The no-binding theorem and stability

The no-binding theorem states, loosely speaking that atoms do not bind in TF-theory. Group the nuclei into two groups, the \( A \)-group and the \( B \)-group. Denote

\[
m_A = \sum_{k \in A} Z_k \delta(x - R_k) \quad , \quad m_B = \sum_{k \in B} Z_k \delta(x - R_k)
\]

so that

\[
V_A(x) := -\sum_{k \in A} \frac{Z_k}{|x - R_k|} = -\frac{1}{|x|} * m_A \quad , \quad V_B(x) := -\sum_{k \in B} \frac{Z_k}{|x - R_k|} = -\frac{1}{|x|} * m_B.
\]

We are now considering three systems the systems

\[
E_A(\rho) = \frac{3}{5} \gamma \int \rho^{5/3}(x)dx + \int V_A(x) \rho(x) + D(\rho, \rho) + \sum_{k<l \in A} \frac{Z_k Z_l}{|R_k - R_l|}
\]

and \( E_B(\rho) \) is defined similarly. The third system is the combined system

\[
E(\rho) = \frac{3}{5} \gamma \int \rho^{5/3}(x)dx + \int V(x) \rho(x) + D(\rho, \rho) + \sum_{k<l} \frac{Z_k Z_l}{|R_k - R_l|}.
\]

Using the above notation we can write the above energies in the form

\[
E_A(\rho) = \frac{3}{5} \gamma \int \rho^{5/3}(x)dx - 2D(m_A, \rho) + D(\rho, \rho) + \sum_{k<l \in A} \frac{Z_k Z_l}{|R_k - R_l|}
\]

and likewise \( E_B \). Denote the corresponding ground state energies by \( E_A(\lambda) \), \( E_B(\lambda) \) and \( E(\lambda) \). The goal is to show that the if we divide up the total electronic charge and distribute them over the subsystems in a suitable fashion and push these systems infinitely far apart, the sum of these energies is less than the energy to start with. More precisely we have

**Theorem: No-binding** Assume that \( \lambda \leq Z = \sum Z_k \). Then

\[
\inf \{ E_A(\lambda_1) + E_B(\lambda_2) : \lambda_1 + \lambda_2 = \lambda \} \leq E(\lambda).
\]

This theorem was discovered by Teller. The general proof was given in [LS] and the version we present here is due to Baxter and can also be found in [L].

**PROOF:** Since \( \lambda \leq Z \) we know that we have a minimizer \( \rho \) of the total system with \( \int \rho(x)dx = \lambda \). The goal is to find \( g \) and \( h \) both nonnegative such that \( g + h = \rho \) and

\[
E_A(g) + E_B(h) \leq E(\rho) = E(\lambda).
\]

Since \( a^{5/3} + b^{5/3} \leq (a + b)^{5/3} \) for nonnegative numbers \( a, b \) we have that

\[
\int g^{5/3}dx + \int h^{5/3}(x)dx \leq \int \rho^{5/3}dx
\]
which goes in the right direction. Thus the proof of the no binding theorem is reduced to comparing Coulomb potentials. For any $g, h$ nonnegative with $g + h = \rho$ the sum of the Coulomb energies of the subsystems is given by

$$-2D(m_A, g) + D(g, g) + \sum_{k<l \in A} \frac{Z_kZ_l}{|R_k - R_l|} - 2D(m_B, h) + D(h, h) \sum_{k<l \in B} \frac{Z_kZ_l}{|R_k - R_l|}$$

which has to be compared with

$$-2D(m_A + m_B, g + h) + D(g + h, g + h) + \sum_{k<l} \frac{Z_kZ_l}{|R_k - R_l|} .$$

Thus, we have to find $g$ and $h$ so that

$$0 \leq -2D(m_A, h) - 2D(m_B, g) + 2D(g, h) + \sum_{k \in A, l \in B} \frac{Z_kZ_l}{|R_k - R_l|}$$

The last term can be written as

$$2D(m_A, m_B)$$

and hence we have to find $g, h$ nonnegative with $g + h = \rho$ such that

$$2D(g - m_A, h - m_B) \geq 0 .$$

The following Lemma is a very special case of a Lemma of Baxter.

**Lemma, Baxter** Assume that $\rho \in L^p \cap L^1$, $p > 3/2$. There exists $g$ with $0 \leq g \leq \rho$ so that

$$\frac{1}{|x|} * g \leq \frac{1}{|x|} * m_A$$

everywhere. Moreover,

$$\frac{1}{|x|} * g = \frac{1}{|x|} * m_A \text{ on } \{x : g < \rho\} .$$

With the help of Baxter’s lemma we can immediately finish the proof of the no-binding theorem since

$$2D(g - m_A, h - m_B) = \int \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] (h - m_B) dx$$

$$= \int_{g < \rho} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] (h - m_B) dx + \int_{g = \rho} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] (h - m_B) dx$$

$$= -\int_{h = 0} \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] m_B dx \geq 0 .$$
PROOF of Baxter’s lemma. We follow [L]: Consider the problem of minimizing

\[ D(g, g) - \int g \frac{1}{|x|} \ast m_A \]

subject to the constraint that \( 0 \leq g \leq \rho \). Notice that this is a convex minimization problem. Moreover, since \( \rho \in L^p \cap L^1 \) we have that

\[ \int g \frac{1}{|x|} \ast m_A = \int \frac{1}{|x|} g \ast m_A = \sum_{k \in A} \frac{1}{|x|} g(R_k) \leq \sum_{k \in A} \frac{1}{|x|} \rho(R_k) < \infty . \]

