Linear response

perturbation of eigenvalue

density matrix

time dependent density matrix.

$\to$ perturbation of Green's function.

$$G_\lambda = (\lambda - H)^{-1} = \sum_{p=1}^{d} \psi_p (\lambda - \varepsilon_p)^{-1} \psi_p^* = \sum_{p=1}^{d} |\psi_p\rangle (\lambda - \varepsilon_p)^{-1} \langle \psi_p|$$

$H \psi_i = \varepsilon_i \psi_i$. $\lambda \notin \mathrm{spec}(H)$. resolvent

perturbation $H_\epsilon = H + \varepsilon W$, $H_0 = H$.

$$G_{\lambda,\epsilon} = (\lambda - H - \varepsilon W)^{-1}$$

Neumann series.

$$= \sum_{m=0}^{\infty} \epsilon^m (\lambda - H)^{-1} \left[W (\lambda - H)^{-1} \right]^m$$

$$= G_\lambda + \varepsilon G_\lambda W G_\lambda + \varepsilon^2 G_\lambda W G_\lambda W G_\lambda + \cdots$$

Convergence: $\varepsilon \| W G_\lambda \|_2 < 1$

Another perspective: resolvent identity

$$(\lambda - H_1)^{-1} - (\lambda - H_2)^{-1} = (\lambda - H_1)^{-1} (H_1 - H_2)(\lambda - H_2)^{-1}$$

$$= (\lambda - H_2)^{-1} (H_1 - H_2)(\lambda - H_1)^{-1}$$

$$G_{\lambda,\epsilon} - G_\lambda = \varepsilon G_\lambda W G_{\lambda,\epsilon}$$

$$\Rightarrow G_{\lambda,\epsilon} = G_\lambda + \varepsilon G_\lambda W G_{\lambda,\epsilon}$$

non-perturbative. Dyson equation.

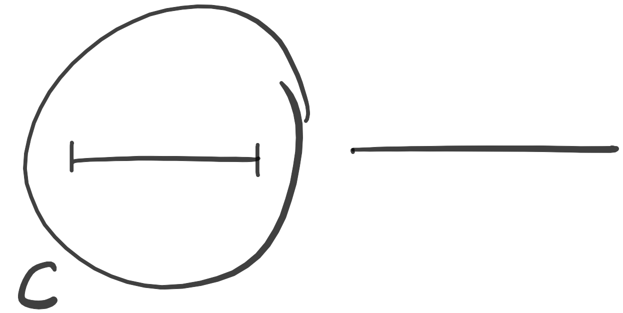
Fixed point iteration. $G_{\lambda,\epsilon}^{(0)} = G_\lambda$

$$G_{\lambda,\epsilon}^{(n)} = G_\lambda + \varepsilon G_\lambda W G_{\lambda,\epsilon}^{(n-1)} = \sum_{m=0}^{n} \varepsilon^{m} G_\lambda (W G_\lambda)^{m}$$

Neumann expansion.

perturbation of density matrix (w. gap)

$$P = \frac{1}{2\pi i} \oint_C (\lambda - H)^{-1} \, d\lambda$$



$$P_\epsilon - P = \frac{1}{2\pi i} \oint_C (\lambda - H)^{-1} \varepsilon W (\lambda - H_\epsilon)^{-1} \, d\lambda$$

$$= \frac{\varepsilon}{2\pi i} \oint_C (\lambda - H)^{-1} W (\lambda - H)^{-1} \, d\lambda + O(\varepsilon^2).$$

$$=: \varepsilon \mathcal{X}_0 W + O(\varepsilon^2)$$

$\mathcal{X}_0$: matrix $\longrightarrow$ matrix. super operator.

$$\left. \frac{d P(H + \varepsilon W)}{d\varepsilon} \right|_{\varepsilon = 0} = \mathcal{X}_0 W$$

spectral representation of χ_0.

