A model for periodicity of atomic structure

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Joint work with August Bjerg

Outline of Talk

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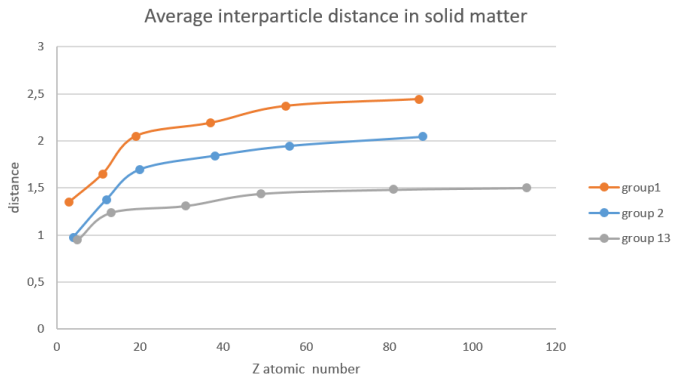
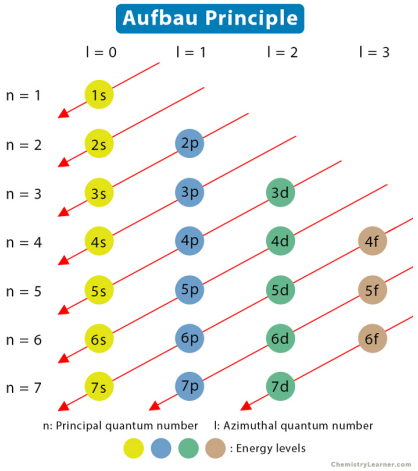
The periodic table

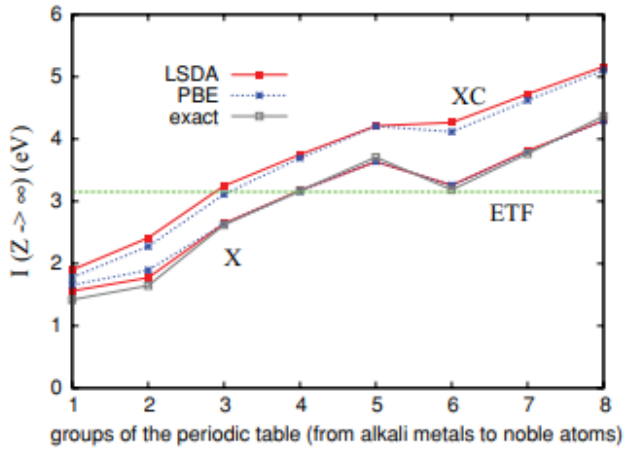
Group → / Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
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
6	55 Cs	56 Ba	* 71 Lu	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
7	87 Fr	88 Ra	** 103 Lr	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
			* 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		
			** 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		

As its name suggests, one of the key features of the periodic table is that it illustrates a **periodicity** of the properties of the elements. Elements in the same group are "more similar" than elements from different groups. We want to discuss a theory in which this periodicity is apparent even in the $Z \to \infty$ limit, i.e. beyond the classical periodic table.



The Aufbau Principle





How do we predict which atoms are in the same group? According to chemists this may be understood from the **Aufbau Principle** (the left figure). Can this be explained?

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 right plot shows **Density Functional Calculations** of $Z \to \infty$ (assuming the Aufbau Principle) from:

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

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)

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

Thomas-Fermi theory

The simplest atomic model

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

First term kinetic energy as free Fermi gas. From microlocal=semiclassical analysis:

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

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

Theorem (Energy approximation of TF, Lieb-Simon '73)

$$\lim_{Z\to\infty} E_Z^{\mathrm{Q}}(Z)/E_Z^{\mathrm{TF}}(Z) = 1, \qquad E_Z^{\mathrm{TF}}(Z) = C_{\mathrm{TF}}Z^{7/3}$$

The Thomas-Fermi potential

It is natural to consider the **Thomas-Fermi mean field potential**

$$\Phi_Z^{\mathrm{TF}}(x) := \frac{Z}{|x|} - \int_{\mathbb{R}^3} \frac{\rho_Z^{\mathrm{TF}}(y)}{|x-y|}\, dy.$$

It is spherically symmetric. For our purposes it has 2 key properties.

