The correlation energy of charged quantum systems

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Quantum Mechanics of charged Particles

PROBLEM: Describe ground state/ground state energy of N charged particles, either identical fermions or identical bosons moving in a background electric field.

FERMIONS: The **state** is a normalized wave function $\psi \in \mathcal{H}_F = \underbrace{\bigwedge^N}_{\text{antisym}} L^2(\mathbb{R}^3; \underbrace{\mathbb{C}^2}_{\text{spin states}})$

BOSONS: The **state** is a normalized wave function $\psi \in \bigotimes^N_{\text{sym}} L^2(\mathbb{R}^3)$.

The system is given by a Hamilton (energy) operator

$$H_{N,V} = \sum_{n=1}^{N} \left[-\tfrac{1}{2}\Delta_n + V(x_n)\right] + \sum_{n<m} |x_n - x_m|^{-1}.$$

Here V is the background electric potential. Units: $\hbar = e = 2m = 1$, $H_{N,V}$ is a semi-bounded, self-adjoint operator if

$$V \in \mathcal{W} := L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$$

Def of ground state: A ground state ψ (if it exists) minimizes the energy $E(\psi) = (\psi, H_{N,V}\psi)$, i.e., ψ is an eigenfunction of the Hamiltonian with smallest possible eigenvalue (recall $(\psi, \psi) = 1$). We denote the minimizing, i.e., ground state energy $E(N, V)$.

The background field: We consider fields produced by static charges:

$$V(x) = -\int |x-y|^{-1} d\mu(y)$$

Two particular cases:

(a) **Molecule** with K nuclei, positions $R_1, \ldots, R_k \in \mathbb{R}^3$, charges $Z_1, \ldots, Z_K$

$$\mu(y) = \sum_{k=1}^{K} Z_k \delta(y - R_k)$$

(b) A **uniformly charged background** (*Jellium*), approximation for electrons in crystals or nuclei in sea of electrons

$$\mu(x) = \rho \mathbf{1}_{[0,L]^3}(x) dx$$

$\rho > 0$, $\rho L^3 = N$ (neutrality), L large.

The wave function ψ is an extremely complicated object. A simpler object which contains much (but far from all) of the information about the state is the 1-particle density

$$\rho_\psi(x) = N \int |\psi(x; x_2, \ldots ; x_N)|^2 \, dx_2 \cdots dx_N.$$

Note $\int \rho = N$. In case of spin there is also a sum over spin (for **all** N particles).

Hohenberg-Kohn 'Theorem': The density determines the ground state.

Really not that simple: *On the set of ρ that are ground state densities for some $H_{N,V}$, for which the ground state is unique and V is "well-behaved" then ρ determines V and hence the ground state.*

The HK 'Theorem' is one of the most significant results in quantum chemistry, but it is never actually used:

- V depends on ρ in a completely unknown way
- The set of ρ coming from 'unique' ground states is completely uncontrollable.

What is being used in density functional theories is that one may find energy functionals depending in an explicit way on the density that are good approximations, e.g. in the high density limit. An example is the Thomas-Fermi functional for molecules and its various improvements.

There are really two issues. Understanding the non-interacting problem and understanding the effect of correlations. For fermions the non-interacting problem in the high density limit is related to Weyl type semiclassical estimates.

Here I shall be interested in correlations. I therefore restrict attention to Jellium where the non-interacting problem is almost trivial. *Locally charged systems may look like Jellium.*

$$H_N^{\text{Jellium}} = \sum_{i=1}^{N} -\tfrac{1}{2}\Delta_i - \rho \sum_{i=1}^{N} \int_{\Lambda} |x_i - y|^{-1} dy$$
$$+ \sum_{i<j} |x_i - x_j|^{-1} + \underbrace{\tfrac{1}{2}\rho^2 \iint_{\Lambda\times\Lambda} |x - y|^{-1} dx dy}_{\text{background self-energy}},$$

$\Lambda = [0, L]^3$ and $N = \rho L^3$ (neutrality). Here ρ is simply a constant, i.e., the density of the background *not* of the ground state, but the two are in fact nearly the same for large ρ. We are interested in the energy asymptotics for large ρ. Note the extra term above, which is the background self-energy. When we include it we have for both fermions and bosons:

THEOREM 1 (Lieb-Narnhofer 1973).
The thermodynamic limit exists:

$$\lim_{\substack{L\to\infty \\ \frac{N}{L^3}=\rho}} \frac{E(N)}{L^3} = e(\rho)$$

FERMIONIC JELLIUM:

THEOREM 2 (Graf-Solovej 1994).

$$e(\rho) = C_{\mathrm{TF}}\rho^{5/3} - C_{\mathrm{D}}\rho^{4/3} + o(\rho^{4/3})$$

as $\rho \to \infty$

TF=THOMAS-FERMI (1927), D=Dirac (1931).

Uses method of Bach, who proved that the Dirac correction $C_{\mathrm{D}} \int \rho(x)^{4/3} dx$ is good for molecules (where $\rho(x)$ is not a constant, i.e., locally molecules almost like Jellium.

