Metals vs insulators: screening and charge sloshing

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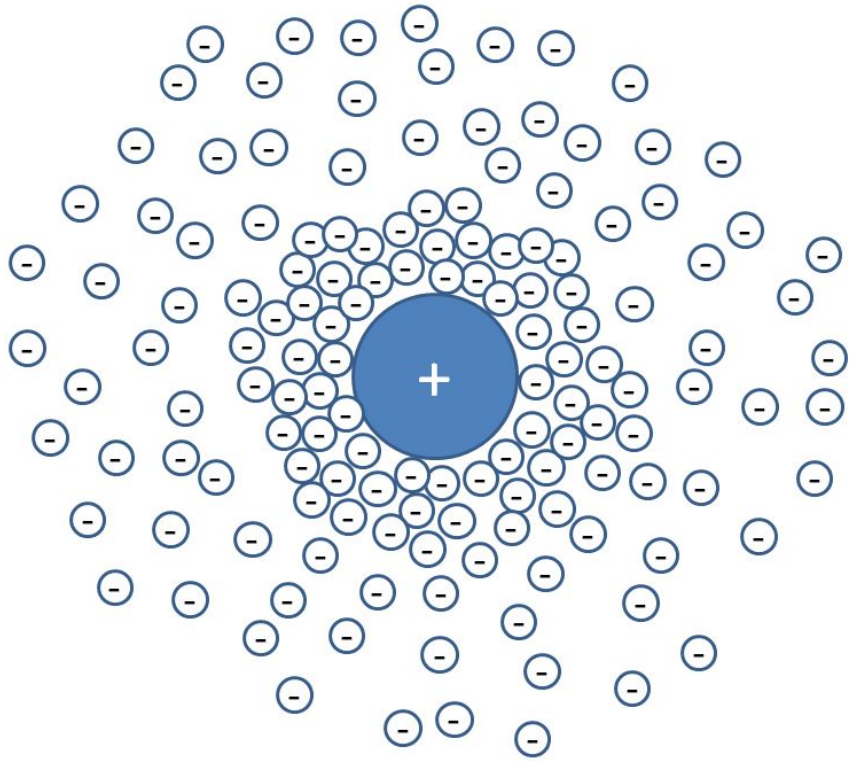
Summary

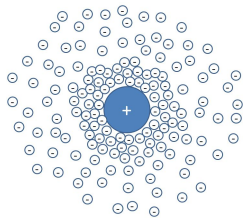
Screening

Place a free charge Q in an environment, and observe its electric field V far away.
In a material, the electrons reorganize around the charge:



V is reduced

Screening



Macroscopic explanation: Debye-Hückel (ions in liquid) or Thomas-Fermi (uniform electron gas)

$$-\Delta V = f(V) + \rho_{\text{ext}}$$

$$f(V) = \begin{cases} \rho_0 e^{-\frac{V}{k_B T}} & \text{Debye-Hückel} \\ \propto (\varepsilon_F - V)^{3/2} & \text{Thomas-Fermi} \end{cases}$$

Linearize around an equilibrium $\rho = \text{cst}_\rho + \delta\rho$, $V = \text{cst}_V + \delta V$, $\chi_0 = f'(V)(\text{cst}_V)$:

$$-\Delta\delta V - \chi_0 \delta V = \delta\rho_{\text{ext}}$$

$$\delta V \propto \rho_{\text{ext}} * \frac{e^{-\sqrt{-\chi_0}|x|}}{|x|}$$

δV is short-ranged! $\sqrt{-\chi_0}$ inverse screening length

Screening

System	Potential $V(x)$	Features
Vacuum	$\frac{Q}{4\pi\lvert x\rvert}$	No screening
Insulator	$\frac{Q}{4\pi\varepsilon_r\lvert x\rvert}$	Partial screening
Conductor (Debye-Hückel, Thomas-Fermi)	$\propto \frac{Qe^{-k\lvert x\rvert}}{\lvert x\rvert}$	Full screening
Metal (Lindhard response)	$\propto \frac{Q\cos(2k_F\lvert x\rvert)}{\lvert x\rvert^3}$	Friedel oscillations

In insulators, electrons are bound to atoms and do not move much (partial screening), in conductors (metals, systems at $T \neq 0$) they are free to flock towards the charge (full screening).

How does this arise from QM?

Screening interesting on its own, but also: SCF iterations, many-body perturbation theory, locality, thermodynamic limits...

