Hartree–Fock Theory and its Generalizations

Volker Bach (TU Braunschweig, @IPAM, UCLA)

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The Hilbert space for nonrelativistic quantum mechanical electrons is as follows.

- The 1-electron Hilbert space is $\mathfrak{h} := L^2\big(\mathbb{R}^3 \times \{\uparrow, \downarrow\}\big)$.
- The N-electron Hilbert space is

$$\mathfrak{H}^{(N)} \;:=\; \mathfrak{h}^{\wedge N} \;=\; \mathrm{span}\Big\{ f_1 \wedge \cdots \wedge f_N \;\Big|\, f_i \in \mathfrak{h}, \langle f_i | f_j \rangle = \delta_{i,j} \Big\},$$

where $f_1 \wedge \cdots \wedge f_N := (N!)^{-1/2} \sum_\pi (-1)^\pi f_1 \otimes \cdots \otimes f_N$ is a Slater determinant.

- The electron Fock space is $\mathfrak{F}_f[\mathfrak{h}] = \bigoplus_{N=0}^\infty \mathfrak{H}^{(N)}$.
- With fermion creation and annhilation ops obeying CAR, we have $f_1 \wedge \cdots \wedge f_N = c^*(f_1) \cdots c^*(f_N)\Omega$ and hence

$$\mathfrak{H}^{(N)} = \mathrm{span}\Big\{ c^*(f_1) \cdots c^*(f_N)\Omega \;\Big|\; f_1, \ldots, f_N \in \mathfrak{h} \Big\} \quad \text{and}$$

$$\mathfrak{F} = \mathrm{span}\Big\{ c^*(f_1) \cdots c^*(f_N)\Omega \;\Big|\; N \in \mathbb{Z}_0^+, \;\; f_1, \ldots, f_N \in \mathfrak{h} \Big\},$$

- Dynamics of Coulomb system of K nuclei and $N \in \mathbb{N}$ electrons is generated by Hamiltonian

$$H_N(\underline{Z}, \underline{R}) \ := \ \sum_{n=1}^{N} h_n(\underline{Z}, \underline{R}) \ + \ \sum_{1 \leq m < n \leq N} V(x_m, x_n)$$

$$h_n(\underline{Z}, \underline{R}) \ := \ -\Delta_n - \sum_{k=1}^{K} \frac{Z_k}{|x_n - R_k|} \, , \quad V(x, y) \ := \ \frac{1}{|x-y|} \, .$$

- Its 2^{nd} quantization is $\mathbb{H} \equiv \mathbb{H}(\underline{Z}, \underline{R}) = \bigoplus_{N=0}^{\infty} H_N(\underline{Z}, \underline{R})$ with

$$\mathbb{H} \ = \mathbb{h} \ + \ \tfrac{1}{2} \mathbb{V} \, ,$$
$$\mathbb{h} \ := \sum_{k,m=1}^{\infty} \langle f_k | \, h(\underline{Z}, \underline{R}) \, f_m \rangle \, c_k^* c_m \, ,$$
$$\mathbb{V} \ := \sum_{k,\ell;m,n=1}^{\infty} \langle f_k \otimes f_\ell | V(f_m \otimes f_n) \rangle \, c_\ell^* c_k^* c_m c_n \, ,$$

where $c_k^* := c^*(f_k)$ and $\{f_k\}_{k=1}^{\infty} \subseteq \mathfrak{h}$ is ONB of suff. regular orbitals.

- The ground state energy $E_{\mathrm{gs}}(N)$ of the Coulomb system is defined as

$$E_{\mathrm{gs}}(N) \;:=\; \inf\Big\{ \langle \psi_N | H_N \psi_N \rangle \;\Big|\; \psi_N \in \mathfrak{H}^{(N)}\,,\; \|\psi_N\| = 1 \Big\}\,,$$

- the total gr. state energy $E_{\mathrm{gs}}(\mu) := \inf_{N \geq 0}\{E_{\mathrm{gs}}(N) - \mu N\}$ is

$$E_{\mathrm{gs}}(\mu) \;=\; \inf\Big\{ \langle \Psi |\, \mathbb{H}_\mu \Psi \rangle \;\Big|\; \Psi \in \mathfrak{F}\,,\; \|\Psi\| = 1 \Big\}\,,$$

where $\mathbb{H}_\mu := \mathbb{H} - \mu \mathbb{N}$ and $\mathbb{N} = \sum_{k=1}^{\infty} c_k^* c_k$ is the number op.

