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The Universal Structure of Large Atoms and Molecules

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LECTURE 4

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QMATH

Consider RHF. Assume we have a minimizer γ with $\mathrm{Tr}\gamma \geq Z$.

<u>Claim:</u> $\exists\, \varepsilon > 0$, $C_0 > 0$, $R_0 > 0$ indep. of Z

$$\left| \int_{|x|\leq R} \rho_\gamma - \int_{|x|\leq R} \rho_Z^{TF} \right| \leq C_0 R^{-3(1-\varepsilon)} \qquad (*)$$

ρ_Z^{TF} neutral TF: $\int \rho_Z^{TF} = Z$. for $\boxed{R \leq R_0.}$

Equivalently, for the screened nuclear charge $\nu(R) = Z - \int_{|x|\leq R} \rho(x)\,dx$.

$$|\nu_\gamma(R) - \nu^{TF}(R)| \leq C_0 R^{-3(1-\varepsilon)} \qquad (**)$$

$$|\nu_\gamma(R) - \nu^{TF}(R)| \leq C_0 R^{-3(1-\varepsilon)} \qquad (**)$$

Recall $\rho^{TF}(x) \leq D|x|^{-6}$

$$\nu^{TF}(R) = Z - \int_{|x|\leq R} \rho^{TF}(x)dx = \int_{|x|\geq R} \rho^{TF}(x)dx \leq D'R^{-3}$$

correct asymtotic tour for large R.

Introduce Coulomb norm

$$\|f\|_C^2 = \frac{1}{2}\iint \frac{\overline{f(x)}\,f(y)}{|x-y|}\,dxdy$$

$$= c\int |\hat{f}(p)|^2 |p|^{-2}dp$$

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

$$= \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \tfrac{Z}{|x|}\right)\gamma\right] + \tfrac{1}{2}\|\rho_\gamma - \rho^{TF}\|_C^2 - \tfrac{1}{2}\|\rho^{TF}\|_C^2 + \int \rho^{TF} * |x|^{-1} \rho_\gamma$$

$$= \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \phi^{TF}\right)\gamma\right] - \tfrac{1}{2}\|\rho^{TF}\|_C^2 + \tfrac{1}{2}\|\rho_\gamma - \rho^{TF}\|_C^2 \geq$$

Upper bound

$$\mathcal{E}_Z^{RHF}(\gamma) \leq \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \phi^{TF}\right)_-\right] - \tfrac{1}{2}\|\rho^{TF}\|_C^2 + C Z^{\frac{7}{3}(1-\eta)} \quad \text{for } \eta > 0.$$

We conclude that

$$\|\rho_\gamma - \rho^{TF}\|_C \le C\, Z^{\frac{7}{6}(1-\gamma)}$$

Recall

$$\|\rho_\gamma\|_{5/3},\ \|\rho^{TF}\|_{5/3} \le c\left(Z^{\frac{7}{3}}\right)^{3/5} = C\, Z^{7/5}$$

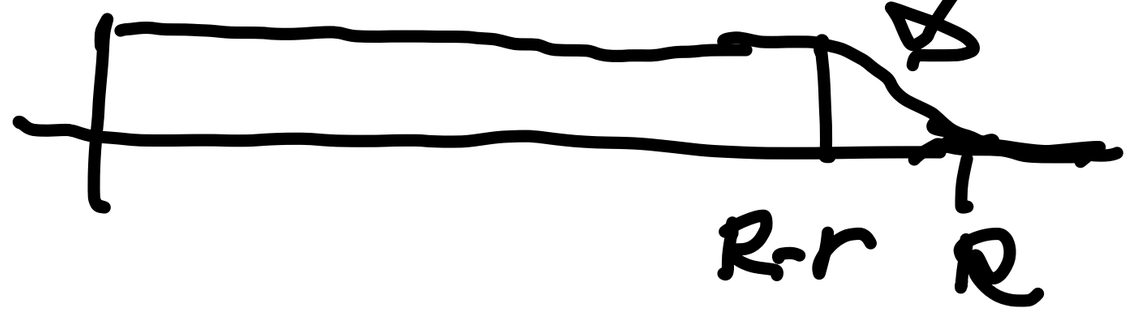
Lemma: If ρ_1, ρ_2 satisfy

$\|\rho_1\|_{5/3}, \|\rho_2\|_{5/3} \le A$, $\|\rho_1 - \rho_2\|_C \le B$ then

$$\left| \int_{|x|\le R} \rho_1 - \int_{|x|\le R} \rho_2 \right| \le C\, R^{8/9} B^{4/9} A^{5/9}$$

$$\left| \int_{|x|\le R} \rho_1 - \int_{|x|\le R} \rho_2 \right| \le C R^{8/9} B^{4/9} A^{5/9}$$

