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 $Z_1, \ldots, Z_M$.

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

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

$x_1, \ldots, x_N \in \mathbb{R}^3$ 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 $M = 1 \quad U = 0$).

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

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

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

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

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

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

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

Energy (E)**.**

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

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

Binding Energy (BE)**.**

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

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

E_* is lowest energy of any break-up.

Ionozation Energy (I)**.**

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

Stability. Two conditions

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

(b) $I(N,\underline{Z}) > 0$, (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: $\rho_Q(x) = N \int \|\psi(x, x_2, \ldots, x_N)\|^2 dx_2 \cdot \ldots \cdot dx_N$.

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

II Results

THEOREM (E) *Neutral case* $N = Z_{\mathrm{tot}}$. *Fermions* $(\mathcal{H} = \mathcal{H}_p)$. *If* $R_n \gg Z_{\mathrm{tot}}^{-2/3}$

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

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* $R_n \gg Z_{\mathrm{tot}}^{-1}$,

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

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

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

"$<$" Lieb-Thirring '86 (van der Waals attraction).

"$>$" Corollary of Theorem (E).

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

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

Seco-Sigal-Solovej '90.

THEOREM (Q). (*Fermions*).

Non-Asymptotic:

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

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

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

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

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

(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 ($\mathcal{H} = \mathcal{H}_0$), ($M = 1$)

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

"$\geq$" Benguria-Lieb '83.

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

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 ψ of the form

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

$\varphi_1, \ldots, \varphi_N$ orthonormal set

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

kernel of projection onto span $\{\varphi_1, \ldots, \varphi_N\}$. Hartree-Fock functional

$$\varepsilon^{HF}(\gamma) \equiv \langle\psi|H(N, \underline{Z}, \underline{\mathcal{R}})|\psi\rangle =$$

$$\mathrm{Tr}[\gamma h] + \tfrac{1}{2} \iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} dx dy - \tfrac{1}{2} \iint \frac{|\gamma(x,y)|^2}{|x-y|} + U$$

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:

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

(2) Extend set of γ's:

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

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

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

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

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

THEOREM

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

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

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

Screened nuclear charge:

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

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

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

as $R \to 0$ *uniformly in* Z_{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 ρ_γ is $\mathrm{Tr}[-\Delta\gamma]$.

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

[semiclassics: $W \geq 0$

$$\mathrm{Tr}[(-\Delta - W)\gamma] \approx 2\cdot(2\pi)^{-3}\int [p^2 - W(x)]_- dpdx$$
$$= -\frac{2}{15\pi^2}\int W(x)^{5/2}dx$$

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

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

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

[In the Bosonic case one gets the Hartree functional

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

We can again define E^{TF}, BE^{TF}, $I^{TF}, \ldots$ studied by Lieb-Simon '73–'77.

Exact scaling:

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

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

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

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

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

as $R\to\infty$. *Recall main theorem where* $R \to 0$.

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

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

$$\nu^Q(R) \approx \nu^{RHF}(R) \approx \nu^{TF}(R) \text{ for } O(Z^{-1/3}) \le R \le O(Z^{-1/3(1-\varepsilon)}) .$$

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 depends on inside only through $\nu(R_1)$ (because of perfect spherical symmetry) except for the separation error (localization 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 controling 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 γ 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-asymptotique bounds on N_+ but now on the outside problem, which has nuclear charge $\nu(R)$, we get

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