# Structure of complex atoms and the periodic table of the elements

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QMATH

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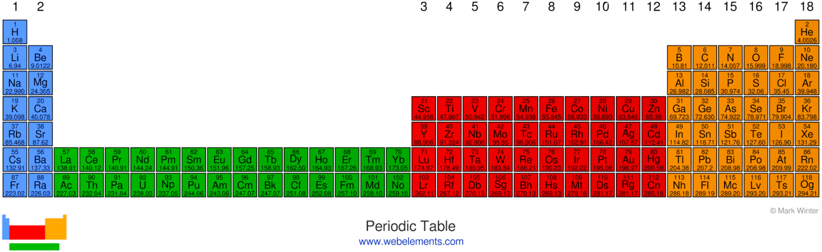
# Outline of Lectures I

# Outline of Lectures II

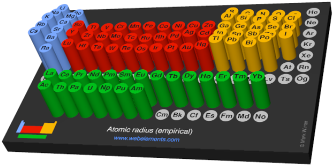
# Periodic Table of the Elements

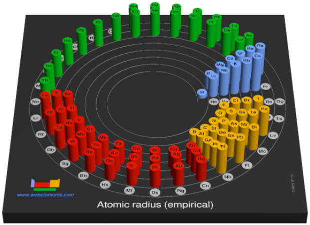


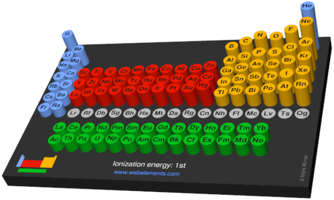

| Reihen | Gruppe I. — R²O | Gruppe II. — RO | Gruppe III. — R²O³ | Gruppe IV. RH⁴ RO² | Gruppe V. RH³ R²O⁵ | Gruppe VI. RH² RO³ | Gruppe VII. RH R²O⁷ | Gruppe VIII. — RO⁴ |
|---|---|---|---|---|---|---|---|---|
| 1 | H=1 | | | | | | | |
| 2 | Li=7 | Be=9,4 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Na=23 | Mg=24 | Al=27,3 | Si=28 | P=31 | S=32 | Cl=35,5 | |
| 4 | K=39 | Ca=40 | —=44 | Ti=48 | V=51 | Cr=52 | Mn=55 | Fe=56, Co=59, Ni=59, Cu=63. |
| 5 | (Cu=63) | Zn=65 | —=68 | —=72 | As=75 | Se=78 | Br=80 | |
| 6 | Rb=85 | Sr=87 | ?Yt=88 | Zr=90 | Nb=94 | Mo=96 | —=100 | Ru=104, Rh=104, Pd=106, Ag=108. |
| 7 | (Ag=108) | Cd=112 | In=113 | Sn=118 | Sb=122 | Te=125 | J=127 | |
| 8 | Cs=133 | Ba=137 | ?Di=138 | ?Ce=140 | — | — | — | — — — — |
| 9 | (—) | — | — | — | — | — | — | |
| 10 | — | — | ?Er=178 | ?La=180 | Ta=182 | W=184 | — | Os=195, Ir=197, Pt=198, Au=199. |
| 11 | (Au=199) | Hg=200 | Tl=204 | Pb=207 | Bi=208 | — | — | |
| 12 | — | — | — | Th=231 | — | U=240 | — | — — — — |

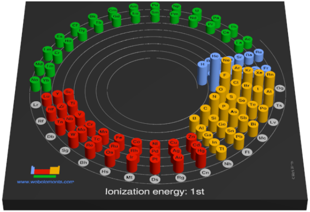
Dmitry Mendeleev (1834-1907)

# Ionization Energy and Radius of Atoms

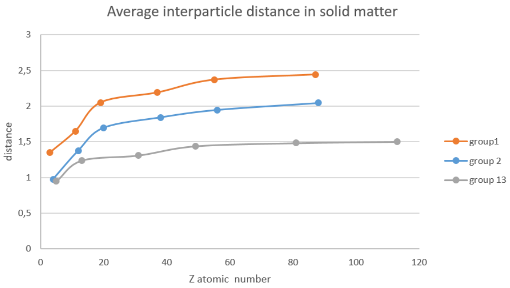


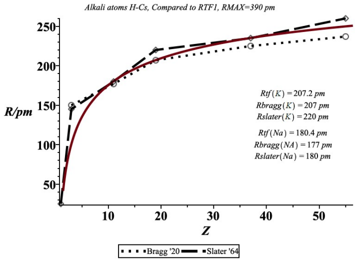



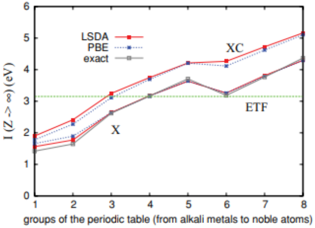



# More Data

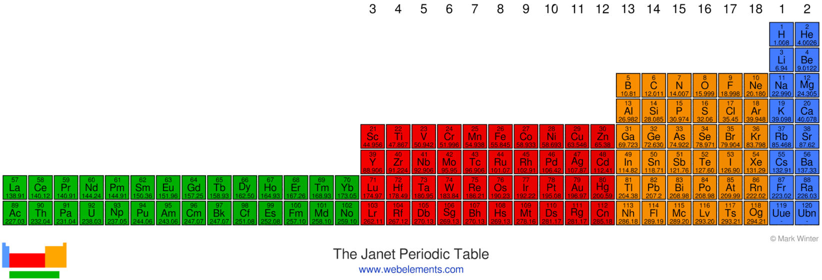



From Constantin, Snyder, Perdew and Burke, Ionization Potentials in the limit of large atomic number *J. Chem. Phys.* *2010,* $Z \approx 3000$

# Janet Periodic table, Madelung rule (Aufbau Principle)

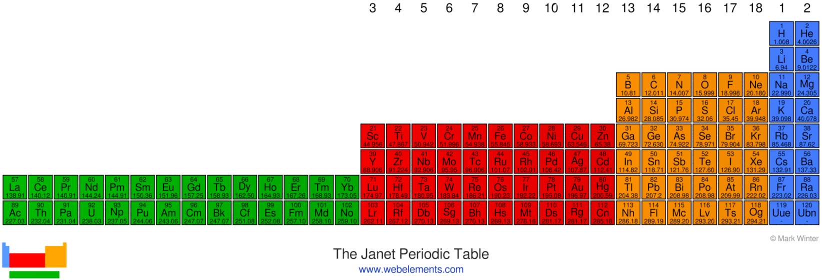



This form illustrates the Madelung rule (Aufbau principle).

**QUESTION: Is the Periodic Table (approximately) periodic in some sense?**

**QUESTION: Does it become exactly periodic as $Z \to \infty$?**

Let us consider the filled group (column) in each block (color).




The Janet Periodic Table
www.webelements.com

The filled groups for $\ell = 0, 1, 2, 3$ $(s, p, d, f)$ $(n_\ell = \#$ of $\ell$ levels-filled$)$:

$$Z_\ell^{\mathrm{Aufbau}}(n_\ell = 2j) = \frac{4}{3}(j+\ell)(j+\ell+\frac{1}{2})(j+\ell+1) - 2\ell^2$$

$$Z_\ell^{\mathrm{Hydrogen}}(n_\ell) = \frac{2}{3}(n_\ell+\ell)(n_\ell+\ell+\frac{1}{2})(n_\ell+\ell+1)$$

Note then $n_\ell = 2j \approx 2(3Z/4)^{1/3} - \ell)$ as $Z \to \infty$. If $\ell \approx \lambda Z^{1/3}$:

$$N_\ell^{\mathrm{Aufbau}}(Z) = 2(2\ell+1)n_\ell \approx 4\lambda[6^{1/3} - 2\lambda]_+ Z^{2/3}$$

$$N_\ell^{\mathrm{Hydrogen}}(Z) \approx 4\lambda[(3/2)^{1/3} - \lambda]_+ Z^{2/3}.$$

# Atomic Model Q: Many-body Quantum

Hamiltonian of atom no. $Z$ with $N$ electrons

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

acting on antisymmetric wave functions $\mathcal{H}_N = \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$. The domain is $H^2$. We use atomic or Hartree units with $\hbar = e = m = 1$.

