

1 Theory of Linear Response in a Nutshell

Classically Consider an electron system subject to small external perturbation $V_{\text{ext}}(\mathbf{r}, t)$. By definition of the *inverse dielectric function* the total potential $V(\mathbf{r}, t)$ is given by

$$V(\mathbf{r}, t) = \int d^3r' \int_{-\infty}^t dt' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', t'). \quad (1)$$

The upper bound of the integral over t' is t in place of ∞ due to causality: the “effect” cannot precede the “cause”. This is equivalent to saying that $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau) = 0$ whenever $\tau < 0$. The Fourier transform of $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau)$ is

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \int_0^{\infty} d\tau e^{i\omega\tau} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau). \quad (2)$$

Applying Titchmarsh’s theorem to ε^{-1} , we get that $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ is the limit $\eta \rightarrow 0+$ of $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega + i\eta)$ which is holomorphic in the upper complex plane. Taking Fourier transform of eq. (1), we obtain¹

$$V(\mathbf{r}, \omega) = \int d^3r' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega). \quad (3)$$

Eqs. (2) and (3) may equivalently be formulated as

$$\begin{aligned} V_{\text{ext}}(\mathbf{r}, \omega) &= \int d^3r' \varepsilon(\mathbf{r}, \mathbf{r}', \omega) V(\mathbf{r}'), \text{ where} \\ \varepsilon(\mathbf{r}, \mathbf{r}', \omega) &= \lim_{\eta \rightarrow 0+} \varepsilon(\mathbf{r}, \mathbf{r}', \omega + i\eta) = \lim_{\eta \rightarrow 0+} \int_0^{\infty} d\tau e^{i(\omega + i\eta)\tau} \varepsilon(\mathbf{r}, \mathbf{r}', \tau). \end{aligned} \quad (4)$$

Quantum Mechanically Now consider a system of non-interacting electrons described in a single-particle approximation by a Hamiltonian \hat{H}_0 . Let E_i denote single-particle energy levels with corresponding eigenstates $|i\rangle$. One-particle density matrix is then

$$\hat{\rho}_0 = \sum_i n_i |i\rangle\langle i|, \quad (5)$$

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$$\begin{aligned} V(\mathbf{r}, \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} V(\mathbf{r}, t) \\ &= \int d^3r' \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i\omega t} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', t') \\ &= \int d^3r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i\omega t} e^{-i\omega' t'} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', \omega') \\ &= \int d^3r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} V_{\text{ext}}(\mathbf{r}', \omega') \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i(\omega - \omega')t} e^{i\omega'(t - t')} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') \\ &= \int d^3r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} V_{\text{ext}}(\mathbf{r}', \omega') \int_{-\infty}^{\infty} dt e^{i(\omega - \omega')t} \int_{\infty}^0 (-d\tau) e^{i\omega'\tau} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau) \\ &= \int d^3r' \int_{-\infty}^{\infty} d\omega' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega') V_{\text{ext}}(\mathbf{r}', \omega') \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega')t} \\ &= \int d^3r' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega). \end{aligned}$$

where n_i denotes the occupational number at energy E_i which, in equilibrium, is given by the Fermi-Dirac distribution. Electron density operator is $\hat{N}(\mathbf{r}) = |\mathbf{r}\rangle\langle\mathbf{r}|$. Equation of motion reads

$$i\hbar \frac{d\hat{\rho}_0}{dt} = [\hat{H}_0, \hat{\rho}_0] = 0 .$$

Within RPA (Random Phase Approximation) we are interested in the reponse of the system to the perturbation of the form $\hat{V}e^{-i(\omega+i\eta)t}$ (**TODO:** explain η). In the first order approximation, $\hat{\rho} = \hat{\rho}_0 + \hat{\rho}' + \mathcal{O}(\hat{V}^2)$, where $\hat{\rho}_0$ is defined by eq. (5) and $\hat{\rho}' \propto \hat{V}$. We thus have

