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

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

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]

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

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

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

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

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

[1]

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

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

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

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 $\delta\langle\hat{N}(\mathbf{r})\rangle$, also called the *polarizability matrix*:

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

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

$$\hat{V}_{\text{tot}}(t) = \hat{V}_{\text{ext}}(t) + \hat{V}_{\text{Coulomb}}\hat{\chi}(t) \; . \tag{9}$$

where $\hat{V}_{\text{Coulomb}}$ is the Coulomb interaction potential. Using the fact that $\hat{V}$ is diagonal, in

[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

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

position representation eq. (9) reads[3]

$$\langle \mathbf{r}|\hat{V}_{\text{ext}}(t)|\mathbf{r}\rangle = \left(\langle \mathbf{r}|\hat{V}|\mathbf{r}\rangle - \sum_{i,j} G_{i,j} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \; \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \; \langle j|\mathbf{r}'\rangle\langle \mathbf{r}'|i\rangle\langle i|\mathbf{r}''\rangle\langle \mathbf{r}''|j\rangle\langle \mathbf{r}''|\hat{V}|\mathbf{r}''\rangle \right) e^{-i(\omega+i\eta)t} \; .$$

which can be rewritten as

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

Using Titchmarsh's theorem once again, we obtain

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

which is the exact equivalent of eq. (4) in the classical description.

2 Application

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

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