$$\frac{\partial\langle\hat{B}\rangle_\rho}{\partial\lambda_i} = \langle\delta\hat{B};\delta\hat{A}_i^+\rangle_\rho = \langle\delta\hat{B};\hat{A}_i^+\rangle_\rho = \langle\hat{B};\delta\hat{A}_i^+\rangle_\rho = \langle\hat{B};\hat{A}_i^+\rangle_{\rho c}$$

Vamos considerar $\hat{B} = \hat{A}_j$ tq $\hat{A}_j = \hat{A}_j^+$

$$\Rightarrow \frac{\partial\langle\hat{A}_i\rangle_\rho}{\partial\lambda_j} = \frac{\partial^2 \ln Z}{\partial\lambda_j\,\partial\lambda_i} = \langle\delta\hat{A}_i;\delta\hat{A}_j\rangle_\rho = C_{ij}$$

C_{ij} é simétrica e $> 0 \Rightarrow \exists\ C^{-1}_{ij}$

Assim, $d\langle\hat{A}_i\rangle_\rho = \sum_j C_{ij}\,d\lambda_j \Rightarrow d\lambda_i = \sum_j C^{-1}_{ij}\,d\langle\hat{A}_j\rangle_\rho$

$$\Rightarrow d\langle\hat{B}\rangle_\rho = \sum_j \langle\delta\hat{B};\delta\hat{A}_j\rangle_\rho\,d\lambda_j = \sum_{jk}\langle\delta\hat{B};\delta\hat{A}_j\rangle_\rho\,C^{-1}_{jk}\,d\langle\hat{A}_k\rangle_\rho$$

$$d\langle\hat{B}\rangle_\rho = \sum_{jk} C^{-1}_{jk}\langle\delta\hat{B};\delta\hat{A}_j\rangle_\rho\,d\langle\hat{A}_k\rangle_\rho$$

$\langle\hat{B}\rangle_\rho$ depende de $\langle\hat{A}_j\rangle_\rho$ porque $\hat{\rho}$ é determinado por

$$\langle\hat{A}_i\rangle_\rho = \mathrm{Tr}(\hat{\rho}\hat{A}_i) = A_i$$

<u>A função de Kubo quântica</u>

Como anteriormente $H \to H_1 = H - \sum_i \hat{A}_i f_i$

$$\Rightarrow e^{-\beta H} \to e^{-\beta H_1} = e^{-\beta(H - \sum_i \hat{A}_i f_i)} \quad \text{e} \quad Z \to Z_1$$

$$\hat{A}_0 \leftrightarrow H \quad \text{e} \quad \lambda_0 \leftrightarrow -\beta \Rightarrow \hat{\rho}_{eq} = \frac{1}{Z(H)}e^{-\beta H}$$

$$Z(H) = \mathrm{Tr}\, e^{-\beta H}$$

Novamente $f_i(t) = e^{\eta t}\,\theta(-t)\, f_i \qquad \eta \to 0$

$\Rightarrow$ se $\hat{B} = \hat{A}_i$ temos $\hat{A}_i(t) = e^{iHt/\hbar}\,\hat{A}_i\, e^{-iHt/\hbar}$

onde $\hat{A}_i = \hat{A}_i(0)$ está na versão de Schrödinger.

Se $\delta\hat{B} = \delta\hat{A}_i(t)$ temos, na aproximação linear,

$$\delta\bar{A}_i(t) = \beta \sum_j \langle \delta\hat{A}_i(t); \delta\hat{A}_j(0)\rangle f_j$$

onde $\langle \delta\hat{A}_i(t); \delta\hat{A}_j(0)\rangle = C_{ij}(t) =$

$$= \int_0^1 dx\, \mathrm{Tr}\left(\delta\hat{A}_i(t)\,\hat{\rho}^{x}\,\delta\hat{A}_j(0)\,\hat{\rho}^{1-x}\right)$$

$$= \int_0^1 dx\, \mathrm{Tr}\left(\delta\hat{A}_i(t)\,\frac{e^{-\beta H x}}{\cancel{Z^{x}}}\,\delta\hat{A}_j(0)\,\frac{e^{-\beta H}}{Z}\,\cancel{Z^{x}}\, e^{\beta H x}\right)$$

$$= \int_0^1 dx\, \mathrm{Tr}\left(\frac{e^{-\beta H}}{Z}\,\delta\hat{A}_i(t)\, e^{-\beta H x}\,\delta\hat{A}_j(0)\, e^{\beta H x}\right)$$