- For Coulomb systems, stability of matter holds, i.e.,

$$E_{\mathrm{gs}}(\mu) + \sum_{1 \leq k < \ell \leq K} Z_k Z_\ell |R_k - R_\ell|^{-1} \geq \mu K,$$

for suff. small μ [Dyson + Lenard 67], [Lieb + Thirring 75].

- The Hartree–Fock (HF) energy is

$$E_{\mathrm{HF}}(N) := \inf\left\{ \mathcal{E}_{\mathrm{HF}}(\underline{f}) \;\middle|\; \underline{f} = (f_1, \ldots, f_N) \in \mathfrak{h}^N, \ \langle f_k | f_m \rangle = \delta_{k,m} \right\},$$

$$\mathcal{E}_{\mathrm{HF}}(\gamma_{\underline{f}}) := \langle \phi_{\underline{f}} | H_N \phi_{\underline{f}} \rangle$$

$$= \sum_{k=1}^{N} \langle f_k | h f_k \rangle + \frac{1}{2} \sum_{k,m=1}^{N} \langle f_k \wedge f_m | V(f_k \wedge f_m) \rangle ,$$

$\phi_{\underline{f}} := f_1 \wedge \cdots \wedge f_N$ and $\gamma_{\underline{f}} := \sum_{k=1}^{N} |f_k\rangle\langle f_k|$.

- Using 1-RDM $\gamma_{\underline{f}}(x,y) := \sum_{n=1}^{N} f_n(x)\overline{f_n(y)}$ and 1-particle density $\rho_{\underline{f}}(x) = \gamma(x,x)$, we have

$$\mathcal{E}_{\mathrm{HF}}(\gamma_{\underline{f}}) = \mathrm{Tr}[h\gamma_{\underline{f}}] + \tfrac{1}{2} D_V(\rho_{\underline{f}}) - \tfrac{1}{2} X_V(\gamma_{\underline{f}}) ,$$

$$D_V(\rho) := \tfrac{1}{2} \int \rho_{\underline{f}}(x)\, \rho_{\underline{f}}(y)\, V(x,y)\, dx\, dy ,$$

$$X_V(\rho) := \tfrac{1}{2} \int |\gamma_{\underline{f}}(x,y)|^2\, V(x,y)\, dx\, dy .$$

- For Coulomb systems:

$$\mathcal{E}_{\mathrm{HF}}(\gamma_{\underline{f}}) \;=\; T(\gamma_{\underline{f}}) + U(\rho_{\underline{f}}) + \tfrac{1}{2} D(\rho_{\underline{f}}) - \tfrac{1}{2} X(\gamma_{\underline{f}}) \,,$$

$$T(\gamma) \;:=\; \mathrm{Tr}[(-\Delta)\gamma] \,, \quad U(\rho) \;:=\; -\textstyle\sum_{k=1}^{K} \int \frac{Z_k \, \rho(x) \, dx}{|x - R_k|} \,,$$

$$D(\rho) \;:=\; \iint \frac{\rho(x) \, \rho(y) \, dx}{|x-y|} \,, \quad X(\gamma) \;:=\; \iint \frac{|\gamma(x,y)|^2 \, dx}{|x-y|} \,.$$

- Large neutral Coulomb systems [Lieb + Simon 77], [Hughes 86], [Siedentop + Weikard 87-89], [Ivrii + Sigal 93], [Solovej + Spitzer 03, 10], [Fefferman + Seco 90-95]: If $Z = N \gg 1$, $\underline{Z} = Z\underline{z}$, $\underline{z} = (z_1, \ldots, z_k)$ fixed, $\underline{R} = (R_1, \ldots, R_k)$ not too close, then $\exists \delta > 0$ s.th.

$$E_{\mathrm{HF}}(Z) \; = E_{\mathrm{TF}}(Z) \, + \, \tfrac{1}{4}\textstyle\sum_{k=1}^{K} Z^2 z_k^2 \, + \, C_{\mathrm{DS}} Z^{5/3} \, + \, \mathcal{O}\big(Z^{5/3-\delta}\big) \, .$$

