Time dependent perturbation theory

$$i \partial_t \psi_i (t) = H(t) \psi_i (t) , \qquad i = 1, \cdots, N$$

$$P(t) = \sum_{i=1}^{N} \psi_i(t) \psi_i^*(t)$$

$$i \partial_t P = \sum_{i=1}^{N} i \partial_t \psi_i \psi_i^* + i \psi_i \partial_t \psi_i^*$$

$$= HP - PH = [H, P]$$

Quantum Liouville eq.

$$i\partial_t A(t) = H(t)A(t).$$

$$H(t) \equiv H. \qquad A(t) = e^{-iHt}A(0)$$

In general.

$$A(t) = \mathcal{T}\left[e^{-i\int_0^t H(s)\,ds}\right]A(0)$$

$\mathcal{T}$: time ordering operator

$$\mathcal{T}\left[A_1(s_1)A_2(s_2)\right] = \begin{cases} A_1(s_1)A_2(s_2), & s_1 \geq s_2 \\ +A_2(s_2)A_1(s_1), & s_1 < s_2 \end{cases}$$

no sign change

$$\mathcal{T}[A_1(s_1)\cdots A_n(s_n)] = A_{\pi(1)}(s_{\pi(1)})\cdots A_{\pi(n)}(s_{\pi(n)})$$

$$s_{\pi(1)} \geq s_{\pi(2)} \geq \cdots \geq s_{\pi(n)}$$

Time ordered exponential

$$\mathcal{T}\left[e^{-i\int_0^t H(s)ds}\right] = \mathcal{T}\left[\sum_{n=0}^{\infty}\frac{1}{n!}\int_0^t\cdots\int_0^t H(s_n)\cdots H(s_1)\, ds_1\cdots ds_n\right]$$

$$= \sum_{n=0}^{\infty}\int_0^t\int_0^{s_n}\cdots\int_0^{s_2} H(s_n)\cdots H(s_1)\, ds_1\cdots ds_n$$

Verify (exer)

$$i\,\partial_t \underbrace{\mathcal{T}\left[e^{-i\int_0^t H(s)\,ds}\right]}_{U(t,0)} = H(t)\,\mathcal{T}\left[e^{-i\int_0^t H(s)\,ds}\right]$$

$U(t,0)$ propagator.

$$\Rightarrow \quad P(t) = U(t,0)\,P(0)\,U(0,t)$$

Perturbation

$$H_\epsilon(t) = H_0(t) + \epsilon W(t)$$

$$\mathcal{U}_\epsilon(t,0) = \mathcal{T}\left[e^{-i\int_0^t H_0(s) + \epsilon W(s)\,ds}\right]$$

Duhamel principle (exer)

$$\mathcal{U}_\epsilon(t,0) = \mathcal{U}(t,0) - i\epsilon\int_0^t \mathcal{U}(t,s)\,W(s)\,\mathcal{U}_\epsilon(s,0)\,ds$$

$$= \mathcal{U}(t,0) - i\epsilon\int_0^t \mathcal{U}(t,s)\,W(s)\,\mathcal{U}(s,0)\,ds$$

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

$$P_\epsilon(t) - P(t) = U_\epsilon(t,0)\, P(0)\, U_\epsilon(0,t) - P(t)$$

$$= -i\epsilon \int_0^t U(t,s)\, W(s)\, U(s,0)\, P(0)\, U(0,t)\, ds$$

$$+ h.c. + O(\epsilon^2)$$

$$:= \epsilon\, (\chi_0 W)(t) + O(\epsilon^2)$$

χ_0 : time-dependent independent particle polarizability matrix.