$$\left. \begin{aligned} i\hbar \frac{d\hat{\rho}}{dt} &= i\hbar \frac{d\hat{\rho}_0}{dt} + i\hbar \frac{d\hat{\rho}'}{dt} \\ [\hat{H}, \hat{\rho}] &= [\hat{H}_0, \hat{\rho}_0] + [\hat{H}_0, \hat{\rho}'] + [\hat{V}, \hat{\rho}_0]e^{-i(\omega+i\eta)t} + \mathcal{O}(\hat{V}^2) \end{aligned} \right\} \implies i\hbar \frac{d\hat{\rho}'}{dt} = [\hat{H}_0, \hat{\rho}'] + [\hat{V}, \hat{\rho}_0]e^{-i(\omega+i\eta)t} . \quad (6)$$

Using an ansatz $\hat{\rho}' = \tilde{G}\hat{V}e^{-i(\omega+i\eta)t}$, where \tilde{G} is some time-independent operator, we obtain²

$$\begin{aligned} \langle i|\tilde{G}\hat{V}|j\rangle &= \frac{n_i - n_j}{E_i - E_j - \hbar(\omega + i\eta)} \langle i|\hat{V}|j\rangle \\ &\equiv \langle i|\hat{G}|j\rangle \langle i|\hat{V}|j\rangle , \end{aligned}$$

where we have defined a new operator \hat{G} by

$$\langle i|\hat{G}|j\rangle = \frac{n_i - n_j}{E_i - E_j - \hbar(\omega + i\eta)} . \quad (7)$$

We can now calculate the induced electron density $\delta\hat{N}(t)$:

$$\begin{aligned} \langle \mathbf{r}|\delta\hat{N}(t)|\mathbf{r}\rangle &= \text{Tr}(\hat{N}(\mathbf{r})\hat{\rho}) - \text{Tr}(\hat{N}(\mathbf{r})\hat{\rho}_0) = \text{Tr}(\hat{N}(\mathbf{r})\hat{\rho}') \\ &= \sum_{i,j} \langle j|\mathbf{r}\rangle \langle \mathbf{r}|i\rangle \langle i|\tilde{G}\hat{V}|j\rangle e^{-i(\omega+i\eta)t} \\ &= \sum_{i,j} \langle i|\hat{G}|j\rangle \langle j|\mathbf{r}\rangle \langle \mathbf{r}|i\rangle \langle i|\hat{V}|j\rangle e^{-i(\omega+i\eta)t} . \end{aligned} \quad (8)$$

The total potential \hat{V} is the sum of external potential \hat{V}_{ext} and the potential induced by the variation of the charge density, i.e.

$$\langle \mathbf{r}|\hat{V}_{\text{tot}}(t)|\mathbf{r}\rangle = \langle \mathbf{r}|\hat{V}_{\text{ext}}(t)|\mathbf{r}\rangle + \int d^3r' \langle \mathbf{r}|\hat{V}_{\text{Coulomb}}|\mathbf{r}'\rangle \langle \mathbf{r}'|\delta\hat{N}(t)|\mathbf{r}'\rangle , \quad (9)$$

where \hat{V}_{Coulomb} is the Coulomb interaction potential. We have also used the fact that \hat{V} is

²Calculating matrix elements:

$$\begin{aligned} \langle i|i\hbar \frac{d\hat{\rho}'}{dt}|j\rangle &= \hbar(\omega + i\eta) \langle i|\hat{\rho}'|j\rangle , \\ \langle i|[\hat{H}_0, \hat{\rho}']|j\rangle &= (E_i - E_j) \langle i|\hat{\rho}'|j\rangle , \\ \langle i|[\hat{V}, \hat{\rho}_0]|j\rangle &= (n_j - n_i) \langle i|\hat{V}|j\rangle . \end{aligned}$$

