

Time dependent perturbation theory

$$i\partial_t \psi_i(t) = H(t) \psi_i(t), \quad i=1, \dots, N$$

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

$$\begin{aligned} i\partial_t P &= \sum_{i=1}^N i \partial_t \psi_i \psi_i^* + i \psi_i \partial_t \psi_i^* \\ &= H P - P H = [H, P] \end{aligned}$$

Quantum Liouville eq.

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

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

In general.

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

T: time ordering operator

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

↑ 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)

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

$\mathcal{U}(t,0)$ propagator.

$$\Rightarrow P(t) = \mathcal{U}(t,0) P(0) \mathcal{U}(0,t)$$

Perturbation

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

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

Duhamed principle (exer)

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

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

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

$$\begin{aligned}
 P_\epsilon(t) - P(t) &= U_\epsilon(t, 0) P(0) U_\epsilon(0, t) - P(t) \\
 &= -i\epsilon \int_0^t U(t, s) W(s) U(s, 0) P(0) U(0, t) ds \\
 &\quad + h.c. + O(\epsilon^2) \\
 &:= \epsilon (\mathbb{I}_0 W)(t) + O(\epsilon^2)
 \end{aligned}$$

\mathbb{I}_0 : time-dependent independent particle polarizability matrix.

Ground state starting point

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

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

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

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

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

$$(\bar{X}_0 W)(t) = -i \int_{-\infty}^t e^{-i(t-s)H_0} [W(s), P_0] e^{i(t-s)H_0} ds$$

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

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 $(\bar{X}_0 W)(t)$

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

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

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

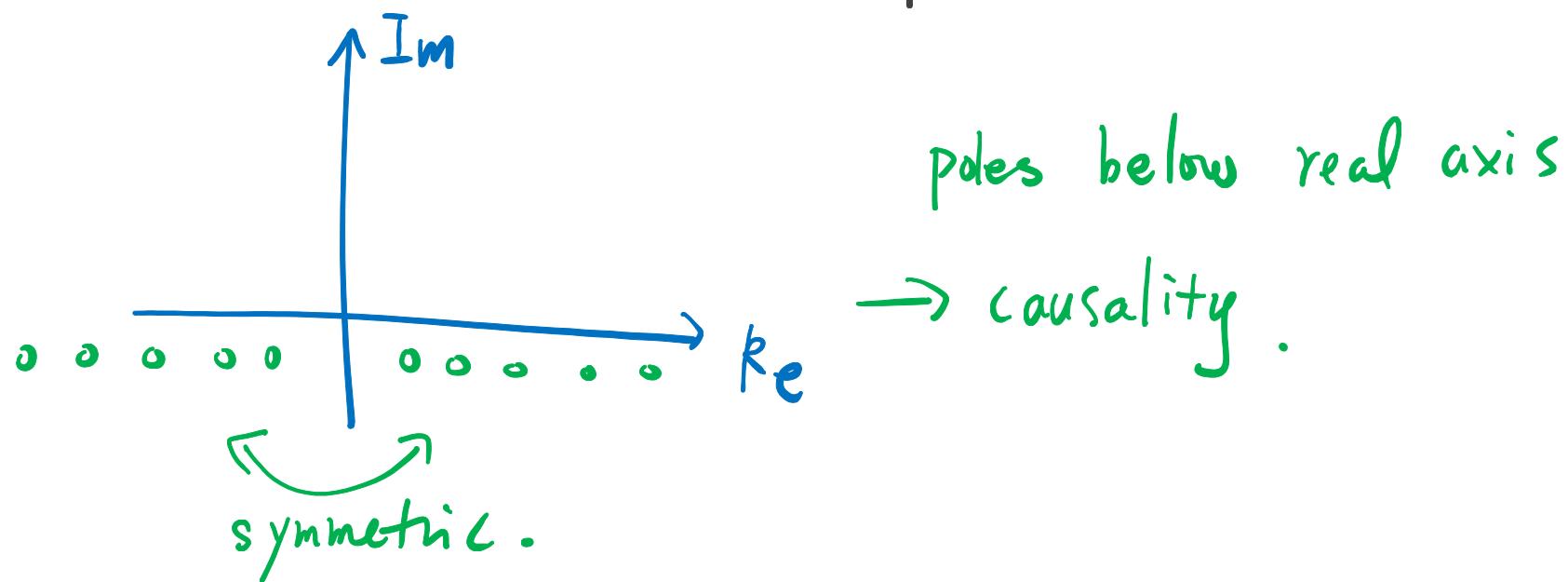
$$= \hat{\Theta}(\omega - \omega_0) \hat{W}(\omega)$$

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

$$F(X_0, W)(\omega) = \lim_{\eta \rightarrow 0^+} \sum_{pq} \frac{|\psi_p\rangle \langle \psi_p| [\hat{N}(\omega), P_0] |\psi_q\rangle \langle \psi_q|}{\omega - (\epsilon_p - \epsilon_q) + i\eta}$$

