Friedel Oscillations
in the reduced Hartree–Fock model

Jack Thomas. Joint work with Antoine Levitt.

Département de Mathématiques d'Orsay

Abstract: When a defect potential is placed in a material, the material rearranges and the total potential at long-range is screened by the electrons. In the finite temperature reduced Hartree–Fock model, small defects are completely screened [3]; the total change in potential decays exponentially. On the other hand, in metals at zero temperature, the presence of the Fermi-surface introduces non-analytic behaviour into the independent-particle susceptibility χ_0, leading to what are known as Friedel oscillations; the total potential oscillates and decays algebraically, with exponent depending on the dimensionality.

Introduction

Suppose we have a lattice $\mathcal{R} \subset \mathbb{R}^d$ and an associated unit cell Γ, we let $L^2_{\mathrm{per}} := \{f \in L^2(\Gamma) \colon f \text{ is } \mathcal{R}\text{-periodic}\}$. For a fixed periodic potential $W_{\mathrm{per}} \in L^2_{\mathrm{per}}$, associated Fermi level ε_{F}, consider the response to an effective potential V:

$$\begin{aligned} \rho_V(x) &= F_{\varepsilon_{\mathrm{F}}}\big(-\Delta + W_{\mathrm{per}} + V\big)(x,x) \\ &= \rho_0(x) + \chi_0 V(x) + \cdots \end{aligned} \tag{1}$$

where
- $F_{\varepsilon_{\mathrm{F}}}(x) := \big(1 + e^{\frac{x-\varepsilon_{\mathrm{F}}}{k_{\mathrm{B}}T}}\big)^{-1}$ is the Fermi–Dirac distribution with temperature $T \geq 0$ and
- χ_0 is the independent particle susceptibility operator.

$$\begin{aligned} &\text{Linear model:} && V = V_{\mathrm{def}}, \\ &\text{Reduced Hartree–Fock (rHF):} && V = V_{\mathrm{def}} + \big(\rho_V - \rho_0\big) \star |\cdot|^{-1}, \end{aligned} \tag{2}$$

Finite temperature:
- $\chi_0 V$ decays "as quickly as" V,
- rHF: small defects are completely screened; $V(V_{\mathrm{def}})$ in (2) decays exponentially [3].

Zero temperature:
- Fermi surface leads to fundamentally different behaviour,
- $\chi_0 V$ oscillates and decays algebraically with rate depending on the Fermi surface.

Decay of the Green's Function

Non-interacting response given in terms of the Green's function G^E_V:

$$\rho_V(x) = -\frac{1}{\pi}\operatorname{Im}\int_{-\infty}^{\varepsilon_{\mathrm{F}}} G^E_V(x,x)\,\mathrm{d}E \tag{3}$$

where

$$\begin{aligned} G^E_V &:= \lim_{\eta\downarrow 0}\big(E + i\eta - H_0 - V\big)^{-1} \qquad \big[H_0 := -\Delta + W_{\mathrm{per}}\big] \\ &= G^E_0 + G^E_0 V G^E_0 + G^E_0 V G^E_0 V G^E_0 + G^E_0 V G^E_0 V G^E_0 V G^E_0 + \cdots . \end{aligned} \tag{Dyson}$$

In particular, we have

$$\rho_V(x) = \rho_0(x) + \chi_0 V(x) + \cdots + \chi_0^{(N)}[V](x) + \cdots \tag{4}$$

$$\chi_0(x,y) = -\frac{1}{\pi}\operatorname{Im}\int_{-\infty}^{\varepsilon_{\mathrm{F}}} G^E_0(x,y)G^E_0(y,x)\,\mathrm{d}E. \tag{5}$$

Therefore, the off-diagonal decay of G^E_0 leads to corresponding rates of decay for χ_0 and $\rho_V - \rho_0$.

