Screening in the reduced Hartree–Fock model

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Mathematical Physics and PDEs
Herrsching, 16 December 2024,

Slides are online: `jack.thomaslabs.co.uk/Herrsching`

Electrostatic Screening: $\mu_{\mathrm{def}} = Q\delta_0$

- Point charge in vacuum $\implies$ long-range Coulomb potential
- In a material $\implies$ material reorganises itself, total potential (Coulomb + response) is screened,
- Behaviour depends on whether charge carriers are mobile,
- Empirical models:

Vacuum

$$V(x) = v_c \mu_{\mathrm{def}}(x) = \frac{Q}{4\pi|x|},$$

Coulomb potential

Total screening

$$V(x) = \frac{Q}{4\pi|x|} e^{-k|x|}$$

Yukawa potential with screeening length k^{-1}

Partial screening

$$V(x) = \frac{Q}{4\pi\varepsilon_r|x|}$$

Dielectric constant of the material $\varepsilon_r > 1$

Reduced Hartree–Fock (rHF) - finite systems

Coulomb operator:

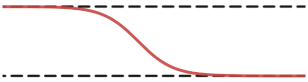
$$v_c\rho(x) = \frac{1}{4\pi}\int \frac{\rho(y)}{|x-y|}\mathrm{d}y$$

Potential-to-density:

$$F_\varepsilon(V)(x) = f_{\varepsilon_\mathrm{F}}\big(-\Delta + V\big)(x,x)$$

$$f_{\varepsilon_\mathrm{F}}(x) = \left(1 + e^{\frac{x-\varepsilon_\mathrm{F}}{k_B T}}\right)^{-1}$$

Fermi–Dirac distribution:



k_B - Boltzmann const.
T - temperature
ε_F - Fermi level

Finite Systems

Total potential V satisfies:

$$V = V_\mathrm{ext} + v_c F_{\varepsilon_F}(V)$$

$$\int_{\mathbb{R}^3} F_{\varepsilon_F}(V) = N_\mathrm{el}$$

where: N_el – number of electrons,
V_ext – external potential

- Hartree
- RPA
- Schrödinger–Poisson
- KSDFT w/o XC
- Hartree–Fock w/o exchange

Reduced Hartree–Fock (rHF)

$$\mathcal{E}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int V_{\mathrm{ext}}\rho_\gamma + \frac{1}{2}\int \rho_\gamma v_c \rho_\gamma$$

Convex variational problem

- existence γ and uniqueness ρ_γ
  (neutral or positively charged systems)
  [J-P Solovej, 1991]
- thermodynamic limit / periodic problem
  [I. Catto, C. Le Bris, and P-L Lions, 2001]
  [É. Cancès, A. Deleurence, and M. Lewin, 2008]

Finite Systems

Total potential V satisfies:

$$V = V_{\mathrm{ext}} + v_c F_{\varepsilon_F}(V)$$

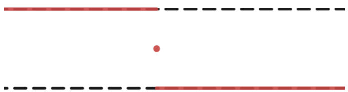
$$\int_{\mathbb{R}^3} F_{\varepsilon_F}(V) = N_{\mathrm{el}}$$

N_{el} = # of electrons

V_{ext} = external potential

$$v_c\rho(x) = \frac{1}{4\pi}\int \frac{\rho(y)}{|x-y|}\mathrm{d}y$$

$$F_\varepsilon(V)(x) = f_{\varepsilon_{\mathrm{F}}}\big(-\Delta + V\big)(x,x)$$



Reduced Hartree–Fock (rHF)

$\Longrightarrow \quad W_{\text{per}} = W_{\text{nucl}} + v_{\text{per}} F_{\varepsilon_{\text{F}}}(W_{\text{per}})$
unique solution of the periodic rHF problem

Defect Problem

Change in potential V satisfies:

$$V = V_{\text{def}} + v_c\big(\rho_V - \rho_0\big)$$
$$\rho_V = F_{\varepsilon_{\text{F}}}\big(W_{\text{per}} + V\big)$$

Finte temperature: small defects are totally screened

[A. Levitt, 2020]

e.g. $V_{\text{def}} = \frac{Q}{|x|}$ for Q small enough,
$V(V_{\text{def}})$ decays exponentially

Zero temperature: partial screening

[É. Cancès, M. Lewin, 2010]

Finite Systems

Total potential V satisfies:

$$V = V_{\text{ext}} + v_c F_{\varepsilon_F}(V)$$
$$\int_{\mathbb{R}^3} F_{\varepsilon_F}(V) = N_{\text{el}}$$