Hence the functional is bounded below. Next we write

\[ \frac{1}{|x|} = \frac{1}{|x|} \zeta(x) + \frac{1}{|x|} (1 - \zeta(x)) \]

where \( \zeta \) is a smooth function of compact support, identically equals to 1 in the vicinity of the origin. In other words we split the Coulomb potential into two pieces, the first is in \( L^q \) for all \( 1 \leq q < 3/2 \) and the second is in \( L^r \) for all \( r > 3/2 \).

Let \( g_j \) be a minimizing sequence. Since \( 0 \leq g_j \leq \rho \) this sequence is bounded in \( L^p \). Thus there exists a subsequence (again denoted by \( g_j \)) which converges to some function \( g \) weakly in \( L^p \). Hence

\[ \frac{1}{|x|} \ast g_j \to \frac{1}{|x|} \ast g \]

pointwise since \( \frac{1}{|x|} \zeta \) is in the dual of \( L^p \). Since \( \rho \in L^1 \) we can extract a further subsequence so that \( g_j \) converges weakly to \( g \) in some \( L^s \) space dual to \( L^r \). This ensures that

\[ \frac{1}{|x|} (1 - \zeta) \ast g_j \to \frac{1}{|x|} (1 - \zeta) \ast g \]

and hence

\[ \int g_j \frac{1}{|x|} \ast m_A \to \int g \frac{1}{|x|} \ast m_A . \]

Since \( D(g, g) \) is weakly lower semicontinuous we have that

\[ \lim \inf D(g_j, g_j) \geq D(g, g) . \]

The fact that \( 0 \leq g \leq \rho \) is left as a simple exercise. Thus the minimizer \( g \) exists. Note, that since \( g \in L^p \cap L^1 \) we know that \( \frac{1}{|x|} \ast g \) is a continuous function which vanishes at \( \infty \).

Using the calculus of variation we learn that

\[ \frac{1}{|x|} \ast g = \frac{1}{|x|} \ast m_A \text{ on } \{ x : 0 < g(x) < \rho(x) \} \]

\[ \frac{1}{|x|} \ast g \leq \frac{1}{|x|} \ast m_A \text{ on } \{ x : g(x) = \rho(x) \} \]
\[ \frac{1}{|x|} * g \geq \frac{1}{|x|} * m_A \text{ on } \{ x : g(x) = 0 \} \]

Consider the set
\[ P := \{ x : \frac{1}{|x|} * g - \frac{1}{|x|} * m_A > 0 \} \]

This set is open since \( \frac{1}{|x|} * g \) is continuous and \( P \) does not contain the points \( R_k, k \in A \).

The function \( \frac{1}{|x|} * g \) vanishes on the boundary of \( P \) since \( \frac{1}{|x|} * g \) tends to zero at infinity. Finally, \( P \) is a subset of \( \{ x : g(x) = 0 \} \). On \( P \) we have
\[ \Delta \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] = -g \]

Hence
\[ \left[ \frac{1}{|x|} * g - \frac{1}{|x|} * m_A \right] \]

is harmonic. Since it vanishes on the boundary it must vanish in \( P \) and hence \( P \) is empty.

An immediate corollary from the no-binding theorem is the following electrostatic inequality.

**Corollary:** for any nonnegative function \( \rho \in L^{5/3} \) and for any positions \( R_1, \ldots, R_K \)
\[ \frac{3}{5} \varepsilon \int \rho^{5/3}(x)dx - \sum Z_k \int \frac{1}{|x - R_k|} \rho(x)dx + D(\rho, \rho) + \sum_{k<l} \frac{Z_kZ_l}{|R_k - R_l|} \geq -\frac{3.678}{\varepsilon} \sum Z^{7/3}_k \]

We are now ready to apply TF-theory to the problem of stability of matter. There are two terms in the Hamiltonian that are not expressed in terms of the one particle density, the kinetic energy and the Coulomb repulsion among the electrons. The former was dealt with when we considered the Lieb-Thirring inequalities and now we deal with the second problem. Again, we follow Lieb and Thirring [LT]. We consider the previous Corollary but with the positions of the nuclei replaced by the positions of the electrons, in other words we have for any \( \rho \) and all positions \( x_1, \ldots, x_N \)
\[ \sum_{i<j} \frac{1}{|x_i - x_j|} \geq -\frac{3}{5} \varepsilon \int \rho^{5/3}(x)dx + \sum_j \int \frac{1}{|x - x_j|} \rho(x)dx - D(\rho, \rho) - \frac{3.678}{\varepsilon} N . \]

