1 Theory of Linear Response in a Nutshell

Consider an electron system subject to small external perturbation $V_{\text{ext}}(\mathbf{r}, t)$. The total potential $V(\mathbf{r}, t)$ is then given by

$$\begin{aligned} V(\mathbf{r}, t) &= \left(\hat{\varepsilon}^{-1} V_{\text{ext}}\right)(\mathbf{r}, t) \\ &= \int\limits_{\text{all space}} \mathrm{d}^3 r' \int\limits_{-\infty}^{t} \mathrm{d}t' \, \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', t') \; . \end{aligned}$$

Linear operator $\hat{\varepsilon}^{-1}$ is called the *inverse dielectric function.* Applying Fourier transformation to V and V_{ext}, we obtain[1]

$$\begin{aligned} V(\mathbf{r}, \omega) &= \left(\hat{\varepsilon}^{-1} V_{\text{ext}}\right)(\mathbf{r}, t) \\ &= \int\limits_{\text{all space}} \mathrm{d}^3 r' \, \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega) \; , \\ \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) &= \int\limits_{0}^{\infty} \mathrm{d}t \; e^{i\omega t} \, \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t) \; . \end{aligned}$$

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

$$\hat{\rho}_0 = \sum_i n_i \, |i\rangle\langle i| \; , \tag{1}$$

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 $\hat{V} e^{-i\omega t + \eta t}$ (**TODO:** explain η). In the first order approximation,

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[1]

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

$\hat{\rho} = \hat{\rho}_0 + \hat{\rho}' + \mathcal{O}(\hat{V}^2)$, where $\hat{\rho}_0$ is defined by eq. (1) and $\hat{\rho}' \propto \hat{V}$. We thus have

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

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

$$\begin{aligned} \langle i|\hat{G}\hat{V}|j\rangle &= \frac{n_i - n_j}{E_i - E_j - \hbar(\omega + i\eta)}\langle i|\hat{V}|j\rangle \\ &\equiv G_{i,j}\,\langle i|\hat{V}|j\rangle \; . \end{aligned} \tag{3}$$

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*:

$$\begin{aligned} \langle \mathbf{r}|\hat{\chi}(t)|\mathbf{r}\rangle &= \delta\langle\hat{N}(\mathbf{r})\rangle \\ &= \mathrm{Tr}(\hat{N}(\mathbf{r})\hat{\rho}) - \mathrm{Tr}(\hat{N}(\mathbf{r})\hat{\rho}_0) = \mathrm{Tr}(\hat{N}(\mathbf{r})\hat{\rho}') \\ &= \sum_{i,j}\langle j|\mathbf{r}\rangle\langle\mathbf{r}|i\rangle\langle i|\hat{G}\hat{V}|j\rangle e^{-i\omega t + \eta t} \\ &= \sum_{i,j} G_{i,j}\langle j|\mathbf{r}\rangle\langle\mathbf{r}|i\rangle\langle i|\hat{V}|j\rangle e^{-i\omega t + \eta t} \\ \implies \hat{\chi}(t) &= \sum_{i,j} G_{i,j}\,\langle i|\hat{V}|j\rangle\, e^{-i\omega t + \eta t}\; |i\rangle\langle j| \end{aligned} \tag{4}$$

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.

$$\hat{V}_{\mathrm{tot}}(t) = \hat{V}_{\mathrm{ext}}(t) + \hat{V}_{\mathrm{Coulomb}}\hat{\chi}(t) \; . \tag{5}$$

where $\hat{V}_{\mathrm{Coulomb}}$ is the Coulomb interaction potential. If we assume that $\hat{V}$ is diagonal (**TODO:**

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[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. (2) now reads

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

why?), then in position representation eq. (5) reads[3]

$$\langle \mathbf{r}|\hat{V}_{\text{ext}}(\omega)|\mathbf{r}\rangle = \langle \mathbf{r}|\hat{V}|\mathbf{r}\rangle - \sum_{i,j} G_{i,j} \int \mathrm{d}^3r' \int \mathrm{d}^3r'' \, \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \, \langle j|\mathbf{r}'\rangle\langle \mathbf{r}'|i\rangle\langle i|\mathbf{r}''\rangle\langle \mathbf{r}''|j\rangle\langle \mathbf{r}''|\hat{V}|\mathbf{r}''\rangle \, .$$

2 Application

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

$$\begin{aligned}
\langle \mathbf{r}|\hat{V}_{\text{ext}}(t)|\mathbf{r}\rangle &= \langle \mathbf{r}|\hat{V}_{\text{tot}}(t)|\mathbf{r}\rangle - \int \mathrm{d}^3r' \, \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \, \delta\langle \hat{N}(\mathbf{r}')\rangle \\
&\overset{(4)}{=} \langle \mathbf{r}|\hat{V}|\mathbf{r}\rangle e^{-i\omega t+\eta t} - \int \mathrm{d}^3r' \, \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \sum_{i,j} G_{i,j} \, e^{-i\omega t+\eta t} \, \langle j|\mathbf{r}'\rangle\langle \mathbf{r}'|i\rangle\langle i|\hat{V}|j\rangle \\
&= \left(\langle \mathbf{r}|\hat{V}|\mathbf{r}\rangle - \sum_{i,j} G_{i,j} \int \mathrm{d}^3r' \int \mathrm{d}^3r'' \int \mathrm{d}^3r''' \, \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \, \langle j|\mathbf{r}'\rangle\langle \mathbf{r}'|i\rangle\langle i|\mathbf{r}''\rangle\langle \mathbf{r}'''|j\rangle\langle \mathbf{r}''|\hat{V}|\mathbf{r}'''\rangle \right) e^{-i\omega t+\eta t} \\
&= \left(\langle \mathbf{r}|\hat{V}|\mathbf{r}\rangle - \sum_{i,j} G_{i,j} \int \mathrm{d}^3r' \int \mathrm{d}^3r'' \, \frac{e^2}{\|\mathbf{r}-\mathbf{r}'\|} \, \langle j|\mathbf{r}'\rangle\langle \mathbf{r}'|i\rangle\langle i|\mathbf{r}''\rangle\langle \mathbf{r}''|j\rangle\langle \mathbf{r}''|\hat{V}|\mathbf{r}''\rangle \right) e^{-i\omega t+\eta t} \, .
\end{aligned}$$

Now take the Fourier transform of the above equation to obtain **TODO:** what?