$\beta x \equiv \alpha$

$$= \frac{1}{\beta}\int_0^\beta \left\langle \hat{A}_i(t)\, e^{-H\alpha}\,\hat{A}_j(0)\, e^{H\alpha}\right\rangle_c d\alpha.$$

Como $\hat{A}_j(t) = e^{iHt/\hbar}\,\hat{A}_j(0)\, e^{-iHt/\hbar}$, se fizermos $t = +i\hbar\alpha$ temos

$$e^{-H\alpha}\,\hat{A}_j(0)\, e^{H\alpha} = \hat{A}_j(i\hbar\alpha)$$

$$\Rightarrow C_{ij}(t) = \frac{1}{\beta}\int_0^{\beta} \langle \hat{A}_i(t)\hat{A}_j(i\hbar\alpha)\rangle_c \, d\alpha .$$

$$\alpha' = \hbar\alpha \Rightarrow C_{ij}(t) = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} \langle \hat{A}_i(t)\hat{A}_j(i\alpha')\rangle_c \, d\alpha'$$

Devido às propriedades de analiticidade, que por sua vez decorrem da causalidade, podemos ainda escrever:

$$\chi_{ij}(t) = -\beta\,\Theta(t)\,\dot{C}_{ij}(t) \quad \text{ou} \quad \chi''_{ij}(t) = \frac{i}{2}\beta\,\dot{C}_{ij}(t)$$

Teorema de flutuação-dissipação.

Pela invariância de translação no tempo temos

$$\dot{C}_{ij}(t) = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha \, \langle \dot{\hat{A}}_i(t)\hat{A}_j(i\alpha)\rangle_c$$

$$= -\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha \left\langle \hat{A}_i(t)\frac{d}{du}\hat{A}_j(i\alpha)\right\rangle_c$$

$$= \frac{i}{\hbar\beta}\int_0^{\hbar\beta} d\alpha \left\langle \hat{A}_i(t)\frac{d}{d\alpha}\left(e^{-\frac{\alpha H}{\hbar}}\hat{A}_j(0)\,e^{\frac{\alpha H}{\hbar}}\right)\right\rangle_c$$

$$= \frac{i}{\hbar\beta}\int_0^{\hbar\beta} d\alpha \frac{d}{d\alpha}\left\langle \hat{A}_i(t)\,e^{-\frac{\alpha H}{\hbar}}\hat{A}_j(0)\,e^{\frac{\alpha H}{\hbar}}\right\rangle_c$$

$$= \frac{i}{\hbar\beta}\left\{\langle \hat{A}_i(t)\,e^{-\beta H}\hat{A}_j(0)\,e^{\beta H}\rangle_c - \langle \hat{A}_i(t)\hat{A}_j(0)\rangle\right\}$$

$$\Rightarrow \dot{C}_{ij}(t) = -\frac{i}{\hbar\beta}\left(\langle \hat{A}_i(t)\hat{A}_j(0)\rangle_c - \langle \hat{A}_i(t) e^{-\beta H} \hat{A}_j(0) e^{\beta H}\rangle_c \right)$$

Mas $\langle \hat{A}_i(t) e^{-\beta H} \hat{A}_j(0) e^{\beta H}\rangle_c = \mathrm{Tr}\left(e^{-\beta H}\hat{A}_i(t) e^{-\beta H}\hat{A}_j(0) e^{\beta H}\right)$

$$= \mathrm{Tr}\left(\hat{A}_i(t) e^{-\beta H}\hat{A}_j(0)\right) = \mathrm{Tr}\left(e^{-\beta H}\hat{A}_j(0)\hat{A}_i(t)\right)$$

$$\Rightarrow \dot{C}_{ij}(t) = -\frac{i}{\hbar\beta}\langle [\hat{A}_i(t), \hat{A}_j(0)]\rangle = -\frac{2i}{\beta}\chi''_{ij}(t)$$

$$\Rightarrow \chi''_{ij}(t) = \frac{1}{2\hbar}\langle [\hat{A}_i(t), \hat{A}_j(0)]\rangle \quad \text{e}$$

$$\chi_{ij}(t) = \frac{i\Theta(t)}{\hbar}\langle [\hat{A}_i(t), \hat{A}_j(0)]\rangle$$