Ground state starting point

$$H_0(t) \equiv H_0, \qquad P_0 = \mathbb{1}_{(-\infty,\mu)}(H_0)$$

$$\mathcal{U}(t,s) = e^{-i(t-s)H_0}, \qquad [\mathcal{U}(t,s), P_0] = 0.$$

$$(\mathcal{I}_0 W)(t) = -i \int_0^t e^{-i(t-s)H_0} W(s) e^{i(t-s)H_0} \, ds \, P_0 + h.c.$$

$$= -i \int_0^t e^{-i(t-s)H_0} [W(s), P_0] e^{i(t-s)H_0} \, ds.$$

shift initial point to $t_0 = -\infty$.

$$(\Phi_0 W)(t) = -i\int_{-\infty}^{t} e^{-i(t-s)H_0}[W(s), P_0]e^{i(t-s)H_0}\,ds$$

$$= -i\int_{-\infty}^{t} \sum_{pq} |\psi_p\rangle\langle\psi_p| e^{-i(t-s)(\varepsilon_p-\varepsilon_q)} [W(s),P_0]\,|\psi_q\rangle\langle\psi_q|\,ds$$

Use

$$\int_{-\infty}^{t} e^{-i(t-s)\omega_0} W(s)\,ds$$

$$= \int_{-\infty}^{\infty} e^{-i(t-s)\omega_0} W(s)\;\theta(t-s)\,ds$$

Fourier transform

Write down Fourier transform of $(\Phi_0 W)(t)$

$$\mathcal{F}(f)(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} f(t)\, dt$$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\omega(t-s)} f(s)\, ds\, d\omega = f(t)$$

$$\Rightarrow \mathcal{F}\left(\int_{-\infty}^{t} e^{-i(t-s)\omega_0} W(s)\, ds \right)$$

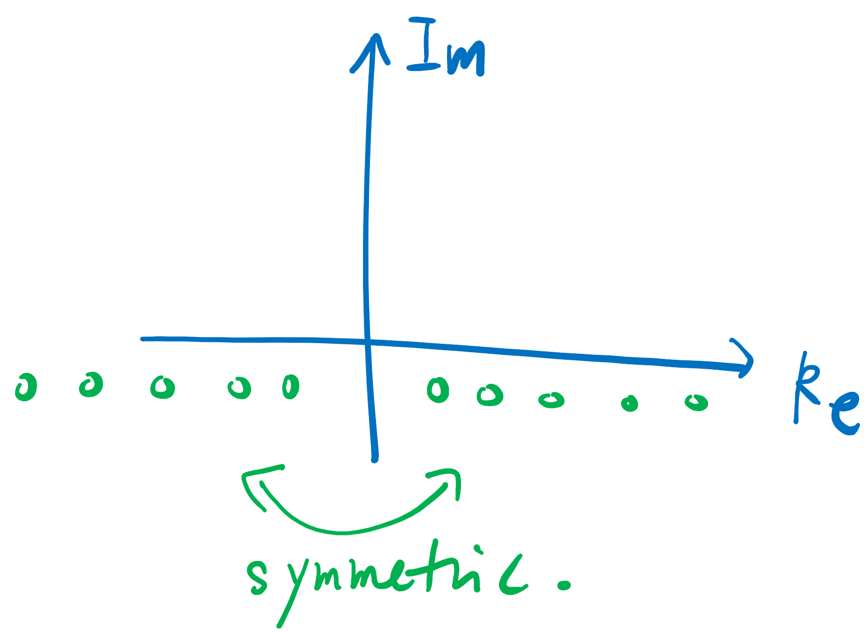
$$= \hat{\Theta}(\omega - \omega_0)\, \hat{W}(\omega)$$

$$= i \lim_{\eta \to 0^+} \frac{\hat{W}(\omega)}{\omega - \omega_0 + i\eta}$$

$$\mathcal{F}(\mathbb{X}\circ W)(\omega) = \lim_{\eta\to 0^+} \sum_{pq} \frac{|\psi_p\rangle\langle\psi_p| \, [\hat{W}(\omega), P_0] \, |\psi_q\rangle\langle\psi_q|}{\omega - (\varepsilon_p - \varepsilon_q) + i\eta}$$

$$= \lim_{\eta\to 0^+} \sum_{ia} \frac{|\psi_a\rangle\langle\psi_a| \hat{W}(\omega) |\psi_i\rangle\langle\psi_i|}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta}$$

$$- \sum_{ia} \frac{|\psi_i\rangle\langle\psi_i| \hat{W}(\omega) |\psi_a\rangle\langle\psi_a|}{\omega - (\varepsilon_i - \varepsilon_a) + i\eta}$$



poles below real axis

$\longrightarrow$ causality.