$$\chi_0 W = \frac{1}{2\pi i} \oint_C \sum_{pq} \frac{|\psi_p\rangle\langle\psi_p| W |\psi_q\rangle\langle\psi_q|}{(\lambda-\varepsilon_p)(\lambda-\varepsilon_q)} d\lambda$$

$$= \frac{1}{2\pi i} \oint_C \sum_{pq} \frac{|\psi_p\rangle\langle\psi_p| W |\psi_q\rangle\langle\psi_q|}{\varepsilon_p-\varepsilon_q} \cdot \left(\frac{1}{\lambda-\varepsilon_p} - \frac{1}{\lambda-\varepsilon_q} \right)$$

$$= \sum_i^{occ} \sum_a^{unocc} \frac{|\psi_i\rangle\langle\psi_i| W |\psi_a\rangle\langle\psi_a|}{\varepsilon_i-\varepsilon_a}$$

$$- \sum_a^{unocc} \sum_i^{occ} \frac{|\psi_a\rangle\langle\psi_a| W |\psi_i\rangle\langle\psi_i|}{\varepsilon_a-\varepsilon_i}$$

$$= 2\,\mathrm{Re} \sum_i \sum_a \frac{|\psi_i\rangle\langle\psi_i| W |\psi_a\rangle\langle\psi_a|}{\varepsilon_i-\varepsilon_a}.$$

Perturbation of density

$$\rho = \mathrm{diag}\, P. \qquad W = \mathrm{diag}\, w$$

$$\rho_\varepsilon - \rho = \mathrm{diag}\,(P_\varepsilon - P)$$

$$= \varepsilon\, \mathrm{diag} \left(\sum_i \sum_a \frac{|\psi_i\rangle\langle\psi_i| \,\mathrm{diag}\, w\, |\psi_a\rangle\langle\psi_a|}{\varepsilon_i - \varepsilon_a} + h.c. \right) + O(\varepsilon^2)$$

$$\chi_0 w := \left. \frac{d \rho(H + \varepsilon\, \mathrm{diag}\, w)}{d\varepsilon} \right|_{\varepsilon = 0}$$

$$= \mathrm{diag} \left(\sum_i \sum_a \frac{|\psi_i\rangle\langle\psi_i| \,\mathrm{diag}\, w\, |\psi_a\rangle\langle\psi_a|}{\varepsilon_i - \varepsilon_a} + h.c. \right)$$

$$|\psi_i\rangle\langle\psi_i| \,\mathrm{diag}\, w | Q (\varepsilon_i - H)^{-1} Q$$

$\rho(r)$, $w(r)$. $\psi_i(r)$

$$(\chi_0 w)(r) = \sum_i \sum_a \frac{\psi_i(r) \int \psi_i^*(r') w(r') \psi_a(r') dr' \, \psi_a^*(r)}{\varepsilon_i - \varepsilon_a} + h.c.$$

$$\chi_0(r, r') = \sum_i \sum_a \frac{\psi_i(r) \psi_a^*(r) \quad \psi_i^*(r') \psi_a(r')}{\varepsilon_i - \varepsilon_a} + h.c.$$

$$\varepsilon_a - \varepsilon_i \geq \varepsilon_g > 0.$$

$$0 \geq \int w^*(r) \chi_0(r, r') w(r') \, dr \, dr' = 2 \sum_i \sum_a \frac{\left| \int \psi_i^*(r) w(r) \psi_a(r) dr \right|^2}{\varepsilon_i - \varepsilon_a}$$

$$\geq -2 \sum_i \sum_a \frac{|\langle \psi_i | \mathrm{diag}\, w | \psi_a \rangle|^2}{\varepsilon_g}$$

$$\geq -\sum_{pq} \frac{|\langle \psi_p | \mathrm{diag}\, w | \psi_q \rangle|^2}{\varepsilon_g} = -\frac{1}{\varepsilon_g} \|w\|_2^2$$

$$-\frac{1}{\varepsilon_g} \le \chi_0 \le 0 .$$

bounded response.

