Introduction to Green's functions methods for valence spectroscopies

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Miniworkshop REST in Paris

Common problems and solutions in core and valence theoretical spectroscopies

Paris, 7-8 December 2017

ETSF
European Theoretical Spectroscopy Facility

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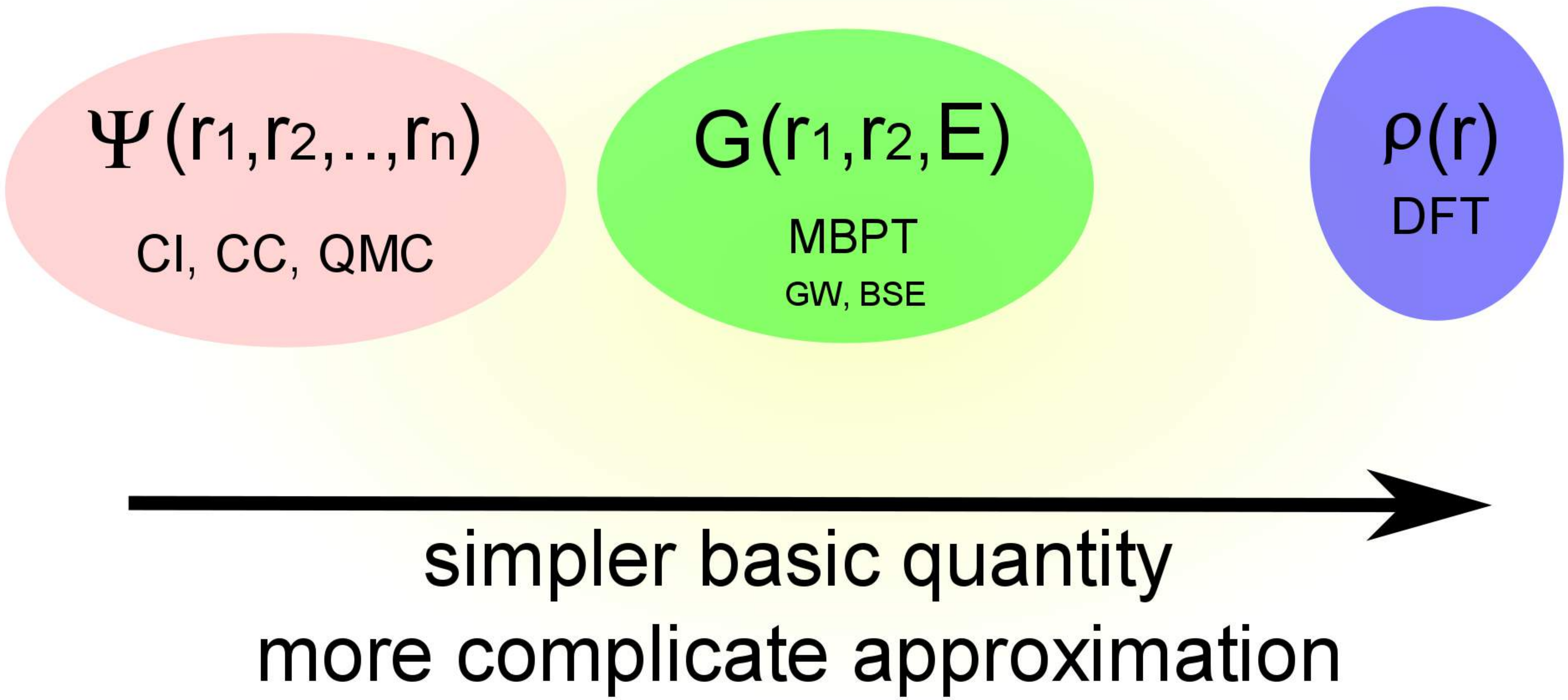
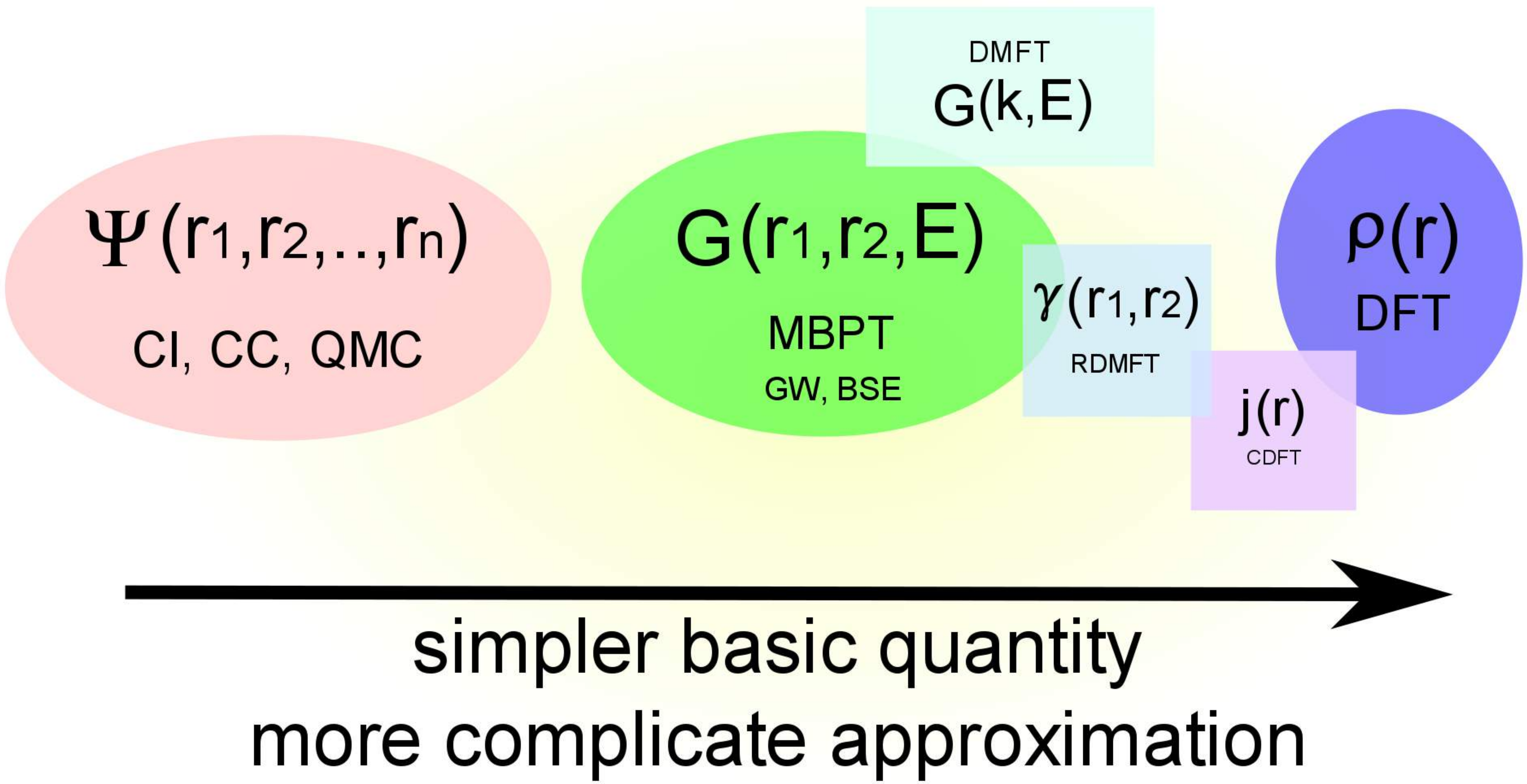

Ψ(r1,r2,..,rn)
CI, CC, QMC
G(r1,r2,E)
MBPT
GW, BSE
ρ(r)
DFT
simpler basic quantity
more complicate approximation



DMFT
G(k,E)
Ψ(r1,r2,..,rn)
CI, CC, QMC
G(r1,r2,E)
MBPT
GW, BSE
γ(r1,r2)
RDMFT
ρ(r)
DFT
j(r)
CDFT
simpler basic quantity
more complicate approximation

$$\Sigma(1,2) = i\int d(34) G(1,3)\Gamma(3,2,4)W(4,1^+)$$

$$G(1,2) = G^0(1,2) + \int d(34) G^0(1,3)\Sigma(3,4)G(4,2)$$

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4567)\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7,3)$$

$$P(1,2) = -i\int d(34) G(1,3)G(4,1^+)\Gamma(3,4,2)$$

$$W(1,2) = v(1,2) + \int d(34) v(1,3)P(3,4)W(4,2)$$

Hedin's equations

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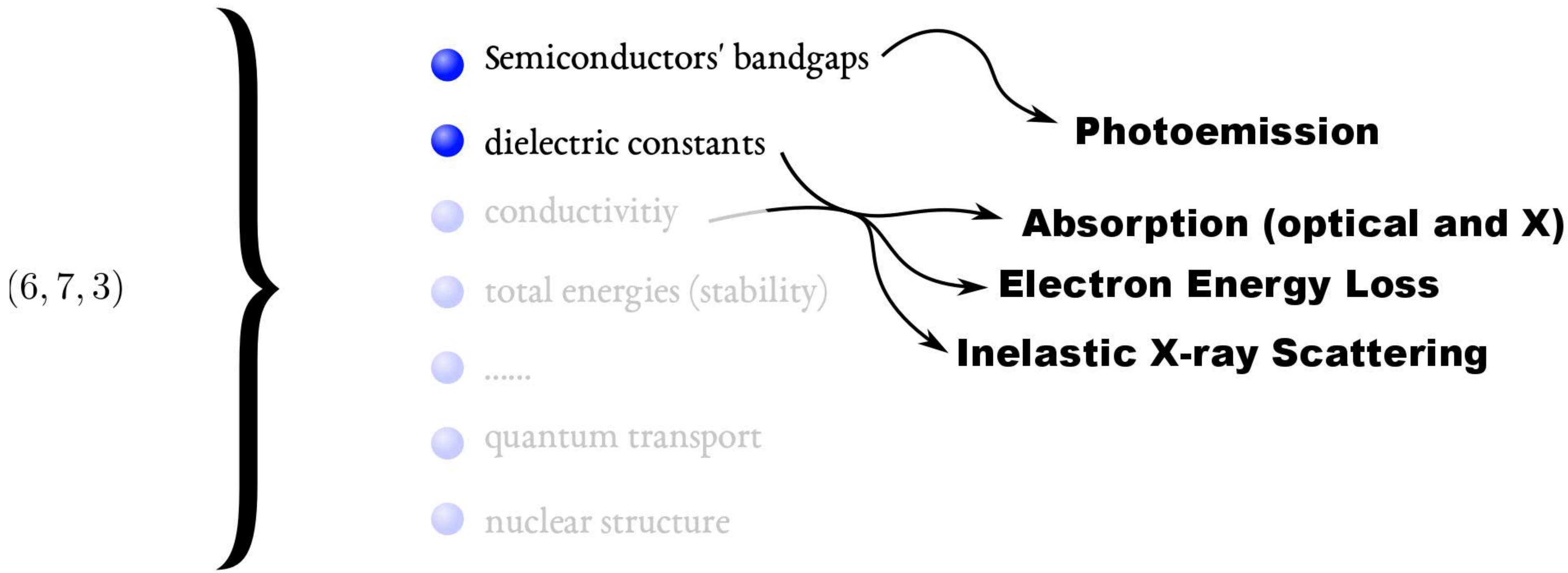
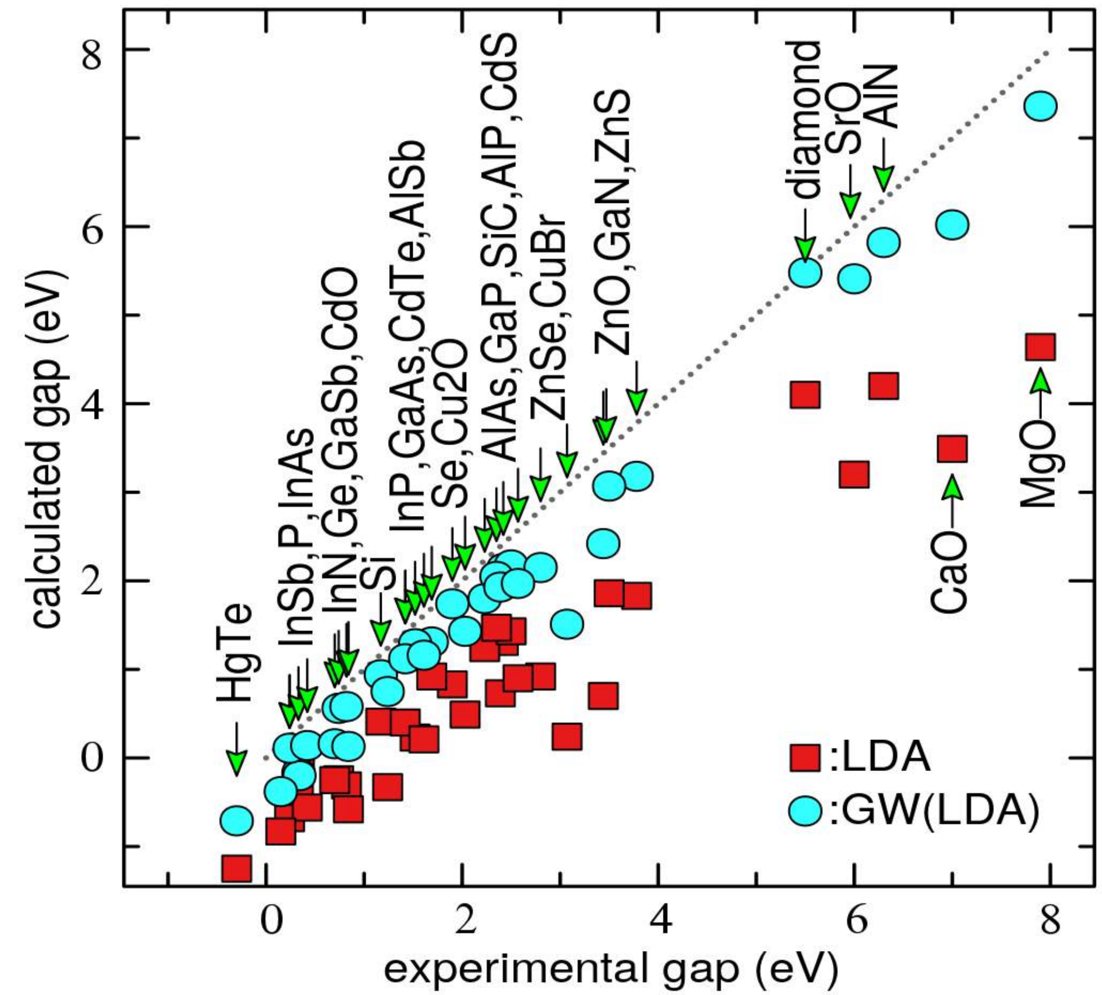
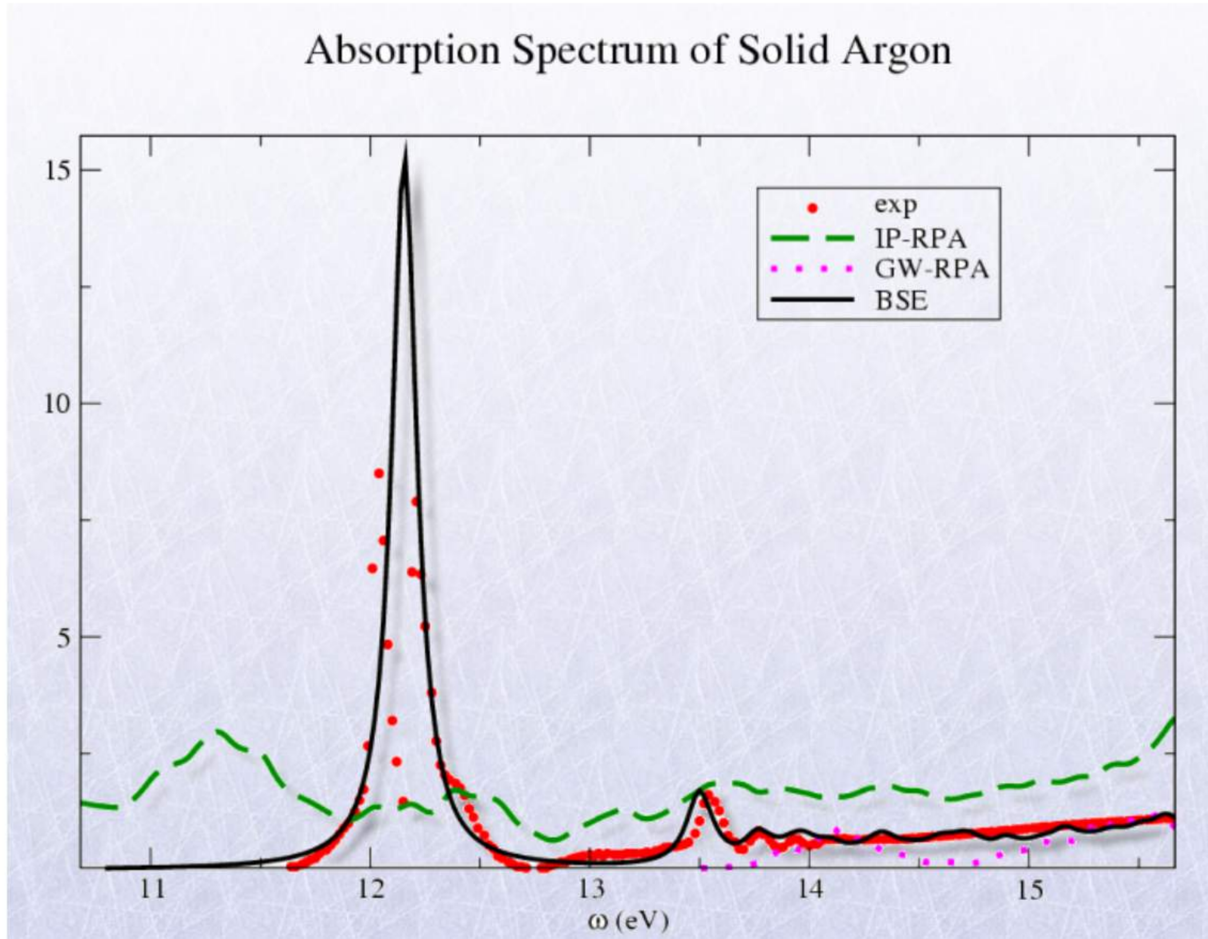
- Semiconductors' bandgaps
- dielectric constants
- conductivitiy
- total energies (stability)
- ......
- quantum transport
- nuclear structure