Notation: H_0 is Bloch diagonal with eigenpairs: $\varepsilon_{n\boldsymbol{k}},\ \psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$ for $\boldsymbol{k} \in \mathcal{B}$, $[u_{n\boldsymbol{k}}$ is $\mathcal{R}$-periodic$]$
$S(E) = \bigcup_n S_n(E)$, $S_n(E) := \{\boldsymbol{k} \in \mathcal{B} \colon \varepsilon_{n\boldsymbol{k}} = E\}$. $[S(\varepsilon_{\mathrm{F}}) = \text{Fermi surface}]$
Fix $x, y \in \mathbb{R}^d$, define $\underline{R} := R\hat{\underline{R}} := x - y$ where $R \geq 0, |\hat{\underline{R}}| = 1$.

Proposition 1: Decay of the Green's function. Suppose that, at points $\boldsymbol{k} \in S(E)$ with normal in the direction $\hat{\underline{R}}$, the surface $S(E)$ has non-zero Gauss curvature. Then,

$$G^E_0(x,y) = R^{-\frac{d-1}{2}} \sum_{\substack{\boldsymbol{k}\in S_n(E): \\ \frac{\nabla\varepsilon_{n\boldsymbol{k}}}{|\nabla\varepsilon_{n\boldsymbol{k}}|}\cdot\hat{\underline{R}} = 1}} c_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\underline{R}} + O\big(R^{-\frac{d+1}{2}}\big) \tag{6}$$

as $R = |x-y| \to \infty$, where $c_{\boldsymbol{k}} := C_d \frac{u_{n\boldsymbol{k}}(x)u^\star_{n\boldsymbol{k}}(y)}{|\nabla\varepsilon_{n\boldsymbol{k}}|}\frac{e^{-i\frac{\pi}{4}\sum_{j=1}^{d-1}\operatorname{sgn}\kappa_{\boldsymbol{k}j}}}{\prod_{j=1}^{d-1}\sqrt{|\kappa_{\boldsymbol{k}j}|}}$ and $\{\kappa_{\boldsymbol{k}j}\}$ are the principal curvatures of $S(E)$ at $\boldsymbol{k}$.

Remark: If $S(E)$ has κ non-zero principal curvatures, we have $|G^E_0(x,y)| \lesssim R^{-\frac{\kappa}{2}}$. The exact asymptotic behaviour is more complicated: e.g. [2].