$W(t)$: time dependendent local potential.

$\rho(t)$: response of density.

$$\chi_0(r,r';t,t') = \frac{\delta \rho(r,t)}{\delta W(r',t')} \quad , \quad W(r,t) = \delta(r-r')\,\delta(t-t')$$

$$\hat{\chi}_0(r,r';\omega) = \mathcal{F}\left(\chi_0(r,r';t,0)\right)$$

$$= \lim_{\eta \to 0^+} \sum_i \sum_a \frac{\psi_i^*(r)\psi_a(r)\psi_a^*(r')\psi_i(r')}{\omega-(\varepsilon_a-\varepsilon_i)+i\eta}$$

$$- \sum_a \sum_i \frac{\psi_a^*(r)\psi_i(r)\psi_i^*(r')\psi_a(r')}{\omega+(\varepsilon_a-\varepsilon_i)+i\eta}$$

Self-consistent TD perturbation (Dyson eq.)

Sternheimer formulation

} exercise.

Casida formalism for excitation.

reducible polarization operator.

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega) f_{Hxc}(\omega) \chi(\omega)$$

poles :

$$\chi(\omega) f = \infty \quad \text{or.} \quad \chi^{-1}(\omega) f = 0.$$

$$\chi^{-1}(\omega) = \chi_0^{-1}(\omega) - f_{Hxc}(\omega)$$

$$\Rightarrow \quad \chi_0(\omega) f_{Hxc}(\omega) f = f$$

projection.

$$\Psi_{ia}(r) = \psi_i(r)\psi_a^*(r) , \quad \Psi_{ai}(r) = \psi_a(r)\psi_i^*(r), \; D_{ai} = \varepsilon_a - \varepsilon_i$$

$$f(r) = \sum_{ai} f_{ai}\Psi_{ai}(r) + f_{ia}\Psi_{ia}(r)$$ (not necessarily $f_{ia} = f_{ai}^*$)

$$\Rightarrow \lim_{\eta\to 0^+} \sum_{ij}\sum_{ab}\Bigg[\frac{|\Psi_{ai}\rangle\langle\Psi_{ai}| f_{Hxc} |\Psi_{bj}\rangle}{\omega - D_{ai} + i\eta} f_{bj}$$

$$+ \frac{|\Psi_{ai}\rangle\langle\Psi_{ai}| f_{Hxc} |\Psi_{jb}\rangle}{\omega - D_{ai} + i\eta} f_{jb}$$

$$
- \frac{|\Psi_{ia}\rangle\langle\Psi_{ia}|f_{Hxc}|\Psi_{bj}\rangle}{\omega + D_{ai} + i\eta} f_{bj}
$$

$$
\left. - \frac{|\Psi_{ia}\rangle\langle\Psi_{ia}|f_{Hxc}|\Psi_{jb}\rangle}{\omega + D_{ai} + i\eta} f_{jb} \right]
$$

$$
= \sum_{ai} f_{ai} |\Psi_{ai}\rangle + f_{ia} |\Psi_{ia}\rangle
$$

Match coef for $|\Psi_{ia}\rangle$, $|\Psi_{ai}\rangle$

(NOT a standard Galerkin)

$$\sum_{jb} \langle \Phi_{ai} | f_{Hxc} | \Phi_{bj} \rangle f_{bj} + \langle \Phi_{ai} | f_{Hxc} | \Phi_{jb} \rangle f_{jb}$$

$$= \left[(\omega + i\eta) - D_{ai} \right] f_{ai}$$

$$\sum_{jb} \langle \Phi_{ia} | f_{Hxc} | \Phi_{bj} \rangle f_{bj} + \langle \Phi_{ia} | f_{Hxc} | \Phi_{jb} \rangle f_{jb}$$

$$= - \left[(\omega + i\eta) + D_{ai} \right] f_{ia}$$

$$\tilde{D} = \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix}, \qquad \tilde{C} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

$$\tilde{K} = \begin{bmatrix} A & B \\ \bar{B} & \bar{A} \end{bmatrix}$$

$$A_{ai,bj} = \langle \Phi_{ai} | f_{Hxc} | \Phi_{bj} \rangle$$

$$B_{ai,bj} = \langle \Phi_{ai} | f_{Hxc} | \Phi_{jb} \rangle$$

$$\tilde{\Omega} = \tilde{D} + \tilde{K}$$

$$\tilde{\Omega} \tilde{f} = \omega \tilde{C} \tilde{f}.$$ Casida eq.