Conjecture (Gell-Mann & Bruckner (1959)):

The next terms in the expansion above are

$$C_1 \rho \log(\rho) + C_2 \rho$$

Sawada (1959) explains the Gell-Mann and Bruckner results in terms of a Bogolubov type approximation.

BOSONIC JELLIUM:

Foldy 1961: Using Bogolubov approximation gets

$$e(\rho) = -0.402(3/4\pi)^{1/4}\rho^{5/4}.$$

Should be good for large ρ. Using the variational principle Girardeau (1962) 'rigorously' establishes:

$$e(\rho) \leq -0.402(3/4\pi)^{1/4}\rho^{5/4} + o(\rho^{5/4}),$$

as $\rho \to \infty$

THEOREM 3 (Lieb-Solovej 2000). *Foldy's calculation is correct:*

$$e(\rho) \geq -0.402(3/4\pi)^{1/4}\rho^{5/4} + o(\rho^{5/4})$$

as $\rho \to \infty$.

Foldy's calculation and pairing theory:
Not rigorous
Step 1: Motivation is Bose condensation: Almost all particles are in the state of momentum $p = 0$ (periodic BC).

Use 2nd quantization: a_0^* creates. particles in the condensate. Keep only the following terms

$$
\begin{aligned}
H_{\text{appr}} \;=\; & \sum_p |p|^2 a_p^* a_p + \sum_{p\neq 0} L^{-3}|p|^{-2}[a_p^* a_0^* a_p a_0 \\
& + a_0^* a_{-p}^* a_0 a_{-p} + a_p^* a_{-p}^* a_0 a_0 + a_0^* a_0^* a_p a_{-p}]
\end{aligned}
$$

i.e., all quartic terms have presicely two $a_0^\sharp$ (ignore terms with one or no $a_0^\sharp$).
Note $|p|^{-2}$ comes from Coulomb potential.

Step 2 in Bogolubov appr.: Replace the *operators* $a_0^\sharp$ by the *number* $\sqrt{N}$:

$$
\begin{aligned}
H_{\text{Foldy}} = \sum_{p\neq 0} \; & |p|^2 a_p^* a_p + \rho|p|^{-2}[a_p^* a_p + a_{-p}^* a_{-p} \\
& + a_p^* a_{-p}^* + a_p a_{-p}]
\end{aligned}
$$

Note: not particle number preserving.

Complete the square:

$$\begin{aligned} H_{\mathrm{Foldy}} &= \sum_p A_p(a_p^* + \beta_p a_{-p})(a_p + \beta_p a_{-p}^*) \\ &\quad + A_p(a_{-p}^* + \beta_p a_p)(a_{-p} + \beta_p a_p^*) \\ &\quad -2 \sum_{p \neq 0} A_p \beta_p^2 \end{aligned}$$

Last term due to $[a_p, a_q^*] = \delta_{pq}$.

$$\begin{aligned} A_p(1+\beta_p^2) &= \tfrac{1}{2}|p|^2 + \rho |p|^{-2} \\ 2A_p\beta_p &= \rho |p|^{-2} \end{aligned}$$

The ground state energy is given by the last term above.

$$e = \lim_{L\to\infty} -\frac{2}{L^3} \sum_{p\neq 0} A_p \beta_p^2 = -2 \int A_p \beta_p^2 = -C_F \rho^{5/4}.$$

Ground state wave function ψ satisfies

$$(a_p + \beta_p a_{-p}^*)\psi = 0,$$

for all $p \neq 0$.

In the original language (a_0 an operator) this corresponds to function of the form

$$\psi = 1 + \sum_{i<j} f(x_i - x_j) + c \sum_{\substack{i,j,l,k \\ \text{different}}} f(x_i - x_j) f(x_l - x_k) + \ldots$$

where $\widehat{f}(p) = \beta_p$. In fact, $\widehat{f}(p) = G(|p|^4/\rho)$, G independent of ρ.
Thus f varies on a length scale $\rho^{-1/4}$ (the typical interpair distance).

Ideas in rigorous proof: No need to prove Bose condensation globally enough to do it on short scale $\ell \gg \rho^{-1/4}$.

- Localize by Neumann bracketing in "small" boxes of size ℓ.
  - Condensate not affected: Constant function 1 always Neumann ground state
  - The Function f "not affected" since $\ell \gg \rho^{-1/4}$. We choose ℓ close to $\rho^{-1/4}$.

- Control electrostatics between boxes using an averaging method of Conlon-Lieb-Yau. Error $= N/\ell \ll N\rho^{1/4}$.

- Establish condensation on scale ℓ: First non-zero Neumann eigenvalue $\sim \ell^{-2}$. The expected number N_+ of particles not in condensate in the "small box". Their energy: $N_+\ell^{-2} \sim N_+\rho^{1/2}$. if consistent with total energy $-N\rho^{1/4}$ we should expect $N_+ \ll N\rho^{-1/4}$, i.e., local condensation.

One establishes this through a bootstrapping procedure. Having established local condensation one starts the hard work of establishing the Bogolubov approximation. Difficulty: We cannot use periodic b.c.