$N_{\text{el}} = \#$ of electrons
$V_{\text{ext}} =$ external potential

$$v_c\rho(x) = \frac{1}{4\pi}\int \frac{\rho(y)}{|x-y|}\mathrm{d}y$$
$$F_\varepsilon(V)(x) = f_{\varepsilon_{\text{F}}}\big(-\Delta + V\big)(x,x)$$

$$\begin{cases} -\Delta(v_{\text{per}}\rho) = \rho - \frac{1}{|\Gamma|}\int_\Gamma \rho \\ \int_\Gamma v_{\text{per}}\rho = 0 \end{cases}$$

Ideas in the proof

- Linearise: $V = V_{\mathrm{def}} + v_c \chi_0 V$ and thus

$$V(V_{\mathrm{def}}) = \varepsilon^{-1} V_{\mathrm{def}} := (1 - v_c \chi_0)^{-1} V_{\mathrm{def}}$$

  where $\rho_V = \rho_0 + \chi_0 V + \cdots$.
- $\chi_{0,KK'}(q) := \langle e_K, \chi_{0,q} e_{K'} \rangle$ where $e_K := e^{iK\cdot x}$,
- For example, $K = K' = 0$

$$V = V_{\mathrm{def}} + v_c \left(\rho_V - \rho_0 \right)$$

Notation:
$V = \fint_{\mathcal{B}} V_q(x) e^{iq\cdot x} \mathrm{d}q$
$AV = \fint_{\mathcal{B}} (A_q V_q)(x) e^{iq\cdot x} \mathrm{d}q$

$H_0 := -\Delta + W_{\mathrm{per}}$
$H_{0,q} = \sum_n \varepsilon_{nq} \left| u_{nq} \right\rangle \left\langle u_{nq} \right|$

$$\chi_{0,00}(q) \approx \sum_n \fint_{\mathcal{B}} f'_{\varepsilon_{\mathrm{F}}}(\varepsilon_{nk}) |u_{nk}|^2 \mathrm{d}k + \sum_{n \neq m} \fint_{\mathcal{B}} \frac{f_{\varepsilon_{\mathrm{F}}}(\varepsilon_{nk}) - f_{\varepsilon_{\mathrm{F}}}(\varepsilon_{mk})}{(\varepsilon_{n,k} - \varepsilon_{mk})^3} \left| \langle q \cdot \nabla u_{mk}, u_{nk} \rangle \right|^2 \mathrm{d}k$$

$$= -\mathrm{DOS} - q^T L q$$

where $0 \leq L \in \mathbb{R}^3_{\mathrm{sym}}$.

more details

$$V(V_{\mathrm{def}}) \approx \varepsilon^{-1} V_{\mathrm{def}} = (1 - v_c \chi_0)^{-1} V_{\mathrm{def}}$$

- Finite temperature: $\chi_0(q) \approx -\mathrm{DOS}$ and $V_{\mathrm{def}} = \frac{Q}{|x|}$, then

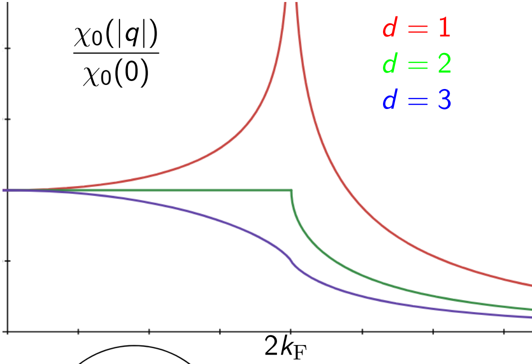
$$\widehat{V}(q) = \frac{1}{1 + \frac{\mathrm{DOS}}{|q|^2}} \frac{Q}{|q|^2} = \frac{Q}{|q|^2 + \mathrm{DOS}} \qquad \text{i.e.} \quad V = Q \frac{e^{-\sqrt{\mathrm{DOS}}|x|}}{|x|}$$

- Insulators: $\chi_0(q) \approx -q^T L q$ and

$$\widehat{V}(q) = \frac{1}{1 + \frac{q^T L q}{|q|^2}} \frac{Q}{|q|^2} = \frac{Q}{q^T M q} \qquad \text{i.e.} \quad V = \frac{Q}{\sqrt{\det M}} \frac{1}{|x^T M^{-1} x|^{\frac{1}{2}}}$$

Metals at Zero Temperature

$$\chi_{0,00}(q) = \fint_{\mathcal{B}} \frac{f_{\varepsilon_{\mathrm{F}}}(\varepsilon_{k+q}) - f_{\varepsilon_{\mathrm{F}}}(\varepsilon_k)}{\varepsilon_{k+q} - \varepsilon_k} \, |\langle u_k, u_{k+q}\rangle|^2 \, \mathrm{d}k$$