Alternative linear algebra perspective

$$\bar{\Psi}_{ai}(r) = \psi_i(r)\,\psi_a^*(r) \qquad \Psi_{ai}(r) = \psi_a(r)\,\psi_i^*(r)$$

$$D_{ai} = \epsilon_a - \epsilon_i$$

$$\chi_0(\omega) = \Psi\left((\omega+i\eta)I - D\right)^{-1} \overset{\Psi^*}{\bar{\Psi}^T}$$

$$- \bar{\Psi}\left((\omega+i\eta)I + D\right)^{-1} \Psi^T$$

$$= \underbrace{[\Psi, \bar{\Psi}]}_{\tilde{\Psi}} \underbrace{\begin{bmatrix} (\omega+i\eta)I - D & 0 \\ 0 & -(\omega+i\eta)-D \end{bmatrix}^{-1}}_{(\omega+i\eta)\tilde{C} - \tilde{D}} \underbrace{\begin{bmatrix} \bar{\Psi}^* \\ \bar{\Psi}^* \end{bmatrix}}_{\tilde{\Psi}^*}$$

$$\tilde{C} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \qquad \tilde{D} = \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix}$$

$$\chi(\omega) = \left(I - \chi_0(\omega) f_{Hxc}\right)^{-1} \chi_0(\omega)$$

Use Sherman-Morrison formula

$$= \left(I - \tilde{\Psi}\left[(\omega+i\eta)\tilde{C} - \tilde{D}\right]^{-1} \tilde{\Psi}^* f_{Hxc}\right)^{-1} \tilde{\Psi}\left[(\omega+i\eta)\tilde{C} - \tilde{D}\right]^{-1} \tilde{\Psi}^*$$

$$(A + UCV)^{-1} = A^{-1} - A^{-1}U\left(C^{-1} + VA^{-1}U\right)^{-1} VA^{-1}$$

$$= \left(I + \tilde{\Psi} \left[(\omega + i\eta) \tilde{C} - \tilde{D} - \tilde{\Psi}^* f_{Hxc} \tilde{\Psi} \right]^{-1} \tilde{\Psi}^* f_{Hxc} \right)$$

$$\tilde{\Psi} \left[(\omega + i\eta) \tilde{C} - \tilde{D} \right]^{-1} \tilde{\Psi}^*$$

$$\left(\tilde{\Omega} := \tilde{D} + \tilde{\Psi}^* f_{Hxc} \tilde{\Psi} \right)$$

$$= \tilde{\Psi} \left[I + \left((\omega + i\eta) \tilde{C} - \tilde{\Omega} \right)^{-1} \left(\tilde{\Omega} - \tilde{D} \right) \right] \left[(\omega + i\eta) \tilde{C} - \tilde{D} \right]^{-1} \tilde{\Psi}^*$$

$$\overset{\text{exer}}{=} \tilde{\Psi} \left[(\omega + i\eta) \tilde{C} - \tilde{\Omega} \right]^{-1} \tilde{\Psi}^*$$

Hence poles of $\chi(\omega)$ solves the generalized eigenvalue problem.

$$\tilde{\Omega}\,\tilde{f} = \omega\,\tilde{C} f$$

Casida eq.