- If $\underline{f}^{(\mathrm{HF})}$ is (approx.) minim., $\gamma_{\mathrm{HF}} = \gamma_{\underline{f}^{(\mathrm{HF})}}$, $\rho_{\mathrm{HF}} = \rho_{\underline{f}^{(\mathrm{HF})}}$, then

$$c\, Z^{7/3} \; \leq \; T(\underline{f}^{(\mathrm{HF})}) \, , \; U(\rho_{\mathrm{HF}}) \, , \; D(\rho_{\mathrm{HF}}) \; \leq \; C\, Z^{7/3} \, ,$$

$$c\, Z^{5/3} \; \leq \; X(\gamma_{\mathrm{HF}}) \; \leq \; C\, Z^{5/3}, \quad X(\gamma_{\mathrm{HF}}) \; \sim \; \tfrac{9}{11} C_{\mathrm{DS}} Z^{5/3} \, .$$

- $\exists \delta > 0$ s.th. [B. 92, 93]:

$$0 \; \leq \; E_{\mathrm{HF}}(Z) - E_{\mathrm{gs}}(Z) \; \leq \; C\, Z^{5/3-\delta} \, .$$

- If $N < Z + 1$ then HF-minimizer $\underline{\varphi}^{(\mathrm{HF})} = (\varphi_1, \ldots, \varphi_N)$ exists and fulfills HF self-consistent equations [Lieb + Simon 77]:

$$h_{\mathrm{HF}}[\underline{\varphi}^{(\mathrm{HF})}]\, \varphi_i^{(\mathrm{HF})} \;=\; e_i\, \varphi_i^{(\mathrm{HF})} \,,$$

where

$$\big(h_{\mathrm{HF}}[\underline{f}]\,\varphi\big)[\vec{x},\tau] \;:=\; \big(h\,\varphi\big)[\vec{x},\tau] + \Big(\int \frac{\rho_{\underline{f}}(\vec{y})\, d^3y}{|\vec{x}-\vec{y}|}\Big) \varphi(\vec{x},\tau) - \int \frac{\gamma_{\underline{f}}(\vec{x},\vec{y})\, \varphi(\vec{y},\tau)\, d^3y}{|\vec{x}-\vec{y}|} \,.$$

- If $K = 1$ (atom) then Ionization Conjecture holds true, i.e., $\exists C_{\mathrm{Sol}} < \infty$ s.th., for $N > Z + C_{\mathrm{Sol}}$, there is no minimizer of $\mathcal{E}_{\mathrm{HF}}$ [Solovej 03].

- No unfilled shells thm. holds [B.+ Lieb + Loss + Solovej 94]:
$e_1 \leq \ldots \leq e_N \; < \; e_{N+1} = \inf \left[\sigma(h_{\mathrm{HF}}[\underline{\varphi}^{(\mathrm{HF})}]) \setminus \{e_1, \ldots, e_N\}\right]$
- Kohn-Sham approximation results from replacing exchange term $X(\gamma_{\underline{f}})$ in $\mathcal{E}_{\mathrm{HF}}(\gamma_{\underline{f}})$ by LDA or refinements thereof, e.g. GGA (see [Anantharaman + Cancès 09]).
- Existence of excited states [stationary points of $\mathcal{E}_{\mathrm{HF}}$ other than $\underline{\varphi}^{(\mathrm{HF})}$] under HVZ-type condition [Lions 87], [Friesecke 03], [Lewin 11, 18].

- Relativistic analogue of HF eqs. are Dirac–Fock (DF) eqs.
  - * Exist. of sol'ns of DF eqs. in [Esteban + Séré 99], [Paturel 00], [Barbaroux + Farkas + Helffer+ Siedentop 05], [Barbaroux + Esteban + Séré 05], [Huber + Siedentop 07].
  - * DF eqs. do not result from energy minimization because energy functional is unbounded below. Need to involve positrons and renormalize energy functional [BDF model].
  - * Lack of relative boundedness causes instability for $Z > 87$ (with $\alpha = 1/137$). [Chaix + Iracaine (+ Lions) 89], [B.+ Barbaroux + Helffer + Siedentop 99].
  - * Exist. of minimizers for BDF model in [Hainzl + Lewin + Séré 05, 09].
- Overview article by [Esteban + Lewin + Séré 08].