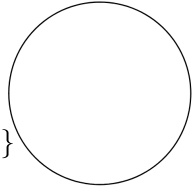
Free electron gas, $\varepsilon_k = |k|^2$

$$V(V_{\mathrm{def}}) \approx \varepsilon^{-1} V_{\mathrm{def}} = (1 - v_c \chi_0)^{-1} \frac{Q}{|x|}$$

$$\sim Q \frac{\sin(2k_{\mathrm{F}}|x| + (d-2)\frac{\pi}{2})}{|x|^d}$$

as $|x| \to \infty$.

$\{k : \varepsilon_k = \varepsilon_{\mathrm{F}} =: (k_{\mathrm{F}})^2\}$



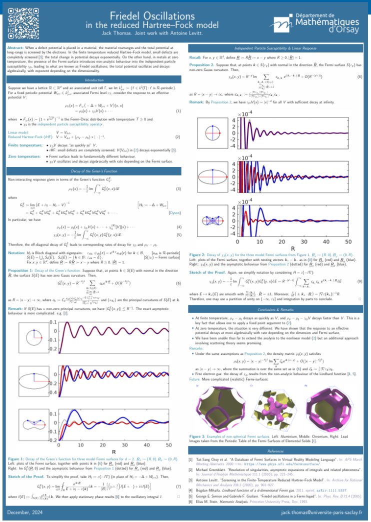
More generally,

$$\chi_0 V(x) = \frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\varepsilon_{\mathrm{F}}}\int_{\mathbb{R}^d} G_0(x,y;E)V(y)G_0(y,x;E)\,\mathrm{d}y\,\mathrm{d}E$$

where

$$G_0(x,y;E) := \lim_{\eta\downarrow 0} \fint_{\mathcal{B}} \frac{u_k(x)u_k^\star(y)}{E + i\eta - \varepsilon_k} e^{ik\cdot(x-y)}\mathrm{d}k.$$

- Asymptotic behaviour of the Green's function (contour deformation + stationary phase argument) $\implies$ linear response behaviour



Scattering Theory: Eigenfunction Expansions

- Want: $\rho_V - \rho_0$,

$$\rho_0(x) = f_{\varepsilon_F}(H_0)(x,x) = \fint_{\mathcal{B}} f_{\varepsilon_F}(\varepsilon_k)|\Psi_k(x)|^2 \mathrm{d}k$$

$$\rho_V(x) \stackrel{?}{=} \sum_{j:\,\lambda_j \le \varepsilon_F} |\varphi_i(x)|^2 + \fint_{\mathcal{B}} f_{\varepsilon_F}(\varepsilon_k)|\Psi_k^+(x)|^2 \mathrm{d}k$$

- Idea: $\Psi_k^+ = \Omega^+ \Psi_k$ that "looks like" Ψ_k in the distant past:

$$\lim_{t\to-\infty} \left(e^{-iHt}\Psi_k^+ - e^{-iH_0 t}\Psi_k \right) = 0$$

- " $\Omega^+ = \lim_{t\to-\infty} e^{iHt}e^{-iH_0 t}$ ", $\quad \Omega^+ H = H_0 \Omega^+$
- Lippmann-Schwinger: $\Psi_k^+ = \Psi_k + G_0(\varepsilon_k) V \Psi_k^+$ Proof

Notation:
$H_0 = -\Delta + W_{\text{per}}$,
$\Psi_k = u_k(x)e^{ik\cdot x}$ with
$H_0\Psi_k = \varepsilon_k \Psi_k$,
$G_0(E) := (E + i0^+ - H_0)^{-1}$

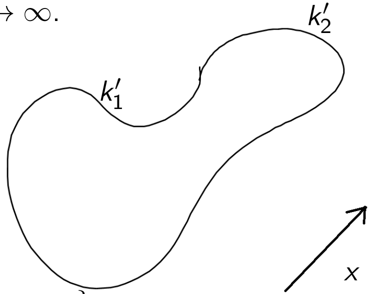
$H = H_0 + V$,
$G(E) := (E + i0^+ - H)^{-1}$
$H\varphi_i = \lambda_i \varphi_i$

Scattering Theory: Eigenfunction Expansions

- For $V \in L^p \cap L^{\frac{d}{d-1}}$, $\exists! \Psi_k^+$ with $|V|^{\frac{p}{2}} \Psi_k^+ \in L^2 \quad (1 \leq p < \frac{d}{d-1})$
- Asymptotics Green's function (see poster) $\implies$

$$\Psi_k^+(x) \approx \Psi_k(x) + \sum_{k'} c_{k'} \frac{e^{ik' \cdot x}}{|x|^{\frac{d-1}{2}}} \underbrace{\left\langle \Psi_{k'} \,\middle|\, V \,\middle|\, \Psi_k^+ \right\rangle}_{=: T(k', k)}$$

as $|x| \to \infty$.



