Constitution and Stability of Atoms and Molecules

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Ascona July 1996

OVERVIEW OF LECTURES

Schrödinger Theory (QM)

- Definition of ground state energi
  ionization energy
  binding energy
  stability
  radius of atoms
  size of molecules
- Review of known (rigorous) results
- Qualitative features of the periodic table and their possible formulations as conjectures

Hartree-Fock Theory (HF)

- Differences and similarities with QM
- Validity as approximation

Thomas-Fermi Theory (TF)

- No-binding
- Sommerfeld asymptotics
- Validity as approximation (semiclassics)
- Consequences for QM and HF

I. The Schrödinger Theory (QM) of Atoms and Molecules:

Molecule of N electrons and K nuclei. Nuclear charges $\underline{Z} = (Z_1, \ldots, Z_K)$. Hamiltonian:

$$H^{\text{tot}}_{N,\underline{Z}} = H = \sum_{k=1}^{K} T_k + \sum_{i=1}^{N} t_i + V_C.$$

The nuclear kinetic energy operator:

$$T_k = -\frac{1}{2M_k}\Delta_{R_k}, \quad M_k = \text{Nuclear mass}$$

The electron kinetic energy operator:

$$t_i = -\frac{1}{2}\Delta_{x_i}.$$

The Coulomb potential V_C is the function

$$\begin{aligned} V_C \;&=\; -\sum_{k=1}^{K}\sum_{i=1}^{N} Z_k|x_i - R_k|^{-1} + \sum_{i<j}|x_i - x_j|^{-1} \\ &\quad + \sum_{k<\ell} Z_k Z_\ell |R_k - R_\ell|^{-1} \end{aligned}$$

Units: $m_e = \hbar = e$.

The Pauli principle: The electrons are Fermions. The physical Hilbert space is

$$\mathcal{H}^{\text{tot}}_{\text{physical}} = \bigotimes_{k}^{K} L^2(\mathbb{R}^3_{R_k}) \otimes \bigwedge_{i}^{N} L^2(\mathbb{R}^3;\mathbb{C}^2).$$

$H^{\text{tot}}_{N,\underline{Z}}$ is Friderichs' extended from C_0^∞ functions.

Removing the Center of Mass Motion:

Define $H_{N,\underline{Z}}$:

$$H^{\text{tot}}_{N,\underline{Z}} = -(2(N+\sum_k M_k))^{-1}\Delta_{\text{CM}}\otimes\mathbf{1}+\mathbf{1}\otimes H_{N,\underline{Z}}$$

$H_{N,\underline{Z}}$ acts in the space $\mathcal{H}_{\text{physical}}$ such that

$$\mathcal{H}^{\text{tot}}_{\text{physical}} = L^2(\mathbb{R}^3_{\text{CM}}) \otimes \mathcal{H}_{\text{physical}}.$$

$\mathcal{H}_{\text{physical}}$ is a subspace (because of the symmetry properties) of the Hilbert space of $\mathbb{C}^{2N}$-valued L^2 functions on a $\mathbb{R}^{3(N+K)-1}$ dimensional space.

Definition: Ground State Energy:

$$E^{\text{QM}}(N,\underline{Z}) := \inf \text{Spec}_{\mathcal{H}_{\text{physical}}} H_{N,\underline{Z}}$$

Definition: Atomic and Molecular Stability:

$E^{\mathsf{QM}}(N, \underline{Z})$ is an eigenvalue of $H_{N,\underline{Z}}$.

Strong Stability: $E^{\mathsf{QM}}(N, \underline{Z})$ is a discreet eigenvalue.

HVZ Criterion: Strong Stability follows if

$$E^{\mathsf{QM}}(N, \underline{Z}) < \inf \{ E^{\mathsf{QM}}(N', \underline{Z'}) + E^{\mathsf{QM}}(N'', \underline{Z''}) \ : \ N' + N'' = N,\ \underline{Z'} \oplus \underline{Z''} = \underline{Z} \}$$

"It costs energy to break into two clusters."

Result: The neutral molecule H_2 (i.e., $(N, Z_1, Z_2) = (2, 1, 1)$) is stable.
Refr: Richard, Fröhlich, Graf & Seifert, *PRL*'93.

Bounds on Stability for diatomic molecules: N cannot be too small. Refr: Ruskai, *LMP*'89 Sol., *CMP*'90

Definition: Stability of Matter:

$$E^{\mathrm{QM}}(N,\underline{Z}) \geq C(\max Z_k)(N+K)$$

Refr: Dyson&Lenard,*JMP*'67&'68, Lieb&Thirring,*PRL*'75.