(6, 7, 3)
Semiconductors' bandgaps
dielectric constants
conductivitiy
total energies (stability)
......
quantum transport
nuclear structure
Photoemission
Absorption (optical and X)
Electron Energy Loss
Inelastic X-ray Scattering

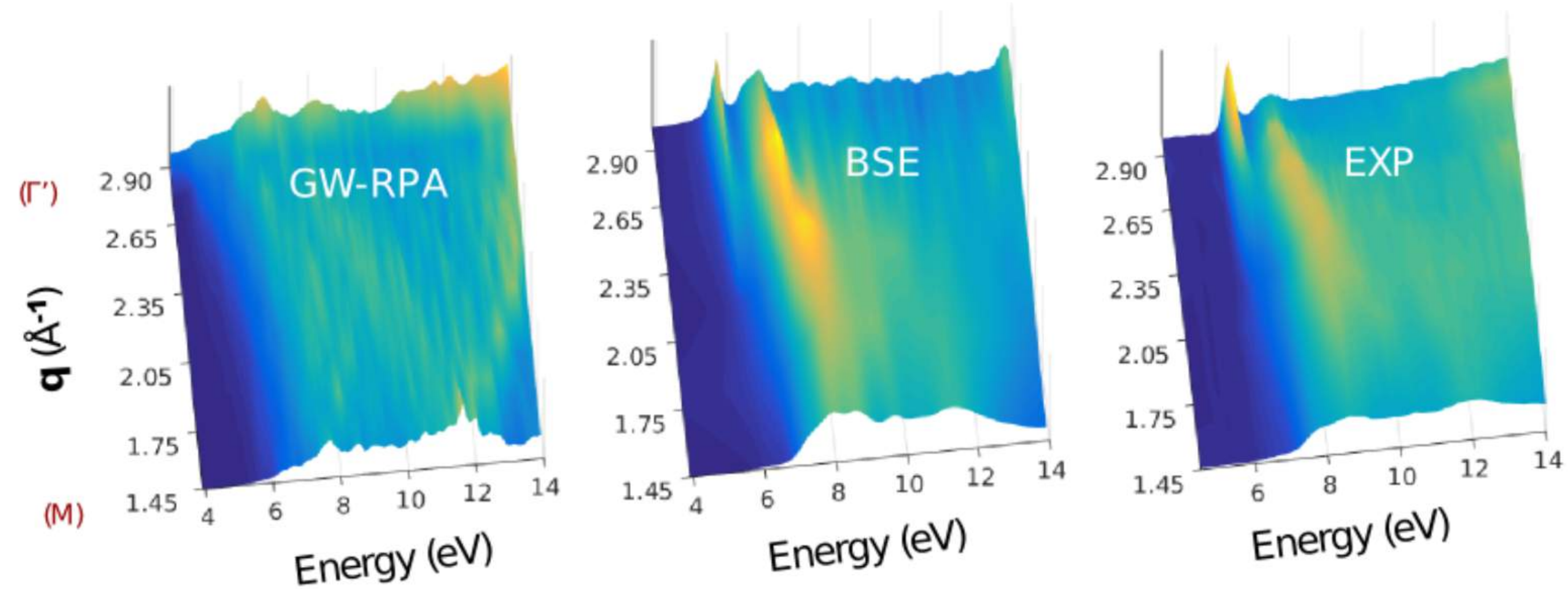


M. van Schilfgaarde *et al.*, PRL **96**, 226402 (2006).



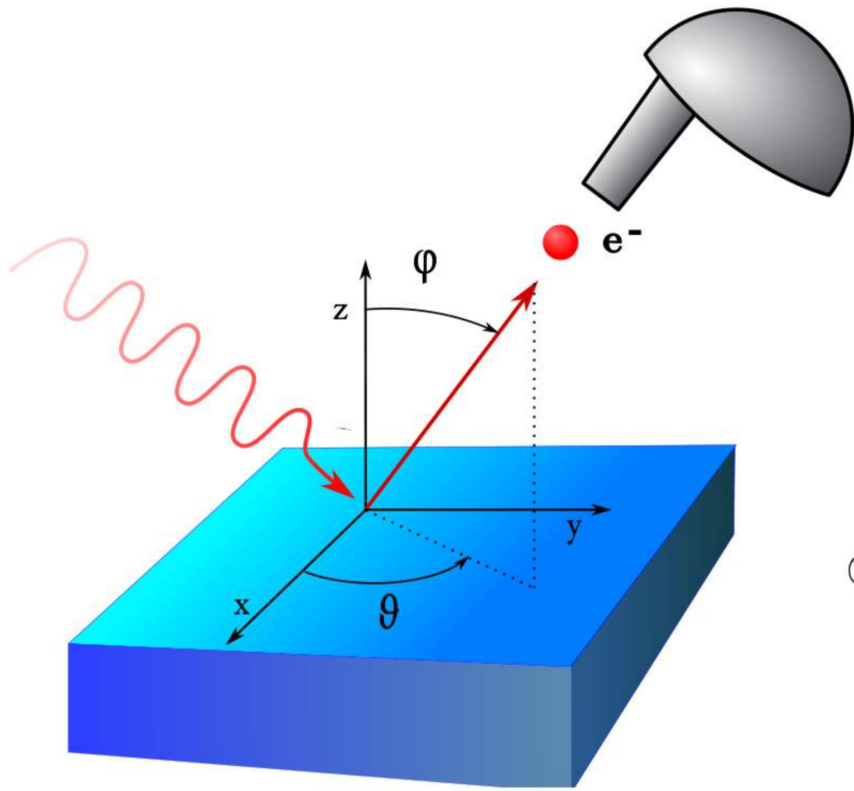
F. Sottile *et al.*, PRB **76**, 116103 (2007).

Exciton dispersion of h BN



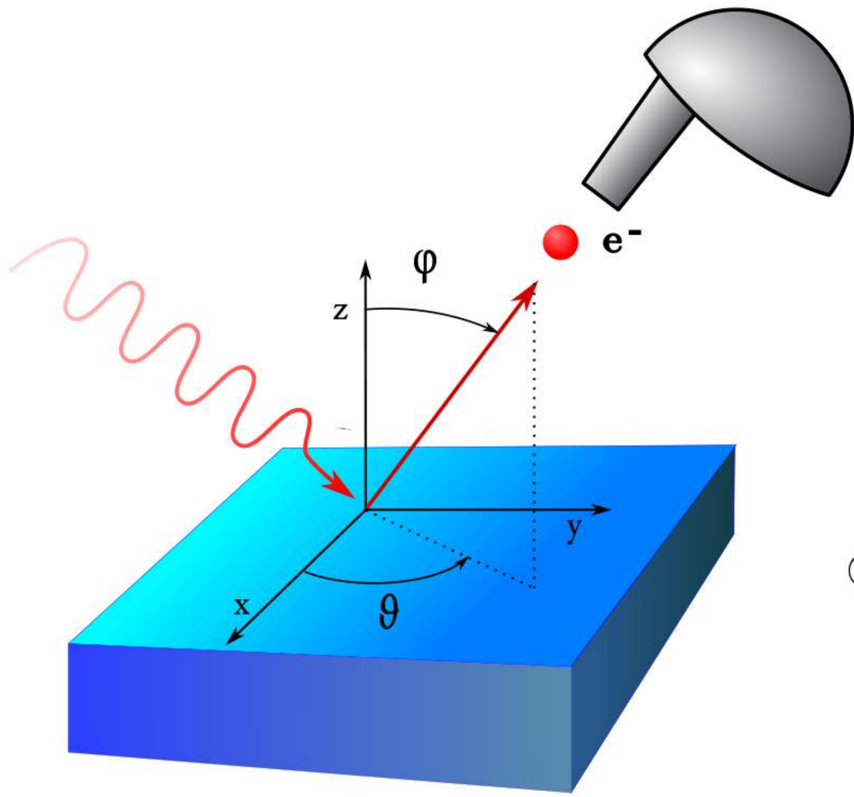
ID20 beamline 5/2015

G. Fugallo et al. Phys. Rev. B **92**, 165122 (2015)



Photoemission spectroscopy

$$\propto |\langle\Psi_f|\Delta|\Psi_i\rangle|^2\delta(\omega - \frac{\mathbf{p}^2}{2} - E(N-1,s) + E(N))$$



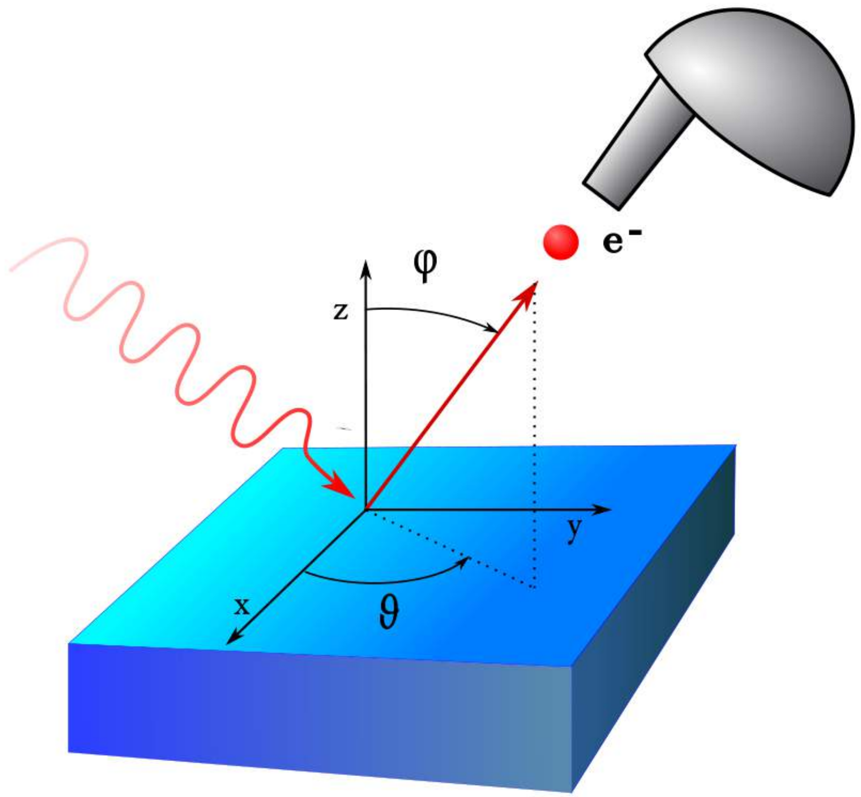
Photoemission spectroscopy

$$\propto |\langle \Psi_f|\Delta|\Psi_i\rangle|^2 \delta(\omega - \frac{\mathbf{p}^2}{2} - E(N-1,s) + E(N))$$