## Definition (Ground state energy )

$$E_Z^{\mathrm{Q}}(N) = \inf\{\langle \Psi, H_Z(N)\Psi\rangle \ : \ \Psi \in \mathcal{H}_N \cap H^2, \ \|\Psi\| = 1\}$$

This energy is bounded below, as we show next.

# Simple Lower Bound on the Energy

We can get a simple lower bound on the energy $E_Z^{\mathrm{Q}}(N)$ by ignoring interactions

$$H_Z(N) \geq \sum_{i=1}^{N} \left( -\frac{1}{2}\Delta_i - \frac{Z}{|x_i|} \right)$$

The non-interacting model on the left has the hydrogen Hamiltonian

$$-\frac{1}{2}\Delta - \frac{Z}{|x|}.$$

Rescaling $x \to Z^{-1}x$ we see that this Hamiltonian is unitarily equivalent to

$$Z^2 \left( -\frac{1}{2}\Delta - \frac{1}{|x|} \right).$$

The energies are known explicitly:

$$E_n = -\frac{1}{2}\frac{Z^2}{n^2} \quad n = 1, 2, \ldots.$$

# Lower Bound Continued

The degeneracy is that level $n$ contains angular momenta

$$l = 0, \ldots, n-1.$$

Hence the total degeneracy is $\sum_{\ell=0}^{n-1} 2(2\ell+1) = 2n^2$. The factor 2 is counting spin. To get $N$ electrons we use $k$ levels with

$$N = \sum_{n=1}^{k} 2n^2 = \frac{2}{3}k(k+\frac{1}{2})(k+1).$$

We therefore get the lower bound on the ground state energy

$$E_Z^{\mathrm{Q}}(N) \geq \sum_{n=1}^{k} -2n^2 \frac{1}{2}\frac{Z^2}{n^2} = -kZ^2 \geq -(3/2)^{1/3} Z^2 N^{1/3}.$$

**Exercise:** Give similar upper bound (we return to this).

Note $n_\ell = \sum_{n=\ell+1}^{k} 1 = k - \ell \approx (3Z/2)^{1/3} - \ell$.

# The Ground State Energy and the Maximal Ionization

### Proposition

*$N \mapsto E_Z^{\mathrm{Q}}(N)$ is non-increasing*

### Theorem (Hunziker- van Winter-Zhislin (HVZ) Theorem)

*If $E_Z^{\mathrm{Q}}(N) < E_Z^{\mathrm{Q}}(N-1) <$ then $E_Z^{\mathrm{Q}}(N)$ is an eigenvalue (possibly degenerate). The eigenfunction is the ground state.*

### Theorem (Zhislin's Theorem)

*$N \mapsto E_Z^{\mathrm{Q}}(N)$ is strictly decreasing for $N \leq Z$.*

### Definition (Maximal Negative Ionization)

*The maximal number of electrons the atom can bind is*

$$N_c^{\mathrm{Q}}(Z) = \min\{N \in \mathbb{Z} \mid N \mapsto E_Z^{\mathrm{Q}}(N) \text{ is constant for } N \geq N_c^{\mathrm{Q}}\}.$$

*By Zhislin $N_c^{\mathrm{Q}} \geq Z$. The maximum negative ionization is $N_c^{\mathrm{Q}} - Z \geq 0$.*

## Theorem (Lieb's Bound on the Maximal Ionization)

*If* $E_Z^{\mathrm{Q}}(N) < E_Z^{\mathrm{Q}}(N-1)$ *then* $N < 2Z+1$. *Thus* $N_c^{\mathrm{Q}} < 2Z+1$.

## Proof.

We will use Hardy's inequality in 3-dimensions

$$\begin{aligned}-|x|\Delta - \Delta|x| =& -2|x|^{1/2}\Delta|x|^{1/2} - [[\Delta, |x|^{1/2}], |x|^{1/2}] \\ =& 2|x|^{1/2}\left(-\Delta - \frac{1}{4}|x|^{-2}\right)|x|^{1/2} \geq 0.\end{aligned}$$

Let $\Psi$ be a real normalized ground state $H_Z(N)\Psi = E_Z(N)\Psi$. Then

$$\begin{aligned}E_Z^{\mathrm{Q}}(N)\||x_1|^{1/2}\Psi\|^2 =& \langle\Psi, |x_1|H_Z(N)\Psi\rangle \\ \geq& -Z + \sum_{i=2}^{N}\langle\Psi, \frac{|x_1|}{|x_i - x_1|}\Psi\rangle + \underbrace{\langle|x_1|^{1/2}\Psi, H_Z(N-1)|x_1|^{1/2}\Psi\rangle}_{\geq E_Z^{\mathrm{Q}}(N-1)\||x_1|^{1/2}\Psi\|^2}\end{aligned}$$

Thus $0 > -NZ + \left\langle\Psi, \sum_{i<j}\frac{|x_i|+|x_j|}{|x_i-x_j|}\Psi\right\rangle \geq -NZ + \frac{1}{2}N(N-1)$. □

# One-particle Density Matrix and Density

**The 1-particle density matrix (1pdm)**: Trace class operator $\gamma_\Psi$ on $L^2(\mathbb{R}^3;\mathbb{C}^2) = L^2(\mathbb{R}^3\times\{-,+\})$. Notation $z=(x,\sigma)\in\mathbb{R}^3\times\{-,+\}$

$$\gamma_\Psi(x,\sigma;y,\tau) = N\int \Psi(x,\sigma,z_2,\ldots,z_N)\overline{\Psi(y,\tau,z_2,\ldots,z_N)}dz_2.\cdots z_N$$

$\mathrm{Tr}\,\gamma_\Psi = N$. Fermionic property: $0\leq\gamma_\Psi\leq\mathbb{1}$.

**Density:** $\rho_\Psi(x)=\sum_\sigma\gamma_\Psi(x,\sigma;x,\sigma)$. $\int\rho_\Psi = N$

**Ionization Energy:** Energy to remove $m$ electrons from neutral atom

$$I_Z^{\mathrm{Q}}(m) = E_Z^{\mathrm{Q}}(Z-m) - E_Z^{\mathrm{Q}}(Z) > 0, \quad I_Z^{\mathrm{Q}} = I_Z^{\mathrm{Q}}(1)$$

**Radius to last *m*-th electron**: $R_Z^{\mathrm{Q}}(m)$ defined by:

$$\int_{|x|\geq R_Z^{\mathrm{Q}}(m)}\rho_\Psi = m.$$

# The Ionization Conjecture

## Conjecture (Ionization Conjecture)

*There is a universal constants $C_1 > 0$ and constants $C_2(m), C_3(m) > 0$ depending only on $m$, but not on $Z$ such that*

$$\begin{aligned} N_c^{\mathrm{Q}}(Z) &\leq Z + C_1 \\ R_Z^{\mathrm{Q}}(m) &\geq C_2(m) \\ I_Z^{\mathrm{Q}}(m) &\leq C_3(m). \end{aligned}$$

An even more ambitious question relates to the limiting behavior of $N_c^{\mathrm{Q}}, R_Z^{\mathrm{Q}}(m), I_Z^{\mathrm{Q}}(m)$ as $Z \to \infty$. They will probably not have a limit, but could have limits through subsequences reflecting the different (infinite) groups of the periodic table.