- Total ground state energy is given by

$$E_{\mathrm{gs}}(\mu) = \inf \left\{ \mathrm{Tr}_{\mathfrak{F}}[\rho \mathbb{H}_\mu] \,\middle|\, \rho = |\Psi\rangle\langle\Psi|, \ \Psi \in \mathfrak{F}, \ \|\Psi\| = 1 \right\}$$

$$= \inf \left\{ \mathcal{E}_\mu\big(\gamma_\rho^{(1)}, \gamma_\rho^{(2)}\big) \,\middle|\, \rho \in \mathfrak{DM} \right\},$$

where $\mathcal{E}_\mu\big(\gamma_\rho^{(1)}, \gamma_\rho^{(2)}\big) := \mathrm{Tr}_1\big[h_\mu \gamma_\rho^{(1)}\big] + \frac{1}{2}\mathrm{Tr}_2\big[V \gamma_\rho^{(2)}\big]$ and

$$\mathfrak{DM} := \left\{ \rho \in \mathcal{L}^1(\mathfrak{F}) \,\middle|\, 0 \le \rho \le 1, \ \mathrm{Tr}[\rho] = 1, \ \rho \text{ even} \right\},$$

$$\langle f_m | \, \gamma_\rho^{(1)} f_k \rangle := \mathrm{Tr}_{\mathfrak{F}}[\rho \, c_k^* \, c_m],$$

$$\langle f_m \otimes f_n | \, \gamma_\rho^{(2)} (f_k \otimes f_\ell) \rangle := \mathrm{Tr}_{\mathfrak{F}}[\rho \, c_k^* \, c_\ell^* \, c_n \, c_m],$$

are density matrices, 1-RDM, and 2-RDM, resp.

- Similarly,

$$E_{\mathrm{gs}}(N) \; = \inf \Big\{ \mathcal{E}_0(\gamma_\rho^{(1)}, \gamma_\rho^{(2)}) \; \Big| \; \rho \in \mathfrak{DM}^{(N)} \Big\} ,$$

$$\mathfrak{DM}^{(N)} \; := \big\{ \rho \in \mathfrak{DM} \big| \; \rho \mathbb{N} = \mathbb{N} \rho = N \cdot \rho \big\}$$

- Note that

$$0 \leq \gamma_\rho^{(1)} \leq 1 \quad \text{and} \quad \mathrm{Tr}_1[\gamma_\rho^{(1)}] = \mathrm{Tr}_{\mathfrak{F}}[\rho \mathbb{N}] .$$

- If $\Phi_{\underline{g}} = c^*(g_1) \cdots c^*(g_N)\Omega$, $\langle g_k | g_m \rangle = \delta_{k,m}$, is a Slater determinant and $\rho = |\Phi_{\underline{g}}\rangle\langle\Phi_{\underline{g}}|$ then

$$\gamma_\rho^{(1)} = \sum_{n=1}^N |g_n\rangle\langle g_n| = \big(\gamma_\rho^{(1)}\big)^2 ,$$

$$\gamma_\rho^{(2)} = \sum_{m,n=1}^N |g_m \wedge g_n\rangle\langle g_m \wedge g_n| = (\mathbf{1} - \mathrm{Ex})(\gamma_\rho^{(1)})^{\otimes 2} ,$$

are (multiples of) orthonormal projections.

- Hence

$$E_{\mathrm{HF}}(N) = \inf\big\{\mathcal{E}_{\mathrm{HF}}(\gamma) \,\big|\, \gamma \in \mathcal{L}(\mathfrak{h}),\ \gamma = \gamma^* = \gamma^2,\ \mathrm{Tr}[\gamma] = N\big\} ,$$

$$\mathcal{E}_{\mathrm{HF}}(\gamma) = \mathrm{Tr}_1[h\gamma] + \tfrac{1}{2} D_V(\rho_\gamma) - \tfrac{1}{2} X_V(\gamma) .$$

- [Lieb 81] proved (see also [B. 92]):

$$E_{\mathrm{HF}}(N) = \inf\big\{\mathcal{E}_{\mathrm{HF}}(\gamma) \,\big|\, \gamma \in \mathcal{L}^1(\mathfrak{h}),\ 0 \le \gamma \le 1,\ \mathrm{Tr}[\gamma] = N\big\} .$$