Proof:



$\theta(x) = 1$ for $|x| \le R-r$

$\theta(x) = 0$ for $|x| \ge R$

$$\int_{|x|\le R} \rho_1 - \rho_2 = \underbrace{\int \theta(\rho_1 - \rho_2)}_{①} + \underbrace{\int_{|x|\ge R-r} (1-\theta)(\rho_1 - \rho_2)}_{②}$$

$$|②| \le \int_{R-r \le |x| \le R} \rho_1 + \rho_2 \overset{\text{Hölder}}{\le} (\|\rho_1\|_{5/3} + \|\rho_2\|_{5/3}) \times (C R^2 r)^{2/5}$$

Volume of annulus.

$$|②| \le CA R^{4/5} r^{2/5}$$

$$|①| = \left| \int \Theta (S_1 - S_2) \right| = \left| c \int \widehat{\Theta} \widehat{(S_1 - S_2)} \right|$$

$$\le c \left(\int |\rho|^2 |\widehat{\Theta}(\rho)|^2 \right)^{1/2} \left(\int \frac{|\widehat{S_1 - S_2}(\rho)|^2}{\rho^2} \right)^{1/2}$$

$$\le c \| \nabla \Theta \|_{L^2} \| S_1 - S_2 \|_C$$

$$\le c r^{-1} (rR^2)^{1/2} B$$

$$= c r^{-1/2} R B$$

Optimize in r $\quad r = cR^{2/9} (B/A)^{10/9}$

$$\left| \int_{|x|\le R} \rho_1 - \int_{|x|\le R} \rho_2 \right| \le C R^{8/9} D^{4/9} A^{5/9}$$

Use for $\rho_1 = \rho_\gamma$, $\rho_2 = \rho^{\gamma_F}$

$$\left| \int_{|x|\le R} \rho_\gamma - \rho^{\gamma_F} \right| \le C R^{8/9} z^{\frac{\gamma}{\gamma}\cdot\frac{7}{6}(1-z)} z^{\frac{7}{7}}$$

$$z^{\frac{14}{27}+\frac{21}{27}} = z^{\frac{35}{27}}$$

If $R \sim z^{-1/3}$
$z \sim R^3$

$$= R^{-\frac{35}{9}}$$

$$R^{8/9} R^{-\frac{35}{9}} = R^{-\frac{27}{9}} = R^{-3}$$

If fact we get that for

$$R < Z^{-\frac{1}{3}(1-\delta)} \text{ then}$$

$$\left| \int_{|x| \le R} \rho_\gamma - \rho^{TF} \right| \subset R^{-3(1-\varepsilon)} \Leftarrow$$

I.e. we get (*) for a small range of R.

Claim: Assume (*) holds for $R \le R_1$ with $R_1 < R_0$ then if holds for $R \le R_2$ with $R_2 > R_1$.

Idea split atom in an inside part $|x| \le R_1$ and an outside part.

Morally:

$$\gamma \to \overbrace{\theta_- \gamma \theta_-}^{\gamma_-} + \overbrace{\theta_+ \gamma \theta_+}^{\gamma_+} + \cdots \qquad \theta_1^2 + \theta_2^2 = 1$$

$$\mathcal{E}_z^{RHF}(\gamma) \approx \mathcal{E}_z^{RHF}(\gamma_-) + \mathcal{E}^{RHF}_{\nu(R_1)}(\gamma_+)$$

+ localization errors.

Note that if θ_-, θ_+ localize in regions R_1, R_1+r

$$-\theta_- \Delta \theta_- - \theta_+ \Delta \theta_+ = -\Delta + \text{error}$$

$$|\text{error}| = (\nabla \theta_-)^2 + |\nabla \theta_+|^2 \sim r^{-2}$$

Total kinetic energy localization area will be $\mathrm{Tr}[\gamma r^{-2} 1\!\!1_{\mathrm{supp}\nabla\theta_\pm}]$

$$\leq r^{-2}\,\underbrace{\mathrm{Tr}[\gamma 1\!\!1_{\mathrm{supp}\nabla\theta_\pm}]}_{\leq R^{-3}} \leq r^{-2}R_1^{-3}$$

$$|\mathcal{E}^{RHF}_{\gamma(R)}| \sim C\,\gamma(R)^{-7/3} \sim C\left(R_1^{-3}\right)^{7/3} = C R_1^{-7}.$$

We can easily estimate the localization to be lower order.