Scaling:

- $\mathcal{E}_Z^{\mathrm{TF}}[Z^2\rho(Z^{1/3}\,\cdot\,)] = Z^{7/3}\mathcal{E}_1^{\mathrm{TF}}[\rho]$
- $\rho_Z^{\mathrm{TF}}(x) = Z^2\rho_1^{\mathrm{TF}}(Z^{1/3}x)$
- $\Phi_Z^{\mathrm{TF}}(x) = Z^{4/3}\Phi_1^{\mathrm{TF}}(Z^{1/3}x)$.

Asymptotics:

- $\Phi_1^{\mathrm{TF}}(x) \sim |x|^{-1}, \quad |x| \ll 1$
- $\Phi_1^{\mathrm{TF}}(x) \sim 9\pi^{-2}|x|^{-4}, \quad |x| \gg 1$
- $\Phi_Z^{\mathrm{TF}}(x) = Z^{4/3}\Phi_1^{\mathrm{TF}}(Z^{1/3}x) \to 9\pi^{-2}|x|^{-4}$ as $Z \to \infty$.

From a periodicity point of view this is **not promising**.

The Thomas-Fermi mean field model for the atom

To uncover the periodicity hidden in the Thomas-Fermi model we introduce for each Z the Schrödinger operator

$$H_Z^{\mathrm{TF}} := -\Delta - \Phi_Z^{\mathrm{TF}} \quad \text{unitarily equivalent to } Z^{4/3}(-Z^{-2/3}\Delta - \Phi_1^{\mathrm{TF}})$$

acting on $L^2(\mathbb{R}^3;\mathbb{C}^2)$. It is self-adjoint on $H^2(\mathbb{R}^3;\mathbb{C}^2)$. We refer to this as the **Thomas-Fermi mean field model** for the atom. Consider the natural infinite counterpart

$$H_\infty^{\mathrm{TF}} := -\Delta - 9\pi^{-2}|x|^{-4}.$$

defined on $C_c^\infty(\mathbb{R}^3\backslash\{0\};\mathbb{C}^2)$. It is, however, **not bounded from below** and has many self-adjoint extensions.

Big question: Does H_Z^{TF} approach an extension of H_∞^{TF} in strong resolvent sense as Z tends to infinity?

The short answer is no, but ....

Angular momentum decomposition

Recall the **angular momentum decomposition** of Schrödinger operators with 3-dimensional radially symmetric potentials, i.e. that for such operator $H = -\Delta + V$ we can write

$$H \cong \bigoplus_{\ell=0}^{\infty} \Big(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V \Big) =: \bigoplus_{\ell=0}^{\infty} H_\ell .$$

The H_ℓ's act on $L^2(\mathbb{R}_+) \otimes \mathbb{C}^{2\ell+1} \otimes \mathbb{C}^2$. Thus

$$H_Z = \bigoplus_{\ell=0}^{\infty} H_{Z,\ell} \qquad \text{and} \qquad H_\infty = \bigoplus_{\ell=0}^{\infty} H_{\infty,\ell}.$$

- Self-adjoint extensions of H correspond to self-adjoint extensions of all H_ℓ's.
- H_{Z_n} converges towards (a self-adjoint extensions of) H_∞ in strong resolvent sense if and only if this is the case in every angular momentum component.

Semiclassics and the Aufbau Principle

According to the Aufbau Principle the number of, say, s electrons i.e., $\ell = 0$, satisfies

$$N_{\ell=0} = (6Z)^{1/3} + o(Z^{1/3}) \text{ as } Z \to \infty.$$

Fermi attempted to explain this from a semiclassical approximation. In fact, the number of all negative eigenvalues of

$$-\frac{d^2}{dr^2} - \Phi_Z^{\mathrm{TF}}$$

on $L^2(\mathbb{R}_+; \mathbb{C}^2)$ is given by

$$N_{\ell=0}^{\mathrm{TF}} = 2\pi^{-1} \int_0^\infty (\Phi_Z^{\mathrm{TF}}(r))^{1/2} dr = 2\pi^{-1} Z^{1/3} \int_0^\infty (\Phi_1^{\mathrm{TF}}(r))^{1/2} dr.$$

The constant, however, does not agree with the Aufbau Principle.

The half-line operators

We briefly describe the theory of self-adjoint realizations of one-dimensional Schrödinger operators of the form $-d^2/dx^2 + W$ on $L^2(\mathbb{R}_+)$ for a large class of real-valued potentials W. The main assumption about W is that the equation $f'' = Wf$ has **two linearly independent** solutions which are L^2 near the origin.