- For $\rho \in \mathfrak{DM}$ define its 1-gRDM $\Gamma_\rho^{(1)} \in \mathcal{L}^1[\mathfrak{h}^2]$

$$\langle G | \, \Gamma_\rho^{(1)} F \rangle \; := \mathrm{Tr}_{\mathfrak{F}} \big[\rho \, \big(c^*(f_1) + c(f_2) \big) \big(c^*(g_1) + c(g_2) \big) \big] \, ,$$

where $F = (f_1, \mathrm{j} f_2), G = (g_1, \mathrm{j} g_2) \in \mathfrak{h}^2$ and $\mathrm{j} : \mathfrak{h} \to \mathfrak{h}$ is an antiunitary involution.

- Note that $0 \leq \Gamma_\rho^{(1)} \leq 1$ and that

$$\Gamma_\rho^{(1)} \; = \begin{pmatrix} \gamma_\rho^{(1)} & \alpha_\rho \\ \alpha_\rho^* & \mathbf{1} - \mathrm{j} \, \gamma_\rho^{(1)} \mathrm{j} \end{pmatrix} \, ,$$

where $\langle g | \, \alpha_\rho(\mathrm{j} f) \rangle \; := \; \mathrm{Tr}_{\mathfrak{F}}[\rho \, c(f) \, c(g)]$ is the pairing operator $\alpha_\rho \in \mathcal{L}^2(\mathfrak{h})$, which obeys $\alpha_\rho = -\mathrm{j} \alpha_\rho^* \mathrm{j}$.

- We call any $\Gamma = \left(\begin{smallmatrix} \gamma & \alpha \\ \alpha^* & 1 - \mathrm{j}\gamma\mathrm{j} \end{smallmatrix} \right) \in \mathcal{B}[\mathfrak{h}^2]$ with $\gamma \in \mathcal{L}^1$, $\alpha^* = -\mathrm{j} \alpha \mathrm{j}$ and $0 \leq \Gamma \leq 1$ a 1-gpdm. If $\rho \in \mathfrak{DM}$ then its 1-gRDM is a 1-gpdm.

- $\rho \in \mathfrak{DM}$ is called quasifree, $\rho \in \mathfrak{QDM}$, if

$$\langle \zeta_1 \cdots \zeta_{2k} \rangle_\rho \; = \; \sum_{\pi \in \mathcal{P}_{2k}} (-1)^\pi \langle \zeta_{\pi(1)} \zeta_{\pi(2)} \rangle_\rho \cdots \langle \zeta_{\pi(2k-1)} \zeta_{\pi(2k)} \rangle_\rho$$

for all $k \in \mathbb{N}$ and all choices $\zeta_1, \ldots \zeta_{2k} \in \{c^*(f), c(f) | f \in \mathfrak{h}\}$, where $\mathcal{P}_{2k} \subseteq \mathcal{S}_{2k}$ are the pairings of $2k$ elements and $\langle \mathbb{A} \rangle_\rho := \mathrm{Tr}_{\mathfrak{F}}[\rho \mathbb{A}]$.

- If $k = 2$ and $\rho \in \mathfrak{QDM}$ then

$$\mathrm{Tr}_{\mathfrak{F}}[\rho \, c_k^* \, c_\ell^* \, c_n \, c_m] \; = \; \langle c_k^* \, c_\ell^* \, c_n \, c_m \rangle_\rho$$

$$= \langle c_k^* \, c_m \rangle_\rho \langle c_\ell^* \, c_n \rangle_\rho \; - \; \langle c_k^* \, c_n \rangle_\rho \langle c_\ell^* \, c_m \rangle_\rho \; + \; \langle c_k^* \, c_\ell^* \rangle_\rho \langle c_n \, c_m \rangle_\rho$$

$$= \big(\gamma_\rho^{(1)}\big)_{m,k} \big(\gamma_\rho^{(1)}\big)_{n,\ell} \; - \; \big(\gamma_\rho^{(1)}\big)_{n,k} \big(\gamma_\rho^{(1)}\big)_{m,\ell} \; + \; \overline{(\alpha_\rho)_{\ell,k}} (\alpha_\rho)_{n,m}$$

