Universality of Born-Oppenheimer curves for diatomic molecules

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Atomic and molecular models

Many-Body Quantum Mechanics: $\psi \in \bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$, $\|\psi\| = 1$, Ground state energy $E^{\mathrm{QM}} = \inf_\psi \langle \psi, H\psi\rangle$,

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

Hartree-Fock Theory: One-particle density matrix $0 \leq \gamma \leq 1$ in $L^2(\mathbb{R}^3;\mathbb{C}^2)$, $\mathrm{tr}\gamma = N$, $E^{\mathrm{HF}} = \inf_\gamma \mathcal{E}^{\mathrm{HF}}(\gamma)$

$$\mathcal{E}(\gamma) = \mathrm{tr}((-\frac{1}{2}\Delta - V)\gamma) + \frac{1}{2}\iint \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|} - \mathrm{tr}_{\mathbb{C}^2} \frac{|\gamma(x,y)|^2}{|x-y|} dxdy + U$$

Thomas-Fermi Theory: $0 \leq \rho \in L^1(\mathbb{R}^3)$, $\int \rho = N$, $E^{\mathrm{TF}} = \inf_\rho \mathcal{E}^{\mathrm{TF}}(\rho)$

$$\mathcal{E}(\rho) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3} - \int V\rho + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|} dxdy + U$$

Atoms and diatomic molecules

We will focus on **atoms**:

$$V(x) = \frac{Z}{|x|}, \quad U = 0, \quad E = E(N, Z)$$

and **diatomic molecules**:

$$V(x) = \frac{Z/2}{|x - \mathbf{R}|} + \frac{Z/2}{|x + \mathbf{R}|}, \quad U = \frac{Z^2/4}{2R}, \quad E = (N, Z, R)$$

- **Ionization energy of atoms:**

$$I_Z(m) = E(Z - m, Z) - E(Z, Z)$$

- **Radius of atoms:** $R_Z(m)$ given by (ρ is ground state density)

$$\int_{|x|>R_m(Z)} \rho(x)dx = m$$

- **Born-Oppenheimer curve for diatomic molecule:**

$$D_Z(R) = E(Z, Z, R) - 2E(Z/2, Z/2)$$

Thomas-Fermi scaling and Large Z asymptotics

Thomas-Fermi scaling

$$E^{\mathrm{TF}}(Z,Z) = C_{\mathrm{TF}} Z^{7/3}, \quad E^{\mathrm{TF}}(Z,Z,R) = f(Z^{1/3}R)Z^{7/3}$$

Here

$$f(t) = \frac{1}{8t} + C_{\mathrm{TF}} + o(1) \quad \text{for small } t$$

$$f(t) = 2^{-4/3} C_{\mathrm{TF}} + C_{\mathrm{BL}} t^{-7} + o(t^{-7}) \quad \text{for large } t.$$

BL=Brezis-Lieb

The large Z asymptotics (semi-classics):

$$E^{\mathrm{HF}}(Z,Z) = E^{\mathrm{TF}}(Z,Z) + \frac{1}{2}Z^2 + C_{\mathrm{DS}} Z^{5/3} + o(Z^{5/3})$$

(Lieb-Simon, Siedentop-Weikard, Hughes, Fefferman-Seco) DS=Dirac-Schwinger.

The second term is the **Scott correction**.

$$E^{\mathrm{HF}}(Z,Z,R) = E^{\mathrm{TF}}(Z,Z,R) + S(Z^{1/3}R)Z^2 + O(Z^{5/3})$$

where $S(t) = 1/4$ for large t and $S(0) = 1/2$ (Ivrii-Sigal, Solovej-Spitzer).

The Hartree-Fock approximation

As $Z \to \infty$

$$E^{\mathrm{QM}}(Z,Z) - E^{\mathrm{HF}}(Z,Z) = o(Z^{5/3})$$

and

$$E^{\mathrm{QM}}(Z,Z,R) - E^{\mathrm{HF}}(Z,Z,R) = o(Z^{5/3})$$

(Fefferman-Seco, Bach, Graf-Solovej)

This is however very far from describing energies relevant to **chemistry**, which are expected to be of order $O(1)$.

We will argue that Thomas-Fermi Theory may say something also to $O(1)$!