# Atomic Model HF: Hartree-Fock

Restrict to Slater determinants: $\phi_1, \ldots, \phi_N \in L^2(\mathbb{R}^3 \times \{-,+\})$ orthonormal **orbitals**

$$\Psi(z_1, \ldots, z_N) = \frac{1}{\sqrt{N!}} \det\left[\phi_i(z_j)\right]$$

The 1-pdm $\gamma_\Psi$ is the projection onto span$\{\phi_1, \ldots, \phi_N\}$. The density is $\rho_\Psi(x) = \sum_i \sum_\sigma |\phi_i(x,\sigma)|^2$.
Note up to a phase $\Psi$ depends only on $\gamma_\Psi$: If $\phi_1', \ldots, \phi_N'$ is another orthonormal basis for Ran$\gamma$. Then $\phi_i = \sum_j U_{ij}\phi_j'$ where $U$ is an $N \times N$ unitary. Hence $\Psi(z_1, \ldots, z_N) = \det(U)(N!)^{-1/2} \det\left[\phi_i'(z_j)\right]$. We have

$$\mathcal{E}_Z^{\mathrm{HF}}(\gamma) = \langle \Psi, H_Z(N)\Psi\rangle = \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\gamma\right] + \overbrace{\frac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy}^{\text{Direct term}}$$
$$\underbrace{-\frac{1}{2}\iint \frac{\sum_{\sigma,\tau}|\gamma(x,\sigma;y,\tau)|^2}{|x-y|}dxdy}_{\text{Exchange term}}$$

# Lieb's variational Principle

We may relax the minimization

$$E_Z^{\mathrm{HF}}(N) = \inf_{\substack{\gamma \text{ projection} \\ \mathrm{Tr}\,\gamma = N}} \mathcal{E}_Z^{\mathrm{HF}}(\gamma) = \inf_{\substack{0 \leq \gamma \leq \mathbb{1} \\ \mathrm{Tr}\,\gamma = N}} \mathcal{E}_Z^{\mathrm{HF}}(\gamma)$$

## Proof following Bach of second equality.

("$\geq$" is clear). "$\leq$ ": May restrict to finite rank $\gamma = \sum_{i=1}^{M} \lambda_i |\phi_i\rangle\langle\phi_i|$, $0 \leq \lambda_i \leq 1$, $\sum_i \lambda_i = N$. Note that

$$\rho_\gamma(x)\rho_\gamma(y) - \sum_{\sigma,\tau} |\gamma(x,\sigma;y,\tau)|^2 = \sum_{i<j} A_{ij}\lambda_i\lambda_j, \qquad \text{with } A_{ij} \geq 0$$

$$A_{ij} = \sum_{\sigma,\tau} (|\phi_i(x,\sigma)|^2 |\phi_j(y,\sigma)|^2 + |\phi_j(x,\sigma)|^2 |\phi_i(y,\sigma)|^2$$
$$- \phi_i(x,\sigma)\overline{\phi_j(x,\sigma)}\phi_j(y,\tau)\overline{\phi_i(y,\tau)} - \phi_j(x,\sigma)\overline{\phi_i(x,\sigma)}\phi_i(y,\tau)\overline{\phi_j(y,\tau)}).$$

If $\gamma$ not a projection at least two coefficients, say $\lambda_1, \lambda_2 \in (0,1)$. $\mathcal{E}_Z^{\mathrm{HF}}(\gamma(\lambda_1 + \delta, \lambda_2 - \delta)) = c + b\delta - a\delta^2$ with $a > 0$. Hence the best is to choose $\delta$ largest or smallest. □

# Atomic model RHF: Reduced Hartree-Fock

We can look at the Reduced Hartree-Fock model where we ignore the exchange term (not to be confused with restricted Hartree-Fock):

$$\mathcal{E}_Z^{\mathrm{RHF}}(\gamma) = \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - \frac{Z}{|x|}\right)\gamma\right] + \frac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy.$$

This is a convex functional of $\gamma$. We define

$$E_Z^{\mathrm{RHF}}(N) = \inf_{\substack{0\leq\gamma\leq\mathbb{1}\\ \mathrm{Tr}\,\gamma=N}} \mathcal{E}_Z^{\mathrm{RHF}}(\gamma)$$

Note that $N$ no longer needs to be an integer.
Summary of properties for HF and RHF:

- $N \mapsto E_Z^{\#}(N)$ is non-increasing. For RHF it is also convex.
- Minimizers exist for $N \leq Z$ (Lieb-Simon (HF), Solovej (RHF)).
- Minimerzers do not exist for $N > Z + const$ (Solovej).

$I_Z^{\#}(m), R_Z^{\#}(m)$ defined as for $Q$ model.

# Comparison Between Atomic Models

We have the following comparisons between the energies in our models

$$E_Z^{\mathrm{Q}}(N) \le E_Z^{\mathrm{HF}}(N) \le E_Z^{\mathrm{RHF}}(N)$$

The first inequality follows because HF is a restricted minimization compared to Q, i.e., restricted to Slater determinants. The second inequality is a consequence of Lieb's Variational Principle and the fact that the exchange term lowers the energy.

It follows from the convexity of $\mathcal{E}_Z^{\mathrm{RHF}}$ that a minimizer $\gamma$ for the RHF functional must have spherically symmetric density $\rho_\gamma$.

The last term in $\mathcal{E}_Z^{\mathrm{RHF}}$ is in fact, strictly convex in $\rho_\gamma$. We are not claiming that the minimizer $\gamma$ is unique, but we are claiming that its density is.

The densities for minimizers of $Q$ and $HF$ are not necessarily spherical.

# Variational Equation for RHF

If $\gamma$ minimizes $\mathcal{E}_Z^{\rm RHF}(\gamma)$ with ${\rm Tr}\,\gamma = N$ then there exists a $\mu \geq 0$ such that

$$\mathrm{Tr}\left[(H_{Z,\rm mf}^{\rm RHF}+\mu)\gamma\right] = \mathrm{Tr}\left[(H_{Z,\rm mf}^{\rm RHF}+\mu)_-\right]$$

where the right side is the sum of the negative eigenvaleus of the mean field operator

$$H_{Z,\rm mf}^{\rm RHF} = -\frac{1}{2}\Delta - \frac{Z}{|x|} + \rho_\gamma * |x|^{-1}$$

**Proof.**

Since $N \to E_Z^{\rm RHF}(N)$ is convex we can find a $\mu \geq 0$ such that $\gamma$ minimizes $\mathcal{E}_Z^{\rm RHF}(\gamma) + \mu{\rm Tr}\,\gamma$ without a restriction on the trace.

