Periodicity of atomic structure in a Thomas-Fermi mean-field model

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QMATH
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Outline

1. Motivation: The periodic table of the elements
2. (Non-)Periodicity of large atoms?
   – 3 (hopefully well know) models
3. The infinite atoms in the TFMF-model
4. Outlook

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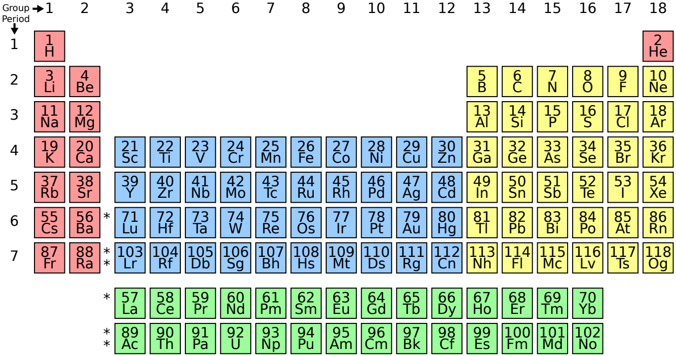
The periodic table

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 the fact that that it illustrates a **periodicity** of the properties of the elements. Elements in the same group are chemically "more similar" than elements from different groups.

THE PERIODIC TABLE



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Blindly continuing this periodicity in the $Z \to \infty$ limit leads to the asymptotic formula $Z_n \approx n^3/6$ for the atomic numbers when "leaving" the red block.

Schrödinger theory for atoms

We will throughout our presentation ignore relativistic effects and use units in which $e = 2m_e = \hbar = 1$. With these choices, the **Schrödinger Hamiltonian**

$$H_Z = \sum_{i=1}^{Z} \left(-\Delta_i - \frac{Z}{|x_i|} + \frac{1}{2} \sum_{j \neq i} \frac{1}{|x_i - x_j|} \right)$$

is believed to describe the behaviour of **neutral** atoms. Here,

$$(x_1, \ldots, x_Z) \in (\mathbb{R}^3)^Z,$$

and the operator H_Z acts on the antisymmetric (fermionic) subspace of the Hilbert space $L^2(\mathbb{R}^3; \mathbb{C}^2)^{\otimes Z}$ including 2 spin degrees of freedom.

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- In the ideal world, we would be able to detect a periodicity in H_Z as $Z \to \infty$, but...
- Taking the $Z \to \infty$ limit in Schrödinger theory is notoriously difficult.

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The TF- and TFMF-models

In Thomas-Fermi theory for atoms the energy of the system is modelled by

$$\mathcal{E}_Z^{\mathrm{TF}}[\rho] = \int_{\mathbb{R}^3} c_{\mathrm{TF}}\,\rho(x)^{5/3} - \frac{Z\rho(x)}{|x|}\,dx + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy$$

where $\rho \geq 0$ is the electronic density. We denote the unique minimizer of this functional ρ_Z^{TF}. This is radially symmetric and has $\int \rho_Z^{\mathrm{TF}} = Z$, thus describes a neutral atom.

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We introduce finally for each Z the Schrödinger operator

$$H_Z^{\mathrm{TF}} := -\Delta - \Phi_Z^{\mathrm{TF}}$$

acting on $L^2(\mathbb{R}^3)$. It is essentially self-adjoint on $C_c^\infty(\mathbb{R}^3)$. We refer to its self-adjoint closure as the *Thomas-Fermi mean-field model for the atom*.

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Thomas-Fermi theory

Here the convergences

$$\rho_Z^{\mathrm{TF}}(x) \longrightarrow 234\pi|x|^{-6} \quad \text{and} \quad \Phi_Z^{\mathrm{TF}}(x) \longrightarrow 81\pi^2|x|^{-4}$$

as $Z \to \infty$ show the non-existence of (an obvious) periodicity.

Periodicity of large atoms?

In the TFMF-model we will study **strong resolvent convergence**. If

$$(A_n + i)^{-1} \longrightarrow (A + i)^{-1}$$

strongly as $n \to \infty$ then one says that $A_n \to A$ in the strong resolvent sense.

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Theorem (Periodicity in TFMF-model)

Consider a sequence $\{Z_n\}_{n=1}^{\infty}$ such that $Z_n \to \infty$ as $n \to \infty$. Then $H^{\mathrm{TF}}_{Z_n}$ is converging in the strong resolvent sense if and only if[a]

$$\frac{1}{4\pi^2} \int_{\mathbb{R}^3} \frac{\Phi^{\mathrm{TF}}_{Z_n}(x)^{1/2}}{|x|^2}\, dx = \frac{Z_n^{1/3}}{\pi} \int_0^\infty \Phi^{\mathrm{TF}}_1(r)^{1/2}\, dr =: Z_n^{1/3} D_{\mathrm{cl}}$$

is convergent modulo 1. Note that we can take $Z_n \approx D_{\mathrm{cl}}^{-3} n^3$ here.

[a] Using the notation $\Phi^{\mathrm{TF}}_Z(|x|) = \Phi^{\mathrm{TF}}_Z(x)$.