The ionization conjectures

The ionization conjectures: For fixed m and R

$$I_Z(m), R_Z(m), \text{ and } D_Z(R)$$

are bounded independently of Z. The same should hold for the maximal ionization $Q_z = N_Z - Z$, where N_Z is the maximal number of electrons an atom can bind.

The ionization conjectures hold in TF theory:

$$\lim_{Z\to\infty} I_Z^{\mathrm{TF}}(m) = a^{\mathrm{TF}} m^{7/3}, \quad \lim_{Z\to\infty} R_Z^{\mathrm{TF}}(m) = b^{\mathrm{TF}} m^{-1/3}, \quad Q_Z^{\mathrm{TF}} = 0$$

$$\lim_{Z\to\infty} D_Z^{\mathrm{TF}}(R) = c^{\mathrm{TF}} R^{-7},$$

(Brezis-Lieb)

The generalized ionization conjectures

The generalized ionization conjectures: In all models

$$\overline{\lim}_{Z\to\infty} I_Z(m) = a^{\mathrm{TF}} m^{7/3} + o(m^{7/3})$$

$$\overline{\lim}_{Z\to\infty} R_Z(m) = b^{\mathrm{TF}} m^{-1/3} + o(m^{-1/3})$$

as $m \to \infty$ and

$$\overline{\lim}_{Z\to\infty} D_Z(R) = c^{\mathrm{TF}} R^{-7} + o(R^{-7})$$

as $R \to 0$.

- The ionization conjectures are still open for many-body QM.
- The generalized ionization conjecture for R_Z for atoms holds in Hartree-Fock theory (Solovej 2003)
- The generalized ionization conjecture for $D_Z(R)$ for molecules holds in reduced Hartree-Fock theory (Samojlow-Solovej in preparation)

Splitting the energy in inside and outside

Fix $cZ^{-1/3} \leq R \leq \sigma$ where σ is independent of Z but small enough.
Smaller R are easy to deal with by a standard TF approximation as $R^{-7} \geq c^{-7} Z^{7/3}$.
For $cZ^{-1/3} \leq r < R/2$ we split the energy in a part coming from an **outside region** and the complimentary **inside region**

$$\Omega_{\text{in}}(r) = \{|x - \mathbf{R}| < r\} \cup \{|x + \mathbf{R}| < r\} = B(\mathbf{R}, r) \cup B(-\mathbf{R}, r).$$

$$E^{\text{RHF}}(Z, Z, R) = E_{\text{in}} + E^m_{\text{out}} + o(r^{-7})$$

$$E^{\text{RHF}}(Z/2, Z/2) = E_{\text{in}}/2 + E^a_{\text{out}} + o(r^{-7})$$

Note E_{in} is the same in both cases (really upper and lower bounds).
The point is now that E^m_{out} and E^a_{out} to the appropriate order is given by outside TF functionals restricted to the **outside region**, but with **screened charges** from the inside.

Iteration

The **main estimates** needed on the charges inside are

$$\left| \left(\rho^{\mathrm{aTF}}_{|B(\pm\mathbf{R},r)} - \rho^{\mathrm{aRHF}}_{|B(\pm\mathbf{R},r)} \right) * |x|^{-1} \right| \leq c r^{-4+\epsilon}$$

for $x \in \partial B(\pm\mathbf{R}, r)$ and

$$\left| \left(\rho^{\mathrm{mTF}}_{|\Omega_{\mathrm{in}}(r)} - \rho^{\mathrm{mRHF}}_{|\Omega_{\mathrm{in}}(r))} \right) * |x|^{-1} \right| \leq c r^{-4+\epsilon}$$

for $x \in \partial\Omega_{\mathrm{in}}(r)$.

These estimates are proved **iteratively**:

- For $r \sim Z^{-1/3}$ these are standard TF approximations
- If estimates above known for some r we can split the energy in and out and approximate by outside TF.
- We now use the fact that the outside TF potential ϕ_{out} satisfies a TF equation $-\Delta\phi_{\mathrm{out}} = c_{\mathrm{TF}}\phi_{\mathrm{out}}^{3/2}$.
- The solution to the TF-equation has a universal **Sommerfeld asymptotics** which allows to prove the estimates above for larger r.