Here, \( \varepsilon > 0 \) is an arbitrary parameter. Multiplying this inequality with \( |\Psi(x_1, \ldots, x_N)|^2 \), replacing \( \rho \) by \( \rho_\Psi \) and integrating over all variables we learn that
\[ \sum_{i<j} \int \frac{|\Psi(x_1, \ldots, x_N)|^2}{|x_i - x_j|} dx_1 \cdots dx_N - D(\rho_\Psi, \rho_\Psi) \geq -\frac{3}{5} \varepsilon \int \rho^{5/3}_\Psi(x)dx - \frac{3.678}{\varepsilon} N . \]

This is the desired inequality.
We could optimize over $\varepsilon$ to get the lower bound

$$-2\left(\frac{3.678 \times 3}{5}\right)^{1/2} \sqrt{N} \sqrt{\int \rho_\Psi^5(x) dx}$$

but we prefer the first version. The difference between the true Coulomb repulsion and the electrostatic repulsion of the single particle density is called the indirect term.

Using the LT -inequality we know that for any antisymmetric function $\Psi$

$$T_\Psi \geq \frac{3}{5}\left(\frac{2}{5L}\right)^{2/3} \int \rho_\Psi^{5/3}(x) dx$$

where $L$ is the sharp constant in the inequality that estimates the sum of the negative eigenvalues. Combining this with (1) we learn that the true quantum energy is bounded below by

$$\frac{3}{5} \left[ \left(\frac{2}{5L}\right)^{2/3} - \varepsilon \right] \int \rho_\Psi^{5/3}(x) dx - \sum_k Z_k \int \frac{1}{|x - R_k|} \rho_\Psi(x) dx + D(\rho_\Psi, \rho_\Psi)$$

$$+ \sum_{k<l} \frac{Z_k Z_l}{|R_k - R_l|} - \frac{3.678}{\varepsilon} N .$$

Using once more the no-binding theorem and the numerical value of the minimum energy of a single atom we get

$$E_0(N, K) \geq -3.678 \left[ \frac{\sum_k Z_{k}^{7/3}}{(2/5L)^{2/3} - \varepsilon} - \frac{N}{\varepsilon} \right] .$$

Optimizing over $\varepsilon$ yields

$$-3.678 \left(\frac{5}{2}\right)^{2/3} L^{2/3} \left[ \left(\sum_k Z_{k}^{7/3}\right)^{1/2} + \sqrt{N} \right]^2 .$$

Using the bound

$$L \leq \frac{4}{15\pi}$$

which was obtained in the chapter on the Birman-Schwinger principle we get the numerical value

$$-1.309 \left[ \left(\sum_k Z_{k}^{7/3}\right)^{1/2} + \sqrt{N} \right]^2 .$$

In the case where all the nuclei have the same charge the true QM ground state energy is bounded below by

$$-2.618 Z^{7/3}(N + K) .$$
in units of four Rydbergs.

So far we have neglected spin. The electron has an additional degree of freedom namely there are electrons with spin ‘up’ and spin ‘down’. Of course the state of an electron can be in any superposition of the two. This leads to consider wave functions

$$\Psi(x_1, \sigma_1; \ldots, x_N, \sigma_N)$$

which are antisymmetric under exchange of the particle label. We shall assume that the \(\sigma\)’s take values in the set \(\{1, \ldots, q\}\) where \(q\) is an integer. The only term in the Hamiltonian that is really sensitive to the spin is the kinetic energy term. Consider the problem of filling up the energy levels of a single particle Hamiltonian with fermions that have \(q\) spin degrees of freedom. The first \(q\) particles sit in the ground state, the next \(q\) in the first excited etc. If we return to the proof of the fermion uncertainty principle for such kind of wave functions we have to consider filling up the levels of the Hamiltonian

$$-\Delta - c\rho_{\Psi}^{2/3}(x).$$

Chasing through the proof we get that for any wave function \(\Phi\) that has \(q\) spin degrees of freedom

$$T_\Phi - c \int \rho_{\Phi}^{2/3}(x)\rho_{\Phi}(x)dx \geq -q \sum_{k=1}^{[\frac{N}{q}]} \lambda_k$$

which in turn can be estimated by the LT-inequality and we obtain

$$T_\Phi - c \int \rho_{\Phi}^{2/3}(x)\rho_{\Phi}(x)dx \geq -qLe^{5/2} \int \rho_{\Phi}^{5/3}(x)dx$$

so that

$$T_\Phi \geq \frac{3}{5} \left( \frac{2}{5qL} \right)^{2/3} \int \rho_{\Psi}^{5/3}(x)dx.$$

Thus we have to augment in all our estimates the LT-constant by a factor of \(q\). With this we get the lower bound on the true quantum energy to be

$$-4.156Z^{7/3}(N + K),$$

which in the case of hydrogen (\(Z = 1\)) is about 17 Rydbergs per atom. One would expect about 1 Rydberg per atom.