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

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



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

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

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

$$\hat{\chi}_o(r, r'; \omega) = \mathcal{F}(\chi_o(r, r'; t, 0))$$

$$\begin{aligned} &= \lim_{\eta \rightarrow 0^+} \sum_i \sum_a \frac{\psi_i^*(r) \psi_a(r) \psi_a^*(r') \psi_i(r')}{\omega - (\epsilon_a - \epsilon_i) + i\eta} \\ &\quad - \sum_a \sum_i \frac{\psi_a^*(r) \psi_i(r) \psi_i^*(r') \psi_a(r')}{\omega + (\epsilon_a - \epsilon_i) + i\eta} \end{aligned}$$

Self-consistent TD perturbation
(Dyson eq.)

Sternheimer formulation

} exercise.

Casida formalism for excitation.

reducible polarization operator.

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

poles :

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

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

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

projection.

$$\Psi_{ia}(r) = \psi_i(r) \psi_a^*(r), \quad \Psi_{ai}(r) = \psi_a(r) \psi_i^*(r), \quad D_{ai} = \epsilon_a - \epsilon_i$$

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

$$\Rightarrow \lim_{\eta \rightarrow 0^+} \sum_{ij} \sum_{ab} \left[\frac{|\Psi_{ai}\rangle \langle \Psi_{ai}| f_{Hxc} |\Psi_{bj}\rangle}{\omega - D_{ai} + i\eta} +_{bj} \right. \\ \left. + \frac{|\Psi_{ai}\rangle \langle \Psi_{ai}| f_{Hxc} |\Psi_{jb}\rangle}{\omega - D_{ai} + i\eta} f_{ib} \right]$$

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

$$- \frac{|\bar{\Psi}_{ia}\rangle \langle \bar{\Psi}_{ia}| f_{Hxc} |\bar{\Psi}_{jb}\rangle}{\omega + D_{ai} + i\eta} f_{jb}]$$

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

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

(NOT a standard Galerkin)

$$\sum_{jb} \langle \bar{\Psi}_{ai} | f_{Hxc} | \bar{\Psi}_{bj} \rangle f_{bj} + \langle \bar{\Psi}_{ai} | f_{Hxc} | \bar{\Psi}_{jb} \rangle f_{jb}$$

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

$$\sum_{jb} \langle \bar{\Psi}_{ia} | f_{Hxc} | \bar{\Psi}_{bj} \rangle f_{bj} + \langle \bar{\Psi}_{ia} | f_{Hxc} | \bar{\Psi}_{jb} \rangle f_{jb}$$

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

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

$$\tilde{K} = \begin{bmatrix} A & B \\ \bar{B} & \bar{A} \end{bmatrix} \quad A_{ai,bj} = \langle \underline{\psi}_{ai} | f_{Hx_c} | \underline{\psi}_{bj} \rangle$$

$$B_{ai,bj} = \langle \underline{\psi}_{ai} | f_{Hx_c} | \underline{\psi}_{jb} \rangle$$

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

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

Alternative linear algebra perspective

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

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

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

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

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

$(\omega + i\eta) \tilde{C} - \tilde{D}$

↑
 $\tilde{\Psi}^*$

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

$$\chi(\omega) = (I - \chi_0(\omega) f_{Hx_C})^{-1} \chi_0(\omega) \quad \text{Use Sherman-Morrison formula}$$

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

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

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

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

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

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

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 et.
T.

Connection w. many body case.

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

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

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

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

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

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

Similar to single body case

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

$$\begin{aligned} \mathcal{F} \left(\bar{X}^{(N)} W^{(N)} \right)(\omega) &= \lim_{\eta \rightarrow 0^+} \sum_{k \neq 0} \frac{\left| \bar{\Psi}_k^{(N)} \right\rangle \langle \bar{\Psi}_k^{(N)} | W^{(N)}(\omega) | \bar{\Psi}_0^{(N)} \rangle \langle \bar{\Psi}_0^{(N)} \right|}{(\omega + i\eta) - (E_k^{(N)} - E_0^{(N)})} \\ &\quad - \sum_{k \neq 0} \frac{\left| \bar{\Psi}_0^{(N)} \right\rangle \langle \bar{\Psi}_0^{(N)} | W^{(N)}(\omega) | \bar{\Psi}_k^{(N)} \rangle \langle \bar{\Psi}_k^{(N)} \right|}{(\omega + i\eta) - (E_0^{(N)} - E_k^{(N)})} \end{aligned}$$

response of density to change of potential.

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

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

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

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

Casida formulation:

compute neutral excitation spectrum
(# electron does not change)

Second quantized formulation.

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

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

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

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

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

$\uparrow \qquad \qquad \uparrow$
First quan. second quan.

In UBPT, 2nd quan. is preferred since it

allows the particle number to fluctuate,

◦ convenient for neutral excitation processes

◦ essential for electron addition/removal processes.

Green's function formalism