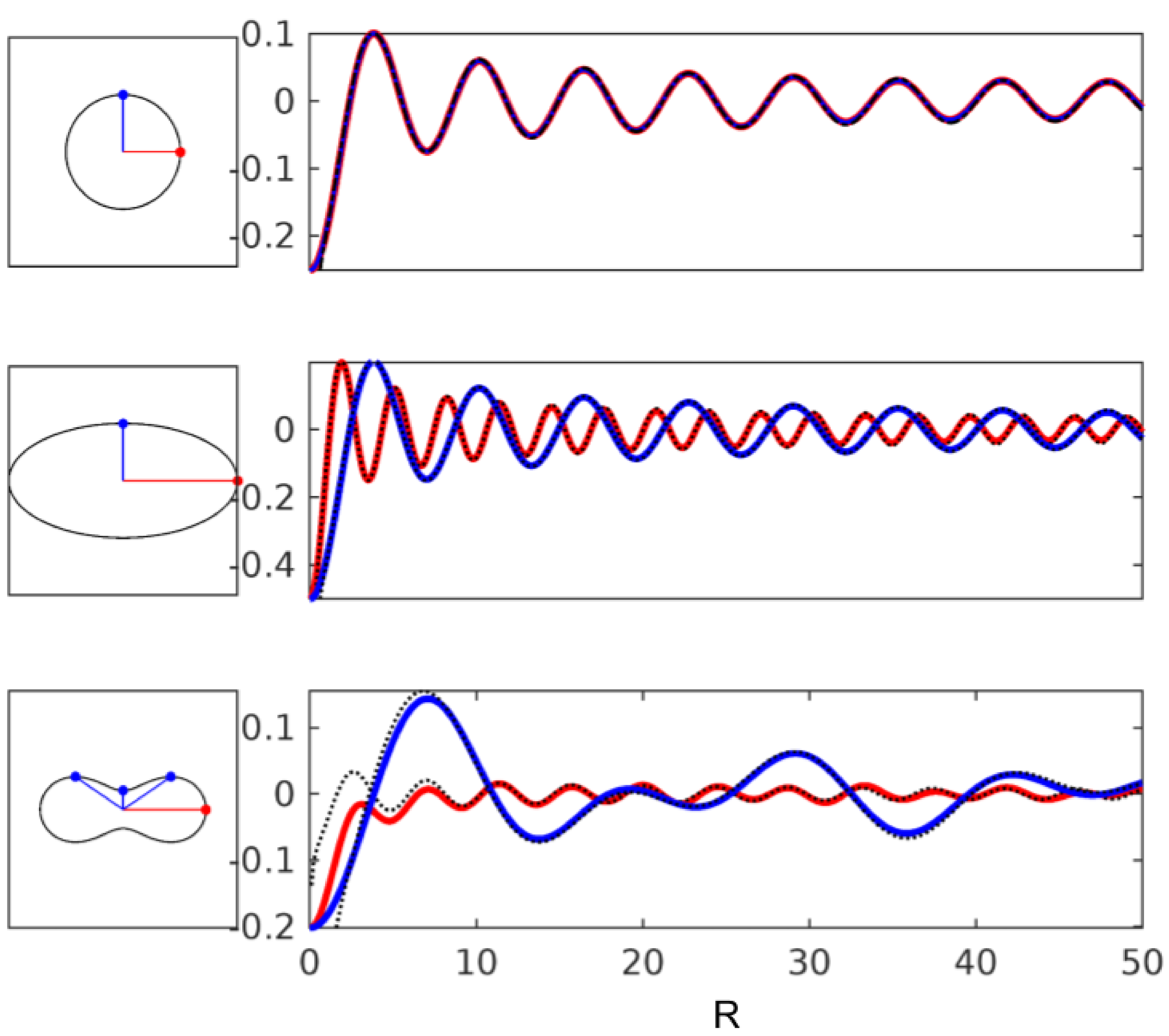

Figure 1: Decay of the Green's function for three model Fermi surfaces for $d = 2$. $\underline{R}_x := (R,0), \underline{R}_y := (0,R)$.
Left: plots of the Fermi surface, together with points $\boldsymbol{k}$ in (6) for $\underline{R}_x$ (red) and $\underline{R}_y$ (blue).
Right: $\operatorname{Im} G^E_0(\underline{R},0)$ and the asymptotic behaviour from Proposition 1 (dotted) for $\underline{R}_x$ (red) and $\underline{R}_y$ (blue).

Sketch of the Proof. To simplify the proof, take $H_0 := \varepsilon(-i\nabla)$ (in place of $H_0 = -\Delta + W_{\mathrm{per}}$). Then,

$$G^E_0(x,y) = \lim_{\eta\downarrow 0} \fint_{\mathcal{B}} \frac{e^{i\boldsymbol{k}\cdot\underline{R}}}{E + i\eta - \varepsilon(\boldsymbol{k})}\mathrm{d}\boldsymbol{k} = -\frac{1}{|\mathcal{B}|}\Big[\Big(\mathrm{p.v.}\tfrac{1}{\varepsilon}\Big) I(E + \cdot\,) + i\pi I(E)\Big] \tag{7}$$

where $I(E) := \int_{S(E)} \frac{e^{i\boldsymbol{k}\cdot\underline{R}}}{|\nabla\varepsilon(\boldsymbol{k})|}\mathrm{d}\boldsymbol{k}$. We then apply stationary phase results [6] to the oscillatory integral I. □

Independent Particle Susceptibility & Linear Response

Recall: For $x, y \in \mathbb{R}^d$, define $\underline{R} := R\hat{\underline{R}} := x - y$ where $R \geq 0, |\hat{\underline{R}}| = 1$.