Isolated systems

DFT of an **isolated** system:

$$\underbrace{V}_{\text{total potential}} = \underbrace{V_{\text{nucl}}}_{\text{ext. potential}} + \underbrace{v_c F_{\varepsilon_F}(V)}_{\text{Hartree potential}} + \underbrace{\cancel{V_{xc}[F_{\varepsilon_F}(V)]}}_{\text{Exchange-correlation}}$$

$$\int_{\mathbb{R}^3} \underbrace{F_{\varepsilon_F}(V)}_{\text{density}} = \underbrace{N_{\text{el}}}_{\text{number of electrons}}$$

where

$$(v_c\rho)(x) = \frac{1}{4\pi}\int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}dy = \mathcal{F}^{-1}\left(\frac{\mathcal{F}(\rho)(q)}{|q|^2}\right)$$

$$F_{\varepsilon_F}(V) = f_{\varepsilon_F}(-\Delta + V)(x,x)$$

$$f_{\varepsilon_F}(\varepsilon) = \begin{cases} \frac{1}{1+\exp\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right)} & \text{(finite temperature)} \\ 1(\varepsilon \leq \varepsilon_F) & \text{(zero temperature)} \end{cases}$$

- No exchange-correlation, because it's hard (non-convex)
- Reduced Hartree-Fock, Hartree, Schrödinger-Poisson, RPA...
- Fixed-point formulation rather than (free-)energetic: less powerful, but simpler for perturbation

Periodic system

Assume W_{nucl} is $2\pi\mathbb{Z}^3$-periodic

$$\underbrace{W}_{\text{total potential}} = \underbrace{W_{\mathrm{nucl}}}_{\text{ext. potential}} + \underbrace{v_{\mathrm{per}} F_{\varepsilon_F}(W)}_{\text{Hartree potential}}$$

$$\int_{[0,2\pi]^3} \underbrace{F_{\varepsilon_F}(W)}_{\text{density}} = \underbrace{N_{\mathrm{el}}}_{\text{electrons per unit cell}}$$

where $v_{\mathrm{per}}\rho$ is the unique periodic solution of

$$\begin{cases} -\Delta(v_{\mathrm{per}}\rho) & = \rho - \frac{1}{(2\pi)^3}\int_{[0,2\pi]^3}\rho \\ \int_{[0,2\pi]^3} v_{\mathrm{per}}\rho & = 0 \end{cases}$$

- Derived from thermodynamic limit at zero temperature (Catto/Le Bris/Lions '01)
- Metal or insulator, depending on whether $\varepsilon_F \in \sigma(-\Delta + W)$ or not
- Existence theory at finite temperature (Nier '93)

Defect model

Fix a solution $(W_{\mathrm{per}}, \varepsilon_F)$ of the periodic rHF equation, and set $V_{\mathrm{def}} : \mathbb{R}^3 \to \mathbb{R}$ be a defect potential (e.g. $Q/|x|$)

$$\boxed{\underbrace{V}_{\text{screened potential}} = V_{\mathrm{def}} + \underbrace{v_{\mathrm{c}} G(V)}_{\text{reaction potential}}}$$

with

$$\begin{aligned} \underbrace{G(V)}_{\text{reaction density}} &= \underbrace{F_{\varepsilon_F}(W_{\mathrm{per}} + V)}_{\text{perturbed density}} - \underbrace{F_{\varepsilon_F}(W_{\mathrm{per}})}_{\text{periodic density}} \\ &= \Big(f_{\varepsilon_F}(-\Delta + W_{\mathrm{per}} + V) - f_{\varepsilon_F}(-\Delta + W_{\mathrm{per}}) \Big)(x, x). \end{aligned}$$

(grand-canonical ensemble)

- Existence theory and derivation from thermodynamic limit at zero temperature (Cancès/Deleurence/Lewin '08)
- Derivation from thermodynamic limit in a tight-binding model (Chen/Lu/Ortner '17)

Linear response

Linear response, e.g. $V_{\mathrm{def}}(x) = Q/|x|$ with $\boxed{Q \text{ small}}$

"Theorem" (Cancès-Lewin '10, modulo regularization/homogenization)