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Form of the infinite TFMF-operators

We now discuss the limits of the sequences $\{H_{Z_n}^{\mathrm{TF}}\}_{n=1}^{\infty}$. For this we consider the natural infinite counterpart of the H_Z^{TF}'s, i.e. the operator

$$H_{\infty}^{\mathrm{TF}} := -\Delta - 81\pi^2|x|^{-4}.$$

At least this is well defined on the dense set $C_c^{\infty}(\mathbb{R}^3\setminus\{0\}) \subseteq L^2(\mathbb{R}^3)$.

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However, H^{TF}_{∞}

- is not essentially self-adjoint,
- is not bounded from below,
- has many and very similar self-adjoint extensions.

One needs to handle this problem as self-adjointness is fundamental in Schrödinger's theory.

Angular momentum decomposition

For a more precise description we need crucially 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

$$H \simeq \bigoplus_{\ell=0}^{\infty} \Big(-\frac{d^2}{dx^2} + \frac{\ell(\ell+1)}{x^2} + V \Big) =: \bigoplus_{\ell=0}^{\infty} H_\ell$$

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

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- Self-adjoint extensions of all H_ℓ's yield a self-adjoint extension of H.
- In this set-up, $H_{Z_n}^{\mathrm{TF}}$ converges towards (a self-adjoint extensions of) H_∞^{TF} if and only if this is the case in every angular momentum component.

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 real-valued potentials $W \in L^2_{\mathrm{loc}}(\mathbb{R}_+)$ (satisfying weak assumptions at ∞).

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Example 2: If W is sufficiently regular, the procedure in ③ amounts to putting boundary conditions at the origin.
Example 3: If $W(x) = -81\pi^2 x^{-4}$ we can take $f(x) = x \cdot \cos(\frac{9\pi}{x} - \theta)$.

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The infinite TFMF-atoms

Theorem

Consider a sequence $\{Z_n\}_{n=1}^{\infty}$. The sequence of operators $\{H_{Z_n}^{\mathrm{TF}}\}_{n=1}^{\infty}$ converges in the strong resolvent sense towards a self-adjoint extension of H_{∞}^{TF} if and only if $Z_n \to \infty$ and

$$\frac{1}{\pi}\int_0^{\infty} (\Phi_{Z_n}^{\mathrm{TF}})^{1/2}\, dr \longrightarrow \tau \qquad (\mathrm{mod} \quad 1)$$

as $n \to \infty$ for some number τ. In the affirmative case the limiting operator $H_{\infty,\tau}^{\mathrm{TF}}$ is defined by the self-adjoint extensions of the $H_{\infty,\ell,\min}^{\mathrm{TF}}$'s with domains $D(H_{\infty,\ell,\min}^{\mathrm{TF}}) \oplus \mathbb{C}\xi g_{\infty,\ell,\tau}$ where ξ is a localizing function and

$$g_{\infty,\ell,\tau}(x) = \sin\left(\tau\pi + \frac{\ell\pi}{2} + \frac{\pi}{4}\right) \cdot j_\ell\left(\frac{9\pi}{x}\right) - \cos\left(\tau\pi + \frac{\ell\pi}{2} + \frac{\pi}{4}\right) \cdot y_\ell\left(\frac{9\pi}{x}\right)$$

with j_ℓ and y_ℓ the spherical Bessel-functions.

Note that in particular $g_{\infty,0,\tau}(x) \propto x \cdot \cos(\frac{9\pi}{x} - \tau\pi - \frac{\pi}{4})$.

The infinite TFMF-atoms: Bonus info

1. The map
$$S^1 \ni (\cos(2\tau\pi), \sin(2\tau\pi)) \longmapsto H^{\mathrm{TF}}_{\infty,\tau}$$
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2. The form of $g_{\infty,\ell,\tau}$ comes from the expression
$$\tau + \frac{\ell}{2} + \frac{1}{4} = \underbrace{-\frac{2\ell+1}{4+2\cdot(-1)} - \frac{1}{4}}_{\Phi_1^{\mathrm{TF}} \sim |x|^{-1} \text{ near } 0} + \tau \underbrace{-\frac{2\ell+1}{4+2\cdot(-4)} - \frac{1}{4}}_{\Phi_1^{\mathrm{TF}} \sim |x|^{-4} \text{ near } \infty}$$
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mod 1. Here, the different contributions come from an analysis of the "regular" solutions to the equation

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

on intervals $(0, (Z\varepsilon(Z))^{-1})$, $((Z\varepsilon(Z))^{-1}, \varepsilon(Z))$ and $(\varepsilon(Z), \infty)$ respectively, with $\varepsilon(Z) \to 0$ very slowly as $Z \to \infty$.

Directions for further research

1. Studying asymptotic periodicity in more advanced models. A starting point could be considering a "Thomas-Fermi-von Weizsäcker mean-field model". Here it is known that

$$\Phi_Z^{\mathrm{TFW}}(x) \xrightarrow{Z\to\infty} \Phi_\infty^{\mathrm{TFW}}(x) = 81\pi^2|x|^{-4} + \mathcal{O}_{|x|\to 0}(|x|^{-2})$$

for small x. Also, one could study real-valued quantities in more advanced models as for example the atomic radius in Hartree-Fock theory.

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Thank you for your attention!