Consequentemente, se $\hat{A}_i = \hat{A}_i^+$ temos

$$(\chi_{ij})^+ = -\frac{i\Theta(t)}{\hbar}\langle (\hat{A}_i(t)\hat{A}_j(0))^+ - (\hat{A}_j(0)\hat{A}_i(t))^+\rangle$$

$$= -\frac{i\Theta(t)}{\hbar}\langle \hat{A}_j(0)\hat{A}_i(t) - \hat{A}_i(t)\hat{A}_j(0)\rangle$$

$$= \frac{i\Theta(t)}{\hbar}\langle [\hat{A}_i(t), \hat{A}_j(0)]\rangle = \chi_{ij} = \chi_{ij}^*$$

$\Rightarrow \chi_{ij} \in \mathbb{R}$!

Seja $|n\rangle$ tq $H|n\rangle = E_n|n\rangle$

1° Termo do comutador: $S_{ij}(t) = \langle \hat{A}_i(t)\hat{A}_j(0)\rangle_c$

$$= \mathrm{Tr}\,\frac{e^{-\beta H}}{Z}\delta\hat{A}_i(t)\delta\hat{A}_j(0) = \sum_{\substack{nm\\k}} \langle n|\frac{e^{-\beta H}}{Z}|m\rangle\langle m|e^{\frac{iHt}{\hbar}}\delta A_i(0)$$

$$e^{-iHt/\hbar}|k\rangle\langle k|\delta\hat{A}_j(0)|n\rangle$$

$$= \sum_{nm} \frac{e^{-\beta E_n}}{Z} e^{i(E_n - E_m)\frac{t}{\hbar}} \langle n | \delta\hat{A}_i(0) | m \rangle \langle m | \delta\hat{A}_j(0) | n \rangle$$

$$\Rightarrow S_{ij}(\omega) = \frac{1}{Z} \sum_{nm} e^{-\beta E_n} \delta\left(\omega + \frac{E_n - E_m}{\hbar}\right) \langle n | \delta\hat{A}_i(0) | m \rangle \langle m | \delta\hat{A}_j(0) | n \rangle$$

2º termo: $S_{ji}(-t)$, mas $S_{ij}(t) = \int S_{ij}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}$

$$\Rightarrow S_{ji}(-t) = \int_{-\infty}^{\infty} S_{ji}(\omega) e^{i\omega t} \frac{d\omega}{2\pi} = -\int_{\infty}^{-\infty} S_{ji}(-\omega) e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$= \int_{-\infty}^{\infty} S_{ji}(-\omega) e^{-i\omega t} \frac{d\omega}{2\pi} \Rightarrow$$

$$S_{ji}(-\omega) = \sum_{nm} \frac{e^{-\beta E_n}}{Z} \delta\left(-\omega + \frac{E_n - E_m}{\hbar}\right) \langle n | \delta\hat{A}_j(0) | m \rangle \langle m | \delta\hat{A}_i(0) | n \rangle$$

$m \leftrightarrow n$

$$= \sum_{nm} \frac{e^{-\beta E_m}}{Z} \delta\left(-\omega + \frac{E_m - E_n}{\hbar}\right) \langle m | \delta\hat{A}_j(0) | n \rangle \langle n | \delta\hat{A}_i(0) | m \rangle$$

$$= \sum_{nm} \frac{e^{-\beta E_n}}{Z} e^{-\beta\hbar\omega} \delta\left(\omega + \frac{E_n - E_m}{\hbar}\right) \langle n | \delta\hat{A}_i(0) | m \rangle \langle m | \delta\hat{A}_j(0) | n \rangle$$

$$\Rightarrow \boxed{\chi''_{ij}(\omega) = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right) S_{ij}(\omega)}$$ Teo. Flutuação-Dissipação.

Para a função simetrizada $\varphi_{ij}(t) = \left\langle \frac{1}{2}\{\hat{A}_i(t), \hat{A}_j(t)\} \right\rangle - \langle \hat{A}_i \rangle \langle \hat{A}_j \rangle$

Temos $\boxed{\varphi_{ij}(\omega) = \hbar \coth \frac{\beta\hbar\omega}{2} \chi''_{ij}(\omega)}$