Eq. (6) now reads

$$\langle i|\hat{\rho}'|j\rangle = \frac{(n_i - n_j) e^{-i\omega t + \eta t}}{E_i - E_j - \hbar(\omega + i\eta)} \langle i|\hat{V}|j\rangle .$$

diagonal in position representation. Using eq. (8) we get³

$$\begin{aligned}\langle \mathbf{r} | \hat{V}_{\text{ext}}(t) | \mathbf{r} \rangle &= \int d^3 r' \langle \mathbf{r} | \hat{\varepsilon}(t) | \mathbf{r}' \rangle \langle \mathbf{r}' | \hat{V} | \mathbf{r}' \rangle, \text{ where} \\ \langle \mathbf{r} | \hat{\varepsilon}(\tau) | \mathbf{r}' \rangle &= \left(\langle \mathbf{r} | \mathbf{r}' \rangle - \sum_{i,j} \langle i | \hat{G} | j \rangle \int d^3 r'' \frac{e^2}{\|\mathbf{r} - \mathbf{r}''\|} \langle j | \mathbf{r}'' \rangle \langle \mathbf{r}'' | i \rangle \langle i | \mathbf{r}' \rangle \langle \mathbf{r}' | j \rangle \right) e^{-i(\omega+i\eta)\tau}.\end{aligned}$$

Using Titchmarsh's theorem once again, we obtain

$$\begin{aligned}\langle \mathbf{r} | \hat{V}_{\text{ext}}(\omega) | \mathbf{r} \rangle &= \int d^3 r' \langle \mathbf{r} | \hat{\varepsilon}(\omega) | \mathbf{r}' \rangle \langle \mathbf{r}' | \hat{V} | \mathbf{r}' \rangle, \text{ where} \\ \langle \mathbf{r} | \hat{\varepsilon}(\omega) | \mathbf{r}' \rangle &= \lim_{\eta \rightarrow 0+} \langle \mathbf{r} | \hat{\varepsilon}(\omega + i\eta) | \mathbf{r}' \rangle = \lim_{\eta \rightarrow 0+} \int_0^\infty d\tau e^{i(\omega+i\eta)\tau} \langle \mathbf{r} | \varepsilon(\tau) | \mathbf{r}' \rangle \\ &= \langle \mathbf{r} | \mathbf{r}' \rangle - \lim_{\eta \rightarrow 0+} \sum_{i,j} \langle i | \hat{G} | j \rangle \int d^3 r'' \frac{e^2}{\|\mathbf{r} - \mathbf{r}''\|} \langle j | \mathbf{r}'' \rangle \langle \mathbf{r}'' | i \rangle \langle i | \mathbf{r}' \rangle \langle \mathbf{r}' | j \rangle \\ &= \langle \mathbf{r} | \mathbf{r}' \rangle - \int d^3 r'' \langle \mathbf{r} | \hat{V}_{\text{Coulomb}} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | \hat{\chi}(\omega) | \mathbf{r}' \rangle, \\ \langle \mathbf{r}'' | \hat{\chi}(\omega) | \mathbf{r}' \rangle &= \lim_{\eta \rightarrow 0+} \sum_{i,j} \langle i | \hat{G} | j \rangle \langle j | \mathbf{r}'' \rangle \langle \mathbf{r}'' | i \rangle \langle i | \mathbf{r}' \rangle \langle \mathbf{r}' | j \rangle, \\ \langle \mathbf{r} | \hat{V}_{\text{Coulomb}} | \mathbf{r}'' \rangle &= \frac{e^2}{\|\mathbf{r} - \mathbf{r}''\|},\end{aligned} \tag{10}$$

which is the exact equivalent of eq. (4) in the classical description. $\hat{\chi}$ is called the *polarizability matrix*.