Proposition 2. Suppose that, at points $\boldsymbol{k} \in S(\varepsilon_{\mathrm{F}})$ with normal in the direction $\hat{\underline{R}}$, the Fermi surface $S(\varepsilon_{\mathrm{F}})$ has non-zero Gauss curvature. Then,

$$\chi_0(x,y) = R^{-d}\operatorname{Im} \sum_{\substack{\boldsymbol{k}_+,\boldsymbol{k}_-\in S(\varepsilon_{\mathrm{F}}): \\ \frac{\nabla\varepsilon_{\boldsymbol{k}_\pm}}{|\nabla\varepsilon_{\boldsymbol{k}_\pm}|}\cdot\hat{\underline{R}} = \pm 1}} c_{\boldsymbol{k}_+\boldsymbol{k}_-} e^{i(\boldsymbol{k}_+ - \boldsymbol{k}_-)\cdot\underline{R}} + O(R^{-(d+1)}) \tag{8}$$

as $R = |x-y| \to \infty$, where $c_{\boldsymbol{k}_+\boldsymbol{k}_-} := \frac{i}{\pi}\frac{|\nabla\varepsilon_{\boldsymbol{k}_+}||\nabla\varepsilon_{\boldsymbol{k}_-}|}{|\nabla\varepsilon_{\boldsymbol{k}_+}| + |\nabla\varepsilon_{\boldsymbol{k}_-}|}c_{\boldsymbol{k}_+}c_{\boldsymbol{k}_-}$.

Remark: By Proposition 2, we have $\chi_0 V(x) \sim |x|^{-d}$ for all V with sufficient decay at infinity.