Infinite Nuclear Mass Approximation:

$$H(N,\underline{Z},\underline{R}) := \sum_{i=1}^{N} t_i + V_c$$

$\underline{R} = (R_1, \ldots, R_K)$ parameters. $H(N,\underline{Z},\underline{R})$ acts in $\mathcal{H}(N) = \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$.

Born-Oppenheimer Energy Function:

$$E^{\mathrm{QM}}(N,\underline{Z},\underline{R}) := \inf\ \mathrm{spec}_{\mathcal{H}(N)} H(N,\underline{Z},\underline{R})$$

Ground State Energy:

$$E^{\mathrm{QM}}(N,\underline{Z}) := \inf_{\underline{R}} E(N,\underline{Z},\underline{R})$$

Stability: There exists $\underline{R}_0$ such that

(i) $E^{\mathrm{QM}}(N,\underline{Z},\underline{R}_0) = E^{\mathrm{QM}}(N,\underline{Z})$
(ii) $E^{\mathrm{QM}}(N,\underline{Z},\underline{R}_0)$ is an eigenvalue of $H(N,\underline{Z},\underline{R})$.
(Notice translation invariance.)

<u>Ground State Configuration:</u> (R_0, ψ) with $\psi \in \mathcal{H}(N)$ ground state eigenfunction for $H(N, \underline{Z}, \underline{R}_0)$.

<u>Density:</u>

$$\rho(x) = N \int \cdots \int \|\psi(x, x_2, \ldots, x_N)\|^2_{\mathbb{C}^{2N}} dx_2 \cdots dx_N$$

<u>Binding energy:</u>

$$BE^{\mathrm{QM}}(N, \underline{Z}) :=$$

$$\inf\{E^{\mathrm{QM}}(N', \underline{Z'}) + E^{\mathrm{QM}}(N'', \underline{Z''})\} - E^{\mathrm{QM}}(N, \underline{Z})$$

Infimum over $N' + N'' = N$ and $\underline{Z'} \oplus \underline{Z''} = \underline{Z}$ where both $\underline{Z'}$ and $\underline{Z''}$ are not empty.

<u>Ionization Energy:</u>

$$IE^{\mathrm{QM}}(N, \underline{Z}) = E^{\mathrm{QM}}(N-1, \underline{Z}) - E^{\mathrm{QM}}(N, \underline{Z}).$$

<u>OBS:</u> Both BE and IE are non-negative.

<u>Strong Stability:</u> (i) $BE^{\mathrm{QM}}(N, \underline{Z}) > 0$
(ii) $IE^{\mathrm{QM}}(N, \underline{Z}) > 0$.

<u>HVZ criterion:</u> Strong Stability $\Rightarrow$ Stability.

- Result: Atoms with $N < Z$ are stable.

- Result: H^- (i.e. $(N, Z) = (2, 1)$) is stable. (variational proof).

- Result: H^{--} (i.e., $(N, Z) = (3, 1)$) is unstable

The last result which was an open problem for many years is a corollary of

Theorem 1 (Lieb,*PRL*'84&*PRA*'84):
If a molecule with $(N, \underline{Z})$ *is stable then*

$$N < 2 \sum_{k=1}^{K} Z_k + K.$$

The proof for atoms (K=1) is remarkably simple. It relies on Hardy's inequality:

$$\begin{aligned} -\mathrm{Re} \int \overline{f}|x|\Delta f &= \int |\nabla |x|^{1/2} f(x)|^2 dx \\ &\quad - \frac{1}{4} \int |x|^{-2} \left| |x|^{1/2} f(x) \right|^2 dx \geq 0 \end{aligned}$$

and a very clever use of the triangle inequality.

+ +

<u>Result:</u> Neutral molecules are *always* stable (in the infinite mass approximation). This is a corollary of

Theorem 2 (van der Waals attraction) Lieb&Thirring *PRA*‘86
If $N = \sum_k Z_k$, $\underline{Z} = \underline{Z'} \oplus \underline{Z''}$, $N' = \sum_k Z'_k$, *and* $N'' = \sum_k Z''_k$ *and* $\max_{k,\ell} |R_k - R_\ell|$ *large enough*

$$E^{\mathrm{QM}}(N, \underline{Z}, \underline{R}) \leq E^{\mathrm{QM}}(N', \underline{Z'}) + E^{\mathrm{QM}}(N'', \underline{Z''}) - C(\underline{Z'}, \underline{Z''}) \left(\max_{k,\ell} |R_k - R_\ell| \right)^{-6}.$$

<u>Radius of Atoms:</u> Define $\mathfrak{R}_\nu$ by

$$\int_{|x-R_1| \geq \mathfrak{R}_\nu} \rho(x) dx = \nu.$$

The radius is naturally defined as $\mathfrak{R}_1$, the radius to last electron.