Let $\gamma'$ satisfy $0 \leq \gamma' \leq \mathbb{1}$. Then

$$\begin{aligned} 0 \leq & \frac{d}{d\alpha}\left(\mathcal{E}_Z^{\rm RHF}((1-\alpha)\gamma+\alpha\gamma') + \mu{\rm Tr}\,((1-\alpha)\gamma+\alpha\gamma')\right)_{|\alpha=0} \\ = & {\rm Tr}\left[(H_{Z,\rm mf}^{\rm RHF}+\mu)(\gamma'-\gamma)\right]. \end{aligned}$$

□

# The Lieb-Thirring Inequality and a-priori Bounds

We will uses the Lieb-Thirring (LT) inequality

$$\mathrm{Tr}\left[-\Delta\gamma\right] \geq c\int \rho_\gamma^{5/3}.$$

We recall that $E_Z^{\mathrm{Q}}(N) \geq -CZ^2N^{1/3}$. The same bound holds for HF and RHF as we used hydrogen to get this bound and that has no electron-electron interaction and therefore is the same for all these models. As we would also have gotten this bound (with a different $C$) with half the kinetic energy we conclude from the LT inequality that all the densities satisfy

$$\int(\rho^{\mathrm{Q}})^{5/3}, \int(\rho^{\mathrm{HF}})^{5/3}, \int(\rho^{\mathrm{RHF}})^{5/3} \leq CZ^2N^{1/3} \leq C'Z^{7/3}.$$

for stable neutral atoms.

# Improved Lower Bound on the Ground State Energy

Let $\chi_a = (4a^3\pi/3)^{-1}\mathbb{1}_{B_a}$ be the normalized characteristic function of a ball of radius $a$. Let $W_a(x) = \chi_a * |x|^{-1} * \chi_a(x) \leq |x|^{-1}$. Then $W_a(x) = |x|^{-1}$ for $|x| > 2a$. Moreover, $\widehat{W_a} \geq 0$ and $W_a(0) = ca^{-1}$. Thus for all $\widetilde{\rho}$

$$
\begin{aligned}
\sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} &\geq \sum_{i<j} W_a(x_i - x_j) \\
&= \frac{1}{2}\iint \sum_i \delta(x - x_i) W_a(x-y) \sum_j \delta(y - x_i)\, dxdy - \frac{1}{2} N W_a(0) \\
&= \frac{1}{2}\iint \Big(\sum_i \delta(x - x_i) - \tilde{\rho}(x)\Big) W_a(x-y) \Big(\sum_j \delta(y - x_i) - \tilde{\rho}(y)\Big) dxdy \\
&\quad + \sum_i W_a * \widetilde{\rho}(x_i) - \frac{1}{2}\iint \widetilde{\rho}(x)\widetilde{\rho}(y) w_a(x-y)\, dxdy - \frac{1}{2} N W_a(0) \\
&\geq \sum_i W_a * \widetilde{\rho}(x_i) - \frac{1}{2}\iint \frac{\widetilde{\rho}(x)\widetilde{\rho}(y)}{|x-y|}\, dxdy - cNa^{-1}.
\end{aligned}
$$

We thus have a lower bound

$$H_N(Z) \geq \sum_{i=1}^{N}\left(-\frac{1}{2}\Delta - \frac{Z}{|x_i|} + W_a * \widetilde{\rho}(x_i)\right) - \frac{1}{2}\iint \frac{\widetilde{\rho}(x)\widetilde{\rho}(y)}{|x-y|}dxdy - cNa^{-1}.$$

We estimate

$$\int \rho(x)(\widetilde{\rho} * |x|^{-1} - W_a * \widetilde{\rho}(x))dx \leq \iint_{|x-y|<2a} \rho(x)\widetilde{\rho}(y)|x-y|^{-1}dxdy$$
$$\leq \|\rho\|_{5/3}\|\widetilde{\rho}\|_{5/3}\||x|^{-1}\mathbb{1}_{|x|<2a}\|_{5/4} \leq Ca^{7/5}\|\rho\|_{5/3}\|\widetilde{\rho}\|_{5/3}$$

We conclude that

$$\langle \Psi, H_Z(N)\Psi\rangle \geq \mathrm{Tr}\left[\gamma_\Psi(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \widetilde{\rho} * |x|^{-1})\right] - \frac{1}{2}\iint \frac{\widetilde{\rho}(x)\widetilde{\rho}(y)}{|x-y|}dxdy$$
$$- cNa^{-1} - C\|\rho_\Psi\|_{5/3}\|\widetilde{\rho}\|_{5/3}a^{7/5}.$$

This is a correct lower bound for *any* $\widetilde{\rho}$. What is the best choice?

# Choosing $\widetilde{\rho}$

We can bind this further below as

$$\langle\Psi, H_Z(N)\Psi\rangle \geq \mathrm{Tr}\,[(-\frac{1}{2}\Delta - \frac{Z}{|x|} + \widetilde{\rho} * |x|^{-1})_-] - \frac{1}{2}\iint \frac{\widetilde{\rho}(x)\widetilde{\rho}(y)}{|x-y|}dxdy$$
$$- cNa^{-1} - C\|\rho_\Psi\|_{5/3}\|\widetilde{\rho}\|_{5/3}a^{7/5}.$$

The best choice for $\widetilde{\rho}$ satisfies that

$$\widetilde{\rho} * |x|^{-1} = \rho_\gamma * |x|^{-1} \qquad (1)$$

where $\rho_\gamma$ is the density of the projection onto the negative spectrum of the operator

$$-\frac{1}{2}\Delta - \frac{Z}{|x|} + \widetilde{\rho} * |x|^{-1}.$$

We see that the self-consistent condition (1) is exactly satisfied for $\widetilde{\rho} = \rho_\gamma$ for $\gamma$ being the RHF minimizer.

We therefore choose $\widetilde{\rho} = \rho_\gamma$ with $\gamma$ the RHF minimizer assuming it exists. Using

$$\|\rho_\Psi\|_{5/3}, \|\widetilde{\rho}\|_{5/3} \leq C(Z^{7/3})^{3/5} = CZ^{7/5}$$

we obtain

$$\begin{aligned}\langle\Psi, H_Z(N)\Psi\rangle \geq & \mathrm{Tr}\left[\gamma_\Psi(H_{Z,\mathrm{mf}}^{\mathrm{RHF}} + \mu)\right] - \mu N - \frac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy \\ & - cZa^{-1} - CZ^{14/5}a^{7/5} \\ \geq & \mathrm{Tr}\left[\gamma(H_{Z,\mathrm{mf}}^{\mathrm{RHF}} + \mu)\right] - \mu N - \frac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy \\ & - cZa^{-1} - CZ^{14/5}a^{7/5} \\ \geq & \mathcal{E}_Z^{\mathrm{RHF}}(\gamma) - CZ^{7/4}\end{aligned}$$

where we chose $a = Z^{-3/4}$. Thus $E_Z^{\mathrm{Q}}(N) \geq E_Z^{\mathrm{RHF}}(N) - CZ^{7/4}$. A much more complicated argument proves an error $O(Z^{5/3})$.

# Atomic Model TF: Thomas-Fermi

The next model we introduce is the Thomas-Fermi model that depends only on the density. We arrive at it by replacing in the RHF functional the kinetic energy $\mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right)$ by the **semiclassical** approximation

$$2(2\pi)^{-3}\iint_{|p|\leq F(x)} \frac{1}{2}p^2 dp dx = \frac{3}{10}(3\pi^2)^{2/3}\int \rho(x)^{5/3}dx$$

where we chose

$$\rho(x) = 2(2\pi)^{-3}\int_{|p|\leq F(x)} 1 dp = (3\pi^2)^{-1}F(x)^3.$$

Thus we define the **Thomas-Fermi Energy Functional:**

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

$\mathcal{E}_Z^{\mathrm{TF}}$ is convex and satisfies the scaling property: If $\rho_Z(x) = Z^2\rho_1(Z^{1/3}x)$ then

$$\mathcal{E}_Z^{\mathrm{TF}}(\rho_Z) = Z^{7/3}\mathcal{E}_1^{\mathrm{TF}}(\rho_1)$$

We set as before

$$E_Z^{\mathrm{TF}}(N) = \inf\{\mathcal{E}_Z^{\mathrm{TF}}(\rho) \ : \ \rho \geq 0, \quad \int \rho = N\}.$$

We will see that a minimizer exists if and only if $N \leq Z$.