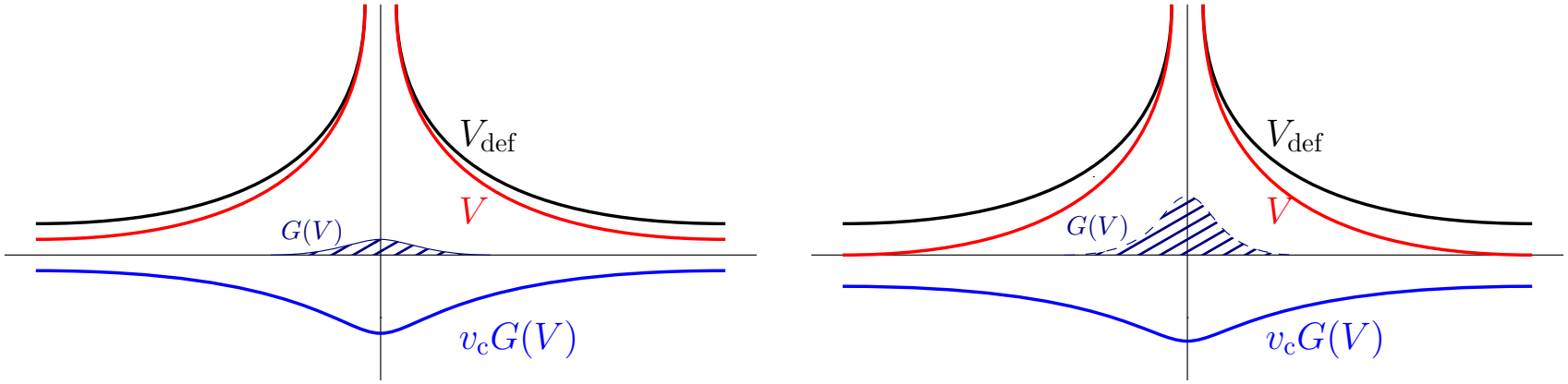
For a zero-temperature isotropic insulator, $V(x) \approx \frac{Q}{\varepsilon_r |x|}$ for large x, for some $\varepsilon_r > 1$.

Theorem (Levitt '18 arxiv)

For any finite-temperature system, V decays faster than any inverse polynomial.

Screening in insulators and conductors

$$V = V_{\mathrm{def}} + v_{\mathrm{c}} G(V)$$



Insulators $T = 0$ Finite temperature

- Insulators attract a charge $\int G(V) < Q$, V is long-range
- Conductors attract a charge $\int G(V) = Q$, V is short-range
- This picture is "homogenized" (ignores lattice-scale oscillations)
- Zero-temperature metals still open (Friedel oscillations)

Summary

Bloch matrices

- **Periodic operators** A (that commute with lattice translations) map Bloch waves $e^{ikx}u_k(x)$ to Bloch waves $e^{ikx}(A_k u_k)(x)$
- In Fourier series representation $u_k(x) = \sum_{K\in\mathbb{Z}^3} c_K e^{iKx}$, **Bloch matrices** A_k

$$e^{i(k+K')x} \mapsto A_k(K,K')e^{i(k+K)x}, \quad K,K' \in \mathbb{Z}^3, k \in [0,1]^3.$$

- Examples:

Operator A	Bloch fiber A_k	Bloch matrix $A_k(K,K')$
$-\Delta$	$(-i\nabla + k)^2$	$\lvert k+K\rvert^2\delta_{KK'}$
W_{per}	W_{per}	$c_{K-K'}(W_{\mathrm{per}})$
$e^{-iqx}Ae^{iqx}$	A_{k+q}	$A_{k+q}(K,K')$

The independent-particle polarizability operator χ_0

A fundamental quantity is the independent-particle polarizability operator $\chi_0 = G'(0)$

$$\begin{aligned} G(V) &= F(W_{\mathrm{per}} + V) - F(W_{\mathrm{per}}) \\ &= \Big(f(-\Delta + W_{\mathrm{per}} + V) - f(-\Delta + W_{\mathrm{per}})\Big)(x, x). \end{aligned}$$

χ_0:

- describes the density response $\delta\rho = \chi_0 \delta V$ of a system of **fictional system of independent** electrons to a perturbation δV of the potential
- is the Hessian of the (concave) non-interacting potential-to-energy map: self-adjoint, non-positive
- has the symmetries of W_{per} (commutes with lattice translations): $\chi_{0,q}(K, K')$
- can be computed from perturbation theory ("sum over states", Lindhard '53, Adler-Wiser '62)
- contains a lot of information, can be generalized to dynamical $\chi_0(\omega)$ (another story)