<u>Size of Molecules:</u> $D = \max_{k,\ell} |R_k - R_\ell|$.

<u>Important Conjecture For Atoms:</u> The ionization energy $IE(N, Z)$ is non-increasing in N.

Hartree-Fock (HF) Theory: Consider only

$$\Psi = \varphi_1 \wedge \cdots \wedge \varphi_N, \quad \varphi_i \in L^2(\mathbb{R}^3;\mathbb{C}^2). \tag{1}$$

Hartree-Fock energy function:

$$E^{\mathrm{HF}}(N,\underline{Z},\underline{R}) = \inf_{\Psi \text{ as in (1)}} \frac{(\Psi, H(N,\underline{Z},\underline{R})\Psi)}{(\Psi,\Psi)}$$

Reformulation: $\gamma =$ proj. on span$\{\varphi_1,\ldots,\varphi_N\}$. 2×2-matrix Kernel $\gamma(x,y)$.

$$\frac{(\Psi,H(N,\underline{Z},\underline{R})\Psi)}{(\Psi,\Psi)} = \mathcal{E}^{\mathrm{HF}}_{\underline{Z},\underline{R}}(\gamma) = \mathrm{Tr}\left[(-\tfrac{\Delta}{2} - \sum_{k=1}^{K}\tfrac{Z_k}{|x-R_k|})\gamma\right] + \mathcal{D}(\gamma) - \mathcal{EX}(\gamma) + \sum_{k<\ell}\tfrac{Z_kZ_\ell}{|R_k-R_\ell|}$$

Direct energy:

$$\mathcal{D}(\gamma) = \frac{1}{2}\iint \rho_\gamma(x)|x-y|^{-1}\rho_\gamma(y)\,dxdy.$$

Density:

$$\rho(x) = \rho_\gamma(x) = \mathrm{Tr}_{\mathbb{C}^2}[\gamma(x,x)].$$

Exchange energy:

$$\mathcal{EX}(\gamma) = \frac{1}{2}\iint \frac{\mathrm{Tr}_{\mathbb{C}^2}[|\gamma(x,y)|^2]}{|x-y|}dxdy.$$

Lieb's variational principle (PRL'81):

$$E^{\mathsf{HF}}(N,\underline{Z},\underline{R}) = \inf\{\mathcal{E}^{\mathsf{HF}}_{\underline{Z},\underline{R}}(\gamma) : 0 \le \gamma \le 1,\ \mathrm{Tr}\gamma = N\}$$

We now proceed as in QM:

Ground state energy:

$$E^{\mathsf{HF}}(N,\underline{Z}) = \inf_{\underline{R}} E^{\mathsf{HF}}(N,\underline{Z},\underline{R})$$

Stability: *There exists* $\underline{R}_0$ *such that*
(i) $E^{\mathsf{HF}}(N,\underline{Z},\underline{R}_0) = E^{\mathsf{HF}}(N,\underline{Z})$
(ii) There exists γ *with* $\mathrm{Tr}\gamma = N$ *such that* $E^{\mathsf{HF}}(N,\underline{Z},\underline{R}_0) = \mathcal{E}^{\mathsf{HF}}_{\underline{Z},\underline{R}_0}(\gamma)$.

Note that eigenvalue (for QM) has been replaced by existence of minimizer.

Just as for QM we have the quantities:
$BE^{\mathsf{HF}}(N,\underline{Z}), IE^{\mathsf{HF}}(N,\underline{Z}), \rho^{\mathsf{HF}}(x), \mathfrak{R}^{\mathsf{HF}}_{\nu}$

(Almost) all previous (infinite nuclear mass) results hold.

Atomic stability for $N < Z+1$: Lieb & Simon CMP '77.

Exception: Van der Waals Theorem.

Remark: As for QM the HF minimizer need not be unique: For atoms the spherical symmetry may be broken: atoms may have angular momentum and spin.