- $N \mapsto E_Z^{\mathrm{TF}}(N)$ is strictly convex and decreasing for $N \leq Z$ and constant for $N \geq Z$. For $N \leq Z$ the minimizer is unique.
- $E_Z^{\mathrm{TF}}(\lambda Z) = Z^{7/3}E_1^{\mathrm{TF}}(\lambda)$

The minimizing $\rho$ satisfies the scaling above and the Thomas-Fermi equation:

$$\frac{1}{2}(3\pi^2)^{2/3}\rho^{2/3} = [\Phi_Z^{\mathrm{TF}}(x) - \mu]_+$$

where $\mu \geq 0$ and the Thomas-Fermi Mean-field potential is

$$\Phi_Z^{\mathrm{TF}}(x) = \frac{Z}{|x|} - \rho * |x|^{-1}, \qquad \Phi_Z^{\mathrm{TF}}(x) = Z^{4/3}\Phi_1^{\mathrm{TF}}(Z^{1/3}x).$$

# Ionization for TF

We cannot have a minimizer for $N > Z$: On the set where $\rho > 0$ we have

$$\Phi_Z^{\mathrm{TF}}(x) \geq \mu \geq 0.$$

Thus

$$\Phi_Z^{\mathrm{TF}}(|x| = r) \leq r^{-1}(Z - \int_{|x|\leq r} \rho_Z^{\mathrm{TF}}(x)dx).$$

On the other hand the absolute minimum $(\mu = 0)$ must be for $N = Z$: If we had $N < Z$ and $\mu = 0$ we see that for large $|x|$

$$\Phi_Z^{\mathrm{TF}}(x) \sim (Z - N)|x|^{-1},$$

but then $\rho$ satisfying the TF equation cannot be integrable.
Hence $N \mapsto E_Z^{\mathrm{TF}}(N)$ is strictly decreasing and convex for $N \leq Z$ and constant for $N > Z$.

# The Neutral TF atom

For $N = Z$ (i.e., $\mu = 0$) we have since $\rho * |x|^{-1} \leq |x|^{-1} \int \rho$ that $\Phi_Z^{\mathrm{TF}}(x) \geq 0$. Thus the Thomas-Fermi equation reads

$$\Phi_Z^{\mathrm{TF}} = \frac{1}{2}(3\pi^2)^{2/3}(\rho_Z^{\mathrm{TF}})^{2/3}.$$

On the set $x \neq 0$ we get

$$\Delta\Phi_Z^{\mathrm{TF}} = A\left(\Phi_Z^{\mathrm{TF}}\right)^{3/2}, \qquad A = \frac{8\sqrt{2}}{3\pi}$$

This equation has a solution $\Phi_\infty^{\mathrm{TF}}(x) = B|x|^{-4}$, $B = \frac{9\pi^2}{8}$. Note that such a function is a fixed point for the scaling

$$\Phi_\infty^{\mathrm{TF}}(x) = Z^{4/3}\Phi_\infty^{\mathrm{TF}}(Z^{1/3}x).$$

We have

$$\Phi_Z^{\mathrm{TF}}(x) \sim \Phi_\infty^{\mathrm{TF}}(x) \text{ as } |x| \to \infty, \quad \text{and} \quad \lim_{Z\to\infty} \Phi_Z^{\mathrm{TF}}(x) = \Phi_\infty^{\mathrm{TF}}(x).$$

# Mean-Field Thomas-Fermi Model

We see that for the Thomas-Fermi model we have a limiting infinite neutral atom

$$\lim_{Z\to\infty} \rho_Z^{\mathrm{TF}}(x) = C \lim_{Z\to\infty} (\Phi_Z^{\mathrm{TF}})^{3/2} = D|x|^{-6}.$$

**We see no emerging periodicity** in TF.

We may however consider a model somewhere between RHF and TF. Namely, the model that describes the neutral atom in terms of the **Mean-Field Thomas-Fermi** Operator

$$H_{Z,\mathrm{mf}}^{\mathrm{TF}} = -\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}}(x)$$

We shall now see that this is actually a very good approximation to the neutral atom.

# The Thomas-Fermi Mean-Field Approximation

Going back to our previous lower bound, but now choosing $\widetilde{\rho} = \rho_Z^{\mathrm{TF}}$ we find

$$H_Z(Z) \geq \sum_{i=1}^{Z} (-\frac{1}{2}\Delta_i - \Phi_Z^{\mathrm{TF}}(x_i)) - \frac{1}{2}\iint \frac{\rho_Z^{\mathrm{TF}}(x)\rho_Z^{\mathrm{TF}}(y)}{|x-y|} dxdy - CZ^{7/4}.$$

While the upper bound $E_Z^{\mathrm{Q}}(N) \leq E_Z^{\mathrm{RHF}}(N)$ was simple. The corresponding bound for the Mean-Field TF is not and is beyond the scope of these lecture notes. We will simply state it here:
If $\Psi$ is a neutral atomic ground state then

$$\langle \Psi, H_Z(Z)\Psi\rangle \leq \mathrm{Tr}\,[\underbrace{-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}}(x)}_{H_{Z,\mathrm{mf}}^{\mathrm{TF}}}]_- - \frac{1}{2}\iint \frac{\rho_Z^{\mathrm{TF}}(x)\rho_Z^{\mathrm{TF}}(y)}{|x-y|} dxdy + CZ^{5/3}.$$

Understanding this is related to calculating the trace as a semiclassical approximation. We will do that next, but not give all the details.

# The Semiclassical Approximation

We consider the TF Mean-Field operator

$$H^{\rm TF}_{Z,\rm mf} = -\frac{1}{2}\Delta - \Phi^{\rm TF}_Z(x) = -\frac{1}{2}\Delta - Z^{4/3}\Phi^{\rm TF}_1(Z^{1/3}x).$$

If we rescale $x \to Z^{-1/3}x$, i.e., perform the unitary transform $(U_Z f)(x) = Z^{1/2}f(Z^{1/3}x)$ we see that $H^{\rm TF}_{Z,\rm mf}$ is unitarily equivialent to the operator

$$U_Z^* H^{\rm TF}_{Z,\rm mf} U_Z = -\frac{1}{2}Z^{2/3}\Delta - Z^{4/3}\Phi^{\rm TF}_1(x) = Z^{4/3}\left(-Z^{-2/3}\frac{1}{2}\Delta - \Phi^{\rm TF}_1\right)$$

We recognize a semiclassical operator with $h = Z^{-1/3}$

$$-Z^{-2/3}\frac{1}{2}\Delta - \Phi^{\rm TF}_1 = -\frac{1}{2}h^2\Delta - \Phi^{\rm TF}_1$$

We have the following semiclassical approximation to leading order, i.e., the **Weyl term**

$$
\begin{aligned}
Tr[-\frac{1}{2}h^2\Delta - \Phi_1^{\mathrm{TF}}]_- &= 2(2\pi h)^{-3}\iint (\frac{1}{2}p^2 - \Phi_1^{\mathrm{TF}}(x))_- dpdx + o(h^{-3}) \\
&= -\frac{2^{5/2}}{15\pi^2 h^3}\int (\Phi_1^{\mathrm{TF}}(x))^{5/2}dx + o(h^{-3}).
\end{aligned}
$$