Compute χ_0 w

① truncating $\sum_a^{unocc}$

② Sternheimer eq.

$$Q = I - \sum_i^{occ} |\psi_i\rangle\langle\psi_i|$$

$$Q(\varepsilon_i - H)^{-1} Q = \sum_a^{unocc} |\psi_a\rangle (\varepsilon_i - \varepsilon_a)^{-1} \langle\psi_a|$$

$$\chi_0(r,r') = \sum_i^{occ} \psi_i(r)\psi_i^*(r')\left[Q(\varepsilon_i - H)^{-1}Q\right](r',r) + h.c.$$

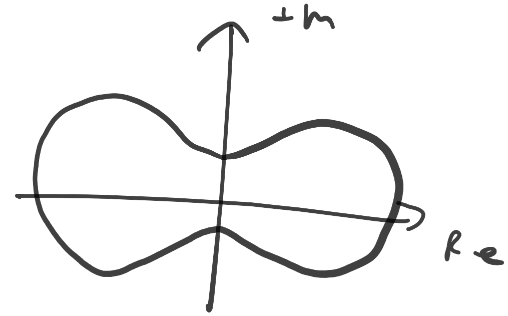
$$\int \chi_0(r,r')\,w(r')\,dr'$$

$$= \sum_i^{occ} \psi_i(r)\,u_i^*(r) + h.c.$$

$$Q(\varepsilon_i - H)\,Q\,u_i(r) = \psi_i(r)\,w(r)$$

Linear system. $O(N)$ eff to solve.

Finite temperature.



$$P_\epsilon - P = \frac{1}{2\pi i}\oint_C \frac{f(\lambda)}{\lambda - H_\epsilon} - \frac{f(\lambda)}{\lambda - H}\, d\lambda$$

$$= \frac{\varepsilon}{2\pi i}\oint_C f(\lambda)\,(\lambda - H)^{-1} W (\lambda - H)^{-1} d\lambda + O(\varepsilon^2)$$

$$=: \varepsilon \mathcal{X}_0 W + O(\varepsilon^2)$$

$$\mathcal{X}_0 W = \frac{1}{2\pi i}\oint_C f(\lambda) \sum_{pq} \frac{|\psi_p\rangle\langle\psi_p|W|\psi_q\rangle\langle\psi_q|}{(\lambda - \varepsilon_p)(\lambda - \varepsilon_q)}\, d\lambda$$

$$= \frac{1}{2\pi i}\sum_{pq}\oint_C \frac{f(\lambda)}{\varepsilon_p - \varepsilon_q} |\psi_p\rangle\langle\psi_p| W |\psi_q\rangle\langle\psi_q| \cdot \left(\frac{1}{\lambda - \varepsilon_p} - \frac{1}{\lambda - \varepsilon_q}\right) d\lambda$$

$$= \sum_{pq} \frac{f(\varepsilon_p) - f(\varepsilon_q)}{\varepsilon_p - \varepsilon_q} |\psi_p\rangle\langle\psi_p| W |\psi_q\rangle\langle\psi_q|$$

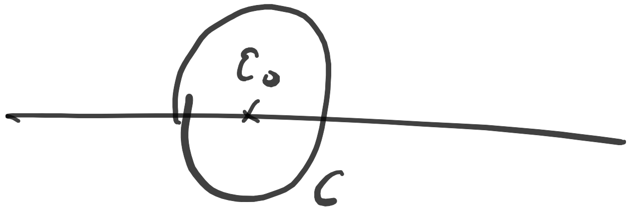
$$\chi_0(r,r') = \sum_{pq} \frac{f(\varepsilon_p)-f(\varepsilon_q)}{\varepsilon_p-\varepsilon_q} \psi_p(r)\,\psi_q^*(r)\,\psi_p^*(r')\,\psi_q(r')$$

$\varepsilon \simeq \varepsilon_p \simeq \varepsilon_q$.

$$\frac{f(\varepsilon_p)-f(\varepsilon_q)}{\varepsilon_p-\varepsilon_q} \simeq f'(\varepsilon)$$

Perturbation of eigenvalues.

First, standard perturbation theory



$$P = \frac{1}{2\pi i}\oint_C (\lambda - H)^{-1}\, d\lambda. \quad \operatorname{rank} P = m.$$

perturbation $H_\epsilon = H + \epsilon W$

$$P_\varepsilon := \frac{1}{2\pi i}\oint_C (\lambda - H_\epsilon)^{-1}\, d\lambda. \quad \operatorname{rank} P_\epsilon = ?$$

$$P_\epsilon - P = \frac{\varepsilon}{2\pi i}\oint_C (\lambda - H)^{-1}\, W\, (\lambda - H)^{-1}\, d\lambda + O(\varepsilon^2)$$

$$\|(\lambda - H)^{-1} W (\lambda - H)^{-1}\| < \infty.$$

$$\Rightarrow \|P_\epsilon - P\|_2 \xrightarrow{\varepsilon \to 0} 0 \quad \Rightarrow \operatorname{rank} P_\varepsilon = \operatorname{rank} P.$$

