Metals vs insulators: screening and SCF convergence

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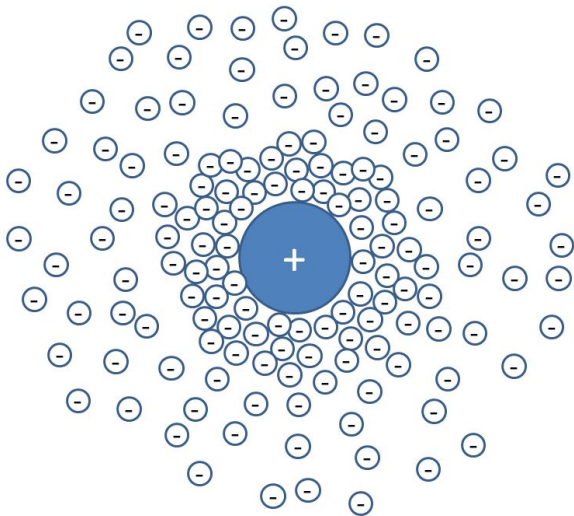Banff

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:

System	Potential $V(x)$	Interpretation
Vacuum	$\dfrac{Q}{|x|}$	No screening
Insulator	$\dfrac{Q}{\varepsilon_r |x|}$	Partial screening
Metal (Thomas-Fermi)	$\dfrac{Qe^{-k_F|x|}}{|x|}$	Full screening
Metal (Lindhard response)	$\propto \dfrac{Q\cos(2k_F|x|)}{|x|^3}$	Friedel oscillations

In insulators, electrons are bound to atoms and do not move much (partial screening), in metals 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:

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

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

where

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

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

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

- Reduced Hartree-Fock, Hartree, Schrödinger-Poisson, RPA...
- No exchange-correlation, because it's hard (non-convex)
- 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. $Q/|x|$)

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

with

$$\underbrace{G(V)}_{\text{reaction density}} = \underbrace{F_{\varepsilon_F}(W_{\mathrm{per}} + V)}_{\text{perturbed density}} - \underbrace{F_{\varepsilon_F}(W_{\mathrm{per}})}_{\text{periodic density}}$$

$$= \Big(f_{\varepsilon_F}(-\Delta + W_{\mathrm{per}} + V) - f_{\varepsilon_F}(-\Delta + W_{\mathrm{per}}) \Big)(x, x).$$

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

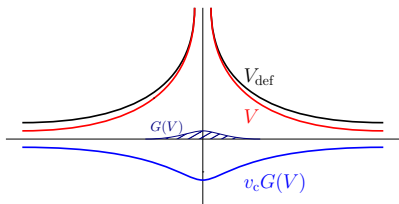**"Theorem" (Cancès-Lewin '10, modulo regularization/homogenization)**

For a zero-temperature isotropic insulator, $V(x) \approx \frac{Q}{\varepsilon_r |x|}$ for large x, for some $\varepsilon_r > 1$.
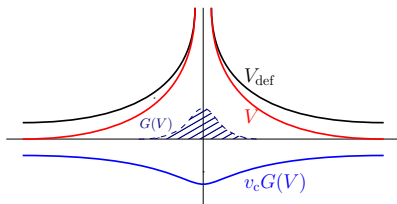
Theorem (Levitt '18 arxiv)

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

Screening in insulators and metals

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

Insulators $T = 0$ Finite temperature

- Insulators attract a charge $\int G(V) < Q$, V is long-range
- Metals attract a charge $\int G(V) = Q$, V is short-range
- This picture is "homogenized" (ignores lattice-scale oscillations)
- Finite temperature as a proxy to study metals: zero-temperature metals still open (Friedel oscillations)

Summary

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

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

χ_0:

- describes the density response $\delta\rho = \chi_0 \delta V$ of a 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)
- 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)

Operators and their symmetries

Formally:

- If A commutes with all translations $R \in \mathbb{R}^3$, then
  $A(x + R, y + R) = A(x, y)$, and A sends plane-waves to plane-waves

  $$\int_{\mathbb{R}^3} A(x, y) e^{iky} \, dy \overset{y = x + y'}{=} e^{ikx} \underbrace{\int_{\mathbb{R}^3} A(x, y' + x) e^{iky'} \, dy'}_{\text{constant}}$$

- If A commutes with all translations $R \in 2\pi\mathbb{Z}^d$, then
  $A(x + R, y + R) = A(x, y)$, and A sends Bloch waves to Bloch waves

  $$\int_{\mathbb{R}^3} A(x, y) e^{iky} \underbrace{u_k(y)}_{\text{periodic}} dy \overset{y = x + y'}{=} e^{ikx} \underbrace{\int_{\mathbb{R}^3} A(x, y' + x) e^{iky'} u_k(y' + x) dy'}_{\text{periodic in } x}$$

  (for mathematicians: A is fibered by the Bloch transform).