The next contribution of order $h^{-2}$ is a non-semiclassical term coming from the Coulomb singularity it is referred to as the **Scott correction**

$$
Tr[-\frac{1}{2}h^2\Delta - \Phi_1^{\mathrm{TF}}]_- = -\frac{2^{5/2}}{15\pi^2 h^3}\int (\Phi_1^{\mathrm{TF}}(x))^{5/2}dx + \frac{1}{2}h^{-2} + o(h^{-2}).
$$

In their monumental work on semiclassics Fefferman and Seco proved

$$
\begin{aligned}
Tr[-\frac{1}{2}h^2\Delta - \Phi_1^{\mathrm{TF}}]_- = &-\frac{2^{5/2}}{15\pi^2 h^3}\int (\Phi_1^{\mathrm{TF}}(x))^{5/2}dx + \frac{1}{2}h^{-2} \\
&+ \frac{2^{1/2}}{24\pi^2 h}\int (\Phi_1^{\mathrm{TF}}(x))^{1/2}\Delta\Phi_1^{\mathrm{TF}}(x)dx + o(h^{-1}).
\end{aligned}
$$

Recall the Thomas-Fermi equation which will give us

$$Tr[-\frac{1}{2}h^2\Delta - \Phi_1^{\mathrm{TF}}]_- = -\frac{2^{5/2}}{15\pi^2 h^3}\int (\Phi_1^{\mathrm{TF}}(x))^{5/2}dx + \frac{1}{2}h^{-2} + \frac{2}{9\pi^3 h}\int (\Phi_1^{\mathrm{TF}}(x))^2 dx + o(h^{-1}).$$

Going back to $Z$ and using $h = Z^{-1/3}$ we find

$$Tr[-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}}]_- = -Z^{7/3}\frac{2^{5/2}}{15\pi^2}\int (\Phi_1^{\mathrm{TF}}(x))^{5/2}dx + \frac{1}{2}Z^2 + Z^{5/3}\frac{2}{9\pi^3}\int (\Phi_1^{\mathrm{TF}}(x))^2 dx + o(Z^{5/3}).$$

Now that we have gotten this far let us estimate also the exchange term that we had ignored up to now. This requires understanding the one-particle density matrix.

# The Semiclassical One-Particle Density Matrix

The semiclassical approximation to the one-particle density is given by the (Weyl quantization)

$$\gamma_{\rm sc}(x,\sigma,y,\tau) = (2\pi h)^{-3}\delta_{\sigma,\tau}\int_{\frac{1}{2}p^2-\Phi_1^{\rm TF}((x+y)/2)\leq 0}\exp(-iph^{-1}(x-y))dp$$

Note this does **not** satisfy $0\leq\gamma_{\rm sc}\leq 1$, but its density is

$$\rho_{\rm sc}(x) = 2(2\pi h)^{-3}\int_{\frac{1}{2}p^2-\Phi_1^{\rm TF}(x)\leq 0}1dp = \frac{2^{3/2}}{3\pi^2h^3}\Phi_1^{\rm TF}(x)^{3/2}$$

which is exactly the Thomas-Fermi density in the rescaled variables $\rho_Z^{\rm TF}(x) = Z\rho_{\rm sc}(Z^{1/3}x)$. Let us use this to approximate the exchange term:

$$-\frac{1}{2}\iint\frac{\sum_{\sigma,\tau}|Z\gamma_{\rm sc}(Z^{1/3}x,\sigma;Z^{1/3}y,\tau)|^2}{|x-y|}dxdy = -C_{\rm D}Z^{5/3}\int(\Phi_1^{\rm TF}(x))^2dx.$$

For completeness let us calculate the constant $C_D$ which is elementary

$$\begin{aligned} C_D =& 2^{-6}\pi^{-6}\int |z|^{-1}\left|\int_{p^2\leq 2} e^{-ipz} d^3p\right|^2 d^3z \\ =& 2^{-6}\pi^{-6}(4\pi)^3\int_0^\infty \left|\int_0^{\sqrt{2}} \sin(st) s ds\right| t^{-3} dt \\ =& \pi^{-3} \end{aligned}$$

Recall that the constant in front of the similar semiclassical term was $\frac{2}{9\pi^3}$. So, the combined constant is $(\frac{2}{9}-1)\pi^{-3} = -\frac{7}{9\pi^3}$

# The Energy Asymptotics

Putting it all together we obtain that

$$E_Z^{\mathrm{Q}}(Z) = Z^{7/3}E_1^{\mathrm{TF}}(1) + \frac{1}{2}Z^2 - Z^{5/3}\frac{7}{9\pi^3}\int(\Phi_1^{\mathrm{TF}}(x))^2dx + o(Z^{5/3}).$$

The leading term was proved by Lieb-Simon and the Scott correction was originally established rigorously by Siedentop-Weikard (upper bound), and Hughes (lower bound). A much more involved (approximately 1000 pages) by Fefferman-Seco that involves understanding the exchange term (see also Bach and Graf-Solovej) led to the last term. In fact, we also have the operator lower bound agreeing with the asymptotics above

$$H_Z(Z) \geq \sum_{i=1}^{Z}(-\frac{1}{2}\Delta_i - \Phi_Z^{\mathrm{TF}}(x_i)) - \frac{1}{2}\iint\frac{\rho_Z^{\mathrm{TF}}(x)\rho_Z^{\mathrm{TF}}(y)}{|x-y|}dxdy$$

$$-\frac{1}{\pi^3}\int(\Phi_Z^{\mathrm{TF}}(x))^2dx - o(Z^{5/3}),$$

$$\boxed{(\Phi_Z^{\mathrm{TF}})^2 = \frac{(3\pi^2\rho_Z^{\mathrm{TF}})^{4/3}}{4}}$$

# Summary of models

- Model Q: $E_Z^{\rm Q}(N) = \inf_{\Psi,\ \|\Psi\|=1}\langle\Psi, H_Z(N)\Psi\rangle$

$$H_Z(N) = \sum_{i=1}^{N}(-\frac{1}{2}\Delta_i - Z|x_i|^{-1}) + \sum_{1\leq i<j\leq N}|x_i - x_j|^{-1}$$

- Model HF: $E_Z^{\rm HF}(N) = \inf_{0\leq\gamma\leq\mathbb{1},\ {\rm Tr}\,\gamma=N}\mathcal{E}_Z^{\rm HF}(\gamma)$.

$$\mathcal{E}_Z^{\rm HF}(\gamma) = \mathcal{E}_Z^{\rm RHF}(\gamma) - \mathcal{E}_{\rm ex}(\gamma)$$

- Model RHF: $E_Z^{\rm RHF}(N) = \inf_{0\leq\gamma\leq\mathbb{1},\ {\rm Tr}\,\gamma=N}\mathcal{E}_Z^{\rm RHF}(\gamma)$

$$\mathcal{E}_Z^{\rm RHF}(\gamma) = {\rm Tr}\left[(-\frac{1}{2}\Delta - Z|x|^{-1})\gamma\right] + \frac{1}{2}\iint\frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}dxdy$$

- Model TF: $E_Z^{\rm TF}(N) = \inf_{0\leq\rho,\ \int\rho=N}\mathcal{E}_Z^{\rm TF}(\rho)$

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

- Model TFMF ($N = Z$): $\sum_{i=1}^{Z}(-\frac{1}{2}\Delta_i - \Phi_Z^{\mathrm{TF}}(x_i))$. This gives a good approximation to the ground state, but the ground state energy has to be corrected by constants: **subtract the (positive) direct term and add the (negative) exchange term.**