$\Rightarrow$ same # eigenvalues.

$$H\psi_i = \epsilon_0 \psi_i, \quad i = 1, \cdots, m.$$

$$P_\varepsilon|\psi_i\rangle = P|\psi_i\rangle + \varepsilon\Bigg(\sum_{\varepsilon_p \neq \varepsilon_0} \frac{1}{\varepsilon_0 - \varepsilon_p} \sum_{k=1}^{m} |\psi_k\rangle\langle\psi_k|W|\psi_p\rangle\langle \cancel{\psi_p}|\psi_i\rangle$$

$$+ \sum_{\varepsilon_p \neq \varepsilon_0} \frac{1}{\varepsilon_0 - \varepsilon_p} \sum_{k=1}^{m} |\psi_p\rangle\langle\psi_p|W|\psi_k\rangle\langle\psi_k|\psi_i\rangle\Bigg) + O(\epsilon^2)$$

$$= |\psi_i\rangle + \varepsilon \sum_{\varepsilon_p \neq \varepsilon_0} \frac{1}{\varepsilon_0 - \varepsilon_p} |\psi_p\rangle\langle\psi_p|W|\psi_i\rangle + O(\epsilon^2)$$

$$= |\psi_i\rangle + \varepsilon \cdot Q(\varepsilon_0 - H)^{-1} Q W|\psi_i\rangle + O(\epsilon^2), \quad Q = I - P.$$

$m=1$. $\quad |\psi_1\rangle = |\psi\rangle$

$$\tilde{\mathcal{E}} = \langle \psi P_\epsilon | H_\epsilon | P_\epsilon \psi \rangle$$

$$= \langle \psi | H | \psi \rangle + \varepsilon \langle \psi | W | \psi \rangle$$

$$+ \varepsilon \left(\langle \psi | \cancel{Q} (\mathcal{E}_0 - H)^{-1} Q W | \psi \rangle + h.\cancel{c.} \right)$$

$$+ O(\varepsilon^2)$$

$m > 1$.

$$H_\varepsilon P_\varepsilon |\psi_i\rangle = P_\epsilon H_\epsilon |\psi_i\rangle$$

$$= P_\epsilon \left(\mathcal{E}_0 |\psi_i\rangle + \epsilon W |\psi_i\rangle \right)$$

$$= \mathcal{E}_0 P_\epsilon |\psi_i\rangle + \epsilon P_0 W |\psi_i\rangle + O(\epsilon^2)$$

$$P_0 W |\psi_i\rangle = \varepsilon_i^{(1)} P_\epsilon |\psi_i\rangle + O(\epsilon).$$

$$\Rightarrow P_0 W|\psi_i\rangle = \sum_{j=1}^{m} |\psi_j\rangle\langle \psi_j|W|\psi_i\rangle = \varepsilon_i^{(1)} |\psi_i\rangle$$

$$\Rightarrow \langle \psi_j|W|\psi_i\rangle = \varepsilon_i^{(1)} \delta_{ij}, \quad i=1,\dots,m.$$

Diagonalize $W|_{\mathrm{range}(P_0)}$.

energy splitting.

Density functional perturbation theory.

$H_0 = H[\rho]$ self consistency.

$V_{ext} \leftarrow V_{ext} + \delta V_{ext}$. $\rho \to \rho + \delta\rho$.

$$V_{Hxc}[\rho + \delta\rho] = V_{Hxc}[\rho] + f_{Hxc}[\delta\rho] + O(\delta\rho^2)$$

$$f_{Hxc}(r, r') = \frac{\delta V_{Hxc}[\rho](r)}{\delta\rho(r')}$$

ex. $V_{Hxc}[\rho] = \int v_c(r, r')\rho(r')dr' + v_{xc}(\rho(r))$

$$f_{Hxc}[\delta\rho] = \int v_c(r, r')\delta\rho(r')dr' + v'_{xc}(\rho(r))\delta\rho(r)$$

$$H = H_0 + \underbrace{\delta V_{ext} + f_{Hxc}[\delta\rho]}_{\text{perturbation}} \quad \text{leading order.}$$

$$\delta\rho = \chi_0 \left[\delta V_{ext} + f_{Hxc}[\delta\rho] \right]$$

$$\Rightarrow \delta\rho = \underbrace{\left(I - \chi_0 f_{Hxc} \right)^{-1} \chi_0}_{\chi} \delta V_{ext} := \chi \, \delta V_{ext}$$

χ: reducible polarizability.