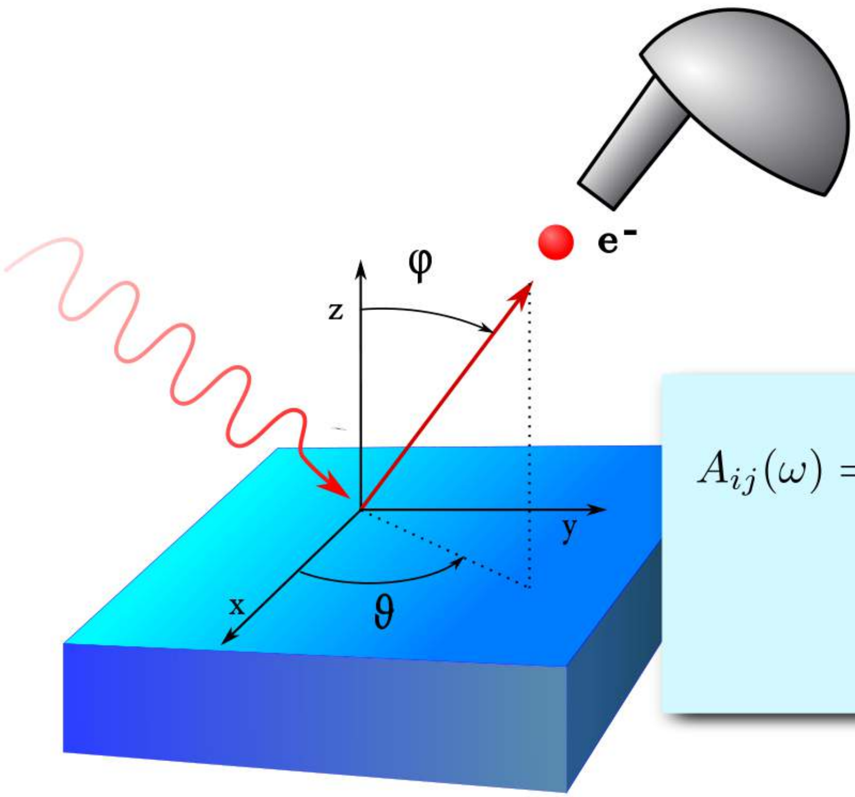
$$\Delta = \sum_{ij} \langle i|\mathbf{A}\mathbf{p} + \mathbf{p}\mathbf{A}|j\rangle\, c_i^\dagger c_j = \sum_{ij} \Delta_{ij} c_i^\dagger c_j$$

$$\Psi_i = |N\rangle$$

$$\Psi_f = c_{\mathbf{p}}^\dagger\, |N-1,s\rangle$$



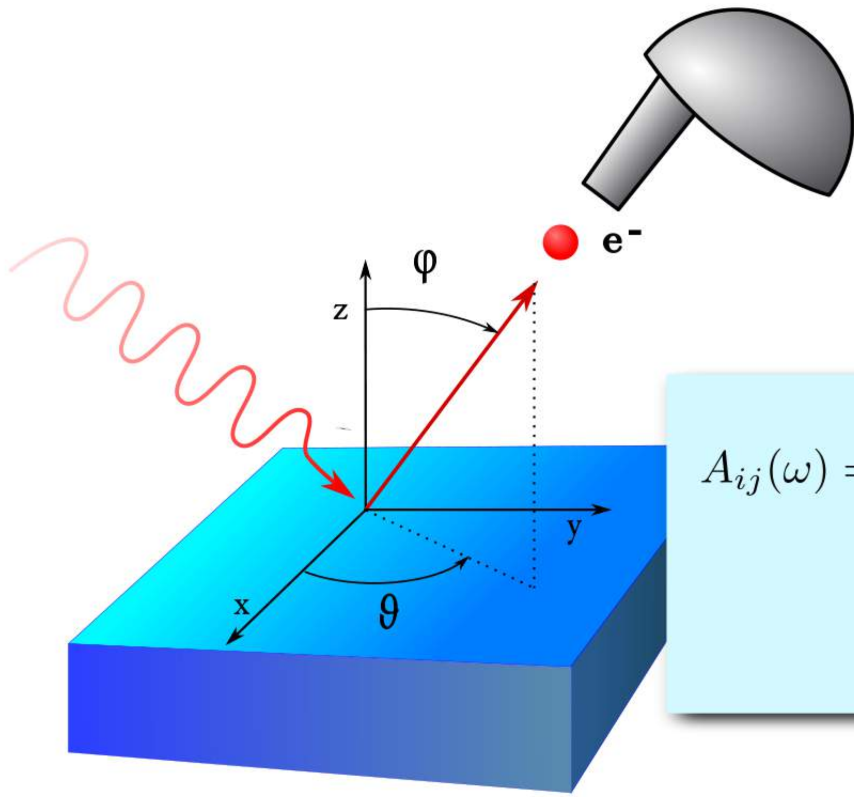
$$\propto \sum_{ij} \Delta_{\mathbf{p}j} A_{ij}(\frac{\mathbf{p}^2}{2} - \omega)\Delta_{i\mathbf{p}}$$



$$\propto \sum_{ij} \Delta_{\mathbf{p}j} A_{ij}(\frac{\mathbf{p}^2}{2} - \omega)\Delta_{i\mathbf{p}}$$

$$A_{ij}(\omega) = \sum_s \langle N| c_i^\dagger |N-1, s\rangle \langle N-1, s| c_j |N\rangle \, \delta(\omega - E(N-1, s) + E(N))$$

Spectral function (intrinsic part of PES)



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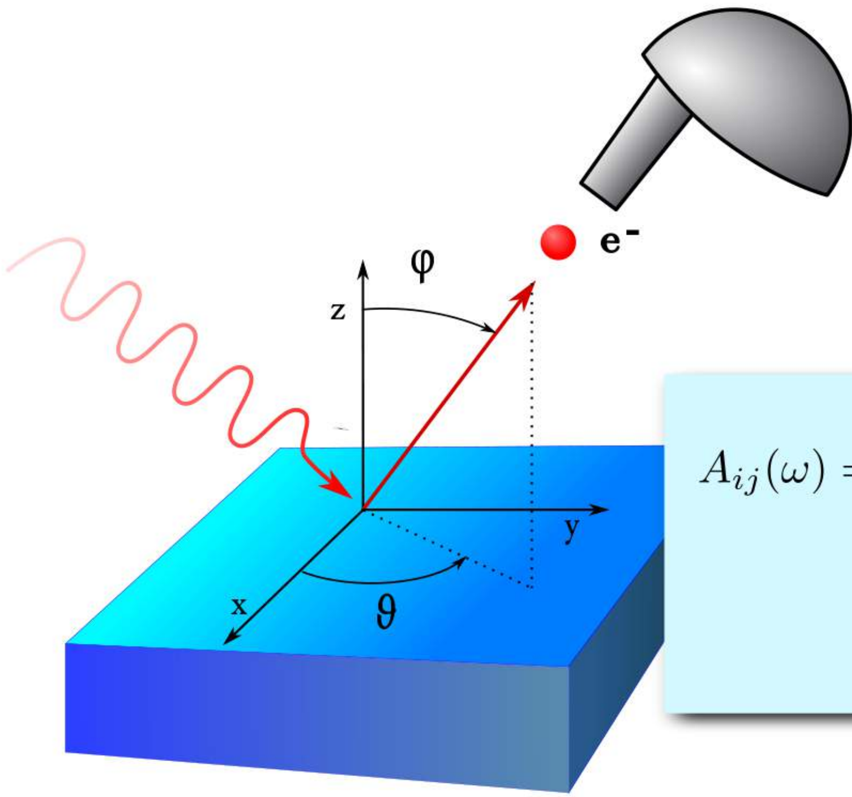
Spectral function (intrinsic part of PES)

$$G_{ij}^{\text{hole}}(\omega) = i \sum_{s} \frac{\langle N|\, c_i^\dagger \,|N-1,s\rangle \, \langle N-1,s|\, c_j \,|N\rangle}{\omega - E(N-1,s) + E(N) - i\eta}$$



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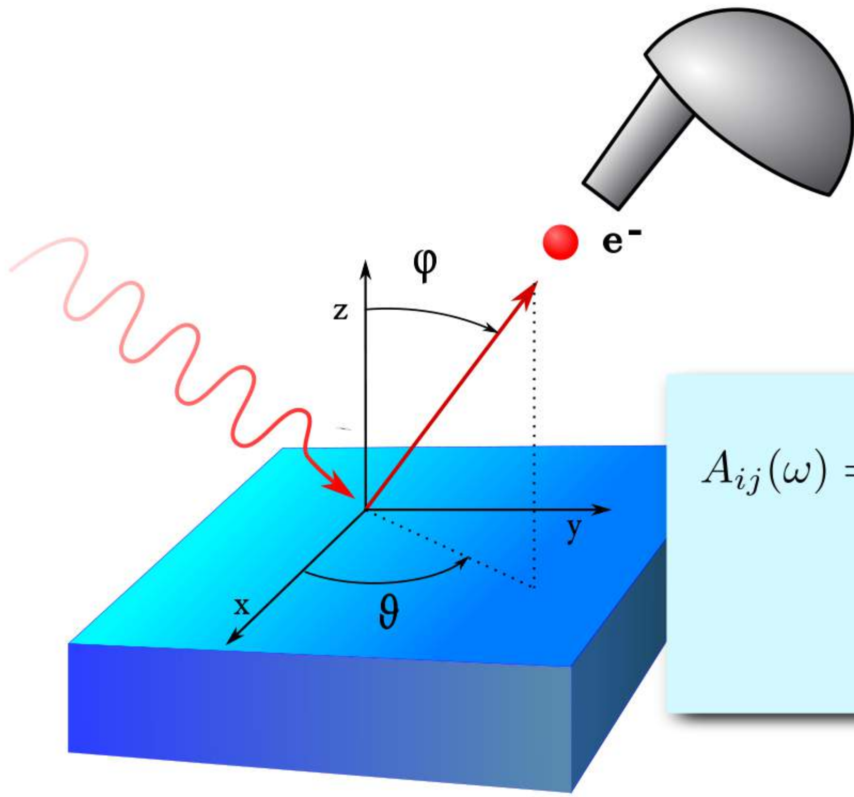
$$A_{ij}(\omega) = \frac{1}{\pi}\text{Im}\left[G_{ij}^{\text{hole}}(\omega)\right]$$

Direct Photo-emission



$$\propto \sum_{ij} \Delta_{\mathbf{p}j} A_{ij}\left(\frac{\mathbf{p}^2}{2} - \omega\right) \Delta_{i\mathbf{p}}$$

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Spectral function (intrinsic part of PES)

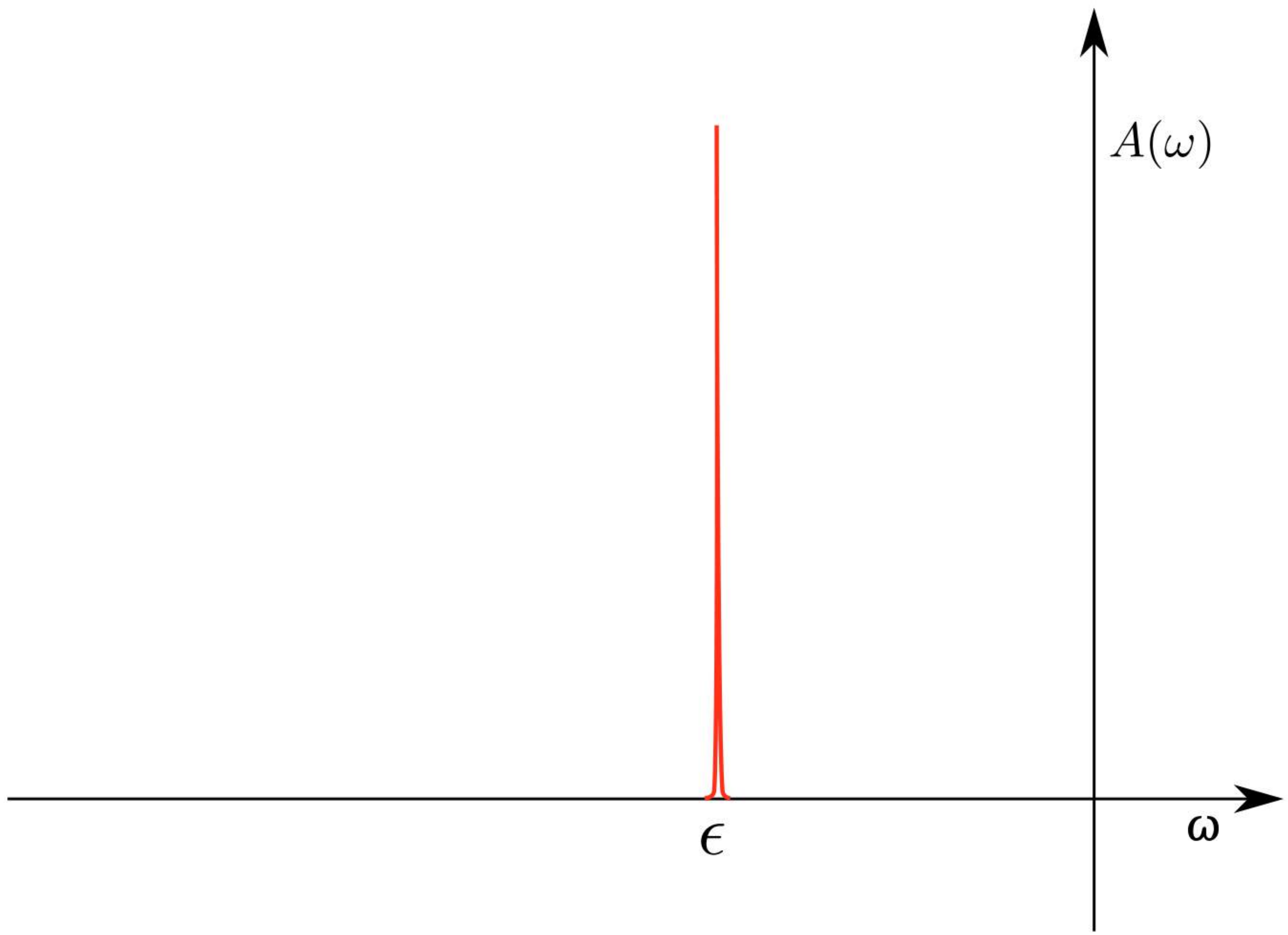
$$G_{ij}^{\text{hole}}(\omega) = i \sum_s \frac{\langle N| c_i^\dagger |N-1,s\rangle \langle N-1,s| c_j |N\rangle}{\omega - E(N-1,s) + E(N) - i\eta}$$