- B.+ Lieb + Solovej 94 showed that if Γ is a 1-gpdm then there exists a unique quasifree state $\eta \in \mathfrak{QDM}$ such that $\Gamma_\eta^{(1)} = \Gamma$.
- This implies that, for every $\rho \in \mathfrak{DM}$ there is a unique quasifree state $q[\rho] \in \mathfrak{QDM}$ such that $\Gamma_{q[\rho]}^{(1)} = \Gamma_\eta^{(1)}$. The idempotent map $q = q^2 : \mathfrak{DM} \to \mathfrak{QDM}$ is called quasifree reduction.
- Among all quasifree density matrices the quasifree reduction $q[\rho]$ is the closest to $\rho \in \mathfrak{DM}$ in the sense that

$$S[\rho, q(\rho)] \;=\; \inf_{\eta \in \mathfrak{QDM}} \big\{ S[\rho, \eta] \big\} \,,$$

$$S[\rho, \eta] \;:= \mathrm{Tr}_{\mathfrak{F}} \big\{ \rho \big(\log[\rho] - \log[\eta] \big) \big\} \,,$$

[Gottlieb + Mauser 07].

- Bogoliubov–Hartree–Fock (BHF) energy (μ fixed):

$$\begin{aligned} E_{\mathrm{BHF}} &:= \inf\left\{\mathrm{Tr}_{\mathfrak{F}}[\rho \mathbb{H}_\mu] \;\middle|\; \rho \in \mathfrak{QDM}\right\} \\ &= \inf\left\{\mathcal{E}_{\mathrm{BHF}}\big(\Gamma_\rho^{(1)}\big) \;\middle|\; \rho \in \mathfrak{QDM}\right\} \\ &= \inf\left\{\mathcal{E}_{\mathrm{BHF}}(\Gamma) \;\middle|\; \Gamma \text{ is a 1-gpdm}\right\}, \end{aligned}$$

$$\mathcal{E}_{\mathrm{BHF}}\big(\Gamma[\gamma,\alpha]\big) := \mathrm{Tr}_1[h\gamma] + \tfrac{1}{2} D_V(\rho_\gamma) - \tfrac{1}{2} X_V(\gamma) + \tfrac{1}{2} X_V(\alpha),$$
$$\Gamma[\gamma,\alpha] := \begin{pmatrix} \gamma & \alpha \\ \alpha^* & 1 - |\gamma| \end{pmatrix}.$$

- If $\Phi_{\underline{g}} = c^*(g_1)\cdots c^*(g_N)\Omega$, $G(\underline{g}) = 1$, is a Slater determinant and $\rho = |\Phi_{\underline{g}}\rangle\langle\Phi_{\underline{g}}|$, then $\alpha_\rho = 0$ and $\rho \in \mathfrak{QDM}$. Hence

$$E_{\mathrm{gs}} \le E_{\mathrm{BHF}} \le E_{\mathrm{HF}}.$$

- For positive temperatures, $\beta = 1/T < \infty$, there is an analogue for the free energy [B.+ Lieb + Solovej 94],

$$-\frac{1}{\beta} \log \Big[\mathrm{Tr}_{\mathfrak{F}}\{ \exp[-\beta \mathbb{H}_\mu] \} \Big] \\ \leq \inf \big\{ \mathcal{E}_{\mathrm{BHF}}(\Gamma) - \tfrac{1}{\beta} S(\Gamma) \,\big|\, \Gamma \text{ is a 1-gpdm} \big\},$$

where $S(\Gamma[\gamma, \alpha]) = \mathrm{Tr}[\gamma \log(\gamma) + (1-\gamma)\log(1-\gamma)]$ is the corresponding entropy.

- If $V(x, y) \geq 0$ is repulsive then

$$X_V(\alpha) = \int |\alpha(x, y)|^2 \, V(x, y) \, dx \, dy \geq 0$$

and

$$E_{\mathrm{BHF}} = E_{\mathrm{HF}} .$$

- If V has an attractive part, $V < 0$ in a region of positive measure, and $\Gamma_{\mathrm{BHF}} = \Gamma[\gamma_{\mathrm{BHF}}, \alpha_{\mathrm{BHF}}]$ is a minimizing 1-gpdm then $\alpha_{\mathrm{BHF}} \neq 0$ for some (but not all) models.

- In case that $\alpha_{\rm BHF} \neq 0$ the particle number symmetry is broken: $[\mathbb{H}, \mathbb{N}] = 0$ but $[\rho_{\rm BHF}, \mathbb{N}] \neq 0$.