$\left(I - \chi_0 f_{Hxc} \right)^{-1}$ exists: stability condition.

Compute, $u = \chi g$. $g = \delta V_{ext}$

$$(I - \chi_0 f_{Hxc}) u = \chi_0 g$$

$$\Rightarrow u = \chi_0 g + \chi_0 f_{Hxc} u$$

$$= \chi_0 g + \chi_0 f_{Hxc} \chi_0 g + \cdots$$ Neumann expansion.

Only matrix-vector mult w. χ_0!

Dielectric screening

$$\delta V_{ext} = V_c\, \delta \rho_{ext} \quad , \quad f_{Hxc} \simeq V_c \leftarrow \text{RPA}.$$

$$\delta \rho = \chi\, \delta V_{ext} = (I - \chi_0 V_c)^{-1} \chi_0 V_c\, \delta \rho_{ext}$$

$$\delta V_{eff} = \delta V_{ext} + V_c\, \delta \rho$$

$$= V_c (I + \chi V_c)\, \delta \rho_{ext}$$

$$= V_c (I + (I - \chi_0 V_c)^{-1} \chi_0 V_c)\, \delta \rho_{ext}$$

$$= V_c (I - \chi_0 V_c)^{-1}\, \delta \rho_{ext}$$

$$= (I - V_c \chi_0)^{-1} V_c\, \delta \rho_{ext}$$

$$= \epsilon_d^{-1} V_c\, \delta \rho_{ext}$$

ϵ_d: dielectric operator.

$W_C = \epsilon_d^{-1} V_c$: screened Coulomb operator.

Ex. jellium.

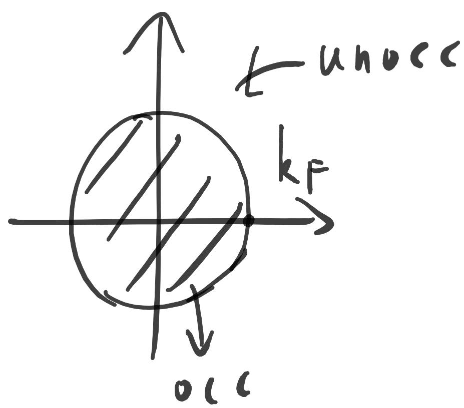
$$H = -\frac{1}{2}\Delta + \int V_c(r,r')\left(\rho(r') - \rho_a(r')\right)dr' \qquad \rho_a(r') \equiv \rho_0$$

SCF: $\rho(r) = \rho_0$.

$$\delta V_{ext}(r) = \int V_c(r,r')\,\delta\rho_{ext}(r')\,dr'$$

$$\delta\rho_{ext}(r) = \epsilon\,\delta(r) \qquad \text{point charge at } r=0.$$

$$\delta V_{eff}(r) = \int (\epsilon_d^{-1} V_c)(r,r')\,\delta\rho_{ext}(r')\,dr' = (\epsilon_d^{-1} V_c)(r,0) \cdot \epsilon.$$



$$\chi_0(r,r') = \sum_i^{occ} \sum_a^{unocc} \frac{\psi_i(r)\psi_a^*(r)\psi_i^*(r')\psi_a(r')}{\varepsilon_i - \varepsilon_a} + c.c.$$

$$\longrightarrow \int_{|\vec{k}|\le k_F} d\vec{k} \int_{|\vec{k}'|>k_F} d\vec{k}' \frac{\psi_{\vec{k}}(\vec{r})\psi_{\vec{k}'}^*(\vec{r})\psi_{\vec{k}}^*(\vec{r}')\psi_{\vec{k}'}(\vec{r}')}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'}} + c.c.$$

