

# Atomic and Molecular Structure

– A RENORMALIZED PICTURE –

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Structure of atomic and molecular ground states:

- 1) Total energy ( $E$ )
- 2) Binding energy ( $BE$ )
- 3) Ionization energy ( $I$ )
- 4) Stability
- 5) Maximal positive and negative ionization charges  
(excess charges) ( $Q$ )
- 6) Nuclear configuration (distance between  $R_n$ )
- 7) Electronic density distribution (radius  $R_e$ )

Organization of talk:

- I Definitions
- II Results
- III Hartree–Fock model
- IV Thomas–Fermi model
- V Renormalized Picture

# I DEFINITIONS (UNITS $e = \hbar = 2m_e = 1$ )

**Molecule.**  $N$  electrons,  $M$  nuclei, charges  $Z_1, \dots, Z_M$ .

Total nuclear charge  $Z_{\text{tot}} = Z_1 + \dots + Z_M$ .

**Hamiltonian.**  $\mathcal{R}_1, \dots, \mathcal{R}_M \in \mathbb{R}^3$  nuclear coordinates

$x_1, \dots, x_N \in \mathbb{R}^3$  electronic coordinates

$$H(N, \underline{Z}, \underline{\mathcal{R}}) = \sum_{i=1}^N [-\Delta_i - V(x_i; \underline{\mathcal{R}})] + \sum_{i<j} |x_i - x_j|^{-1} + U(\underline{\mathcal{R}})$$

$$V(x) = \sum_{k=1}^M Z_k |x - \mathcal{R}_k|^{-1} \quad \text{elec.-nucl. attraction}$$

$$U(\underline{\mathcal{R}}) = \sum_{k<\ell} Z_k Z_\ell |\mathcal{R}_k - \mathcal{R}_\ell|^{-1} \quad \text{nucl.-nucl. repulsion}$$

(Atoms  $M = 1$   $U = 0$ ).

(Born–Oppenheimer Approximation:  $\mathcal{R}_1, \dots, \mathcal{R}_M$  parameters, i.e., we neglect kinetic energy of nuclei).

Break translation invariance: Assume  $\mathcal{R}_1 + \dots + \mathcal{R}_M = 0$ .

**Hilbert Spaces.**  $H(N, \underline{Z}, \underline{\mathcal{R}})$  acts in

$$\mathcal{H}_0 = L^2(\mathbb{R}^{3N}) \quad \text{or the physical space}$$

$$\mathcal{H}_p = \wedge^N L^2(\mathbb{R}^3; \mathbb{C}^2) \quad (\text{Antisymmetric} = \text{Pauli principle})$$

Ground state in  $\mathcal{H}_0 \sim$  Bosonic “electrons”.

Ground state in  $\mathcal{H}_p \sim$  Fermionic electrons.

**Energy ( $E$ ).**

$$E(N, \underline{Z}, \underline{\mathcal{R}}) = \inf \text{spec}_{\mathcal{H}} H(N, \underline{Z}, \underline{\mathcal{R}})$$

$$E(N, \underline{Z}) = \inf_{\underline{\mathcal{R}}, \sum \mathcal{R}=0} E(N, \underline{Z}, \underline{\mathcal{R}})$$

**Binding Energy ( $BE$ ).**

$$0 \leq BE(N, \underline{Z}) = E_*(N, \underline{Z}) - E(N, \underline{Z})$$

$$E_*(N, \underline{Z}) = \liminf_{\underline{\mathcal{R}} \rightarrow \infty} E(N, \underline{Z}, \underline{\mathcal{R}}).$$

$E_*$  is lowest energy of any break-up.

**Ionization Energy ( $I$ ).**

$$0 \leq I(N, \underline{Z}) = E(N-1, \underline{Z}) - E(N, \underline{Z}).$$

**Stability.** Two conditions

$$(a) \quad BE(N, \underline{Z}) > 0$$

$$(b) \quad I(N, \underline{Z}) > 0, \text{ (only condition for atoms.)}$$

(a): All nuclei are bounded – only satisfied if  $N \geq N_-(\underline{Z})$ .

(b): All electrons are bounded – only satisfied if  $N \leq N_+(\underline{Z})$ .