The mean-field operator: For γ with $0 \leq \gamma \leq 1$

$$H_\gamma^{MF} = \; -\tfrac{1}{2}\Delta - \textstyle\sum_{k=1}^{K} Z_k|x - R_k|^{-1}$$

$$+\rho_\gamma * |x|^{-1} - \mathcal{K}_\gamma$$

$$\rho_\gamma(x) = \mathrm{Tr}_{\mathbb{C}^2}[\gamma(x,x)], \quad \mathcal{K}_\gamma(x,y) = \frac{\gamma(x,y)}{|x-y|}$$

Theorem 3 (Self-consistency:) *If γ minimizes $\mathcal{E}^{\mathrm{HF}}_{\underline{Z},\underline{R}}$ with $Tr\gamma = N$ then γ is the projection onto the "lowest" eigenfunctions of H_γ^{MF}.*

Theorem 4 (No unfilled shells) *(Bach, Lieb, Loss & Sol. PRL '94): If γ is a HF minimizer then the space of the N "lowest" eigenfunctions of H_γ^{MF} is unique !*

When is HF a good approximation to QM?
Morally: When the density is big!

Theorem 5 *If* $N \to \infty, \|\underline{Z}\| \to \infty$, $N/\|\underline{Z}\|$ *fixed then (clearly* $E^{\mathsf{HF}}(N,\underline{Z}) \to -\infty$*)* $\exists \varepsilon > 0$ *s.t.*

$$\left| \frac{E^{QM}(N,\underline{Z})}{E^{\mathsf{HF}}(N,\underline{Z})} - 1 \right| \leq c|E^{\mathsf{HF}}(N,\underline{Z})|^{-\frac{2}{7}-\varepsilon}.$$

References:

For atoms: Fefferman, Seco Bull AMS '90

For molecules: Bach CMP '93. Improved in Graf, Sol. Rev. Math. Phys.'94

If $D(H,\underline{Z})$ and $Ex(N,\underline{Z})$ denote the direct and exchange energies then in the limit above

$$\frac{D(N,\underline{Z})}{E^{\mathsf{HF}}(N,\underline{Z})} = 0(1),$$

$$\frac{Ex(N,\underline{Z})}{E^{\mathsf{HF}}(N,\underline{Z})} = 0(|E^{\mathsf{HF}}(N,\underline{Z})|^{-\frac{2}{7}})$$

Thomas-Fermi Theory:

$$\mathcal{E}^{\mathsf{TF}}_{\underline{Z},\underline{R}}(\rho) = \frac{3(3\pi^2)^{2/3}}{10}\int \rho^{5/3} - \sum_{k=1}^{K} Z_k \int |x-R_k|^{-1}\rho(x)dx$$

$$+\frac{1}{2}\iint \rho(x)|x-y|^{-1}\rho(y)dxdy + \sum_{1\le k<l\le K} Z_k Z_l |R_k-R_l|^{-1}$$

Energy Function:

$$E^{\mathsf{TF}}(N,\underline{Z},\underline{R}) = \inf\{\mathcal{E}^{\mathsf{TF}}_{\underline{Z},\underline{R}}(\rho)|\rho,\ \int \rho = N\}.$$

The next theorem from Brezis&Lieb CMP'79 states that Molecules are never stable in TF theory:

Theorem 6 (strong no-binding) *Given* $N,\underline{Z}$ *and* $\underline{R}$ *there exists a decomp.* $N = N_1 + \cdots + N_K$ *such that*

$$E^{\mathsf{TF}}(N,\underline{Z},\underline{R}) \;\ge\; \sum_{k=1}^{K} E^{\mathsf{TF}}(N_k, Z_k\ \cancel{R_k}) + C\min\{\|\underline{Z}\|^{7/3}, |R_k-R_l|^{-7}\}$$

Only neutral and subneutral atoms are stable:

Theorem 7 (Lieb&Simon Adv.Math.'77) *For $K = 1$ there exists a minimizer ρ^{TF} for $\mathcal{E}^{\mathsf{TF}}_{Z,R}$ with $\int \rho^{\mathsf{TF}} = N$ if and only if $N \leq Z$.*

<u>Effective Potential for atoms:</u>

$$\varphi^{\mathsf{TF}}(x) = Z|x|^{-1} - \rho^{\mathsf{TF}} * |x|^{-1},\ R = 0$$

<u>TF equation:</u> φ^{TF} is the unique positive solution to

$$\Delta\varphi^{\mathsf{TF}} = 2^{7/3}(3\pi)^{-1}\varphi_{\mathsf{TF}}^{3/2} - 4\pi Z\delta_0$$

Consequence:

Theorem 8 (Sommerfield Asymptoties)

$0 \leq 3^4 2^{-3}\pi^2|x|^{-4} - \varphi_{\mathsf{TF}}(x) \leq CZ^{(4-\tau)/3}|x|^{-\tau}$, *where* $\tau = (1+\sqrt{73})/2 \approx 4.8$, $4 - \tau \approx -0.8$.