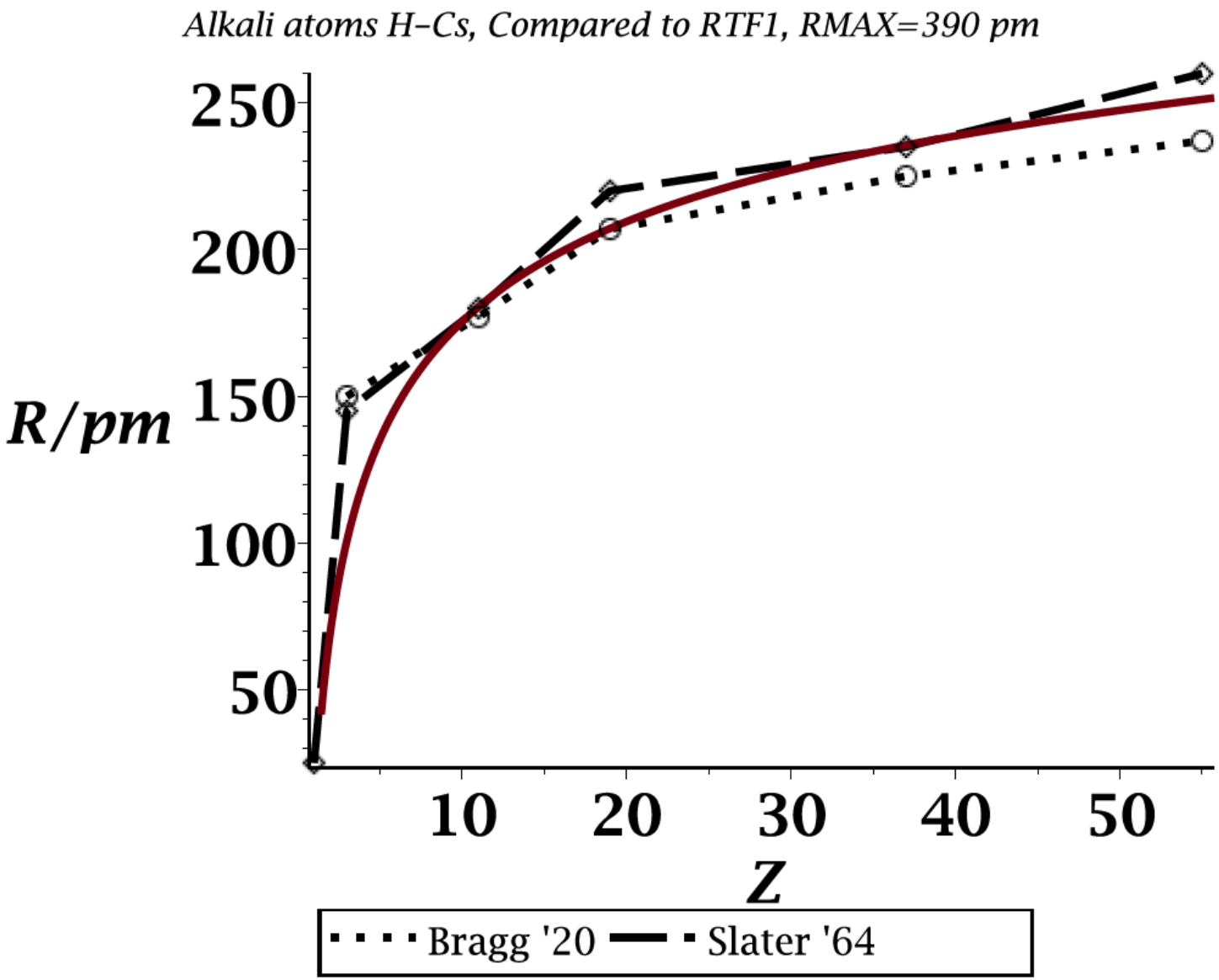
Outlook

- The problem with including the exchange term is to control the exchange interaction between the order Z electrons close to different nuclei.
- We may ask whether these asymptotic estimates are good also for Z ranging in the physically relevant regime

$$1 \leq Z \leq 92 \quad (117) \quad (137)$$

- We present some experimental and numerical comparisons addressing this question.

Comparing with experimental data for $R_Z(1)$



Numerics for $D_Z(R) - Z^2/(8R)$ (joint with Gilka and Taylor and with Samojlow)