

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

$$\begin{aligned} V(\mathbf{r}, t) &= (\hat{\varepsilon}^{-1} V_{\text{ext}})(\mathbf{r}, t) \\ &= \int_{\text{all space}} d^3 r' \int_{-\infty}^t dt' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', t'). \end{aligned}$$

Linear operator $\hat{\varepsilon}^{-1}$ is called the *inverse dielectric function*. Applying Fourier transformation to V and V_{ext} , we obtain¹

$$\begin{aligned} V(\mathbf{r}, \omega) &= (\hat{\varepsilon}^{-1} V_{\text{ext}})(\mathbf{r}, \omega) \\ &= \int_{\text{all space}} d^3 r' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega), \\ \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) &= \int_0^{\infty} dt e^{i\omega t} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t). \end{aligned}$$

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

$$\hat{\rho}_0 = \sum_i n_i |i\rangle\langle i|, \quad (1)$$

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

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

Within RPA (Random Phase Approximation) we are interested in the response 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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$$\begin{aligned} V(\mathbf{r}, \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} V(\mathbf{r}, t) \\ &= \int d^3 r' \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i\omega t} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', t') \\ &= \int d^3 r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i\omega t} e^{-i\omega' t'} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') V_{\text{ext}}(\mathbf{r}', \omega') \\ &= \int d^3 r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} V_{\text{ext}}(\mathbf{r}', \omega') \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' e^{i(\omega - \omega')t} e^{i\omega'(t - t')} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') \\ &= \int d^3 r' \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} V_{\text{ext}}(\mathbf{r}', \omega') \int_{-\infty}^{\infty} dt e^{i(\omega - \omega')t} \int_{-\infty}^0 (-d\tau) e^{i\omega'\tau} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \tau) \\ &= \int d^3 r' \int_{-\infty}^{\infty} d\omega' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega') V_{\text{ext}}(\mathbf{r}', \omega') \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega')t} \\ &= \int d^3 r' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega). \end{aligned}$$

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

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

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

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

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*:

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

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.

$$\hat{V}_{\text{ext}}(t) = \left(\mathbf{1} - \hat{V}_{\text{Coulomb}}\hat{\chi} \right) \hat{V} = \hat{\varepsilon}\hat{V} , \quad (5)$$

where \hat{V}_{Coulomb} is the Coulomb interaction potential and $\hat{\varepsilon}$ is the dielectric function. If we

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. (2) now reads

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

assume that \hat{V} is diagonal (**TODO:** why?), then in position representation eq. (5) reads³

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

2 Application

³At point \mathbf{r} we have

$$\begin{aligned} \langle \mathbf{r} | \hat{V}_{\text{ext}} | \mathbf{r} \rangle &= \langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \int d^3 r' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \delta \langle \hat{N}(\mathbf{r}') \rangle \\ &\stackrel{(4)}{=} \langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \int d^3 r' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \sum_{i,j} G_{i,j} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \hat{V} | j \rangle \\ &= \langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \sum_{i,j} G_{i,j} \int d^3 r' \int d^3 r'' \int d^3 r''' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \mathbf{r}'' \rangle \langle \mathbf{r}'' | j \rangle \langle \mathbf{r}'' | \hat{V} | \mathbf{r}'' \rangle . \\ &= \langle \mathbf{r} | \hat{V} | \mathbf{r} \rangle - \sum_{i,j} G_{i,j} \int d^3 r' \int d^3 r'' \frac{e^2}{\|\mathbf{r} - \mathbf{r}'\|} \langle j | \mathbf{r}' \rangle \langle \mathbf{r}' | i \rangle \langle i | \mathbf{r}'' \rangle \langle \mathbf{r}'' | j \rangle \langle \mathbf{r}'' | \hat{V} | \mathbf{r}'' \rangle . \end{aligned}$$