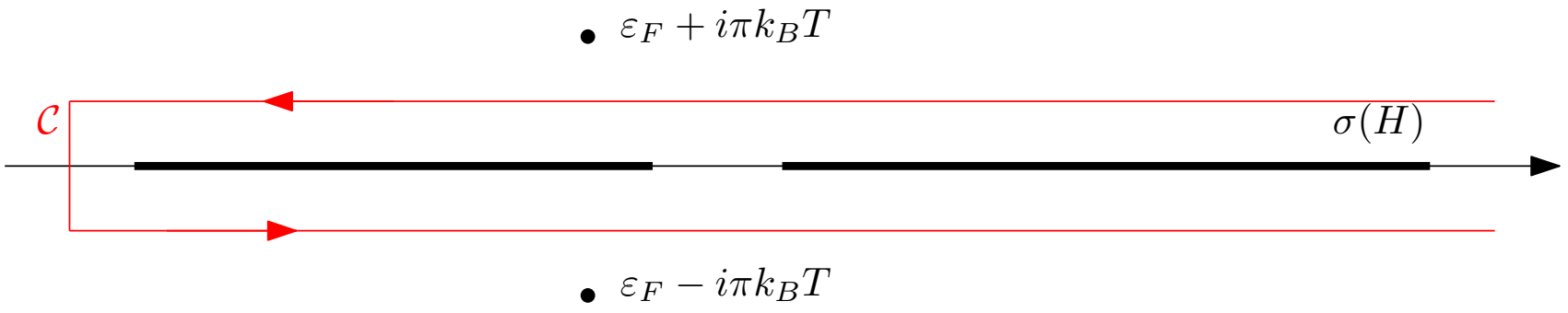
Computing χ_0

Goal: $G'(0)$, where

$$G(V) = \Big(f(H_0 + V) - f(H_0)\Big)(x, x).$$

with $H_0 = -\Delta + W_{\text{per}}$. Classical trick: contour integral representation

$$f(H) = \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - H} f(z) dz$$



$$\begin{aligned} G(V) &= \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \left(\frac{1}{z - (H_0 + V)} - \frac{1}{z - H_0} \right) f(z) dz \right) (x, x) \\ &= \left(\frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - H_0} V \frac{1}{z - H_0} f(z) dz \right) (x, x) + O(\|V\|^2). \end{aligned}$$

with $\left(\frac{1}{z-H_0} V \frac{1}{z-H_0} \right) (x, x) \in L^2(\mathbb{R}^3)$ if $V \in L^2(\mathbb{R}^3)$ (Kato-Seiler-Simon)

χ_0 and $\chi_{0,q}$

$$\boxed{\chi_0 V = \frac{1}{2\pi i}\oint_{\mathcal{C}} \left(\frac{1}{z-H_0} V \frac{1}{z-H_0}\right)(x,x)\, f(z)dz}.$$

If $V = e^{iqx}W$, then

$$\left(\frac{1}{z-H_0} e^{iqx} W \frac{1}{z-H_0}\right)(x,x) = e^{iqx}\Big(\underbrace{e^{-iqx}\frac{1}{z-H_0}e^{iqx}}_{\text{periodic, fibers } \frac{1}{z-H_{k+q}}} W \frac{1}{z-H_0}\Big)(x,x)$$

It follows that, for all $w \in L^2_{\mathrm{per}}$,

$$(\chi_0)_q W = \frac{1}{2\pi i}\oint_{\mathcal{C}} f(z) \int_{\mathcal{B}} \left(\frac{1}{z-H_{0,k+q}} W \frac{1}{z-H_{0,k}}\right)(x,x) dk dz$$

and, inserting $H_{0,k} = \sum_{n=1}^{\infty} \varepsilon_{nk} |u_{nk}\rangle\langle u_{nk}|$ and performing the contour integral,

$$\boxed{\chi_{0,q}(K,K') = \int_{\mathcal{B}} \sum_{n,m\geq 0} \frac{f(\varepsilon_{n,k+q}) - f(\varepsilon_{m,k})}{\varepsilon_{n,k+q} - \varepsilon_{m,k}} \langle e^{iKx} u_{m,k}, u_{nk+q}\rangle \langle u_{nk+q}, e^{iK'x} u_{m,k}\rangle dk}$$