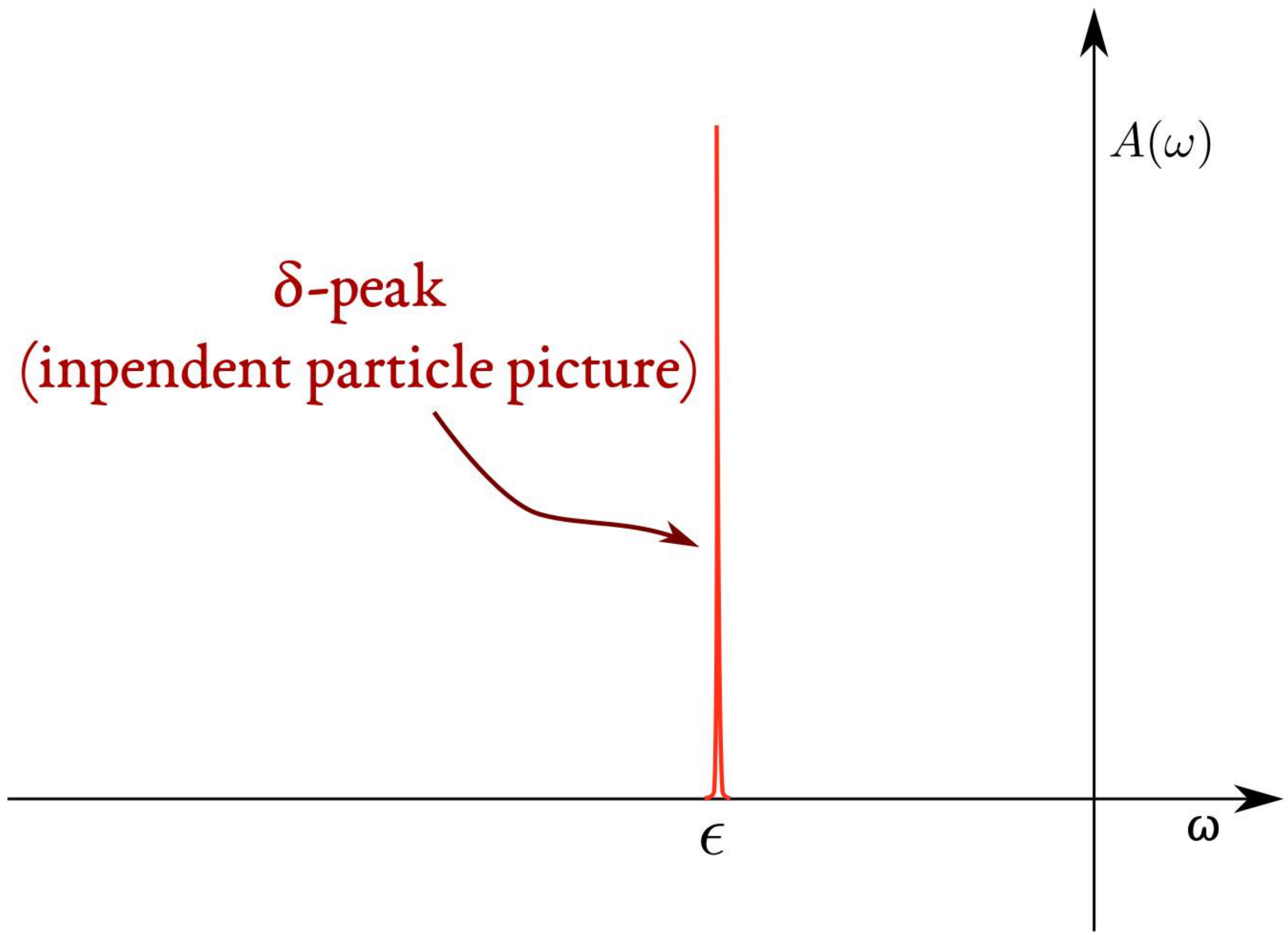
$$A_{ij}(\omega) = \frac{1}{\pi} \text{Im}\left[G_{ij}^{\text{hole}}(\omega)\right]$$

Direct Photo-emission

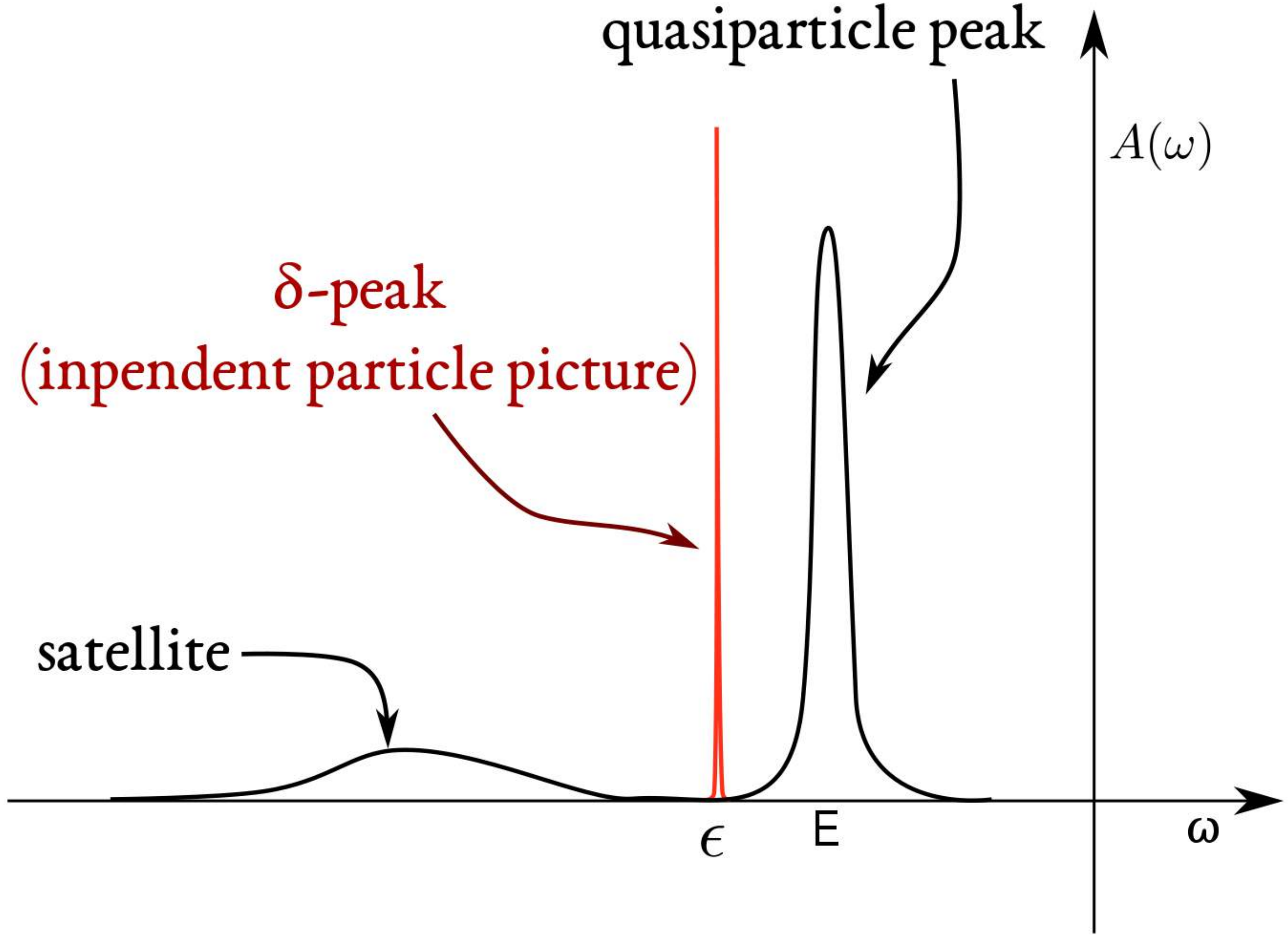
$$A_{ij}(\omega) = -\frac{1}{\pi} \text{Im}\left[G_{ij}^{\text{el}}(\omega)\right]$$

Inverse Photo-emission


A(ω)
ϵ
ω



A(ω)
δ-peak
(inpendent particle picture)
ϵ
ω


quasiparticle peak
$A(\omega)$
δ-peak
(inpendent particle picture)
satellite
ϵ
E
ω

$$G(\mathbf{r},\mathbf{r}',\omega) = i\sum_s \frac{\langle N|\,\hat{\psi}_i^\dagger(\mathbf{r})\,|N\pm 1,s\rangle\,\langle N\pm 1,s|\,\hat{\psi}_j(\mathbf{r}')\,|N\rangle}{\omega - E(N\pm 1,s) + E(N) \mp i\eta}$$

$$
|N\rangle \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(\mathbf{r}_1) & \psi_{\alpha_1}(\mathbf{r}_2) & .. & \psi_{\alpha_1}(\mathbf{r}_n) \\ \psi_{\alpha_2}(\mathbf{r}_1) & \psi_{\alpha_2}(\mathbf{r}_2) & .. & \psi_{\alpha_2}(\mathbf{r}_n) \\ .. & .. & .. & .. \\ \psi_{\alpha_n}(\mathbf{r}_1) & \psi_{\alpha_n}(\mathbf{r}_2) & .. & \psi_{\alpha_n}(\mathbf{r}_n) \end{vmatrix}
$$

$$
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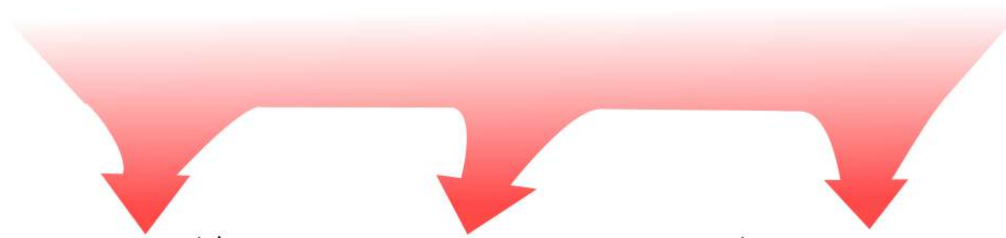

$$G(\mathbf{r}, \mathbf{r}', \omega) = i \sum_s \frac{\langle N | \hat{\psi}_i^\dagger(\mathbf{r}) | N \pm 1, s\rangle \langle N \pm 1, s | \hat{\psi}_j(\mathbf{r}') | N\rangle}{\omega - E(N \pm 1, s) + E(N) \mp i\eta}$$

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$$G^0(\mathbf{r}, \mathbf{r}', \omega) = i \sum_s \frac{\psi_s^*(\mathbf{r})\psi_s(\mathbf{r}')}{\omega - \epsilon_s \mp i\eta}$$

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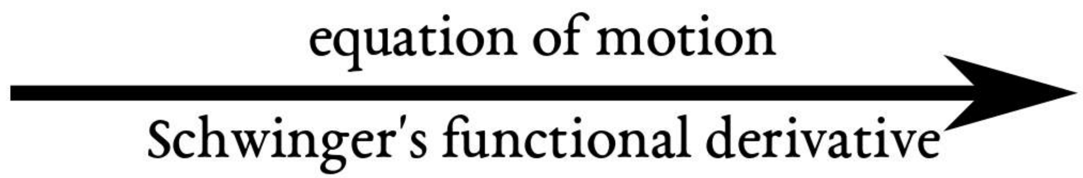
$\psi_s(\mathbf{r}), \epsilon_s$

Hartree, HF, DFT-LDA

calculations

$$\frac{1, s\rangle \langle N \pm 1, s| \hat{\psi}_j(\mathbf{r}') |N\rangle}{\pm 1, s) + E(N) \mp i\eta}$$



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$$W(1,2) = \int d(3)\varepsilon^{-1}(1,3)v(3,2) \quad ; \quad \varepsilon = \delta(1,2) - \int d(3)v(1,3)P(3,2)$$

Hedin's equations

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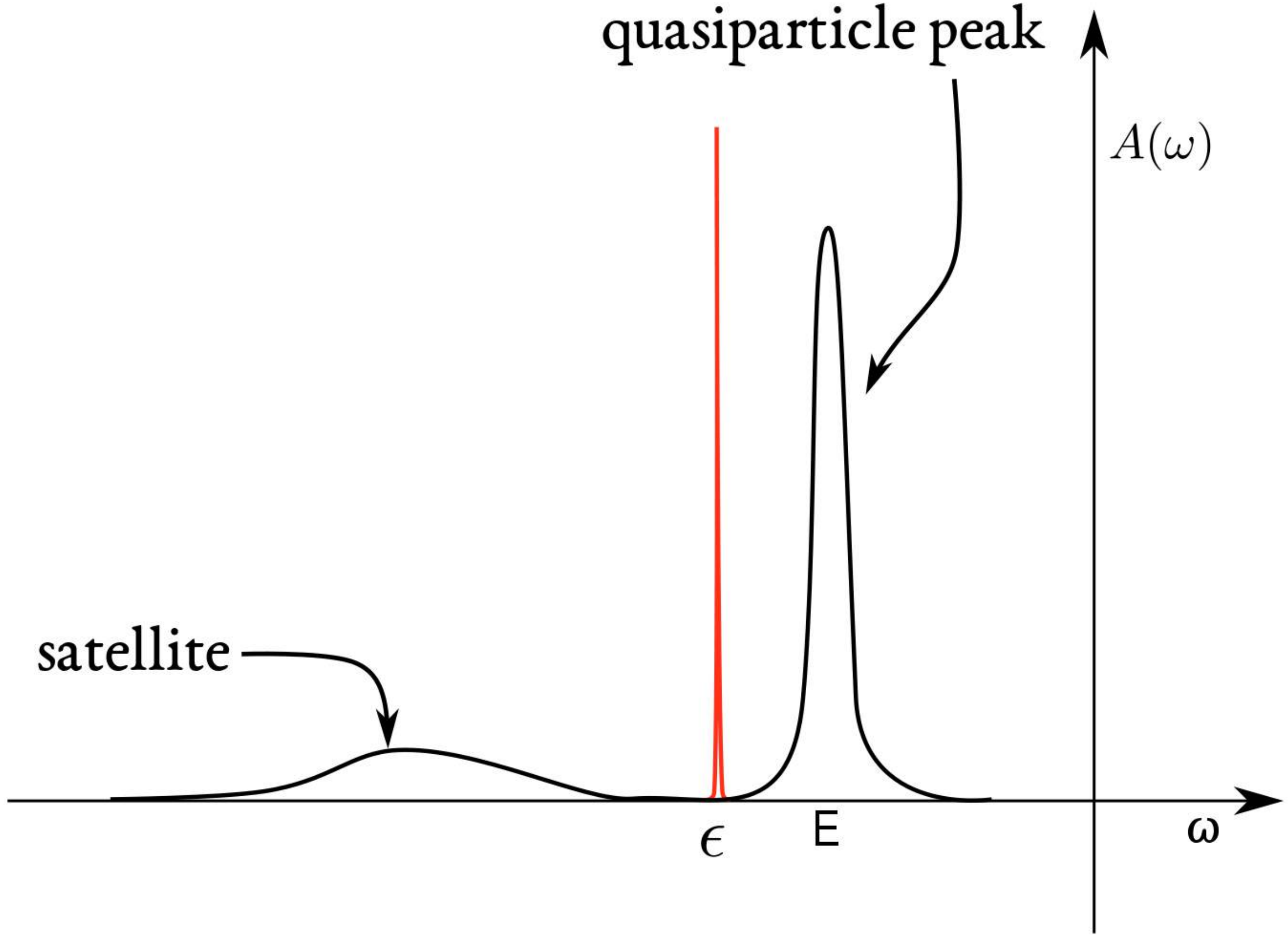
quasiparticle peak
$A(\omega)$
satellite
ϵ
E
ω

Let's focus on the band-structure

Quasiparticle (approx.) equation

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\psi_i(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}') = E_i\psi_i(\mathbf{r})$$

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non-local
non-hermitian
energy dependent