- If $V < 0$, a spin degree of freedom accommodates $\alpha^* = -|\alpha|$ and allows to eliminate α, namely

$$\gamma = \hat{\gamma} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \alpha = \sqrt{\hat{\gamma} - \hat{\gamma}^2} \otimes \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

[B.+ Fröhlich + Jonsson 09], [Lenzman + Lewin 10].

- In analogy to Lieb's variational principle, the variation in the BHF energy over all quasifree density matrices can be restricted to the pure ones [Derezinski + Napiorkowski + Solovej 13], [B.+ Breteaux + Knörr + Menge 14]:

$$E_{\rm BHF} \; = \; \inf \left\{ \langle \Omega | \, \mathbb{U}^* \mathbb{H}_\mu \mathbb{U} \Omega \rangle \; \middle| \; \mathbb{U} \in \mathrm{Bog}_{\mathfrak{F}} \right\}.$$

- $\mathcal{S} \subseteq \mathcal{U}[\mathfrak{F}]$ is a symmetry of $\mathbb{H}_\mu$ if $[U, \mathbb{H}_\mu] = 0$ for all $U \in \mathcal{S}$.
- The restricted BHF energy $E_{\mathrm{BHF}}(\mathcal{S})$ is defined by

$$E_{\mathrm{BHF}}(\mathcal{S}) \ := \ \inf \left\{ \mathrm{Tr}_{\mathfrak{F}}[\rho\, \mathbb{H}_\mu] \,\middle|\, \rho \in \mathfrak{QDM},\ \forall U \in \mathcal{S} :\ U\rho = \rho U \right\}.$$

- If $E_{\mathrm{BHF}}(\mathcal{S}) > E_{\mathrm{BHF}}$ then symmetry $\mathcal{S}$ is broken.
- No unfilled shell theorem does not hold for $E_{\mathrm{BHF}}(\mathcal{S})$, in gen.
- Particle Number I: If $\mathcal{N} = \{e^{i\phi \mathbb{N}}\}_{\phi \in \mathbb{R}}$ and $V \geq 0$ then particle number symmetry $\mathcal{N}$ is never broken.
- Particle Number II: If $\mathcal{N} = \{e^{i\phi \mathbb{N}}\}_{\phi \in \mathbb{R}}$ and $V < 0$ is attractive then particle number symmetry $\mathcal{N}$ may be broken. This then leads to BCS theory.

- Rotations: Consider, e.g., a Lithium atom ($K = 1$, $R = 0$) with $Z = N = 3$. Then the rotation symmetry $\mathcal{R}$ is broken. If, however, $N = 2\sum_{\ell=0}^{L}(2\ell + 1)$ fills up the angular momentum channels up to L and $Z \gg N$, then the rotation symmetry $\mathcal{R}$ is not broken [Griesemer + Hantsch 12].
- Translation Invar. on Torus: Let $\mathfrak{h} = L^2(\Lambda \times \{\uparrow, \downarrow\})$ with Torus $\Lambda := (\mathbb{R}/L\mathbb{Z})^3$. Then $U_{\vec{a}} = \exp[-i\vec{a} \cdot \vec{\mathbb{p}}]$ with $\vec{a} \in \Lambda$ modulo L and $\mathcal{T} := \{U_{\vec{a}} | \vec{a} \in \Lambda\}$ defines the group of translations on the Torus. The model with $h = -\Delta$ is called Fermi gas. Let

$$e_{\mathrm{BHF}} := \lim_{L\to\infty} \{L^{-3} E_{\mathrm{BHF}}\}, \quad e_{\mathrm{BHF}}(\mathcal{T}) := \lim_{L\to\infty} \{L^{-3} E_{\mathrm{BHF}}(\mathcal{T})\}.$$

  * [Overhauser 60, 62, 68] showed that $e_{\mathrm{BHF}} < e_{\mathrm{BHF}}(\mathcal{T})$.
  * [Gontier + Hainzl + Lewin 19] showed that $e_{\mathrm{BHF}}(\mathcal{T}) - e_{\mathrm{BHF}}$ is exponentially small in the coupling constant.