$\{k \colon \varepsilon_k = \varepsilon_{\mathrm{F}}\}$

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$H \varphi_i = \lambda_i \varphi_i$

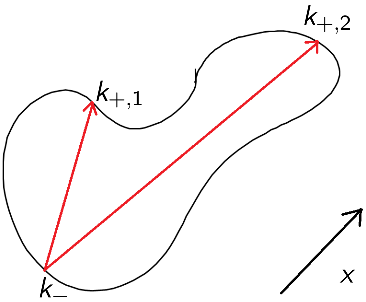
$\Psi_k^+ := \Omega^+ \Psi_k$
$\Psi_k^+ = \Psi_k + G_0(\varepsilon_k) V \Psi_k^+$

Scattering Theory: Eigenfunction Expansions

$$\rho_V(x) - \rho_0(x) = \fint_{\mathcal{B}} f_{\varepsilon_{\mathrm{F}}}(\varepsilon_k) \left[\left|\Psi_k^+\right|^2 - \left|\Psi_k\right|^2 \right] \mathrm{d}k \quad = \cdots =$$

$$= C \frac{\mathrm{Re}}{|x|^d} \sum_{k_-, k_+} c_{k_-} c_{k_+} \Psi_{k_+}(x) T(k_+, k_-) \overline{\Psi_{k_-}(x)}$$

as $|x| \to \infty$.



more details

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$\Psi_k^+ := \Omega^+ \Psi_k$
$\Psi_k^+ = \Psi_k + G_0(\varepsilon_k) V \Psi_k^+$

$T(k', k) := \langle \Psi_{k'} \mid V \mid \Psi_k^+ \rangle$

Summary

- Finite temperature, insulators, metals at zero temperature exhibit different screening behaviour
- Green's function $\implies$ linear response properties (see poster)
- Scattering theory $\implies$ decay of $\rho_V - \rho_0$

Next:

- fixed point arguments to solve $V = V_{\mathrm{def}} + v_c(\rho_V - \rho_0)$
  e.g.

$$V_{n+1} = V_n + \frac{-\Delta}{1-\Delta}\left[V_{\mathrm{def}} + v_c\left(\rho_{V_n} - \rho_0\right) - V_n\right]$$

- More general Fermi surfaces,
- e.g. Graphene, ...

Thank you for your attention!
Slides are online: `jack.thomaslabs.co.uk/Herrsching`

Ideas in the proof

$$
\begin{aligned}
\chi_0 V &= \oint_{\mathscr{C}} f_{\varepsilon_{\mathrm{F}}}(z)\ R_z V R_z(x,x)\ \frac{\mathrm{d}z}{2\pi i} \\
&= \oint_{\mathscr{C}} f_{\varepsilon_{\mathrm{F}}}(z)\ \fint_{\mathcal{B}} R_z e^{iq\cdot x} V_q R_z(x,x)\mathrm{d}q\ \frac{\mathrm{d}z}{2\pi i} \\
&= \oint_{\mathscr{C}} f_{\varepsilon_{\mathrm{F}}}(z)\ \fint_{\mathcal{B}} e^{iq\cdot x}\left[e^{-iq\cdot x} R_z e^{iq\cdot x}\right] V_q R_z(x,x)\mathrm{d}q\ \frac{\mathrm{d}z}{2\pi i} \\
&= \fint_{\mathcal{B}} e^{iq\cdot x}\left[\oint_{\mathscr{C}} f_{\varepsilon_{\mathrm{F}}}(z)\ \fint_{\mathcal{B}} R_{z,k+q} V_q R_{z,k}(x,x)\mathrm{d}k\ \frac{\mathrm{d}z}{2\pi i}\right]\mathrm{d}q
\end{aligned}
$$

$$V = V_{\mathrm{def}} + v_c(\rho_V - \rho_0)$$

Notation:

$$V = \fint_{\mathcal{B}} V_q(x) e^{iq\cdot x}\mathrm{d}q$$

$$AV = \fint_{\mathcal{B}} (A_q V_q)(x) e^{iq\cdot x}\mathrm{d}q$$

$$H_0 := -\Delta + W_{\mathrm{per}}$$

$$H_{0,q} = \sum_n \varepsilon_{nq} \left|u_{nq}\right\rangle \left\langle u_{nq}\right|$$