³At point \mathbf{r} we have

$$\begin{aligned}\langle \mathbf{r} | \hat{V}_{\text{ext}}(t) | \mathbf{r} \rangle &= \langle \mathbf{r} | \hat{V}_{\text{tot}}(t) | \mathbf{r} \rangle - \int d^3 r' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \langle \mathbf{r}' | \delta \hat{N}(t) | \mathbf{r}' \rangle \\ &\stackrel{(8)}{=} \langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle e^{-i(\omega+i\eta)t} - \int d^3 r' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \sum_{i,j} \langle i | \hat{G} | j \rangle e^{-i(\omega+i\eta)t} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \hat{V} | j \rangle \\ &= \left(\langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \sum_{i,j} \langle i | \hat{G} | j \rangle \int d^3 r' \int d^3 r'' \int d^3 r''' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \mathbf{r}'' \rangle \langle \mathbf{r}'' | j \rangle \langle \mathbf{r}'' | \hat{V} | \mathbf{r}''' \rangle \right) e^{-i(\omega+i\eta)t} \\ &= \left(\langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \sum_{i,j} \langle i | \hat{G} | j \rangle \int d^3 r' \int d^3 r'' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \mathbf{r}'' \rangle \langle \mathbf{r}'' | j \rangle \langle \mathbf{r}'' | \hat{V} | \mathbf{r}'' \rangle \right) e^{-i(\omega+i\eta)t}.\end{aligned}$$

2 Application

We now apply the results of sec. 1 to a finite 2D lattice described in the tight binding approximation. We do the calculation in *atomic basis*, i.e. the basis of local site wave functions $|a\rangle$ ($a \in \{0, N-1\}$, where N is the number of sites). The following assumptions are made:

- $\langle a|b\rangle = \delta_{a,b}$,
- atomic basis is complete, i.e. $\sum_a |a\rangle\langle a| = \hat{1}$,
- $|a\rangle$'s are localized around the corresponding sites, i.e. $\langle \mathbf{r}|a\rangle \approx \delta(\mathbf{r} - \mathbf{r}_a)$, where \mathbf{r}_a is the position of a 'th site. This is the key to making a step from analytical formulas to numerical calculations.

These assumptions essentially mean that the step from position representation to atomic basis is performed by $|\mathbf{r}\rangle \rightarrow |a\rangle$, $\mathbf{r} \rightarrow \mathbf{r}_a$ and $\int d^3r \rightarrow \sum_a$. Eq. (10) now reads⁴

$$\begin{aligned}
\langle a|\hat{V}_{\text{ext}}(\omega)|a\rangle &= \sum_b \langle a|\hat{\varepsilon}(\omega)|b\rangle \langle b|\hat{V}|b\rangle, \text{ where} \\
\langle a|\hat{\varepsilon}(\omega)|b\rangle &= \langle a|b\rangle - \sum_c \langle a|\hat{V}_{\text{Coulomb}}|c\rangle \langle c|\hat{\chi}(\omega)|b\rangle, \\
\langle a|\hat{\chi}(\omega)|b\rangle &= \lim_{\eta \rightarrow 0^+} \sum_{i,j} \langle i|\hat{G}|j\rangle \langle j|a\rangle \langle a|i\rangle \langle i|b\rangle \langle b|j\rangle, \\
\langle a|\hat{V}_{\text{Coulomb}}|b\rangle &= \begin{cases} \frac{1}{4\pi\epsilon_0} \frac{e}{\|\mathbf{r}_a - \mathbf{r}_b\|} & , \text{ if } a \neq b, \\ V_0 & , \text{ if } a = b, \end{cases}
\end{aligned} \tag{11}$$

The trick that allows the calculations of $\hat{\chi}(\omega)$ in a reasonable time is to rewrite it in terms of matrices:

$$\begin{aligned}
\langle a|\hat{\chi}(\omega)|b\rangle &= \overbrace{A(a,b)}^{\text{row vector}} \underbrace{\hat{G}}_{\text{square matrix}} \overbrace{A(a,b)^\dagger}^{\text{column vector}} = \overbrace{\left(\underbrace{\hat{G}^T A(a,b)^T}_{\text{GEMV}} \right)^T}_{\text{DOT}} A(a,b)^\dagger, \text{ where} \\
G_{i,j} &= \langle i|\hat{G}|j\rangle \stackrel{(7)}{=} \frac{n_i - n_j}{E_i - E_j - \hbar(\omega + i\eta)} \text{ with } \eta \text{ small, and} \\
A(a,b)_i &= \langle a|i\rangle \langle i|b\rangle = \langle a|i\rangle \langle b|i\rangle^*.
\end{aligned} \tag{12}$$

The second form of $\langle a|\hat{\chi}(\omega)|b\rangle$ with a lot of transposes may seem strange, but it is of utmost importance. It allows us to calculate matrix elements of $\hat{\chi}(\omega)$ using just two BLAS operations: matrix-vector product (GEMV) and dot-product (DOT). It is now straightforward to write a highly parallel implementation of eq. (12) and it will not be discussed here any further.