Connection w. many body case.

$$H_\epsilon^{(N)}(t) = H_0^{(N)} + \epsilon W^{(N)}(t), \qquad H_0^{(N)} \Psi_0^{(N)} = E_0^{(N)} \Psi_0^{(N)}$$

$$W^{(N)}(\{r_i\}_{i=1}^{N}; t) = \sum_{i=1}^{N} w(r_i; t)$$

$$\mathcal{U}_\epsilon^{(N)}(t_2, t_1) = \mathcal{T}\left[e^{-i\int_{t_1}^{t_2} H_\epsilon^{(N)}(s)\,ds} \right]$$

$$\hat{\rho}^{(N)}(r) = \sum_{i=1}^{N} \delta(r_i - r)$$ density operator

$$\langle \Psi | \hat{\rho}^{(N)} | \Psi \rangle = \int |\Psi(r_1, \cdots, r_N)|^2 \sum_{i=1}^{N} \delta(r_i - r)\, dr_1 \cdots dr_N$$

$$= N \int |\Psi(r, r_2, \cdots, r_N)|^2\, dr_2 \cdots dr_N = \rho(r)$$

Similar to single body case

$$P_{\epsilon}^{(N)}(t) - P^{(N)}(t) = \epsilon \left(\underline{X}^{(N)} W^{(N)} \right)(t) + O(\epsilon^2)$$

$$\mathcal{F}\left(\underline{X}^{(N)} W^{(N)}\right)(\omega) = \lim_{\eta \to 0^+} \sum_{k \neq 0} \frac{|\Psi_k^{(N)}\rangle\langle\Psi_k^{(N)}| W^{(N)}(\omega) |\Psi_0^{(N)}\rangle\langle\Psi_0^{(N)}|}{(\omega + i\eta) - (E_k^{(N)} - E_0^{(N)})}$$

$$- \sum_{k \neq 0} \frac{|\Psi_0^{(N)}\rangle\langle\Psi_0^{(N)}| W^{(N)}(\omega) |\Psi_k^{(N)}\rangle\langle\Psi_k^{(N)}|}{(\omega + i\eta) - (E_0^{(N)} - E_k^{(N)})}$$

response of density to change of potential.

$$W^{(N)}(\{r_i\},t) = \sum_{i=1}^{N} \delta(r_i - r')\,\delta(t-t') = \hat{\rho}^{(N)}(r')\,\delta(t-t')$$

$$\chi(r,r';\omega) = \mathrm{Tr}\left[\hat{\rho}(r)\,\mathcal{F}\left[\Xi^{(N)}W^{(N)}\right](\omega)\right]$$

$$\overset{\text{exer}}{=} \lim_{\eta\to 0^+} \sum_{k\neq 0} \frac{\langle \Psi_0^{(N)} | \hat{\rho}^{(N)}(r) | \Psi_k^{(N)} \rangle \langle \Psi_k^{(N)} | \hat{\rho}^{(N)}(r') | \Psi_0^{(N)} \rangle}{\omega + i\eta - (E_k^{(N)} - E_0^{(N)})}$$

$$- \sum_{k\neq 0} \frac{\langle \Psi_k^{(N)} | \hat{\rho}^{(N)}(r) | \Psi_0^{(N)} \rangle \langle \Psi_0^{(N)} | \hat{\rho}^{(N)}(r') | \Psi_k^{(N)} \rangle}{\omega + i\eta + (E_k^{(N)} - E_0^{(N)})}$$

Casida formulation:

compute neutral excitation spectrum

(# electron does not change)

Second quantized formulation.

field operator. spin-less $(\mu=0)$

$$H_0 = \int \hat{\psi}^{+}(r)\left(-\frac{1}{2}\Delta_r + U_{ext}(r)\right)\hat{\psi}(r)\,dr$$

$$+ \frac{1}{2}\int \hat{\psi}^{+}(r)\hat{\psi}^{+}(r')\,v_c(r,r')\,\hat{\psi}(r')\hat{\psi}(r)\,dr\,dr'.$$

$$W_\epsilon(t) = H_0 + \epsilon\int w(r,t)\,\hat{n}(r)\,dr, \qquad \hat{n}(r) = \hat{\psi}^{+}(r)\hat{\psi}(r).$$

$\chi(r,r';\omega)$ same formula, but $\hat{p}^{(N)}(r) \longrightarrow \hat{n}(r)$

First quan. second quan.

In MBPT, 2nd quan. is preferred since it allows the particle number to fluctuate,

- convenient for neutral excitation processes
- essential for electron additional/removal processes.

Green's function formalism