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non-local
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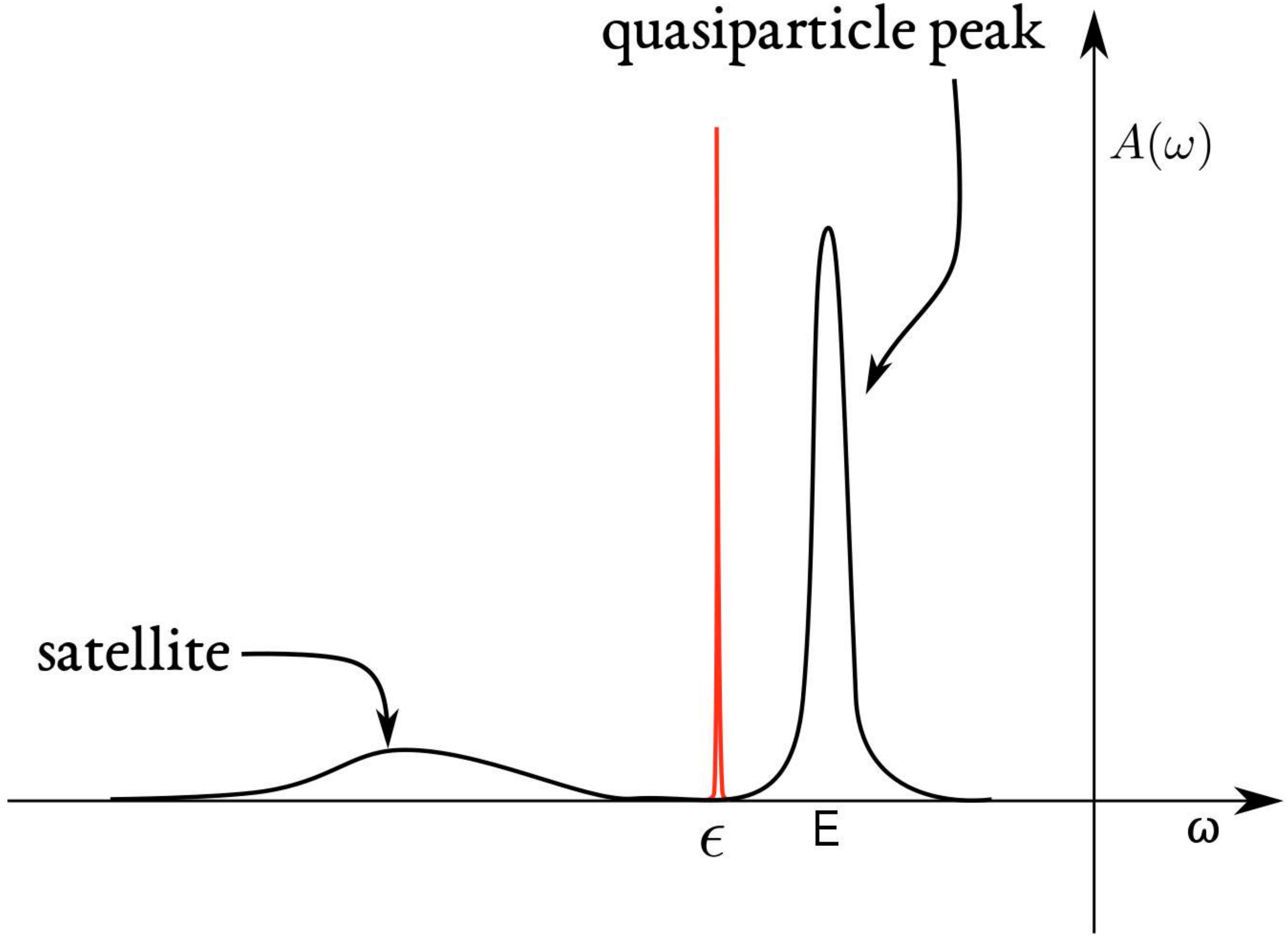
imaginary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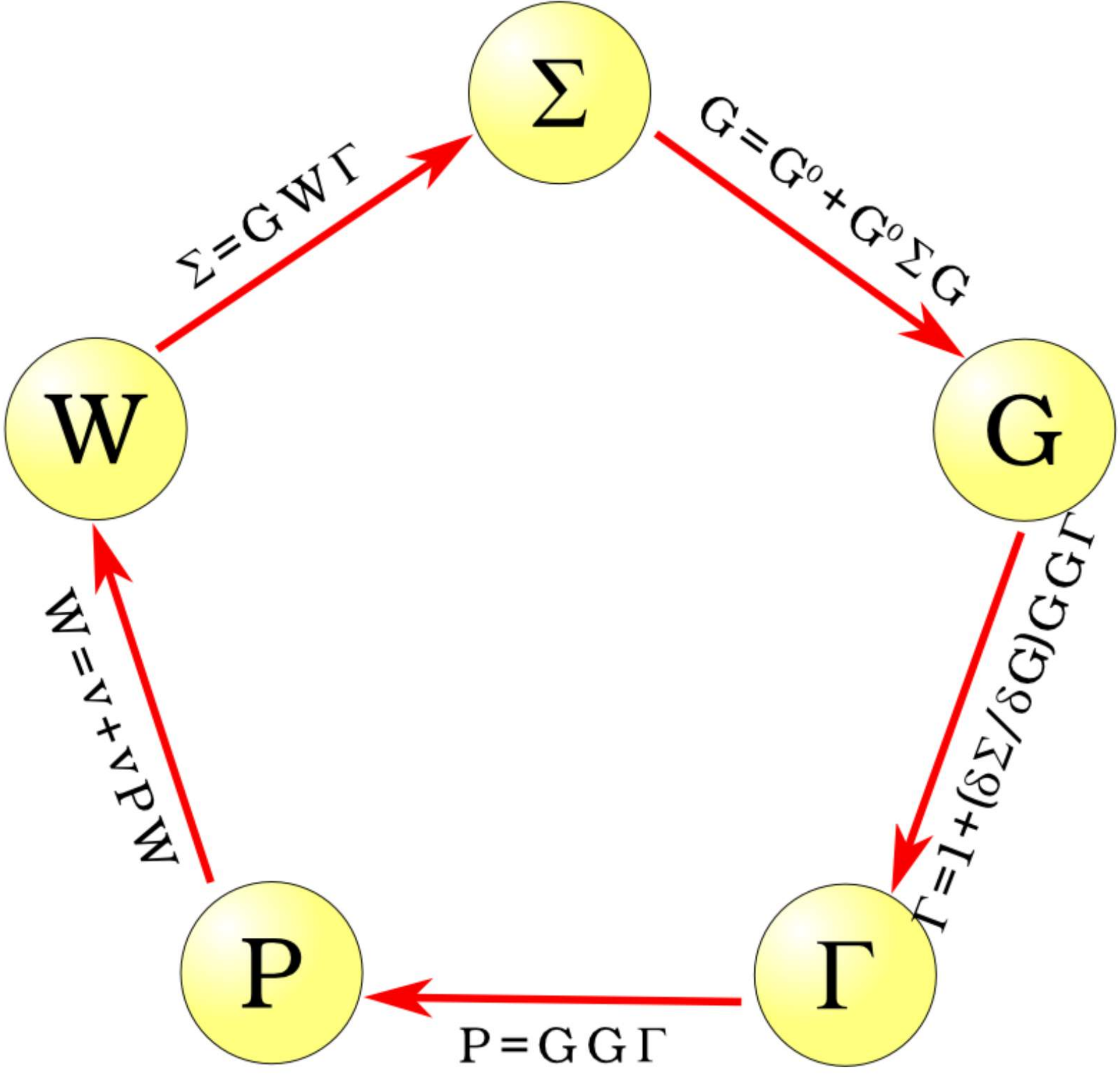
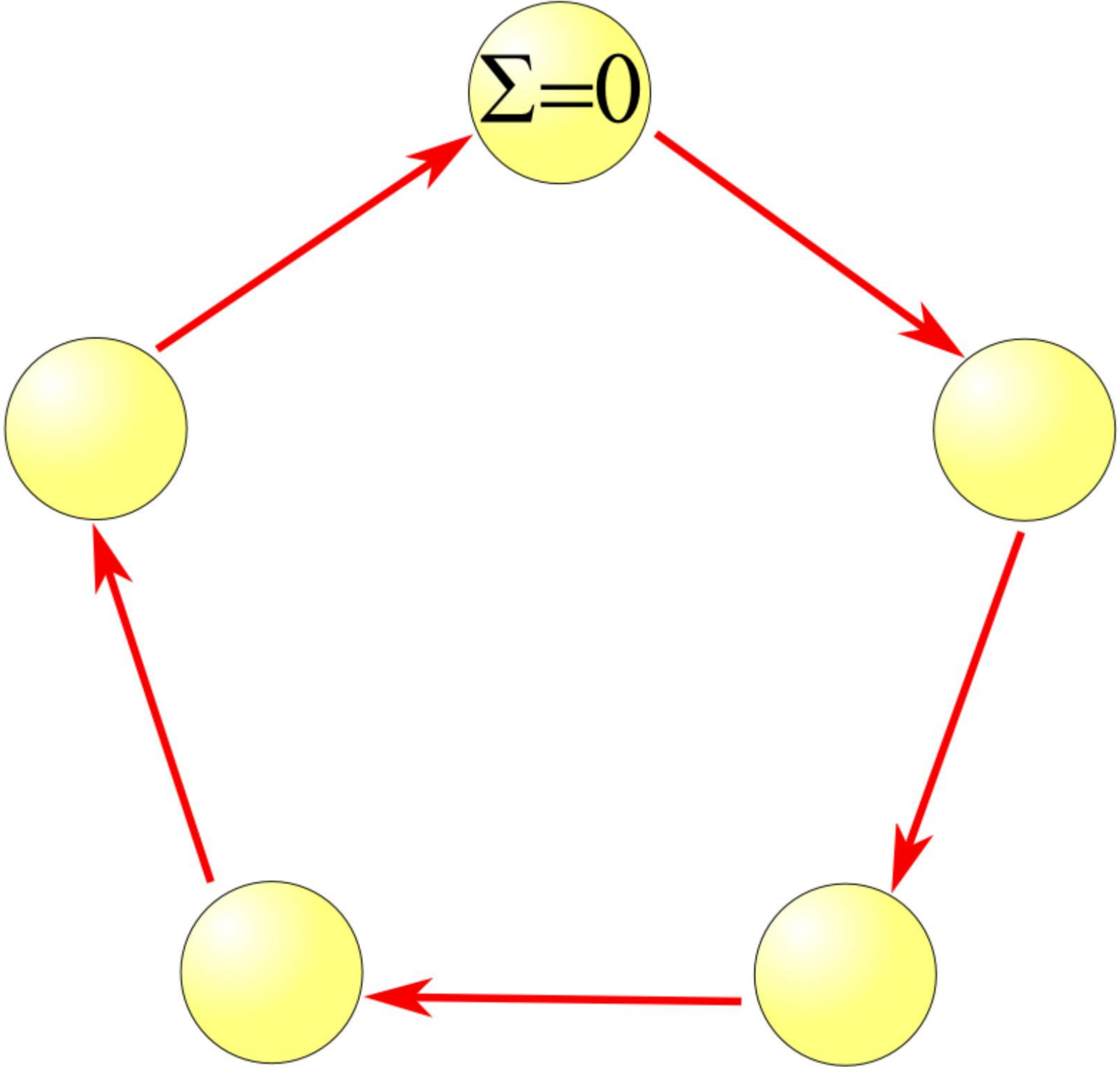
$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\phi_i(\mathbf{r}) + V_{xc}([n],\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

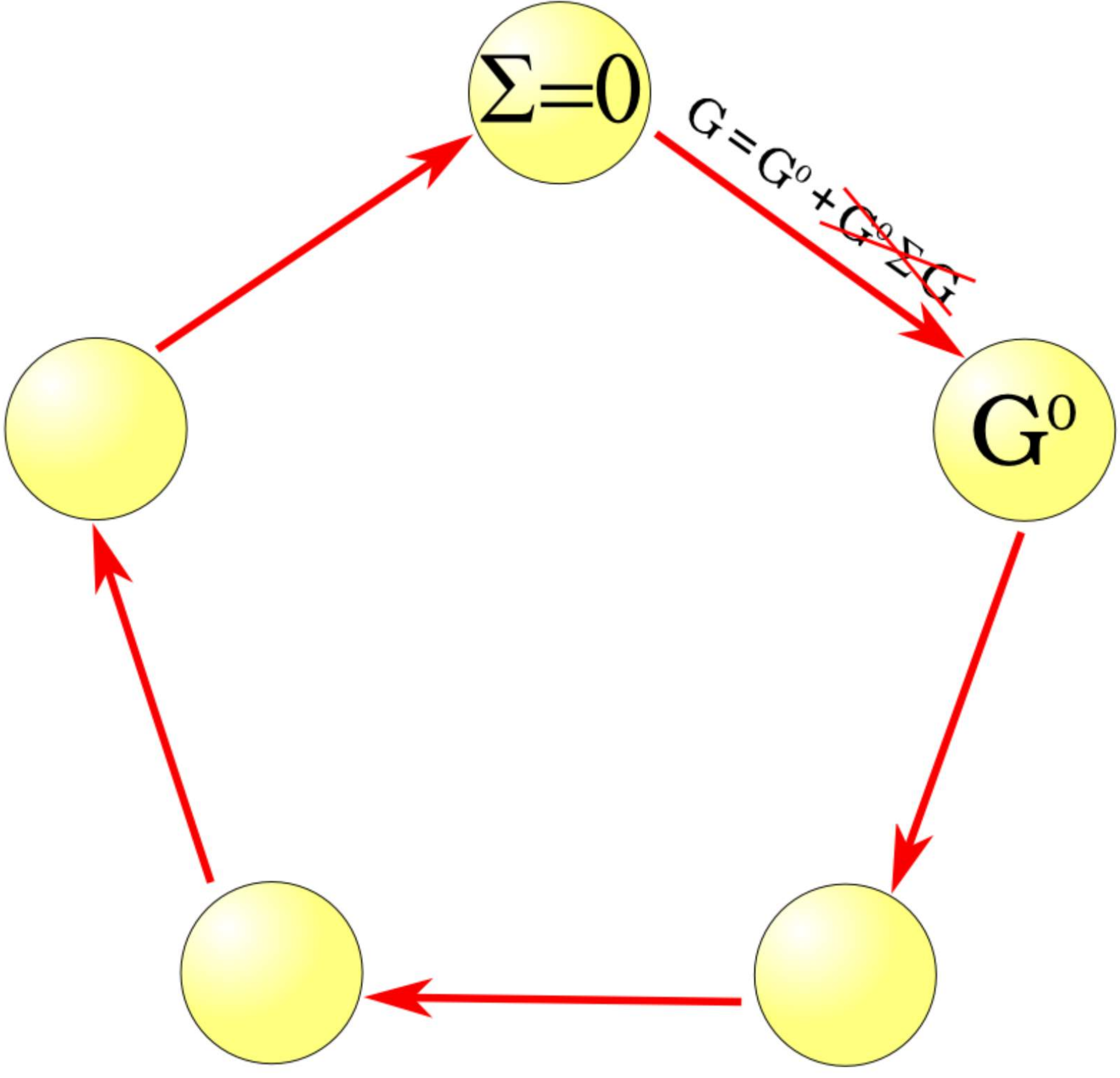
DFT Kohn Sham equations

What about $\sum$?