With eqs. (11) and (12) implemented, we can obtain $\hat{\varepsilon}(\omega)$ for any system, given its tight-binding Hamiltonian \hat{H} and sites positions $\{\mathbf{r}_a | a \in \{0, \dots, N-1\}\}$. The measurable quantity (**TODO**: give links to articles about EELS experiments) is the *loss function* $-\text{Im} [\langle \mathbf{q}|\hat{\varepsilon}^{-1}(\omega)|\mathbf{q}\rangle]$, where $|\mathbf{q}\rangle$'s denote momentum eigenfunctions. Let $\epsilon_n(\omega)$'s be eigenvalues of

⁴Eq. (10) was written in Gauss system. For the calculations it is, however, easier to use electron-volts. We thus replace e^2 by $\frac{e}{4\pi\epsilon_0}$. We also introduce the *self-interaction potential* V_0 to prevent degeneracies in $\langle a|\hat{V}_{\text{Coulomb}}|a\rangle$.

$\hat{\varepsilon}(\omega)$ with the corresponding eigenfunctions $|\phi_n(\omega)\rangle$'s. We can now express the loss function as⁵

$$-\text{Im} [\langle \mathbf{q} | \hat{\varepsilon}^{-1}(\omega) | \mathbf{q} \rangle] = - \sum_n |\langle \mathbf{q} | \phi_n(\omega) \rangle|^2 \cdot \text{Im} \left[\frac{1}{\epsilon_n(\omega)} \right] .$$

Within the tight-binding approximation $\langle \mathbf{q} | \phi_n(\omega) \rangle$ can be calculated as follows

$$\langle \mathbf{q} | \phi_n(\omega) \rangle = \sum_a \int d^3r \langle \mathbf{q} | \mathbf{r} \rangle \langle \mathbf{r} | a \rangle \langle a | \phi_n(\omega) \rangle = \sum_a \langle \mathbf{q} | \mathbf{r}_a \rangle \langle a | \phi_n(\omega) \rangle = \frac{1}{(2\pi)^{3/2}} \sum_a e^{-i\mathbf{q} \cdot \mathbf{r}_a} \langle a | \phi_n(\omega) \rangle .$$

⁵Obviously, if $\epsilon_n(\omega)$ is an eigenvalue of $\hat{\varepsilon}(\omega)$ with an eigenvector $|\phi_n(\omega)\rangle$, then $1/\epsilon_n(\omega)$ is an eigenvalue of $\hat{\varepsilon}^{-1}(\omega)$ with the same eigenvector. We thus have

$$\begin{aligned} -\text{Im} [\langle \mathbf{q} | \hat{\varepsilon}^{-1}(\omega) | \mathbf{q} \rangle] &= -\text{Im} \left[\sum_{n,m} \langle \mathbf{q} | \phi_n \rangle \langle \phi_n | \hat{\varepsilon}^{-1}(\omega) | \phi_m \rangle \langle \phi_m | \mathbf{q} \rangle \right] \\ &= -\text{Im} \left[\sum_n |\langle \mathbf{q} | \phi_n(\omega) \rangle|^2 \frac{1}{\epsilon_n(\omega)} \right] = - \sum_n |\langle \mathbf{q} | \phi_n(\omega) \rangle|^2 \cdot \text{Im} \left[\frac{1}{\epsilon_n(\omega)} \right] . \end{aligned}$$

3 Experiments

3.1 Third iteration Sierpinski carpet