$$
\begin{aligned}
\chi_{0,q} V &= \sum_{nm} \oint_{\mathscr{C}} \fint_{\mathcal{B}} \frac{f_{\varepsilon_{\mathrm{F}}}(z)}{(z-\varepsilon_{n,k+q})(z-\varepsilon_{mk})}\ \left|u_{n,k+q}\right\rangle \left\langle u_{n,k+q}\right| V \left|u_{mk}\right\rangle \left\langle u_{mk}\right| (x,x)\mathrm{d}k\ \frac{\mathrm{d}z}{2\pi i} \\
&= \sum_{nm} \fint_{\mathcal{B}} \frac{f_{\varepsilon_{\mathrm{F}}}(\varepsilon_{n,k+q}) - f_{\varepsilon_{\mathrm{F}}}(\varepsilon_{mk})}{\varepsilon_{n,k+q} - \varepsilon_{mk}}\ \left|u_{n,k+q}\right\rangle \left\langle u_{n,k+q}\right| V \left|u_{mk}\right\rangle \left\langle u_{mk}\right| (x,x)\mathrm{d}k
\end{aligned}
$$

back

Scattering Theory: Eigenfunction Expansions

- Want: $\rho_V - \rho_0$,

$$\rho_0(x) = f_{\varepsilon_F}(H_0)(x,x) = \fint_{\mathcal{B}} f_{\varepsilon_F}(\varepsilon_k)|\Psi_k(x)|^2 \mathrm{d}k$$

$$\rho_V(x) \stackrel{?}{=} \sum_{j:\, \lambda_j \leq \varepsilon_F} |\varphi_i(x)|^2 + \fint_{\mathcal{B}} f_{\varepsilon_F}(\varepsilon_k)|\Psi_k^+(x)|^2 \mathrm{d}k$$

- Idea: $\Psi_k^+ = \Omega^+\Psi_k$ that "looks like" Ψ_k in the distant past:

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- " $\Omega^+ = \lim_{t \to -\infty} e^{iHt} e^{-iH_0 t}$ ", $\quad \Omega^+ H = H_0 \Omega^+$
- Lippmann-Schwinger: $\Psi_k^+ = \Psi_k + G_0(\varepsilon_k) V \Psi_k^+$ back

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Scattering Theory: Eigenfunction Expansions

$$\Omega^+ := \lim_{\eta\downarrow 0} \int_{-\infty}^{0} \eta e^{\eta t} e^{iHt} e^{-iH_0 t} \mathrm{d}t$$

$$\begin{aligned}
\Psi_k^+ &= \lim_{\eta\downarrow 0} \int_{-\infty}^{0} \eta e^{\eta t}\; e^{iHt} e^{-iH_0 t} \Psi_k \mathrm{d}t \\
&= \lim_{\eta\downarrow 0} \eta \int_{-\infty}^{0} e^{-i(\varepsilon_k + i\eta - H)t} \Psi_k \mathrm{d}t \\
&= \lim_{\eta\downarrow 0} \frac{i\eta}{\varepsilon_k + i\eta - H} \Psi_k =: \lim_{\eta\downarrow 0} i\eta\; G(\varepsilon_k + i\eta)\Psi_k \\
&= \lim_{\eta\downarrow 0} i\eta \Big[G_0(\varepsilon_k + i\eta) + G_0(\varepsilon_k + i\eta) V G(\varepsilon_k + i\eta) \Big] \Psi_k \\
&= \Psi_k + G_0(\varepsilon_k + i0^+) V \Psi_k^+
\end{aligned}$$

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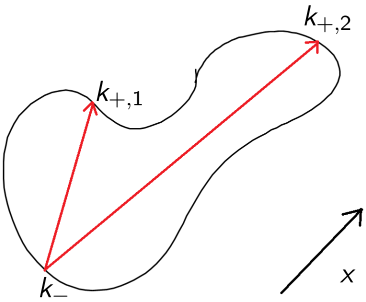
Scattering Theory: Eigenfunction Expansions

Unitarity of T: if $\varepsilon_k = \varepsilon_{k'} = \varepsilon$, then

$$T(k,k') - \overline{T(k',k)} = \frac{2\pi i}{|\mathcal{B}|} \int_{\varepsilon_{k''}=\varepsilon} T(k,k'')T(k'',k') \frac{\mathrm{d}k''}{|\nabla \varepsilon_{k''}|}$$



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