1. Define the operator on $C_c^\infty(\mathbb{R}_+)$ and take the closure to get H_{min}.
2. It has deficiency indices $(1,1)$ and self-adjoint extensions described exactly by the domains $D(H_{\mathsf{min}}) \oplus \mathbb{C}\xi f$ where f is from above and ξ localizes near the origin.

Example 1: If W sufficiently regular. Then $D(H_{\mathsf{min}}) = H_0^2(\mathbb{R}_+)$ and choosing an f corresponds to setting boundary conditions.

Example 2: If $W(x) = -9\pi^{-2}x^{-4}$ we take $f(x) = x \cdot \sin(\frac{3}{\pi x} + \theta)$.

Main result

Theorem (Subsequence convergence, Bjerg-Sol.)

$\{H^{\mathrm{TF}}_{Z_n}\}_{n=1}^{\infty}$ converges in the strong resolvent sense as $Z_n \to \infty$ if and only if there is a $\theta \in [0,\pi)$ such that

$$Z_n^{1/3} \int_0^{\infty} \Phi_1^{1/2}\, dr = \int_0^{\infty} \Phi_{Z_n}^{1/2}\, dr \longrightarrow \theta \qquad (\mathit{mod} \quad \pi)$$

The limiting operator is the self-adjoint extension of H^{TF}_{∞} defined by $D(H^{\mathrm{TF}}_{\infty,\ell,\theta}) = D(H^{\mathrm{TF}}_{\infty,\ell,min}) \oplus \xi g_{\infty,\ell,\theta}$ where ξ is a localizing function,

$$g_{\infty,\ell,\theta}(x) = \cos\left(\theta + \frac{\ell\pi}{2} + \frac{\pi}{4}\right) \cdot j_\ell\left(\frac{3}{\pi x}\right) + \sin\left(\theta + \frac{\ell\pi}{2} + \frac{\pi}{4}\right) \cdot y_\ell\left(\frac{3}{\pi x}\right)$$

where j_ℓ and y_ℓ are the spherical Bessel-functions.

In particular $g_{\infty,0,\theta}(x) = x \cdot \sin(\frac{3}{\pi x} + \theta - \frac{\pi}{4})$.

Sketch of the proof

1. Reduction to the 1-dimensional problem
2. Deducing from the fact that $\Phi_{Z_n} \to 9\pi^{-2}|x|^{-4}$ a convergence of the minimal realizations; "$H^{\mathrm{TF}}_{\infty,\ell,\min} \subseteq \lim H^{\mathrm{TF}}_{Z_n,\ell,\min}$"
3. Realizing that as a consequences of step 2 it suffices to show that for each ℓ a sequence of regular (i.e. from $D(H^{\mathrm{TF}}_{Z_n,\ell})$) approximate solutions to

$$f''(x) = \left[\frac{\ell(\ell+1)}{x^2} - \Phi^{\mathrm{TF}}_{Z_n}(x)\right] f(x)$$

   converges towards $g_{\infty,\ell,\theta}$ in L^2 near the origin
4. Constructing the approximate solutions from step 3. Here, one splits the problem in the **asymptotic parts** (near the origin and ∞) and a **semi-classical part** to which the Green-Liouville approximation (WKB) is applied. As a last step these solutions are glued together.

WKB-type mathching

- Near origin the **true regular solution** is very close to the regular solution $\sqrt{x}J_{2\ell+1}(2\sqrt{Zx})$ of the corresponding asymptotic equation.
- On the "semi-classical" the potential is negative and we apply the Green- Liouville approximation. The **true regular solution** is for some η close to

$$\Phi_Z(x)^{-1/4}\sin\Big(\int_0^x \big[\Phi_Z(x) - \frac{\ell(\ell+1)}{x^2}\big]_+^{1/2}\,dx + \eta\Big).$$

- At large distances we do not control the true regular solution. Instead we consider the exact solutions **asymptotic equation**, i.e., a linear combination of $j_\ell(3/\pi x)$ and $y_\ell(3/\pi x)$.

Gluing, choosing first η then the correct linear combination, is possible since the large Z asymptotics agree on overlap regions.

Note: Maybe not surprising this works for $\ell = 0$. The interesting part is that all the $\ell \neq 0$ solutions seem to follow for free.

Concluding remark

- We have discussed a model of atoms that in the limit of large Z shows a periodic behavior.
- The limiting sequences Z_n that produce converging atoms agree with the Aufbau Principle up to an overall constant factor.
- This is not the full story as we have not discussed which states are occupoied in the infinite atom.
- It would be interesting to understand more complicated atomic models.

Congratulations Anders!