1 Theory of Linear Response in a Nutshell

Clasically 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

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

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

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \int_{0}^{\infty} \mathrm{d}\tau \; e^{i\omega\tau} \, \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau) \; . \tag{2}$$

Applying Titchmarsh's theorem to ε^{-1}, we get that $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ is the limit $\eta \to 0+$ 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 obtain[1]

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

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

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

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

$$\hat{\rho}_0 = \sum_i n_i \, |i\rangle\langle i| \; , \tag{5}$$

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[1]

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

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

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

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

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

Using an ansatz $\hat{\rho}' = \hat{G}\hat{V}e^{-i(\omega+i\eta)t}$, where $\hat{G}$ is some time-independent operator, we obtain[2]

$$\begin{aligned} \langle i|\hat{G}\hat{V}|j\rangle &= \frac{n_i - n_j}{E_i - E_j - \hbar(\omega + i\eta)}\langle i|\hat{V}|j\rangle \\ &\equiv G_{i,j}\,\langle i|\hat{V}|j\rangle \ . \end{aligned} \tag{7}$$

It is important not to confuse $G_{i,j}$ with matrix element $\langle i|\hat{G}|j\rangle$! We can now calculate the induced electron density $\delta\hat{N}(t)$:

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

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

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

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

[2]Calculating matrix elements:

$$\begin{aligned} \langle i|i\hbar\frac{\mathrm{d}\hat{\rho}'}{\mathrm{d}t}|j\rangle &= \hbar(\omega + i\eta)\langle i|\hat{\rho}'|j\rangle \ , \\ \langle i|[\hat{H}_0, \hat{\rho}']|j\rangle &= (E_i - E_j)\langle i|\hat{\rho}'|j\rangle \ , \\ \langle i|[\hat{V}, \hat{\rho}_0]|j\rangle &= (n_j - n_i)\langle i|\hat{V}|j\rangle \ . \end{aligned}$$

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 get[3]

$$\langle \mathbf{r}|\hat{V}_{\text{ext}}(t)|\mathbf{r}\rangle = \int \mathrm{d}^3 r' \ \langle \mathbf{r}|\hat{\varepsilon}(t)|\mathbf{r}'\rangle\langle \mathbf{r}'|\hat{V}|\mathbf{r}'\rangle \ , \text{ where}$$

$$\langle \mathbf{r}|\hat{\varepsilon}(\tau)|\mathbf{r}'\rangle = \left(\langle \mathbf{r}|\mathbf{r}'\rangle - \sum_{i,j} G_{i,j} \int \mathrm{d}^3 r'' \ \frac{e^2}{\|\mathbf{r}-\mathbf{r}''\|} \langle j|\mathbf{r}''\rangle\langle \mathbf{r}''|i\rangle\langle i|\mathbf{r}'\rangle\langle \mathbf{r}'|j\rangle \right) e^{-i(\omega+i\eta)\tau} \ .$$

Using Titchmarsh's theorem once again, we obtain

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

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

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. $\sum_a |a\rangle\langle a| = \hat{\mathbb{1}}$,
- $|a\rangle$'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 formula's to numerical calculations.

[3] At point $\mathbf{r}$ we have

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

These assumptions essentially means that the step from position representation to atomic basis is performed by $|\mathbf{r}\rangle \to |a\rangle$, $\mathbf{r} \to \mathbf{r_a}$ and $\int \mathrm{d}^3 r \to \sum_a$. Eq. (10) now reads[4]

$$\begin{aligned}
\langle a|\hat{V}_{\mathrm{ext}}(\omega)|a\rangle &= \sum_b \langle a|\hat{\varepsilon}(\omega)|b\rangle\langle b|\hat{V}|b\rangle \ , \text{ where} \\
\langle a|\hat{\varepsilon}(\omega)|b\rangle &= \langle a|b\rangle - \sum_c \langle a|\hat{V}_{\mathrm{Coulomb}}|c\rangle\langle c|\hat{\chi}(\omega)|b\rangle \ , \\
\langle a|\hat{\chi}(\omega)|b\rangle &= \lim_{\eta\to 0+} \sum_{i,j} G_{i,j}\langle j|c\rangle\langle c|i\rangle\langle i|b\rangle\langle b|j\rangle \ , \\
\langle a|\hat{V}_{\mathrm{Coulomb}}|b\rangle &= \begin{cases} \dfrac{1}{4\pi\epsilon_0}\dfrac{e}{\|\mathbf{r_a}-\mathbf{r_b}\|} & \text{, if } a \neq b, \\ V_0 & \text{, if } a = b, \end{cases}
\end{aligned} \tag{11}$$

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

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

[4]Eq. (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 $\langle a|\hat{V}_{\mathrm{Coulomb}}|a\rangle$.