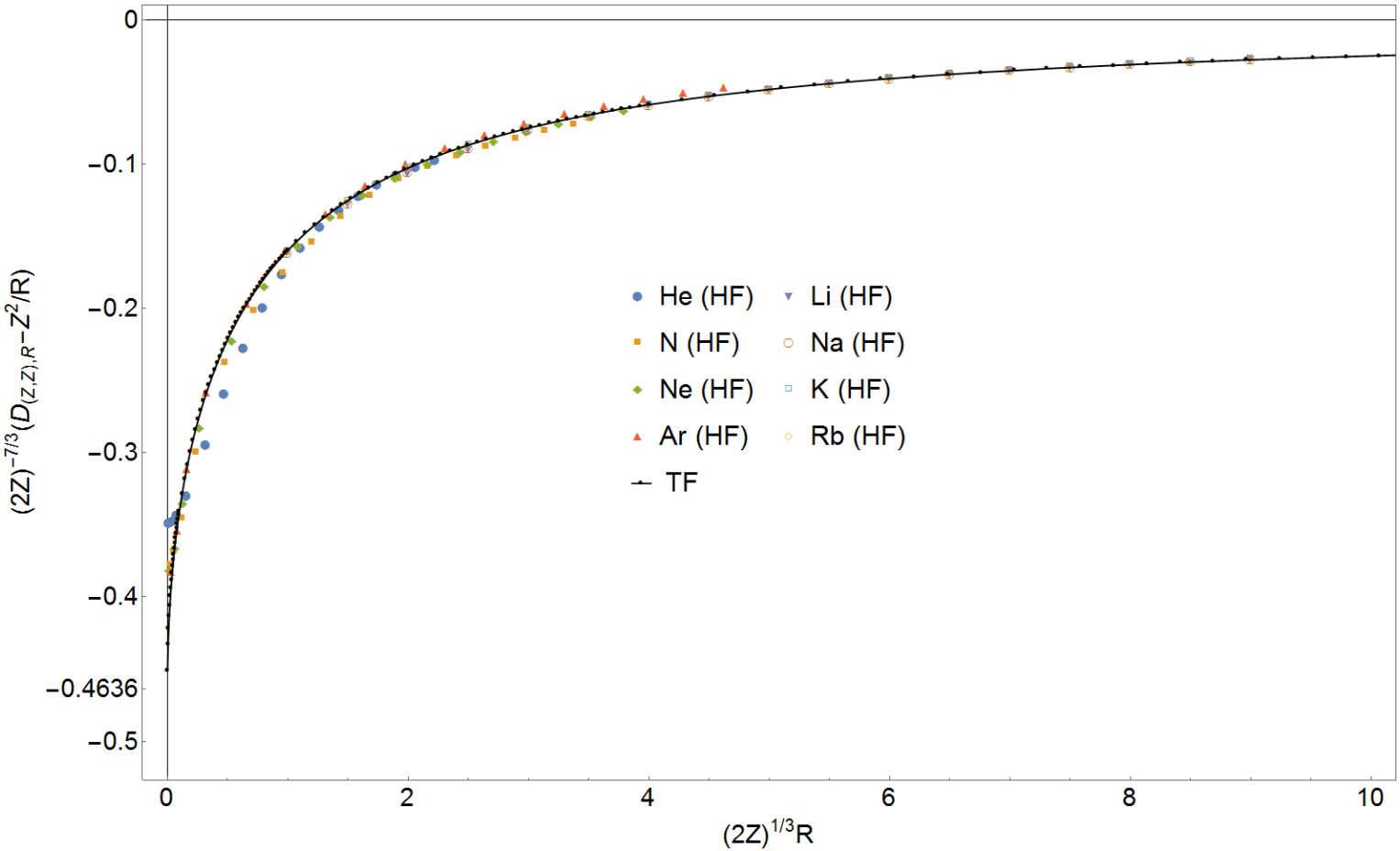
Comparison with experimental/empirical values

Comparision of Alkali radii with R_1^{TF}:



A result for moleules

In works with R. Taylor and N. Gilka using **Dalton** and former Phd. student A. Samojlow we compared rescaled HF diatomic **Born-Oppenheimer curves** with the TF curve. Here plotted without nuclear-nuclear repulsion for clarity:



Conclusion

I have discussed:

- A mathematical formulation of the univesality of complex atomic structure
- Illustrated its validity in Hartree-Fock Theory
- Shown that it leads to a picture with remarkable aggreement with experimental/empirical/numerical values

Open problems:

- Establish universality in the full quantum many body context
- Can we improve the predictions?
- Is there a model of "an infinite" periodic table?
- Can we see the Aufbau principe for large Z?

Thank you for your attention