**Excess Charges ( $Q$ ).**  $Q_{\pm}(\underline{Z}) = Z_{\text{tot}} - N_{\pm}(\underline{Z})$ .

**Nuclear Configuration.** From (a) there exists  $\underline{\mathcal{R}}_0$  such that  $E(N, \underline{Z}) = E(N, \underline{Z}, \underline{\mathcal{R}}_0)$ .

$$R_n = \min_{k \neq \ell} |\mathcal{R}_k - \mathcal{R}_\ell|.$$

**Electronic Density.** From (b) (+ HVZ theorem).  $E(N, \underline{Z})$  eigenvalue for  $H(N, \underline{Z}, \underline{\mathcal{R}}_0)$ . Ground state  $\psi \in \mathcal{H}$ ,  $\|\psi\| = 1$ .

Density:  $\rho_Q(x) = N \int \|\psi(x, x_2, \dots, x_N)\|^2 dx_2 \cdot \dots \cdot dx_N$ .

**Outer Radius ( $R_e$ ).**  $1 = \int_{|x| \geq R_e} \rho_Q(x) dx$ .



## II RESULTS

**THEOREM (E)** *Neutral case*  $N = Z_{\text{tot}}$ . *Fermions*

( $\mathcal{H} = \mathcal{H}_p$ ). If  $R_n \gg Z_{\text{tot}}^{-2/3}$

$$E(Z_{\text{tot}}, \underline{Z}, \underline{\mathcal{R}}) = -C_{TF} Z_{\text{tot}}^{7/3} + \frac{1}{8} Z_{\text{tot}}^2 - C_{DS} Z_{\text{tot}}^{5/3} + o(Z_{\text{tot}}^{5/3})$$

$C_{TF}$ , Thomas-Fermi: Lieb-Simon '73

$C_S = \frac{1}{8}$ , Scott: ( $M = 1$ ) Hughes, Siedentop-Weikard '86–'89

( $M \geq 2$ ) Ivrii-Sigal '91

$C_{DS}$ , Dirac, Schwinger: ( $M = 1$ ) Fefferman-Seco '91

( $M \geq 2$ )??

*Bosons* ( $\mathcal{H} = \mathcal{H}_0$ ): If  $R_n \gg Z_{\text{tot}}^{-1}$ ,

$$E(Z_{\text{tot}}, \underline{Z}, \underline{\mathcal{R}}) = -C_H Z_{\text{tot}}^3 + o(Z_{\text{tot}}^3). \text{ (Benguria-Lieb '83).}$$

**THEOREM (BE).** *Neutral case, Fermions.*

$$0 < BE(Z_{\text{tot}}, \underline{Z}) < o(Z^2).$$

“<” Lieb-Thirring '86 (van der Waals attraction).

“>” Corollary of Theorem (E).

**THEOREM (I).** *Fermions. For  $N \geq Z_{\text{tot}}$*

$$I(N, \underline{Z}) \leq O(Z^{20/21}) \ll O(Z^{4/3}).$$

Seco-Sigal-Solovej '90.

**THEOREM (Q).** *(Fermions).*

*Non-Asymptotic:*

$$N_+ < 2Z + M \text{ (Lieb '84)}$$

$$N_- > \frac{2}{3} \frac{Z_1 Z_2}{Z_1 + Z_2} \text{ (} M = 2, \text{ Solovej '90)}$$

*(Without Born-Oppenheimer approximation, upper and lower bounds by Ruskai).*

*Asymptotic neutrality for fermions ( $\mathcal{H} = \mathcal{H}_p$ )*

$$\lim_{Z_{\text{tot}} \rightarrow \infty} N_+/Z_{\text{tot}} = \lim_{Z_{\text{tot}} \rightarrow \infty} N_-/Z_{\text{tot}} = 1.$$

(For  $M = 1$ , only  $N_+$  : Lieb-Sigal-Simon-Thirring '88, Fefferman-Seco '90, Seco-Sigal-Solovej '90).

(For  $M = 2$  both  $N_{\pm}$  : Solovej '90).

(For  $M > 2$  both  $N_{\pm}$  : Ruskai-Solovej '91).

*Non-neutrality for bosons ( $\mathcal{H} = \mathcal{H}_0$ ), ( $M = 1$ )*

$$\lim_{Z_{\text{tot}} \rightarrow \infty} N_+/Z_{\text{tot}} = 1 + \gamma \quad \gamma > 0, \quad \gamma \approx 0.21$$

“ $\geq$ ” Benguria-Lieb '83.

“ $\leq$ ” Solovej '90 (also  $\liminf_{Z_{\text{tot}} \rightarrow \infty} N_-/Z_{\text{tot}} < 1, M > 1$ ).