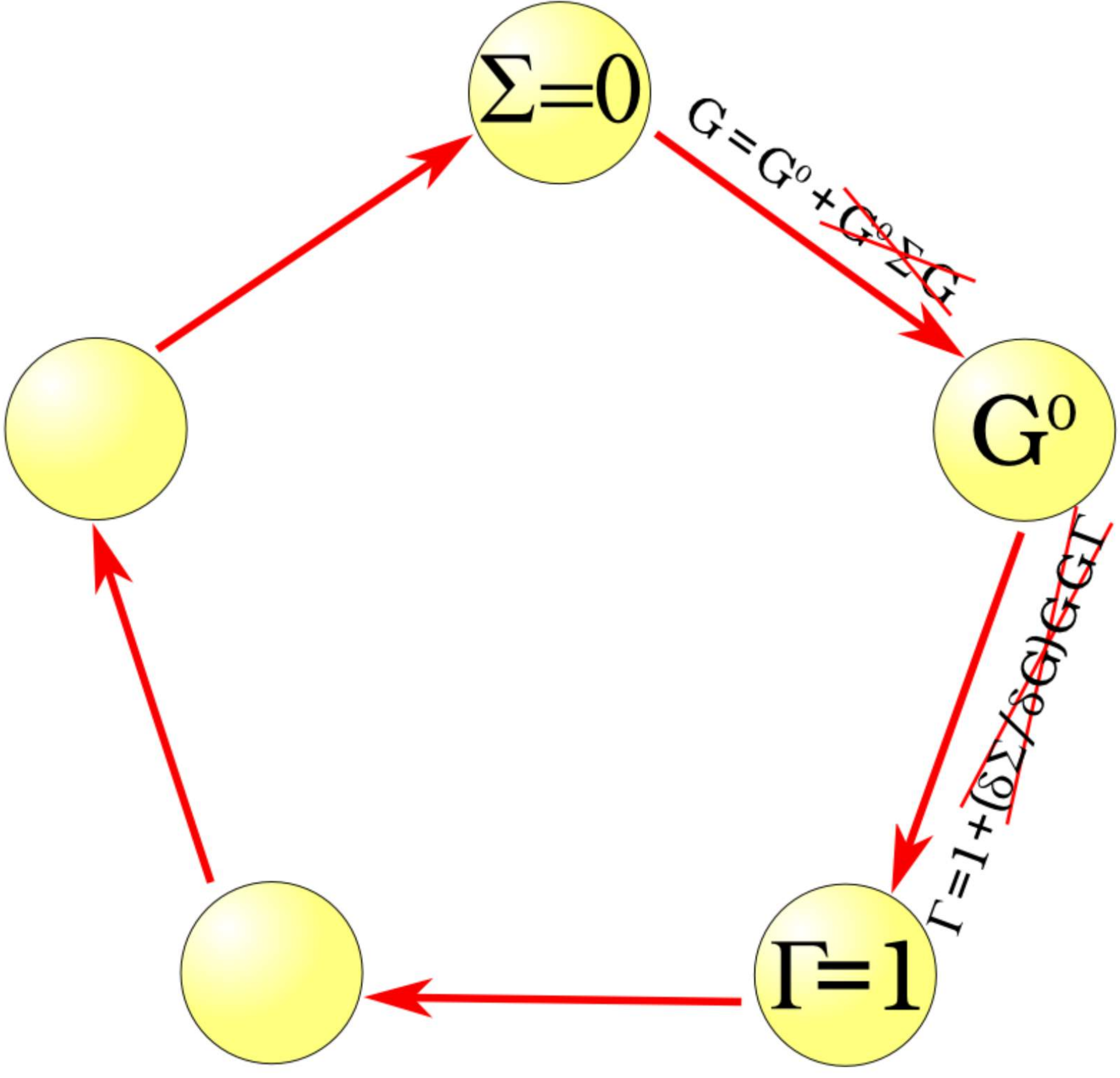


Σ
G
Γ
P
W
G = G0 + G0 Σ G
Γ = 1 + (δΣ/δG) G G Γ
P = G G Γ
W = v + v P W
Σ = G W Γ

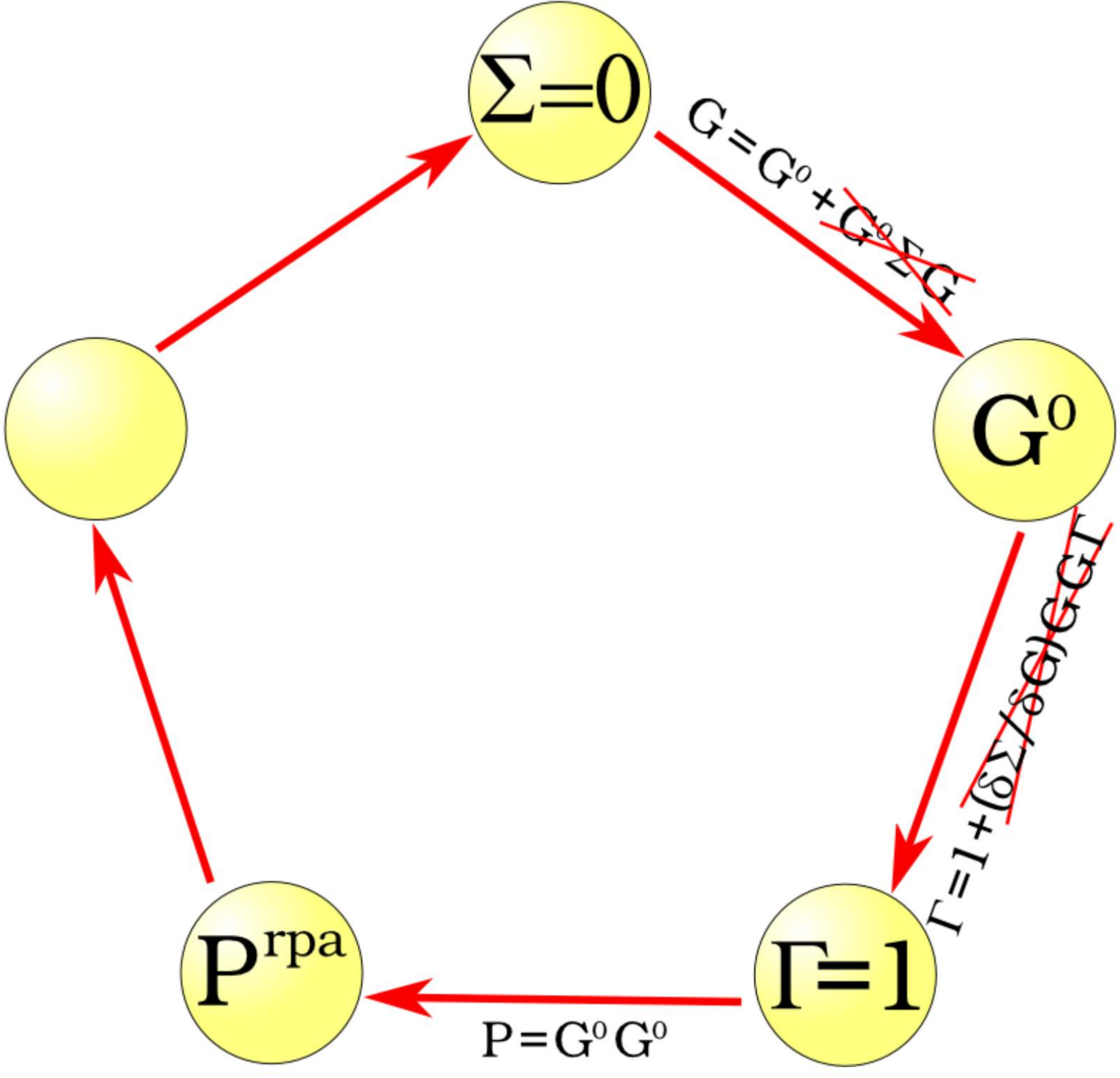

Σ=0



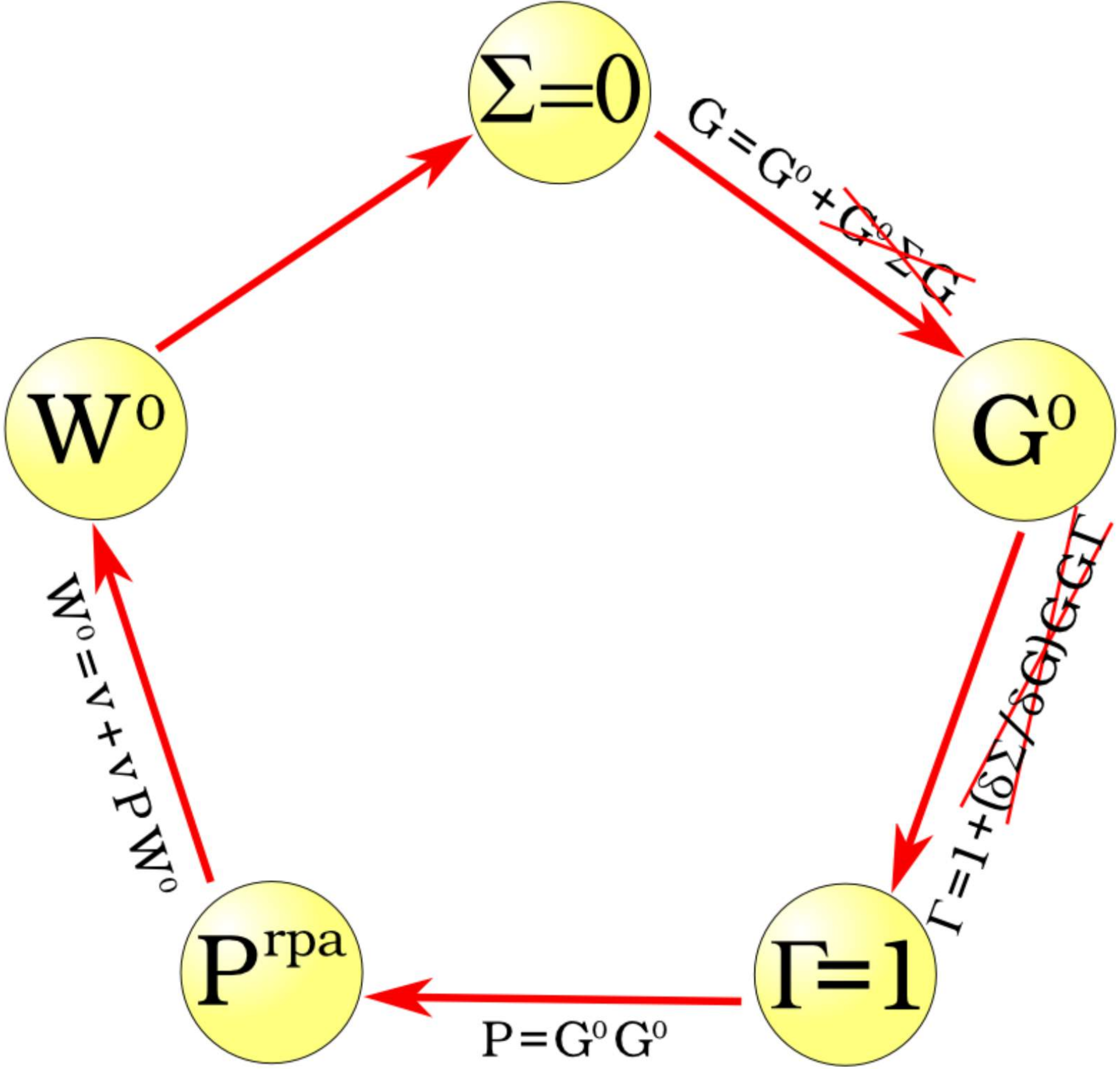
Σ=0
G = G⁰ + G⁰ΣG
G⁰



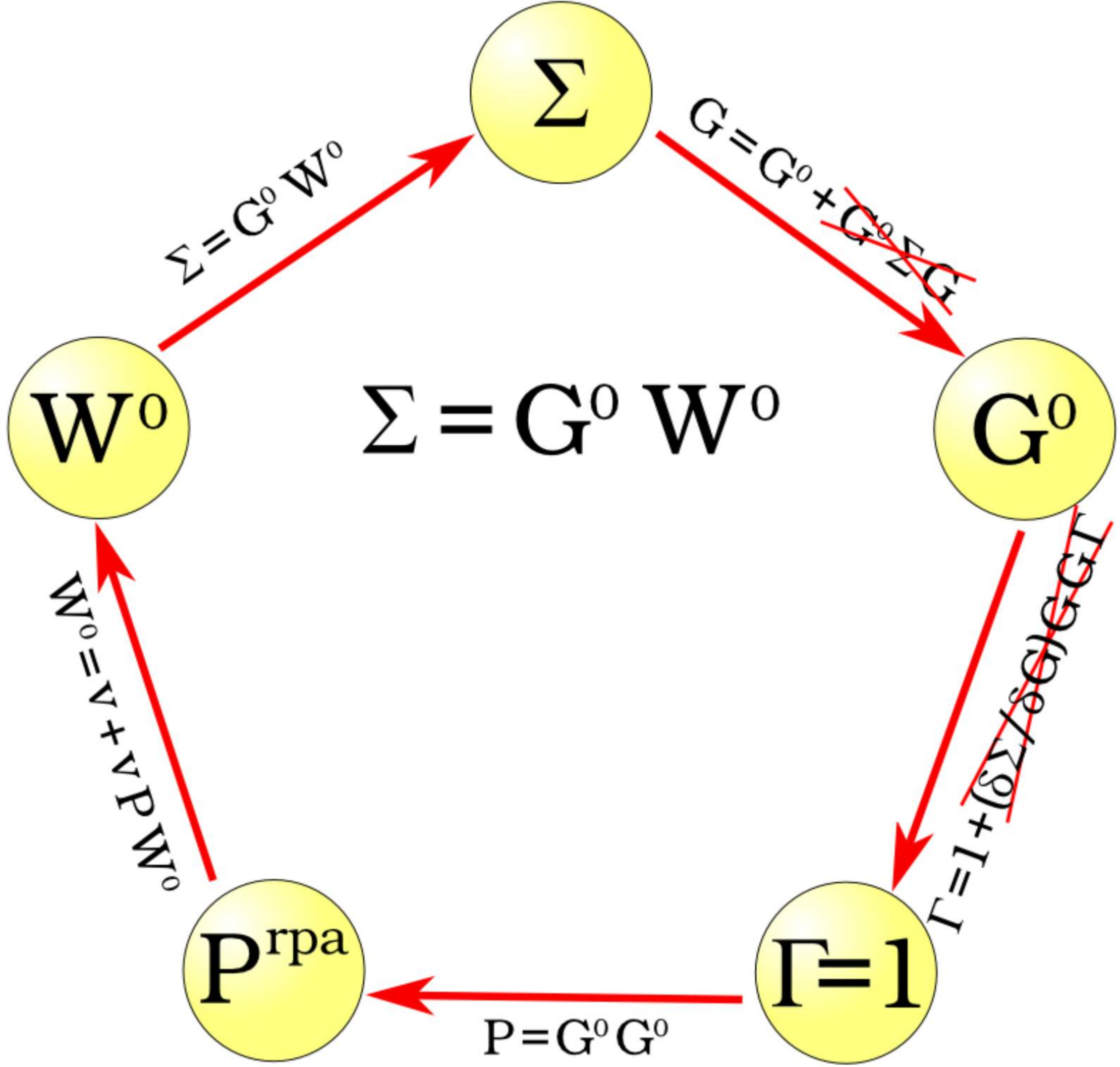
Σ=0
G^0
Γ=1
G = G^0 + G^0ΣG
Γ = 1 + (δΣ/δG)GGΓ