$$\left(\psi_{\vec{k}}(\vec{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\vec{k}\cdot\vec{r}} \qquad \int \psi_{\vec{k}}^*(\vec{r})\psi_{\vec{k}'}(\vec{r})\, d\vec{r} = \delta(\vec{k}-\vec{k}') \right)$$

$$= \frac{1}{(2\pi)^3} \int_{|\vec{k}|\le k_F} \int_{|\vec{k}'|\ge k_F} \frac{e^{i(\vec{k}-\vec{k}')(\vec{r}-\vec{r}')}}{\frac{1}{2}(k^2 - k'^2)} d\vec{k}'\, d\vec{k} + c.c.$$

$$\chi_0(\vec{r},\vec{r}') := \chi_0(\vec{r}-\vec{r}') = \frac{1}{(2\pi)^3}\int \hat{\chi}_0(\vec{q})\, e^{i\vec{q}\cdot\vec{r}}\, d\vec{q}$$

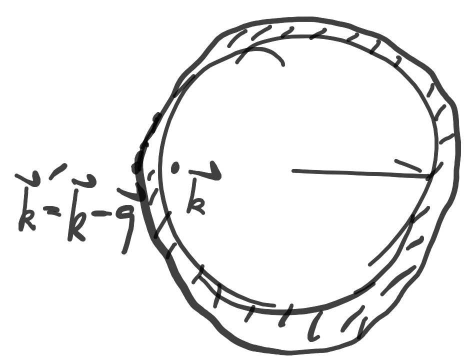
$$\hat{\chi}_0(\vec{q}) = \int e^{-i\vec{q}\cdot\vec{r}}\ \chi_0(\vec{r},0)\, d\vec{r}$$

$$= \int_{|\vec{k}|\le k_F} \int_{|\vec{k}'|\ge k_F} \frac{1}{\frac{1}{2}(k^2-k'^2)}\, \delta(\vec{k}-\vec{k}'-\vec{q})\, d\vec{k}\, d\vec{k}' + c.c.$$

$$\epsilon_d^{-1} V_c = (V_c^{-1} - \chi_0)^{-1}$$

Fourier basis: $\left(-\frac{q^2}{4\pi} - \hat{\chi}_0(\vec{q})\right)^{-1}$

Long range response: $|\vec{q}| << 1$



$\vec{q} = (0, 0, -q)^T$, $\vec{k}' = \vec{k} - \vec{q} = (k_1, k_2, k_3 + q)^T$, $q > 0$.

$k_\parallel = k_3$, $k_\perp^2 = k_1^2 + k_2^2$.

$k_\perp^2 + k_\parallel^2 \leq k_F^2$, $\Rightarrow$ $k_\parallel^2 \leq k_F^2 - k_\perp^2 \leq (k_\parallel + q)^2$

$k_\perp^2 + (k_\parallel + q)^2 \geq k_F^2$,

q small $\Rightarrow$ $k_\parallel \leq 0$.

$k'^2 - k^2 = +2k_\parallel q + q^2 \simeq +2k_\parallel q$. $\vec{k} = (k_\perp, \theta, k_\parallel)$ cylindrical.

$$\hat{\chi}_0(q) \approx 2 \int_0^{k_F} dk_\perp \, k_\perp \cdot 2\pi \int_{\sqrt{k_F^2 - k_\perp^2} - q}^{\sqrt{k_F^2 - k_\perp^2}} \frac{1}{-2k_\parallel q} dk_\parallel$$

$$= -\frac{2\pi}{q}\int_0^{k_F} dk_\perp\, k_\perp \cdot \log \frac{\sqrt{k_F^2 - k_\perp^2}}{\sqrt{k_F^2-k_\perp^2} - q}$$

$$\approx -\frac{2\pi}{q}\int_0^{k_F} dk_\perp \cdot k_\perp \cdot \frac{q}{\sqrt{k_F^2-k_\perp^2}} \qquad k_\perp = k_F \cos\theta.$$

$$= -2\pi k_F \int_0^{\frac{\pi}{2}} d\theta\, \frac{\sin\theta \cos\theta}{\sin\theta} = -2\pi k_F = -\gamma < 0.$$

Screened Coulomb.

$$\left(-\frac{\Delta}{4\pi} + \gamma\right) w_c = \delta \Rightarrow w_c(r,r') = C_1 \frac{e^{-C_2\gamma|r-r'|}}{|r-r'|}$$

exp. decay. screening! Yukawa eq.