- Translation & Spin Invar. on Torus: The BCS model is defined as $E_{\mathrm{BCS}} := E_{\mathrm{BHF}}(\mathcal{T} \times SU(2))$, i.e., the energy is varied over 1-gpdm of the form $\Gamma[\gamma, \alpha]$ with

$$\gamma(k,k') = \delta_{k,k'}\,\hat{\gamma}(k) \otimes \left(\begin{smallmatrix} 1 & 0 \\ 0 & 1 \end{smallmatrix}\right), \quad \alpha(k,k') = \delta_{k,k'}\,\hat{\alpha}(k) \otimes \left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)$$

leading to energy functional ($\beta = \infty$)

$$\mathcal{E}_{\mathrm{BCS}}(\Gamma) = \sum_{k \in \Lambda^*} \big(\omega(k) - \mu\big)\,\hat{\gamma}(k) + \frac{1}{2}\|\widehat{V}\|_1 \|\hat{\gamma}\|_1^2$$

$$- \frac{1}{2}\int_\Lambda V(x)\,|\gamma(x)|^2\,d^3x + \frac{1}{2}\int_\Lambda V(x)\,|\alpha(x)|^2\,d^3x\,,$$

This model has been analyzed by Hainzl and Seiringer et al (Bräunlich, Frank, Freiji, Hamza, Naboko, Seiringer, Solovej), see review [Hainzl + Seiringer 16].

- Hubbard Model: Let $\mathfrak{h} = L^2(\Lambda \times \{\uparrow, \downarrow\})$ with discrete Torus $\Lambda := (\mathbb{Z}/L\mathbb{Z})^3$ and even L. Let $h := t \otimes \mathbf{1}_2$, $t_{x,y} := -\sum_{|e|=1} \delta_{x+e,y}$ and $V_{x,y} := \delta_{x,y} \otimes (\mathbf{1}_2 \otimes \mathbf{1}_2)$. Then

$$\mathbb{H}_{g/2} := \mathbb{h} - \tfrac{g}{2}\mathbb{N} + \tfrac{g}{2}\mathbb{V} = \sum_{x,y;\sigma} h_{x,y}\, c^*_{x,\sigma}\, c_{y,\sigma} + g \sum_{x} n_{x,\uparrow}\, n_{x,\downarrow} \,.$$

- $\mathbb{H}_\mu$ has symmetries $\mathcal{N}$ (particle number), $\mathcal{T}$ (translations), $SU(2)$ (global spin rotations).

- For $g \geq 0$, potential $V \geq 0$ is repulsive and particle number $\mathcal{N}$ is not broken, $E_{\mathrm{BHF}} = E_{\mathrm{BHF}}(\mathcal{N})$.

- $E_{\mathrm{para}} := E_{\mathrm{BHF}}(\mathcal{N} \times \mathcal{T} \times SU(2))$ is the paramagnetic BHF energy. Its minimizer $\gamma_{\mathrm{para}} = \mathbf{1}[h \leq \mu(\rho, g)] \otimes \mathbf{1}_2$ is filled Fermi sea, gr. state for $g = 0$. $E_{\mathrm{BHF}} = E_{\mathrm{para}}$, for $\rho := N/|\Lambda| \leq \rho_0 < 1$ and $0 \leq g \leq g_0(\rho_0)$.

- At low filling $0 < \rho \leq \rho_0 \ll 1$ and strong coupling $g \geq g_0(\rho_0) \gg 1$ the minimizer $\gamma_{\text{ferro}} = \mathbf{1}[h \leq \tilde{\mu}(\rho, g)] \otimes P_\uparrow$ (of HFz-functional) is the ferromagnetic BHF ground state [B.+ Lieb + Travaglia 06] and

$$E_{\text{BHF}} \leq E_{\text{ferro}} := E_{\text{BHF}}(\mathcal{N} \times \mathcal{T}) < E_{\text{para}} .$$

- At half-filling $\rho = 1$ and any $g \geq 0$ the BHF minimizer γ_{af} has antiferromagnetic order, i.e., $\exists \vec{e} \in \mathbb{R}^3$, $|\vec{e}| = 1$:

$$\text{Tr}\big[\gamma_{\text{af}}(\mathbf{1}_x \otimes \vec{\sigma})\big] = \Delta_g \, (-1)^x \, \vec{e} \, ,$$

for all $x \in \Lambda$ [B.+ Lieb + Solovej 94].

– Thank you for your attention! –

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