Σ=0
G = G⁰ + G⁰ΣG
G⁰
Γ = 1 + (δΣ/δG)GGΓ
Γ=1
P = G⁰ G⁰
P^rpa



Σ=0
G⁰
Γ=1
P^rpa
W⁰
G = G⁰ + G⁰ΣG
Γ = 1 + (δΣ/δG)GGΓ
P = G⁰ G⁰
W⁰ = v + v P W⁰



Σ
G⁰
Γ=1
P^rpa
W⁰
Σ = G⁰ W⁰
G = G⁰ + G⁰ΣG
Γ = 1 + (δΣ/δG)GGΓ
P = G⁰ G⁰
W⁰ = v + v P W⁰
Σ = G⁰ W⁰

practical procedure

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\psi_i(\mathbf{r}) + \int d\mathbf{r}' \qquad \Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}') = \qquad E_i\psi_i(\mathbf{r})$$

practical procedure

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\psi_i(\mathbf{r}) + \int d\mathbf{r}' \qquad \Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}') = \qquad E_i\psi_i(\mathbf{r})$$

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\phi_i(\mathbf{r}) + \qquad V_{xc}([n],\mathbf{r})\phi_i(\mathbf{r}) = \qquad \epsilon_i\phi_i(\mathbf{r})$$

practical procedure

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\phi_i(\mathbf{r}) + \int d\mathbf{r}' \qquad \Sigma(\mathbf{r},\mathbf{r}',E_i)\phi_i(\mathbf{r}') = \qquad E_i\phi_i(\mathbf{r})$$

$$\left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right]\phi_i(\mathbf{r}) + \qquad V_{xc}([n],\mathbf{r})\phi_i(\mathbf{r}) = \qquad \epsilon_i\phi_i(\mathbf{r})$$

practical procedure

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H \right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \phi_i^*(\mathbf{r}') \Sigma(\mathbf{r}, \mathbf{r}', E_i) \phi_i(\mathbf{r}') = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) E_i \phi_i(\mathbf{r})$$

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H \right] \phi_i(\mathbf{r}) + \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) V_{xc}([n], \mathbf{r}) \phi_i(\mathbf{r}) = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \epsilon_i \phi_i(\mathbf{r})$$

practical procedure

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \phi_i^*(\mathbf{r}') \Sigma(\mathbf{r}, \mathbf{r}', E_i) \phi_i(\mathbf{r}') = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) E_i \phi_i(\mathbf{r})$$

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) V_{xc}([n], \mathbf{r}) \phi_i(\mathbf{r}) = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \epsilon_i \phi_i(\mathbf{r})$$

$$E_i - \epsilon_i = \langle \phi_i | \Sigma(E_i) - V_{xc} | \phi_i \rangle$$

practical procedure

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \phi_i^*(\mathbf{r}') \Sigma(\mathbf{r}, \mathbf{r}', E_i) \phi_i(\mathbf{r}') = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) E_i \phi_i(\mathbf{r})$$

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + V_{ext} + V_H\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) V_{xc}([n], \mathbf{r}) \phi_i(\mathbf{r}) = \int d\mathbf{r}\ \phi_i^*(\mathbf{r}) \epsilon_i \phi_i(\mathbf{r})$$

$$E_i - \epsilon_i = \langle \phi_i | \Sigma(E_i) - V_{xc} | \phi_i \rangle$$

$$\langle \Sigma(E_i) \rangle = \langle \Sigma(\epsilon_i) \rangle + \langle \left. \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\omega = \epsilon_i} \rangle (E_i - \epsilon_i) + o\big((E_i - \epsilon_i)^2\big)$$

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r})\left[-\frac{\nabla^2}{2}+V_{ext}+V_H\right]\psi_i(\mathbf{r})+\int d\mathbf{r}'\phi_i^*(\mathbf{r}')\Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}')=\int d\mathbf{r}\ \phi_i^*(\mathbf{r})E_i\psi_i(\mathbf{r})$$

$$\int d\mathbf{r}\ \phi_i^*(\mathbf{r})\left[-\frac{\nabla^2}{2}+V_{ext}+V_H\right]\phi_i(\mathbf{r})+\int d\mathbf{r}\ \phi_i^*(\mathbf{r})V_{xc}([n],\mathbf{r})\phi_i(\mathbf{r})=\int d\mathbf{r}\ \phi_i^*(\mathbf{r})\epsilon_i\phi_i(\mathbf{r})$$

$$E_i-\epsilon_i=\langle\phi_i|\Sigma(E_i)-V_{xc}|\phi_i\rangle$$

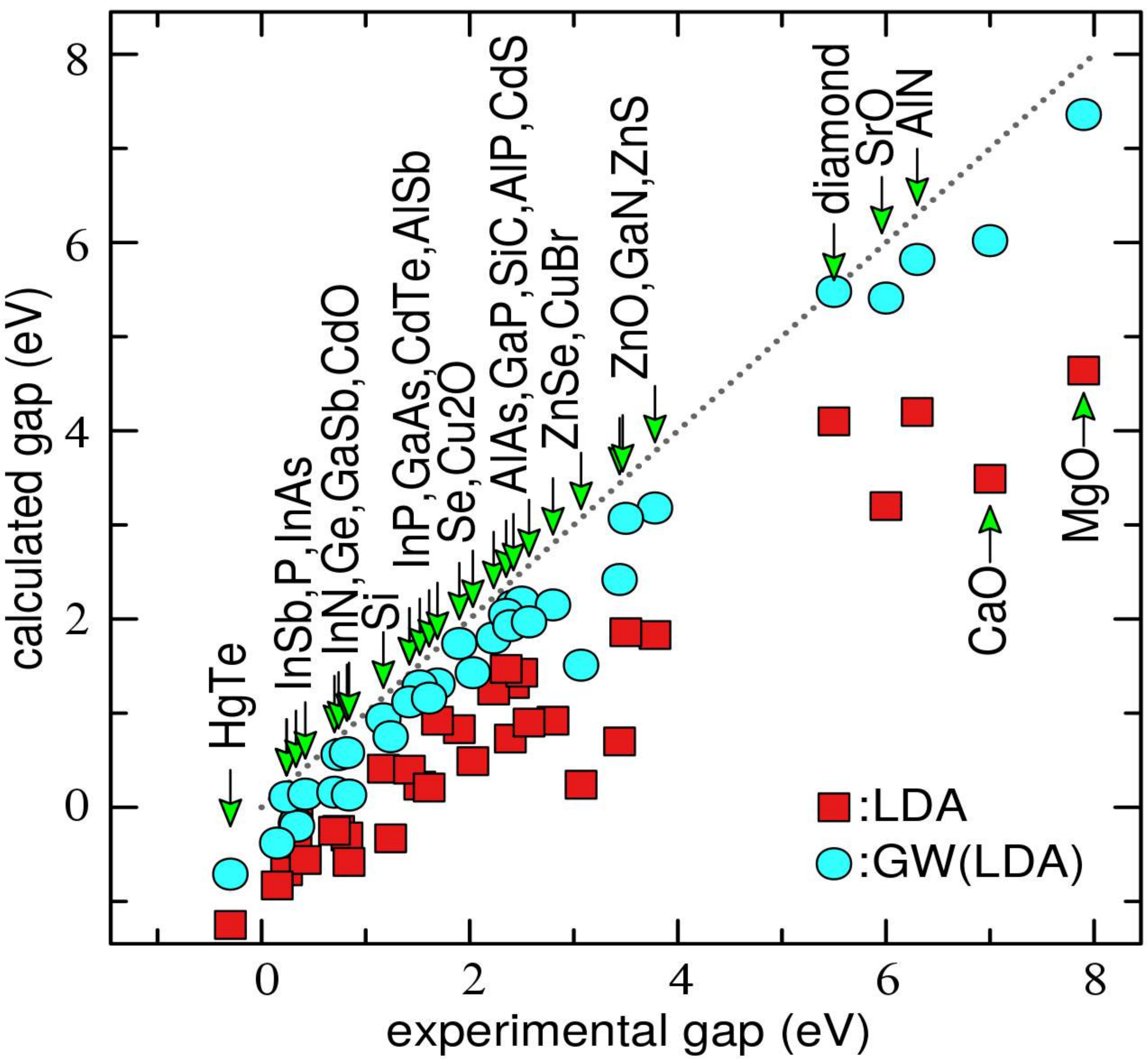
$$\langle\Sigma(E_i)\rangle=\langle\Sigma(\epsilon_i)\rangle+\left\langle\left.\frac{\partial\Sigma(\omega)}{\partial\omega}\right|_{\omega=\epsilon_i}\right\rangle(E_i-\epsilon_i)+o\big((E_i-\epsilon_i)^2\big)$$

$$E_i=\epsilon_i+\frac{\langle\phi_i|\Sigma(\epsilon_i)-V_{xc}|\phi_i\rangle}{1-\left\langle\left.\frac{\partial\Sigma(\omega)}{\partial\omega}\right|_{\omega=\epsilon_i}\right\rangle}$$

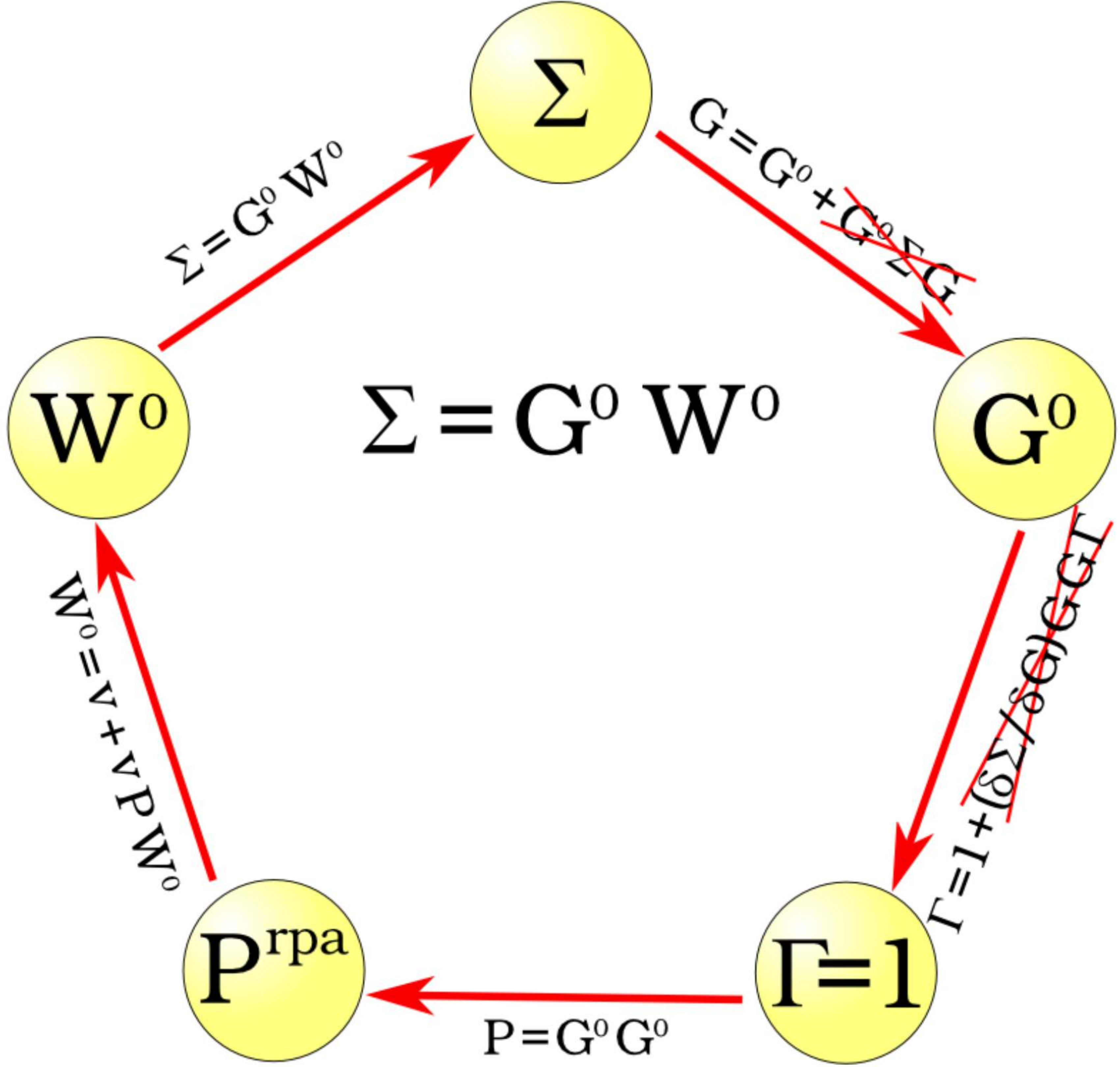
$$E_i - \epsilon_i = \langle \phi_i | \Sigma(E_i) - V_{xc} | \phi_i \rangle$$

$$(E_i)\rangle = \langle \Sigma(\epsilon_i)\rangle + \left\langle \left.\frac{\partial \Sigma(\omega)}{\partial \omega}\right|_{\omega=\epsilon_i} \right\rangle (E_i - \epsilon_i) + o\big((E_i - \epsilon_i$$