The universal infinite TF atom:
$\varphi_{\mathsf{TF}}(x) \to 3^4 \cdot 2^{-3}\pi^2|x|^{-4}$ as $Z \to \infty$.

For large Z, TF theory is a good approximation to HF theory and then in turn to QM.

Theorem 9 (Lieb&Simon Adv.Math.'77) *If $N/\|\underline{Z}\|$ fixed $\exists\varepsilon > 0$ such that*

$$\left|\frac{E^{\mathsf{HF}}(N,\underline{Z},\underline{R})}{E^{\mathsf{TF}}(N,\underline{Z},\underline{R})} - 1\right| \leq C|E^{\mathsf{TF}}(N,\underline{Z},\underline{R})|^{-\varepsilon}$$

Same with HF replaced by QM.

This is a semiclassical approximation:

$$\begin{aligned}\mathrm{Tr}_{L^2(\mathbb{R}^3;\mathbb{C}^2)}[(-\frac{1}{2}h^2\Delta - V)_-] \;=\; & \frac{2^{5/2}}{15\pi^2}h^{-3}\int V^{5/2} \\ & +o(h^{-3}), V \geq 0\end{aligned}$$

The *Legendre transform* of

$$V \mapsto \frac{2^{5/2}}{15\pi^2}V^{5/2}$$

is

$$\rho \mapsto \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}$$

which appeared in the TF functional.

Consequences for QM of no-binding and neutrality:

- Lieb-Thirring proof of stability of matter
- Atoms are asymptotically neutral:

Theorem 10 : *If* $Z_n \to \infty$, *atom* (N_n, Z_n) *stable then*

$$\lim_{n\to\infty}\sup \frac{N_n}{Z_n} \leq 1$$

References:

Lieb&Sigal&Simon&Thirring CMP‘88
Fefferman&Seco CMP‘90
Seco&Sigal&Solovej CMP‘90

Compare: *Without the Pauli principle there exists* $0 < \gamma < 1$ *such that if* $N(Z)$ *denotes the maximal number of electons such that* (N, Z) *is stable then* $\lim \frac{N(Z)}{Z} = 1 + \gamma$.
“$\geq$” Benguria&Lieb PRL‘83,
“$\leq$” Solovej LMP‘90

Consequence for QM of strong no-binding (Brezis-Lieb law): Molecules are asymptotically neutral.

Theorem 11 *: If* $\underline{Z}_n = Z_n \underline{z}$ *with* $\Sigma \underline{z} = 1, Z_n \to \infty$*, molecule* $(N_n, \underline{Z}_n)$ *stable then*

$$\lim \frac{N_n}{Z_n} = 1.$$

(Note upper *and* lower bound).
References:
Solovej CMP'90. (diatomic case)
Ruskai-Solovej, Springer Lecture Notes in Physics **403** (polyatomic case).

Bounds on the size of molecules are also derived.

Consequence for HF of Sommerfeld asymptotics: in the HF theory the radius of atoms is bounded above and below independently of Z

Theorem 12 (Solovej '96) *: Consider the HF effective potential*

$$\varphi^{\mathrm{HF}}(x) = Z|x|^{-1} - \rho^{\mathrm{HF}} * |x|^{-1}, R_1 = 0,$$

$$\rho^{\mathrm{HF}}(x) = T_{R_{\mathbb{C}^2}}[\gamma^{\mathrm{HF}}(x,x)].$$

There exist universal constants, $\varepsilon, D > 0$ *such that*

$$0 < |x| \leq D \Rightarrow |\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x)| \leq |x|^{-4+\varepsilon},$$

Open problems

- Monotonicity of ionization energies

- Understand the effect of relativistic corrections

- Prove bounds uniform in Z on the radius of QM atoms and the size of QM molecules

- Likewise bounds on the binding energies and ionization energies

- Prove bounds on binding energies and size of molecules in HF (still open)

- Prove upper bounds uniform in Z on the density of matter both in HF and QM.