Ex. insulator.

$$\chi_0(r,r') = \sum_i^{occ} \sum_a^{unocc} \frac{\psi_i(r)\psi_a^*(r)\,\psi_i^*(r')\psi_a(r')}{\varepsilon_i - \varepsilon_a}$$

$i = (n, \vec{k})$, $j = (n', \vec{k}')$, $\psi_{nk}(r) = e^{ikr} u_{nk}(r)$

$$\chi_0(r,r') = \sum_{nn'} \int_{\Omega^*} dk \int_{\Omega^*} dk' \, \frac{e^{i(k-k')\cdot(r-r')} u_{nk}(r) u_{n'k'}^*(r) u_{nk}^*(r') u_{n'k'}(r')}{\varepsilon_{nk} - \varepsilon_{n'k'}}$$

$$\hat{\chi}_0(\vec{q},\vec{q}') = \int e^{-i\vec{q}\cdot\vec{r}} \chi_0(\vec{r},\vec{r}') e^{i\vec{q}'\vec{r}'} d\vec{r}\, d\vec{r}'$$

$$\varepsilon_{n'\vec{k}'} - \varepsilon_{n\vec{k}} \geq \varepsilon_g > 0 .$$

$$|\vec{q}|, |\vec{q}'| \approx 0 .$$

$$\hat{\chi}_0(\vec{q}, \vec{q}') = \sum_{nn'} \int_{\Omega^*} d\vec{k} \int_{\Omega^*} d\vec{k}' \frac{\left[\int d\vec{r} e^{i(\vec{k}-\vec{k}'-\vec{q})\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) u^*_{n'\vec{k}'}(\vec{r})\right]}{\varepsilon_{n\vec{k}} - \varepsilon_{n'\vec{k}'}}$$

$$\cdot \int d\vec{r}' e^{-i(\vec{k}-\vec{k}'-\vec{q}')\cdot\vec{r}'} u^*_{n\vec{k}}(\vec{r}') u_{n'\vec{k}'}(\vec{r}')$$

$$\int d\vec{r}\, e^{i(\vec{k}-\vec{k}'-\vec{q})\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) u^*_{n'\vec{k}'}(\vec{r})$$

$$= \sum_{R \in L} \int_{\Omega} d\vec{r}\, e^{i(\vec{k}-\vec{k}'-\vec{q})(\vec{r}+\vec{R})} u_{n\vec{k}}(\vec{r}) u^*_{n'\vec{k}'}(\vec{r})$$

$$\propto \sum_{\vec{G}\in \mathbb{L}^*} \int_\Omega d\vec{r}\;\; \delta(\vec{k}-\vec{k}'-\vec{q}-\vec{G})\, u_{n\vec{k}}(\vec{r})\, u^*_{n'\vec{k}'}(\vec{r})$$

$$= \sum_{\vec{G}\in \mathbb{L}^*} \int_\Omega d\vec{r}\;\, u_{n\vec{k}}(\vec{r})\;\, u^*_{n'(\vec{k}-\vec{q}-\vec{G})}(\vec{r})$$

$$|\vec{q}| << 1. \qquad = \int d\vec{r}\, u_{n\vec{k}}\;\, u^*_{n'(\vec{k}-\vec{q})}(\vec{r})$$

$$\simeq \cancel{\int d\vec{r}\; u_{n\vec{k}} u^*_{n'\vec{k}}} + \int d\vec{r}\; u_{n\vec{k}}\, \nabla_{\vec{k}} u^*_{n'\vec{k}} \cdot (-\vec{q})$$

$$\Rightarrow \hat{\chi}(\vec{q},\vec{q}') \simeq \delta(\vec{q}-\vec{q}') \sum_{nn'} \frac{\vec{q}\cdot \int d\vec{r}\, u_{n\vec{k}} \nabla_{\vec{k}} u^*_{n'\vec{k}} \int d\vec{r}\, u^*_{n\vec{k}} \nabla_{\vec{k}} u_{n\vec{k}} \cdot \vec{q}}{\varepsilon_{n\vec{k}} - \varepsilon_{n'\vec{k}}} + c.c.$$

$$\approx -\delta(\vec{q}-\vec{q}')\ \vec{q}^{T} C \vec{q}\ , \quad C \in \mathbb{R}^{3\times 3}$$

For isotropic material.