Properties of χ_0

$$\chi_{0,q}(K,K') = \int_{\mathcal{B}} \sum_{n,m\geq 0} \frac{f(\varepsilon_{n,k+q}) - f(\varepsilon_{n,k})}{\varepsilon_{n,k+q} - \varepsilon_{m,k}} \langle e^{iKx} u_{m,k}, u_{nk+q} \rangle \langle u_{nk+q}, e^{iK'x} u_{m,k} \rangle dk$$

- χ_0 is bounded, self-adjoint, non-positive on $L^2(\mathbb{R}^3)$, and

$$\chi_{0,q=0}(K=0,K'=0) = \int_{\mathcal{B}} \sum_{n\geq 0} f'(\varepsilon_{nk}) dk$$

  At zero temperature, this is minus the density of states at the Fermi level: finite for a metal and zero for an insulator. In fact:

$$\chi_{0,q}(0,0) \overset{q\to 0}{\approx} \begin{cases} -C_1 & (T \neq 0) \\ -C_2|q|^2 & (\text{insulator } T=0) \end{cases}$$

- In a non-interacting conductor, increasing the potential increases the density; in an insulator, it does not.
- Small-q limit of $T=0$ metals consistent with Thomas-Fermi/Debye-Hückel theory ($\rho \propto f(V) \Rightarrow \delta\rho \propto -\delta V$)

The algebra of linear response

Recall that

$$V = V_{\mathrm{def}} + v_{\mathrm{c}} G(V)$$

Linearize for V_{def} and V small:

$$V \approx V_{\mathrm{def}} + v_{\mathrm{c}} \chi_0 V \quad \text{(Dyson equation)}$$
$$V \approx \varepsilon^{-1} V_{\mathrm{def}}$$

with

$$\boxed{\varepsilon^{-1} = (1 - v_{\mathrm{c}} \chi_0)^{-1}}$$

the dielectric operator (mimics $\frac{Q}{\varepsilon_r |x|}$).

The dielectric operator

$$(1 - v_c\chi_0)^{-1} = \underbrace{(-\Delta - \chi_0)^{-1}}_{\text{defect charge density} \to \text{total potential}} (-\Delta).$$

We split the Bloch matrix $(-\Delta - \chi_0)_q^{-1}$ in $K = 0$ and $K \neq 0$:

$$(-\Delta - \chi_0)_q = \begin{pmatrix} |q|^2 & 0 \\ 0 & \underbrace{|q+K|^2\delta_{K,K'}}_{>0} \end{pmatrix} - \underbrace{\begin{pmatrix} \chi_{0,q}(0,0) & \chi_{0,q}(0,K) \\ \chi_{0,q}(K,0) & \chi_{0,q}(K,K') \end{pmatrix}}_{\leq 0}$$

Invertibility of $(-\Delta + \chi_0)$ determined by behavior of $\chi_{0,q}(0,0)$ near $q = 0$, i.e. the density of states at ε_F.

- For conductors, $\chi_{0,0}(0,0) = -C_1 < 0$ and so $(-\Delta + \chi_0)$ is invertible: $\varepsilon^{-1} \approx \frac{|q|^2}{1+|q|^2}$ (modulo bounded invertible operators)
- For insulators $\chi_{0,q}(0,0) \approx -C_2|q|^2$ and by a Schur complement one can show that ε^{-1} is bounded invertible on $L^2(\mathbb{R}^3)$.

The dielectric operator and screening

$$V \approx \varepsilon^{-1} V_{\mathrm{def}}$$

$$\varepsilon_q^{-1}(0,0) \overset{q\to 0}{\approx} \begin{cases} |q|^2 & (T \neq 0) \\ 1 & (\text{insulator} = 0) \end{cases}$$

When $V_{\mathrm{def}}(x) = \frac{Q}{4\pi|x|}$, $\widehat{V_{\mathrm{def}}}(q) = \frac{Q}{|q|^2}$.
At finite temperature, the singularity $\frac{1}{|q|^2}$ is compensated by ε^{-1} (full screening). For insulators at $T = 0$ it is not (partial screening).