**THEOREM:**  $(R_n, R_e) \quad R_n, R_e \geq O(Z^{-2/7}) \gg O(Z^{-1/3})$ .

**CONJECTURE FOR FERMIONS**

$$BE, I, Q^{\pm}, R_e, R_n = O(1).$$

### III HARTREE-FOCK MODEL

Neglect correlation, consider only  $\psi$  of the form

$$\psi(x_1, \dots, x_N) = N^{-1/2} \det[\varphi_i(x_j)]$$

$\varphi_1, \dots, \varphi_N$  orthonormal set

$$\gamma(x, y) = \sum_i \varphi_i(x) \overline{\varphi_i(y)}$$

kernel of projection onto  $\text{span}\{\varphi_1, \dots, \varphi_N\}$ . Hartree-

Fock functional

$$\begin{aligned} \varepsilon^{HF}(\gamma) &\equiv \langle \psi | H(N, \underline{Z}, \underline{\mathcal{R}}) | \psi \rangle = \\ &\text{Tr}[\gamma h] + \frac{1}{2} \iint \frac{\rho_\gamma(x) \rho_\gamma(y)}{|x - y|} dx dy - \frac{1}{2} \iint \frac{|\gamma(x, y)|^2}{|x - y|} + U \end{aligned}$$

where

$$h = -\Delta - V(x) \quad \text{one-body operator}$$

$$\rho_\gamma(x) = \gamma(x, x) = \sum_i |\varphi_i(x)|^2 .$$

## Change model: (Both Fermions and Bosons)

(1) Drop exchange term:

$$\varepsilon^{RHF}(\gamma) = \text{Tr}[\gamma h] + \frac{1}{2} \iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} dx dy + U$$

(2) Extend set of  $\gamma$ 's:

$$0 \leq \gamma : L^2(\mathbb{R}^3) \rightarrow L^2(\mathbb{R}^3) \quad \text{trace class, } \text{Tr}\gamma = N.$$

Fermionic condition:  $0 \leq \gamma \leq 2\text{Id}$

$$E^{RHF}(N, \underline{Z}, \underline{\mathcal{R}}) = \inf\{\varepsilon^{RHF}(\gamma)\}$$

We can again define  $BE^{RHF}$ ,  $I^{RHF}$ ,  $N_{\pm}^{RHF}$ ,  $\dots$

Stability: Existence of minimizers  $\mathcal{R}_0, \gamma$ .

## THEOREM

*Fermions:*  $|E(N, \underline{Z}, \underline{\mathcal{R}}) - E^{RHF}(N, \underline{Z}, \underline{\mathcal{R}})| = O(Z_{\text{tot}}^{5/3}) \ll Z^{7/3}$ .

*Bosons:*  $|E(N, \underline{Z}, \underline{\mathcal{R}}) - E^{RHF}(N, \underline{Z}, \underline{\mathcal{R}})| = O(Z_{\text{tot}}^{7/3}) \ll Z^3$ .

**MAIN THEOREM:** (*RHF*,  $M = 1$ , Fermions).

*Screened nuclear charge:*

$$\nu^{RHF}(R) = Z_{\text{tot}} - \int_{|x| \leq R} \rho_\gamma(x) dx.$$

For  $O(Z^{-1/3}) \leq R \leq O(1)$

$$\nu^{RHF}(R) = 324\pi^2 R^{-3} + o(R^{-3})$$

as  $R \rightarrow 0$  uniformly in  $Z_{\text{tot}}$ .

Our goal is to give the idea of the proof of the main theorem and along the way the ideas behind some of the other results.

#### IV THOMAS-FERMI MODEL

The only term in  $\varepsilon^{RHF}(\gamma)$  which does not only depend on  $\rho_\gamma$  is  $\text{Tr}[-\Delta\gamma]$ .

Thomas–Fermi theory  $\text{Tr}[-\Delta\gamma] \sim \frac{3}{5}(3\pi^2)^{2/3} \int \rho^{5/3}$

[semiclassics:  $W \geq 0$

$$\begin{aligned} \text{Tr}[(-\Delta - W)\gamma] &\approx 2 \cdot (2\pi)^{-3} \int [p^2 - W(x)]_- dp dx \\ &= -\frac{2}{15\pi^2} \int W(x)^{5/2} dx \end{aligned}$$

$\rho \mapsto \frac{3}{5}(3\pi^2)^{2/3} \rho^{5/3}$  is the Legendre transform of

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

$$\varepsilon^{TF}(\rho) = \frac{3}{5}(3\pi^2)^{2/3} \int \rho^{5/3} - \int \rho V + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} dx dy + U.$$

[In the Bosonic case one gets the Hartree functional

$$\varepsilon_H(\rho) = \int (\nabla \sqrt{\rho})^2 - \int \rho V + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} dx dy + U.]$$

We can again define  $E^{TF}$ ,  $BE^{TF}$ ,  $I^{TF}$ , ... studied by

Lieb-Simon '73–'77.