- Periodic operators can be decomposed as **Bloch matrices**

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

  . Examples:
    - $(-\Delta)_k(K, K') = |k + K|^2 \delta_{KK'}$
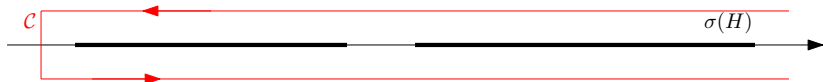   - $(W_{\mathrm{per}})_k(K, K') = c_{K - K'}(W_{\mathrm{per}})$

Goal: $G'(0)$, where

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

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

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

- $\varepsilon_F + i\pi k_B T$

$\mathcal{C}$ $\sigma(H)$

- $\varepsilon_F - i\pi k_B T$

$$G(V) = \frac{1}{2\pi i} \oint_{\mathcal{C}} \Big(\frac{1}{z - (H_0 + V)} - \frac{1}{z - H_0} \Big) f(z) dz$$
$$= \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - H_0} V \frac{1}{z - H_0} f(z) dz + O(\|V\|^2).$$

Computing χ_0

$$\chi_0 V = \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{1}{z - H_0} V \frac{1}{z - H_0} f(z) dz$$

commutes with translations, and, using

$$\int_{\mathcal{C}} \frac{f(z)}{(z - \lambda_1)(z - \lambda_2)} dz = \frac{f(\lambda_1) - f(\lambda_2)}{\lambda_1 - \lambda_2}$$

with $(f(x) - f(x))/(x - x) := f'(x)$ (double pole), we can write its Bloch matrix as

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

where

$$(-\Delta + W_{\mathrm{per}})(e^{ikx} u_{nk}(x)) = \varepsilon_{nk} e^{ikx} u_{nk}(x)$$

For insulators at $T = 0$, $f(\varepsilon_{n,k+q}) - f(\varepsilon_{m,k}) = 0$ unless n is occupied and m virtual (or vice-versa)

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

- 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 metal, increasing the potential increases the density; in an insulator, it does not.
- Small-q limit of metals consistent with Thomas-Fermi theory

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 $\frac{Q}{\varepsilon_r |x|}$).

Assuming $(\varepsilon^{-1})_q(0,0) \approx (\varepsilon_q(0,0))^{-1}$ ("neglect of local field effects"):

$$\varepsilon_q^{-1}(0,0) \approx \frac{1}{1 - \frac{1}{|q|^2} \chi_{0,q}(0,0)}$$

$$\overset{q \to 0}{\approx} \begin{cases} \frac{1}{C_1} |q|^2 & (T \neq 0) \\ \frac{1}{1 + C_2} & (\text{insulator } T = 0) \end{cases}$$

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

$$\varepsilon_q^{-1}(0,0) \overset{q \to 0}{\approx} \begin{cases} \frac{1}{C_1}|q|^2 & (T \neq 0) \\ \frac{1}{1+C_2} & (\text{insulator } T = 0) \end{cases}$$

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

Technical problems and solutions:

- Local field effects $(A_k^{-1})(K, K') \neq (A_k(K, K))^{-1}$: Schur complement
- $v_{\mathrm{c}}\chi_0$ not self-adjoint: $v_{\mathrm{c}}\chi_0 = \sqrt{v_{\mathrm{c}}}(\sqrt{v_{\mathrm{c}}}\chi_0\sqrt{v_{\mathrm{c}}})\sqrt{v_{\mathrm{c}}}^{-1}$
- Asymptotic decay at finite temperature: smoothness of $q \mapsto \varepsilon_q^{-1}$ (not true at $T = 0$: Friedel oscillations)
- Nonlinear terms: implicit function theorem on weighted Sobolev spaces

Summary

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

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

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

does not always work, so use damped iteration

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

with $\alpha > 0$.
Linearize for small V_n, V_{def}:

$$V_{n+1} = (1 - \alpha + \alpha v_c \chi_0) V_n + \alpha V_{\text{def}}$$

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}:

$$V_{n+1} = (1 - \alpha + \alpha v_{\mathrm{c}} \chi_0) V_n + \alpha V_{\mathrm{def}}$$

- v_{c} definite positive, χ_0 definite negative: $v_{\mathrm{c}} \chi_0$ has negative eigenvalues, and damping works
- For insulators at $T = 0$, $\chi_0 \approx |q|^2$, and $v_{\mathrm{c}} \chi_0$ is bounded: when discretized in a $L \times L \times L$ supercell, convergence rate independent of L
- At $T \neq 0$, $\chi_0 \approx C$, and $v_{\mathrm{c}} \chi_0 \approx \frac{C}{|q|^2}$ diverges: charge sloshing
- Number of iterations $\propto L^2$ in a $L \times L \times L$ supercell ($\propto L$ with Anderson).

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

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

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

Theorem (Levitt '18)

At finite temperature, the iteration (1) *with* $V_0 = 0$ *converges for* V_{def} *and* α *small enough.*

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

- Zero temperature metals: Friedel oscillations
- Exchange-correlation ($v_c + \frac{dV_{XC}}{d\rho}$ not necessarily positive)
- Non-perturbative regime
- Coupling to nuclei
- Dynamical properties $\varepsilon^{-1}(q, \omega)$
- Good preconditionners for the SCF cycle