So $\hat{\chi}(\vec{q},\vec{q}') \sim -\delta(\vec{q}-\vec{q}')\, c\, q^2$, $c \in \mathbb{R}$.

$$\Rightarrow \quad \epsilon_d^{-1} V_c(q) \approx (q^2 + c q^2)^{-1} = \frac{1}{(1+\underset{\uparrow\ \text{dielectric}}{c})q^2}$$

$$-\frac{\Delta}{(1+c)} w_c = 4\pi\delta .$$

Ex. Macroscopic polarizability

$$\delta V_{ext} = -\vec{E} \cdot \vec{r} \qquad \vec{E} = \epsilon \vec{e}_\beta$$

$$\delta \rho = \chi \, \delta V_{ext}$$

dipole. $d_\alpha = \int r_\alpha \, \rho(\vec{r}) \, d\vec{r}$

$$= -\epsilon \int \underbrace{r_\alpha \, \chi(\vec{r}, \vec{r}') \, r'_\beta}_{A_{\alpha\beta}} \, d\vec{r} \, d\vec{r}'$$

polarizability.

Ex. SCF. Fixed pt iteration.

$$V_{k+1} = V_{eff}[F_{KS}[V_k]]$$

$$e_k = V_k - V_*$$

$$e_{k+1} = f_{Hxc}\chi_0 e_k + O(\|e_k\|^2)$$

$$e_k \approx (f_{Hxc}\chi_0)^k e_0$$

$r_\sigma(f_{Hxc}\chi_0) < 1$. usually violated.

Simple mixing

$$V_{k+1} = (1-\alpha) V_k + \alpha V_{eff}[F_{ks}[V_k]]$$

$$e_{k+1} \approx (1-\alpha) e_k + \alpha f_{Hxc} \chi_0 e_k$$

$$= \left[I - \alpha \left(I - f_{Hxc} \chi_0 \right) \right] e_k$$

$$= (I - \alpha \epsilon_d) e_k .$$

$$e_k \approx (I - \alpha \epsilon_d)^k e_0 .$$

$$r_\sigma (I - \alpha \epsilon_d) < 1 .$$

If ϵ_d diagonalizable w. positive eigenvalues.

$$-1 < 1-\alpha\lambda < 1$$

$$\Rightarrow 0 < \alpha < \frac{2}{r_\sigma(\epsilon_d)}.$$

Optimal α.

$$\min_\alpha \max_\lambda |1-\alpha\lambda|$$

$$\Rightarrow 1-\alpha\lambda_{min} = \alpha\lambda_{max}-1$$

$$\Rightarrow \alpha = \frac{2}{\lambda_{max}+\lambda_{min}}. \quad \max_\lambda |1-\alpha\lambda| = \frac{\kappa(\epsilon_d)-1}{\kappa(\epsilon_d)+1}.$$

Ex. Phonon.

force

$$E = \inf_{\rho} \mathrm{Tr}\left[\left(-\frac{\Delta}{2} + V_{ext}(\{R_I\})\right)\rho\right] + V_{Hxc}[\rho] + E_{II}[\{R_I\}]$$

$$F = -\frac{\partial E}{\partial R_I} = -\mathrm{Tr}\left[\rho \frac{\partial V_{ext}}{\partial R_I}\right] - \frac{\partial E_{II}}{\partial R_I}$$

$$\frac{\partial^2 E}{\partial^2 R_i \partial R_J} = +\underbrace{\mathrm{Tr}\left[\frac{\partial \rho}{\partial R_J} \frac{\partial V_{ext}}{\partial R_I}\right]}_{D} + \mathrm{Tr}\left[\rho \frac{\partial^2 V_{ext}}{\partial R_I \partial R_J}\right]$$

$$+ \frac{\partial^2 E_{II}}{\partial R_I \partial R_J}$$

$$① = \int \frac{\partial V_{ext}(r)}{\partial R_I} \chi(r, r') \frac{\partial V_{ext}(r')}{\partial R_J} \, dr \, dr'.$$