It leaves us with controlling

$\mathcal{E}^{RHF}_{\nu(R)}(\gamma_t)$ with γ_t supported

outside for $|x| \geq R_1$

We will do this by a semiclassical estimate and compare to a TF theory defined for $|x| \geq R_1$. We will find as before that

$$\|\rho_t - \rho_t^{TF}\|_c^2 \leq c\, R_1^{-7(1-\eta)} \qquad \rho_t = \rho_{\gamma_t}$$

$$\|\rho_t\|_{5/3}, \|\rho_t^{TF}\|_{5/3} \leq (R_1^{-7})^{3/5}.$$

Using the Lemma again we find

$$\left| \int \rho_+ - \rho_+^{TF} \right| \leq C R^{-3(1-\varepsilon)}$$

$$R_1 \leq |x| \leq R$$

$R > R_1$.

Note that $\int \rho_+^{TF} = \nu^{RHF}(R_1)$. If $R > R_1$

$$\nu^{RHF}(R) = Z - \int_{|x| \leq R} \rho_\gamma = Z - \int_{|x| \leq R_1} \rho_\gamma - \int_{R_1 \leq |x| \leq R} \rho_\gamma$$

$$= \nu^{RHF}(R_1) - \int_{R_1 \leq |x| \leq R} \rho_\gamma$$

$$\gamma^{RHF}(R) = \gamma^{RHF}(R_1) - \int_{R_1 \le |x| \le R} \rho_\gamma$$

$$= \gamma^{RHF}(R_1) - \int_{R_1 \le |x| \le R} \rho_+$$

$$= \gamma^{RHF}(R_1) - \int_{R_1 \le |x| \le R} \rho_+^{TF} + O(R^{-3(1-\varepsilon)})$$

$$= \int_{R_1 \le |x|} \rho_+^{TF} - \int_{R_1 \le |x| \le R} \rho_+^{TF} + O(R^{-3(1-\varepsilon)})$$

$$= \int_{|x| \ge R} \rho_+^{TF} + O(R^{-3(1-\varepsilon)})$$

ρ_+^{TF} satisfies a TF equation.
Such solutions have a universal asymptotic form, i.e.

$$\int_{|x|\geq R} \rho_+^{TF} = \int_{|x|\geq R} \rho^{TF} + O\left(R^{-3(1-\varepsilon)}\right)$$

That gives that

$$\mathcal{V}^{RHF}(R) = \int_{|x|\geq R} \rho^{TF} + O\left(R^{-3(1-\varepsilon)}\right)$$

$$= \mathcal{Z} - \int_{|x|\leq R} \rho^{TF} + O\left(R^{-3(1-\varepsilon)}\right) = \mathcal{V}^{TF}(R) + O\left(R^{-3(1-\varepsilon)}\right).$$

I.e., (**).

We have a good estimate on

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

up to $R \le R_0$ indep of Z.

Consider first the neutral case:

$\int \rho_\gamma = Z$. Then

$$\nu^{RHF}(R) = \int_{|x|\ge R} \rho_\gamma(x)\,dx$$

$$\nu^{RHF}\left(R_Z^{RHF}(m)\right) = m$$

We know that

$$\nu^{RHF}(R) \sim c_{TF} R^{-3} \quad \text{for}$$

R small independently of Z.

We get the claimed asymptotic for $R_Z^{RHF}(m)$ for large m: $R_Z^{RHF}(m) \sim R_\infty^{TF} m^{-1/3}$.

Finally let us "prove" that if γ is a minimizer for $\mathcal{E}_Z^{RHF}$ then

$$\mathrm{Tr}\,\gamma \leq Z + \text{const}.$$

We know that if R is indep of Z

$$\mathcal{V}^{RHF}(R) = 2 - \int_{|x|\leq R} \rho_\gamma \sim cR^3 \sim \mathcal{O}(1)$$

We again do inside/outside and use the Lieb method to get a bound on

$$\int_{|x|\geq R} \rho_\gamma \leq 2\nu_{RHF}(R) + 1$$

$$= O(1)$$

$$\int \rho_\gamma = \int_{|x|\leq R} \rho_\gamma + \int_{|x|\geq R} \rho_\gamma$$

$$= Z + O(1) + O(1)$$

$$\leq Z + \text{const.}$$

Solovej, Inventiones 1991 Ion. in RHF

– " – , Annals 2003 Ion in HF.