**Summary of Results:** (in red when not proved in details here)

- For $\# =$ Q, HF, RHF, TF we have that $N \mapsto E_Z^{\#}(N)$ is decreasing and constant for $N \geq N_c^{\#}(Z)$ and $N_c^{\#}(Z) \leq 2Z + 1$.
- For $\# =$HF, RHF, $N_c^{\#}(Z) \leq Z+$const. $N_c^{\mathrm{TF}}(Z) = Z$.
- For $\# =$RHF,TF, $N \mapsto E_Z^{\#}(N)$ is strictly convex for $N \leq N_c(Z)$.
- $E_Z^{\mathrm{RHF}}(N) - cZ^{7/4} \leq E_Z^{\mathrm{Q}}(N) \leq E_Z^{\mathrm{HF}}(N) \leq E_Z^{\mathrm{RHF}}(N)$
- $E_Z^{\mathrm{Q}}(Z) = Z^{7/3}E_1^{\mathrm{TF}}(1)+\frac{1}{2}Z^2 + C_{\mathrm{DS}}Z^{5/3}+ o(Z^{5/3})$ (1st term=Weyl)
- TFMF:

$$H_Z(Z) \geq \sum_{i=1}^{Z}(-\frac{1}{2}\Delta_i-\Phi_Z^{\mathrm{TF}}(x_i))-\frac{1}{2}\iint \frac{\rho_Z^{\mathrm{TF}}(x)\rho_Z^{\mathrm{TF}}(y)}{|x-y|}dxdy-CZ^{7/4}$$

This was proved and we discussed how to get to $o(Z^{5/3})$.

# Universality of Atomic Radius in TF, HF and RHF

In Thomas-Fermi Theory it follows from the existence of $Z \to \infty$ limit and its scaling that

$$\lim_{Z\to\infty} R_Z^{\mathrm{TF}}(m) = R_\infty^{\mathrm{TF}} m^{-1/3}.$$

The following holds in RHF and HF Theories. We will not give details.

**Theorem (Radius in RHF and HF,** Solovej, 1991 (RHF) and 2003 (HF)**)**

*As $m \to \infty$*

$$\liminf_{Z\to\infty} R_Z^{\mathrm{HF}}(m) = R_\infty^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3})$$
$$\limsup_{Z\to\infty} R_Z^{\mathrm{HF}}(m) = R_\infty^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3})$$
$$\liminf_{Z\to\infty} R_Z^{\mathrm{RHF}}(m) = R_\infty^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3})$$
$$\limsup_{Z\to\infty} R_Z^{\mathrm{RHF}}(m) = R_\infty^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3}).$$

Note $\liminf$ and $\limsup$: We expect periodicity not convergence.

# Fermi's Aufbau Formula

We will next discuss results on the periodicity. We begin with what can be proved regarding the Aufbau principle

## Theorem (Fermi's Aufbau formula)

*Let $\Psi_Z$ be a neutral Q ground state for atom Z and let $P_\ell$ be the projection onto angular momentum $\ell$ in $L^2(\mathbb{R}^3;\mathbb{C}^2)$. Consider the occupation $N_\ell(Z) = \mathrm{Tr}\,(P_\ell \gamma_{\Psi_Z})$. (Need not be an integer and may depend on $\Psi$.) We get Fermi's Formula for almost all $\lambda \geq 0$*

$$\liminf_{\substack{Z\to\infty \\ \ell=\lceil \lambda Z^{1/3}\rceil}} \frac{N_\ell(Z)}{Z^{2/3}} = \frac{4\lambda}{\pi}\int_0^\infty [2\Phi_1^{\mathrm{TF}}(r) - \lambda^2 r^{-2}]_+^{1/2} dr := 4\lambda\kappa(\lambda).$$

The function $\kappa(\lambda)$ appeared in the work of Fefferman and Seco. They needed that this function is strictly concave (on its support) and gave a computer assisted (or interval arihtmetic) proof of this fact.

# Comparing the Aufbau Formulas

Before discussing the proof of Fermi's Formula

$$\liminf_{\substack{Z\to\infty\\ \ell=\lceil\lambda Z^{1/3}\rceil}} \frac{N_\ell(Z)}{Z^{2/3}} = \frac{4\lambda}{\pi}\int_0^\infty [2\Phi_1^{\mathrm{TF}}(r)-\lambda^2 r^{-2}]_+^{1/2}dr := 4\lambda\kappa(\lambda).$$

We note that it is different from what we would get from the Aufbau principle or from hydrogen:

$$N_\ell^{\mathrm{Aufbau}}(Z)Z^{-2/3} \approx 4\lambda[6^{1/3}-2\lambda]_+$$
$$N_\ell^{\mathrm{Hydrogen}}(Z)Z^{-2/3} \approx 4\lambda[(3/2)^{1/3}-\lambda]_+.$$

Note these are clearly not strictly concave! All three asymptotic formulas satisfy

$$\int_0^\infty 4\lambda\kappa(\lambda)d\lambda = 1,$$

$$\int_0^\infty 4\lambda[6^{1/3}-2\lambda]_+ d\lambda = 1,\ \int_0^\infty 4\lambda[(3/2)^{1/3}-\lambda]_+ d\lambda = 1$$

as they should.

# Proof of Fermi's Aufbau Formula

This is a preprint (on ArXiv) with August Bjerg, Søren Fournais, and Peter Hearnshaw. We begin with the bound

$$\mathrm{Tr}\,[\gamma_{\psi_Z}(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})] \leq \mathrm{Tr}\,[-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})]_- + o(Z^2)$$

Using the spherical symmetry we may write

$$\mathrm{Tr}\,[\gamma_{\psi_Z}(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})] = \sum_{\ell=0}^{\infty} \mathrm{Tr}\,[P_\ell \gamma_{\psi_Z} P_\ell(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})]$$

and likewise

$$\mathrm{Tr}\,[-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})]_- = \sum_{\ell=0}^{\infty} \mathrm{Tr}\,[P_\ell(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})]_-$$

Thus for each $\ell = 0, 1, \ldots$

$$\mathrm{Tr}\,[P_\ell \gamma_{\psi_Z} P_\ell(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})] \leq \mathrm{Tr}\,[P_\ell(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})]_- + o(Z^2)$$

The operator $P_\ell(-\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}})$ acting on the space $P_\ell L^2(\mathbb{R}^3;\mathbb{C}^2)$ is unitarily equivalent to the operator

$$-\frac{1}{2}\frac{d^2}{dr^2} - \Phi_Z^{\mathrm{TF}} + \frac{\ell(\ell+1)}{2r^2}$$

acting on $L^2(\mathbb{R}_+;\mathbb{C}^2\otimes\mathbb{C}^{2\ell+1})$. This is in turn unitarily equivalent to

$$Z^{4/3}\left[-Z^{-2/3}\frac{1}{2}\frac{d^2}{dr^2} - \Phi_1^{\mathrm{TF}} + \frac{\ell(\ell+1)}{2Z^{2/3}r^2}\right].$$

We now use that $\ell(\ell+1)Z^{-2/3}\approx\lambda^2$ and we are left with analyzing the operator

$$h_{\lambda,Z} = -Z^{-2/3}\frac{1}{2}\frac{d^2}{dr^2} - \Phi_1^{\mathrm{TF}} + \frac{\lambda^2}{2r^2}.$$

Note this is again a semiclasical problem with $h = Z^{-1/3}$ now in 1 dimension. The Weyl law gives

$$\mathrm{Tr}\,[h_{\lambda,Z}]_- = -2(2\ell+1)\frac{1}{3\pi}\int_0^\infty [2\Phi_1^{\mathrm{TF}}(r)-\lambda^2 r^{-2}]_+^{3/2}dr(h^{-1}+o(h^{-1})).$$