- Asymptotic decay at finite temperature: smoothness of $q \mapsto \varepsilon_q^{-1}$. Not true at $T = 0$, singularities in $\frac{f(\varepsilon_{n,k+q}) - f(\varepsilon_{n,k})}{\varepsilon_{n,k+q} - \varepsilon_{m,k}}$ when q connects points in the Fermi surface: Friedel oscillations.
- Nonlinear terms: implicit function theorem on weighted Sobolev spaces

Summary

Convergence of the SCF cycle

$$\underbrace{V}_{\text{screened potential}} = V_{\text{def}} + \underbrace{v_{\text{c}} G(V)}_{\text{reaction potential}}$$

How to compute this numerically? Truncation to a finite $L \times L \times L$ supercell, discretization, then self-consistent algorithms

$$V_{n+1} = V_{\text{def}} + v_{\text{c}} G(V_n)$$

usually does not converge, so use damped iteration

$$\boxed{V_{n+1} = V_n + \alpha(V_{\text{def}} + v_{\text{c}} G(V_n) - V_n)}$$

with $\alpha > 0$.
This is a good idea because it decreases the energy if $\alpha > 0$ is small enough. Speed of convergence?

Charge sloshing

$$V_{n+1} = V_n + \alpha(V_{\mathrm{def}} + v_{\mathrm{c}} G(V_n) - V_n)$$

Linearize for small V_n, V_{def}:

$$\begin{aligned} V_{n+1} &= (1 - \alpha + \alpha v_{\mathrm{c}}\chi_0) V_n + \alpha V_{\mathrm{def}} \\ &= (1 - \alpha\varepsilon) V_n + \alpha V_{\mathrm{def}} \end{aligned}$$

Speed of convergence of SCF $\Leftrightarrow$ ratio of eigenvalues of $\varepsilon = 1 - v_{\mathrm{c}}\chi_0$

- $\varepsilon = 1 - v_{\mathrm{c}}\chi_0$ has eigenvalues ≥ 1: damping works for $\alpha > 0$ small enough
- For insulators at $T = 0$, $\chi_0 \approx |q|^2$, and $v_{\mathrm{c}}\chi_0$ is bounded: convergence rate independent of L
- For conductors, $\chi_0 \approx C$, and $v_{\mathrm{c}}\chi_0 \approx \frac{C}{|q|^2}$ diverges: charge sloshing. Number of iterations $\propto L^2$ ($\propto L$ with Anderson/Pulay/DIIS).

Kerker preconditioning

Slow convergence for metals with large unit cells (*charge sloshing*).
Kerker preconditioning ('81):

$$V_{n+1} = V_n + \alpha \mathcal{K}(V_{\mathrm{def}} + v_c G(V_n) - V_n) \tag{1}$$

with the operator $\mathcal{K} = \frac{|q|^2}{C+|q|^2}$ (high-pass filter).

Iteration matrix $\mathcal{K}\varepsilon \approx 1$:

Theorem (Levitt '18)

At finite temperature, the iteration (1) *with* $V_0 = 0$ *is a contraction in* $L^2(\mathbb{R}^3)$ *for* $V_{\mathrm{def}} \in v_c H^{-2}$ *and* $\alpha > 0$ *small enough.*

Theorem in $\mathbb{R}^3$: in practice, convergence rate $L-$independent.

Extensions

- Zero temperature metals: Friedel oscillations
- Exchange-correlation ($K = v_c + \frac{dV_{XC}}{d\rho}$ not necessarily positive, but $\chi_0 K \leq 1$ at energy minimum)
- Non-perturbative regime (fixed point $\Rightarrow$ variational)
- Coupling to phonons (do they affect screening?)
- Dynamical properties $\varepsilon^{-1}(q, \omega)$
- Good preconditionners for the SCF cycle

Advertisement: `DFTK.jl`

Why a new code?

- Goal: play with algorithms for DFT, simpler models, etc.
- Physicists have large Fortran codebases, mathematicians have Matlab toy models, computer scientists have artificial kernels
- Julia solves the two-language problem (goodbye Fortran+Python)
- Well-placed to take advantage of modern compiler technology (automatic differentiation, GPU, parallelism, mixed precision...)

`DFTK` (Density Functional ToolKit)

- Similar spirit to KSSOLV
- Lead developer: Michael Herbst
- `http://github.com/mfherbst/DFTK.jl`, MIT licence: contributions welcome!
- Use third-party libraries as far as possible (FFTs, linear algebra, eigensolvers, mixing, optimization, libxc...)
- Started from scratch Jan. 2019, first "real" result Apr. 2019 (LDA/GTH band structure of Silicon), 2kLOC
- Contact us if you're interested!