Exact scaling:

$$\text{Energy} \sim Z^{7/3} \quad \text{Length} \sim Z^{-1/3} \quad \text{Density} \sim Z^2.$$

<sup>14</sup> **THEOREM** (Teller, No-Binding)  $BE^{TF} = 0$ . In fact if  $R_n > O(Z^{-1/3})$ ,  $E^{TF}(N, \underline{Z}, \underline{\mathcal{R}}) - E_*^{TF}(N, \underline{Z}) > CR_n^{-7}$ .

**THEOREM** (Neutrality)  $N_+^{TF} = Z$  ( $N_+ = \max N$  for which minimizers exists). (In Hartree theory  $N_+^H = (1 + \gamma)Z$ )

**THEOREM** (Sommerfeld formula) ( $M = 1$ )

$$\nu^{TF}(R) = Z - \int_{|x| \leq R} \rho^{TF}(x) dx = 324\pi^2 R^{-3} + o(R^{-3})$$

as  $R \rightarrow \infty$ . Recall main theorem where  $R \rightarrow 0$ .

**THEOREM** (Approximation) if  $R_n \geq O(Z^{-1/3})$

$$|E^{RHF}(N, \underline{Z}, \underline{\mathcal{R}}) - E^{TF}(N, \underline{Z}, \underline{\mathcal{R}})| = O(Z^{7/3(1-\varepsilon)})$$

$$\nu^Q(R) \approx \nu^{RHF}(R) \approx \nu^{TF}(R) \text{ for}$$

$$O(Z^{-1/3}) \leq R \leq O(Z^{-1/3(1-\varepsilon)})$$

Estimates on  $E$ ,  $BE$ ,  $R_n$  obtained from this. For  $I$ ,

$N_{\pm}$ ,  $R_e$  we need control outside  $O(Z^{-1/3(1-\varepsilon)})$ .

## V RENORMALIZED PICTURE

(Restrict to atomic case).

Idea: Bootstrap estimate on  $\nu(R)$  from  $O(Z^{-1/3(1-\varepsilon)})$

to  $O(1)$ :

(1) Assume  $\nu^{RHF}(R) \approx 324\pi R^{-3}$  to length scale  $R_1 < 1$ .

(2) Separate inside  $R_1$  from outside  $R_1$ . Outside de-

pends on inside only through  $\nu(R_1)$  (because of perfect

spherical symmetry) except for the separation error (lo-

calization error) =  $O(R_1^{-5})$

(3) Outside problem renormalized, scales:

$$\text{nuclear charge} = \nu(R_1) \sim R_1^{-3} \quad \text{Energy} \sim R_1^{-7}$$

(4) Introduce outside  $TF$ -model to estimate outside energy to order  $R_1^{-7(1-\varepsilon)}$ .

(5) Conclude that outside  $TF$  satisfies original Sommerfeld Formula and from this that

$$\nu^{RHF}(R) \approx 324\pi R^{-3} \quad \text{to}$$

$$\text{length scale } R_1^{(1-\varepsilon)} \gg R_1.$$

(6) Having concluded that  $\nu^{RHF}(R) \approx 324\pi^2 R^{-3}$  out to  $R \approx O(1)$  we get estimate on  $N_+^{RHF}$  and  $I^{RHF}$  by controlling the final outside region  $O(1) \leq R < \infty$ . This does not need refined semiclassics.

As an example let us show that  $|Q_+| < O(1)$ : If  $\gamma$  is the minimizer corresponding to the largest possible  $N$  then

$$0 > Q_+ = Z_{tot} - \int \rho_\gamma = \nu(R) - \int_{|x|>R} \rho_\gamma,$$

where  $R = O(1)$ . But we know now that  $\nu(R)$  is  $O(1)$ , i.e., bounded above and below independent of  $Z$ . We must bound the charge outside  $R$ . Using the methods of the previously stated non-asymptotic bounds on  $N_+$  but now on the outside problem, which has nuclear charge  $\nu(R)$ , we get

$$\int_{|x|>R} \rho_\gamma < C_1 \nu(R) + C_2.$$