We conclude that

$$\mathrm{Tr}\,[P_\ell(-\frac{1}{2}\Delta-\Phi_Z^{\mathrm{TF}})_-] = -Z^2 4\lambda\frac{1}{3\pi}\int_0^\infty[2\Phi_1^{\mathrm{TF}}(r)-\lambda^2r^{-2}]_+^{3/2}dr+o(Z^2).$$

We do not really care about this value only that it is of order $Z^2$.
We can also determine the number of negative eigenvalues of $h_{\lambda,Z}$:

$$\begin{aligned}\mathrm{Tr}\,[\mathbb{1}_{h_{\lambda,Z}<0}] =& 2(2\ell+1)\frac{1}{\pi}\int_0^\infty[2\Phi_1^{\mathrm{TF}}(r)-\lambda^2r^{-2}]_+^{1/2}dr(h^{-1}+o(h^{-1}))\\ =& 4\lambda\frac{1}{\pi}\int_0^\infty[2\Phi_1^{\mathrm{TF}}(r)-\lambda^2r^{-2}]_+^{1/2}dr(Z^{2/3}+o(Z^{2/3})).\end{aligned}$$

This however does not allow us to show that $N_\ell(Z)=\mathrm{Tr}\,[P_\ell\gamma_\Psi]$ is close to this number. But it does allow us to conclude that it cannot be much smaller. Since if it was much smaller we would not get the energy to correct $Z^2$ order. I.e., we find the lower bound

$$N_\ell(Z)Z^{-2/3}=\mathrm{Tr}\,[P_\ell\gamma_\Psi]Z^{-2/3}\geq 4\lambda\frac{1}{\pi}\int_0^\infty[2\Phi_1^{\mathrm{TF}}(r)-\lambda^2r^{-2}]_+^{1/2}dr+o(1).$$

To conclude the proof of Fermi's Formula we observe that $\sum_{\ell=0}^{\infty} N_\ell(Z) = Z$. Thus by Fatou

$$1 = \liminf_{Z\to\infty} \sum_{\ell=0}^{\infty} Z^{-1} N_\ell(Z) \geq \int \liminf_{Z\to\infty} Z^{-2/3} N_{\ell=\lambda Z^{1/3}}(Z) d\lambda,$$

and that finishes the proof when we recall that

$$\int_0^\infty 4\lambda\kappa(\lambda) d\lambda = 1.$$

**Historical remark:** Fermi derived this formula in a paper published as part 2 of a 4 paper series in 1927. Paper 1 of the series is where he introduced the Thomas-Fermi model. Fermi also calculated $\kappa(\lambda)$ numerically and realized that it did not quite agree with the periodic table of the elements.

Interestingly there is another potential $\Phi_Z^{\mathrm{T}}$ introduced by Tietz that does reproduce the asymptotic Aufbau formula in the semiclassical limit. This is often referred to in the chemistry literature as the theoretical explanation of the Madelung rule. This of course does not make much sense as we have just proved that the Madelung rule fails in this limit.

# Periodicity in the Mean-Field Thomas-Fermi Model

To uncover the periodicity hidden in the Thomas-Fermi model we consider again the Thomas-Fermi Mean Field model and its Hamiltonian

$$H_{Z,\mathrm{mf}}^{\mathrm{TF}} := -\frac{1}{2}\Delta - \Phi_Z^{\mathrm{TF}} \quad \text{unitarily equivalent to } Z^{4/3}(-Z^{-2/3}\frac{1}{2}\Delta - \Phi_1^{\mathrm{TF}})$$

It is self-adjoint on $H^2(\mathbb{R}^3;\mathbb{C}^2)$. Consider the natural infinite counterpart

$$H_\infty^{\mathrm{TF}} := -\frac{1}{2}\Delta - B|x|^{-4}.$$

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

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

No! **A periodic family of extensions, indeed, appears in the limit.**

# Self-Adjoint Half-Line Operators

Consider potential $W : \mathbb{R}_+ \to \mathbb{R}$ such that the $f'' = 2Wf$ has **two linearly independent** solutions $f$ which are $L^2$ near the origin.

**Self-adjoint realizations** of the Schrödinger operator $-\frac{1}{2}d^2/dr^2 + W$ on $L^2(\mathbb{R}_+)$:

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 $D(H_{\min}) \oplus \mathbb{C}\xi f$ where $f$ is from above and $\xi$ localizes near the origin.
3. This is the **Weyl limit circle** case at $0$.

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

**Example 2:** If $W(x) = -Bx^{-4}$ we have $f(x) = x\sin(\sqrt{2B}x^{-1} + \theta)$.

# Main Result on Periodicity

## Theorem (Atomic Subsequence Convergence, Bjerg-Solovej)

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

$$Z_n^{1/3}\frac{1}{\pi}\int_0^\infty (2\Phi_1)^{1/2} = \frac{1}{\pi}\int_0^\infty (2\Phi_{Z_n})^{1/2} \longrightarrow t \qquad (mod \quad 1)$$

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

$$g_{\infty,\ell,t}(x) = \cos\Big(t\pi + \frac{\ell\pi}{2} + \frac{\pi}{4}\Big) j_\ell\Big(\frac{\sqrt{2B}}{x}\Big) + \sin\Big(t\pi + \frac{\ell\pi}{2} + \frac{\pi}{4}\Big) y_\ell\Big(\frac{\sqrt{2B}}{x}\Big)$$

*where $j_\ell$ and $y_\ell$ are the spherical Bessel-functions.*

In particular, $g_{\infty,0,t}(x) = x\sin(\frac{\sqrt{2B}}{x} + t\pi - \frac{\pi}{4})$.
We may say that the **infinite atomic periodicity** comes from a **Weyl limit circle** parametrized by $t$.

# Sketch of the Proof

1. Reduction to the 1-dimensional problem
2. Deducing from the fact that $\Phi_{Z_n}(x) \to B|x|^{-4}$ 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 consequence of step 2 it suffices to show that for each $\ell$ a sequence of regular (i.e. from $D(H^{\mathrm{TF}}_{Z_n,\ell})$) approximate solutions to
$$f''(x) = \left[\frac{\ell(\ell+1)}{x^2} - 2\Phi^{\mathrm{TF}}_{Z_n}(x)\right] f(x)$$
converges towards $g_{\infty,\ell,t}$ in $L^2$ near the origin ($O(1)$ scale).
4. Constructing the approximate solutions from step 3. Here, split the problem in the **asymptotic parts** (near the origin $O(Z^{-1})$ scale) and $\infty$) and a **semi-classical part** to which the Green-Liouville approximation (WKB) is applied. As a last step, these solutions are glued together by matching oscillations.

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

# Concluding Remarks

We discussed

- the **ground state energy asymptotics** up to order $o(Z^{7/4})$ (with details of lower bound) and $o(Z^{5/3})$ (without proof details)
- the **failure of the Aufbau Principle** for large atoms and derived the **Fermi Aubau Principle**.
- the **Ionization Conjecture** and its validity for TF, RHF, HF,
- a possible stronger Ionization Conjecture the limiting behavior.
- the **TF Mean Field Model** that in the limit of large $Z$ shows a periodic behavior. The sequences $Z_n$ that produce converging atoms can be interpreted as the groups in the periodic table. These sequences do not agree with prediction of the phenomenological Aufbau Principle, but with the "correct" Fermi asymptotic Aufbau formula.
- **Open problems:** Ionization for Q model, limiting periodic behavior for models more accurate than TFMF, e.g., RHF, HF, and Q.