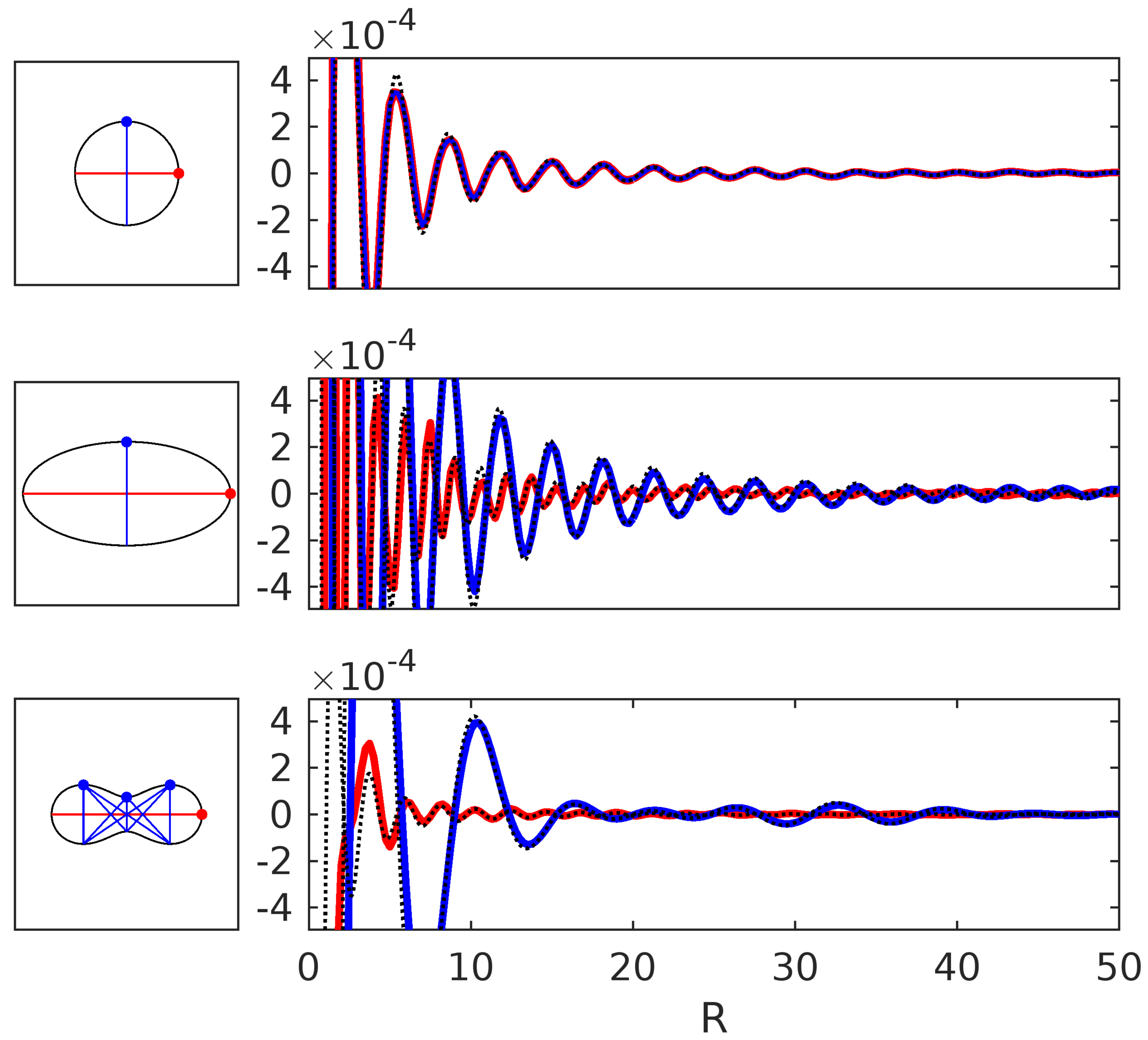

Figure 2: Decay of $\chi_0(x,y)$ for the three model Fermi surfaces from Figure 1, $\underline{R}_x := (R,0), \underline{R}_y := (0,R)$.
Left: plots of the Fermi surface, together with nesting vectors $\boldsymbol{k}_+ - \boldsymbol{k}_-$ as in (8) for $\underline{R}_x$ (red) and $\underline{R}_y$ (blue).
Right: $\chi_0(x,y)$ and the asymptotic behaviour from Proposition 2 (dotted) for $\underline{R}_x$ (red) and $\underline{R}_y$ (blue).

Sketch of the Proof. Again, we simplify notation by considering $H = \varepsilon(-i\nabla)$:

$$\chi_0(x,y) = -\frac{1}{\pi}\operatorname{Im}\int_{-\infty}^{\varepsilon_{\mathrm{F}}} G^E_0(x,y)G^E_0(y,x)\,\mathrm{d}E \sim R^{-(d-1)}\int_{-\infty}^{\varepsilon_{\mathrm{F}}}\sum_{\boldsymbol{k}+,\boldsymbol{k}_-} c_{\boldsymbol{k}_+}c_{\boldsymbol{k}_-}e^{i(\boldsymbol{k}_+ - \boldsymbol{k}_-)\cdot\underline{R}}\,\mathrm{d}E \tag{9}$$

where $E \mapsto \boldsymbol{k}_\pm(E)$ are smooth with $\frac{\nabla\varepsilon(\boldsymbol{k}_\pm)}{|\nabla\varepsilon(\boldsymbol{k}_\pm)|}\cdot\hat{\underline{R}} = \pm 1$. Moreover, $\frac{\mathrm{d}}{\mathrm{d}E}\big(\pm\boldsymbol{k}_\pm\cdot\underline{R}\big) = |\nabla\varepsilon(\boldsymbol{k}_\pm)|^{-1}R$.
Therefore, one may use a partition of unity on $(-\infty, \varepsilon_{\mathrm{F}}]$ and integration by parts to conclude. □

Conclusions & Remarks

- At finite temperature, $\rho_V - \rho_0$ decays as quickly as V, and $\rho_V - \rho_0 - \chi_0 V$ decays faster than V. This is a key fact that allows one to apply a fixed point argument to (2).
- At zero temperature, the situation is very different: We have shown that the response to an effective potential decays at most algebraically with rate depending on the dimension and Fermi surface,
- We have been unable thus far to extend the analysis to the nonlinear model (2) but an additional approach involving scattering theory seems promising.

Remarks:
- Under the same assumptions as Proposition 2, the density matrix $\rho_0(x,y)$ satisfies
$$\rho_0(x,y) = |x-y|^{-\frac{d+1}{2}}\operatorname{Im}\sum_{\boldsymbol{k}}\widetilde{c}_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(x-y)} + O\big(|x-y|^{-\frac{d+3}{2}}\big)$$
as $|x-y| \to \infty$, where the summation is over the same set as in (6) and $\widetilde{c}_{\boldsymbol{k}} := \frac{i}{\pi}|\nabla\varepsilon_{\boldsymbol{k}}|c_{\boldsymbol{k}}$.
- Free electron gas: the decay of χ_0 results from the non-analytic behaviour of the Lindhard function [4, 5].

Future: More complicated (realistic) Fermi-surfaces:

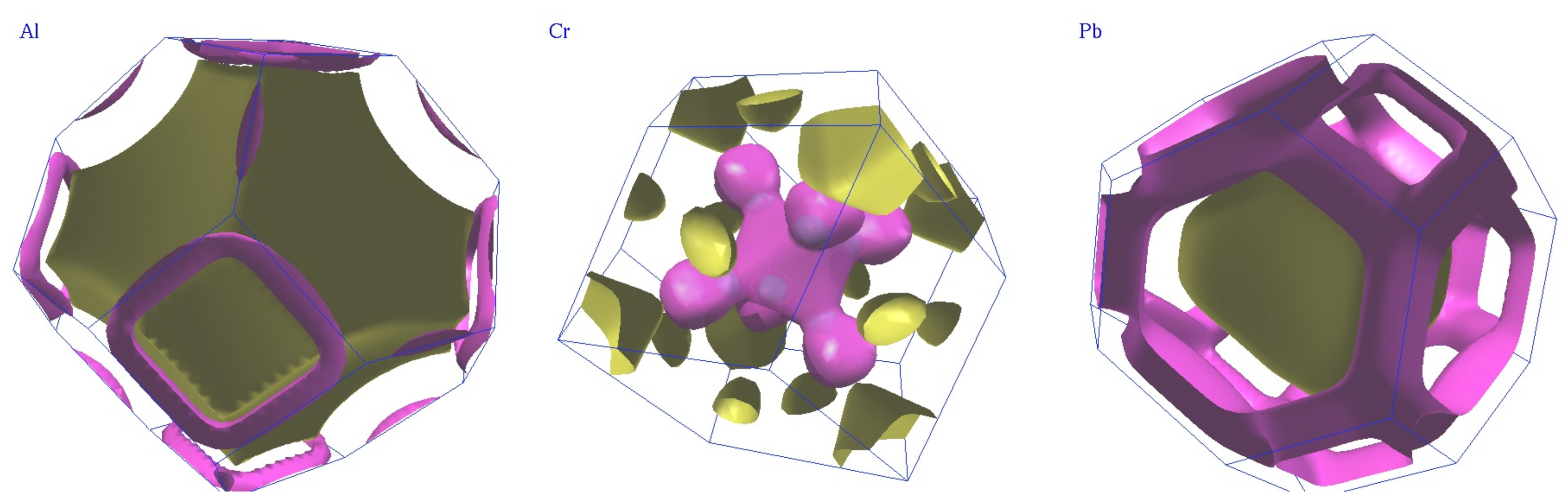

Figure 3: Examples of non-spherical Fermi surfaces. Left: Aluminium, Middle: Chromium, Right: Lead
Images taken from the Periodic Table of the Fermi Surfaces of Elemental Solids [1].

References

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