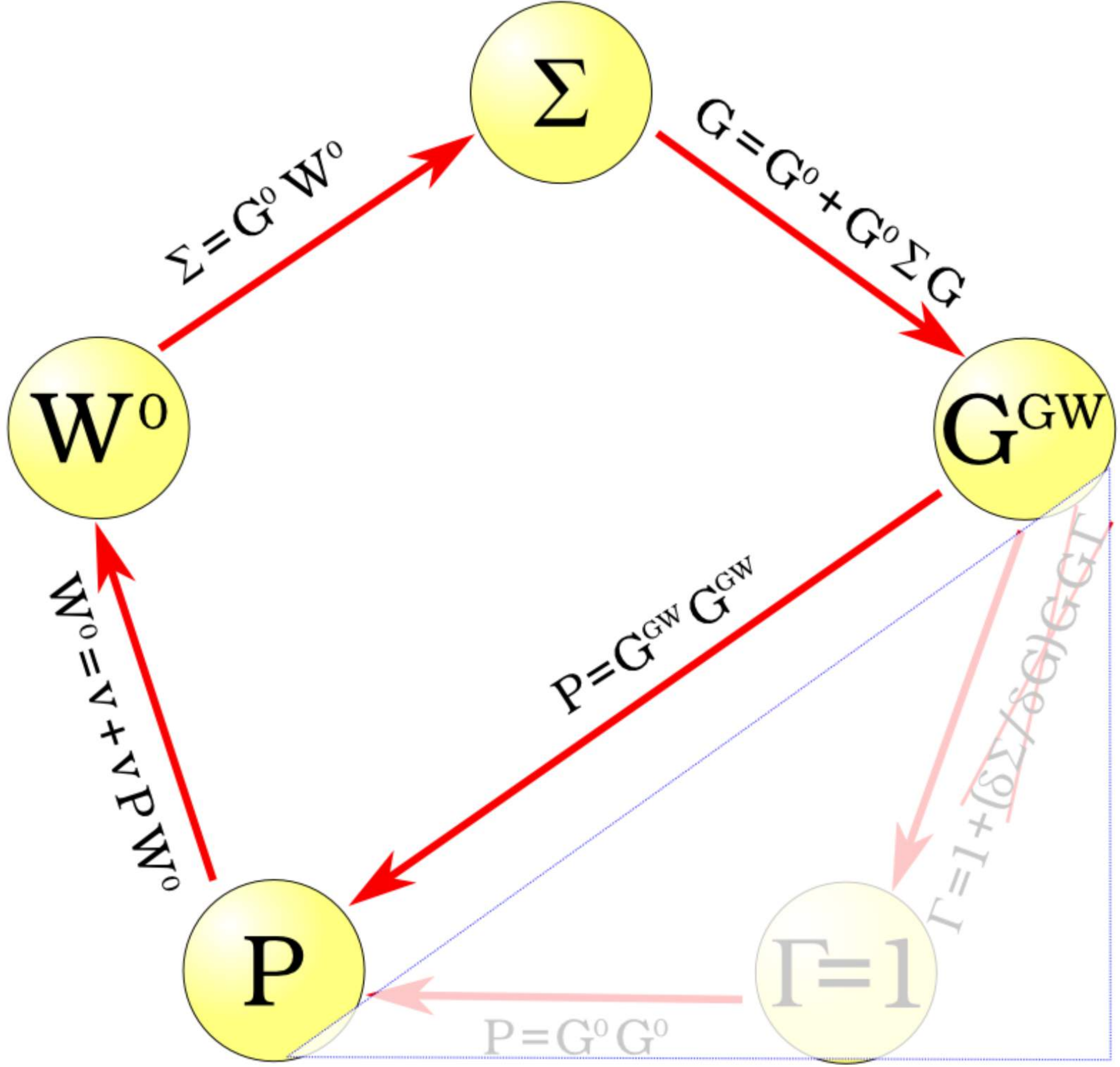
$$E_i = \epsilon_i + \frac{\langle \phi_i | \Sigma(\epsilon_i) - V_{xc} | \phi_i \rangle}{1 - \left\langle \left.\frac{\partial \Sigma(\omega)}{\partial \omega}\right|_{\omega=\epsilon_i} \right\rangle}$$



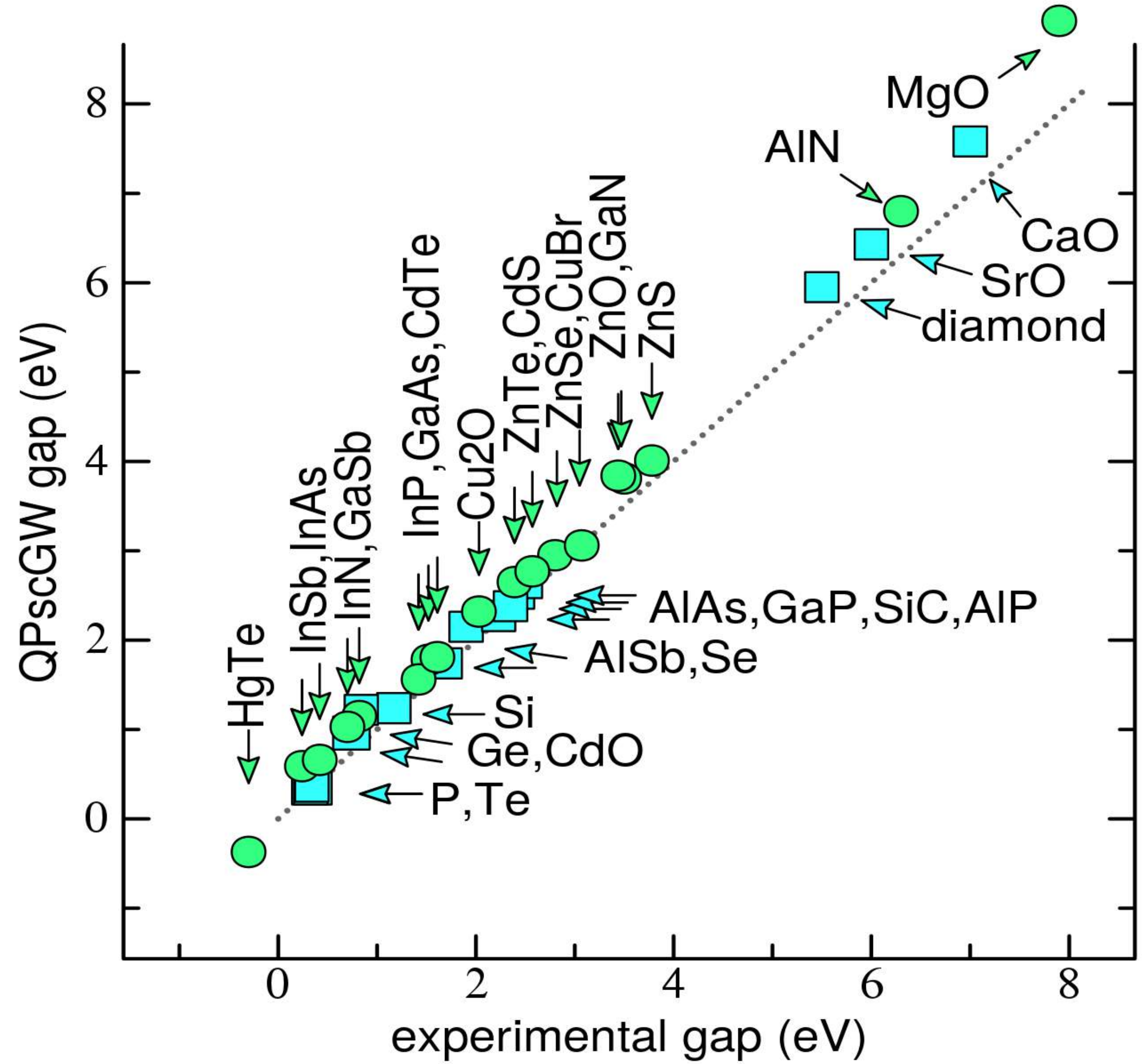
M. van Schilfgaarde *et al.*, PRL **96**, 226402 (2006).



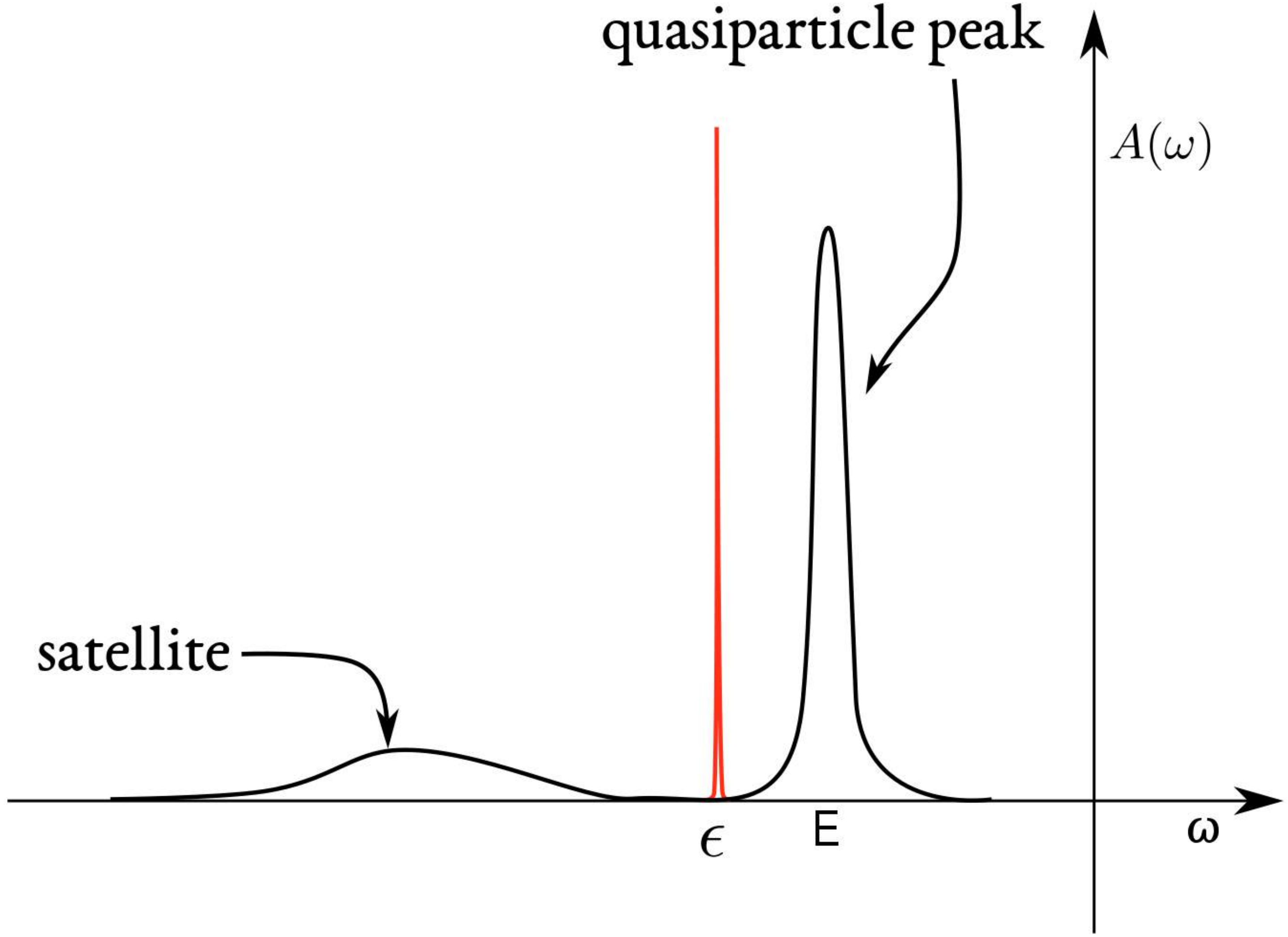
Σ
$G = G^0 + G^0 \Sigma G$
G^0
$\Gamma = 1 + (\delta\Sigma/\delta G) G G \Gamma$
$\Gamma = 1$
$P = G^0 G^0$
P^{rpa}
$W^0 = v + v P W^0$
W^0
$\Sigma = G^0 W^0$
$\Sigma = G^0 W^0$



Σ
G = G⁰ + G⁰ Σ G
G^GW
Σ = G⁰ W⁰
W⁰
P=G^GW G^GW
W⁰ = v + v P W⁰
P
Γ = 1 + (δΣ/δG) G G Γ
Γ=1
P = G⁰ G⁰

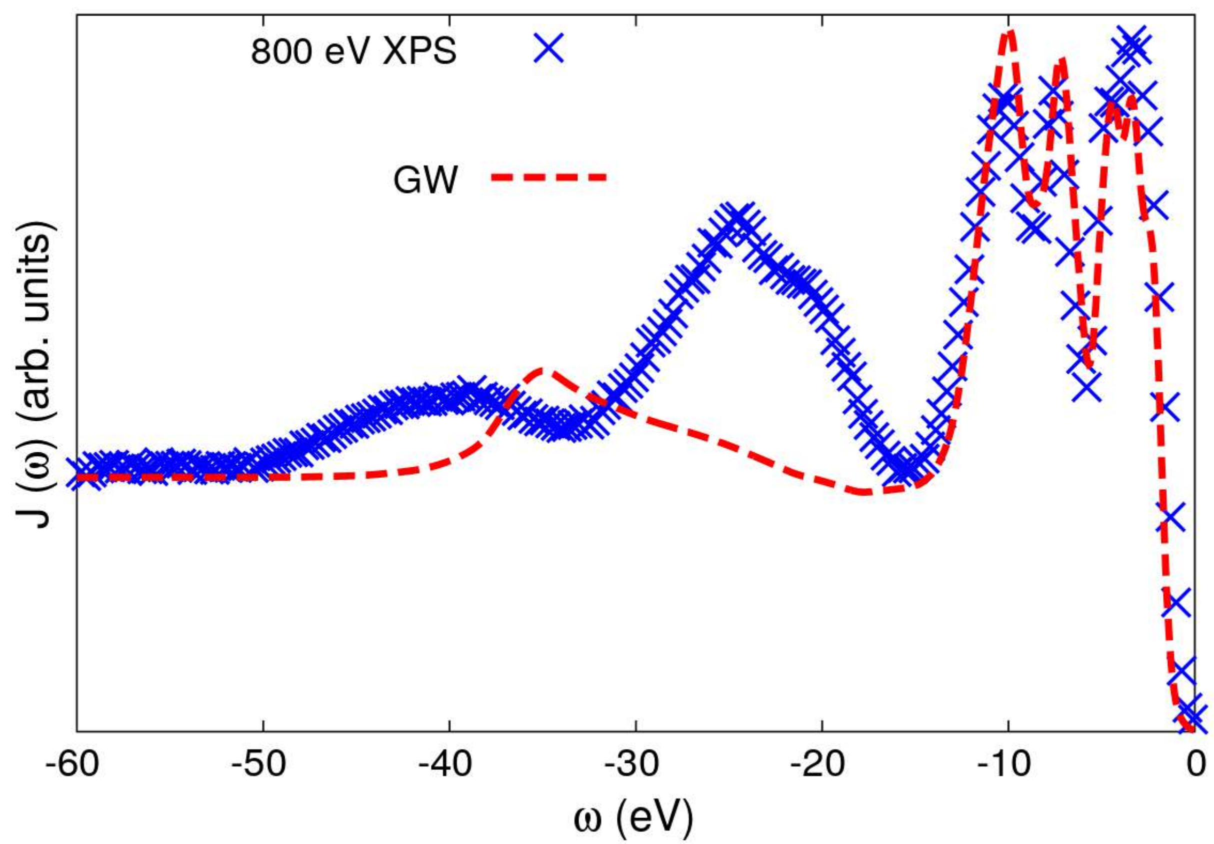


M. van Schilfgaarde *et al.*, PRL **96**, 226402 (2006).



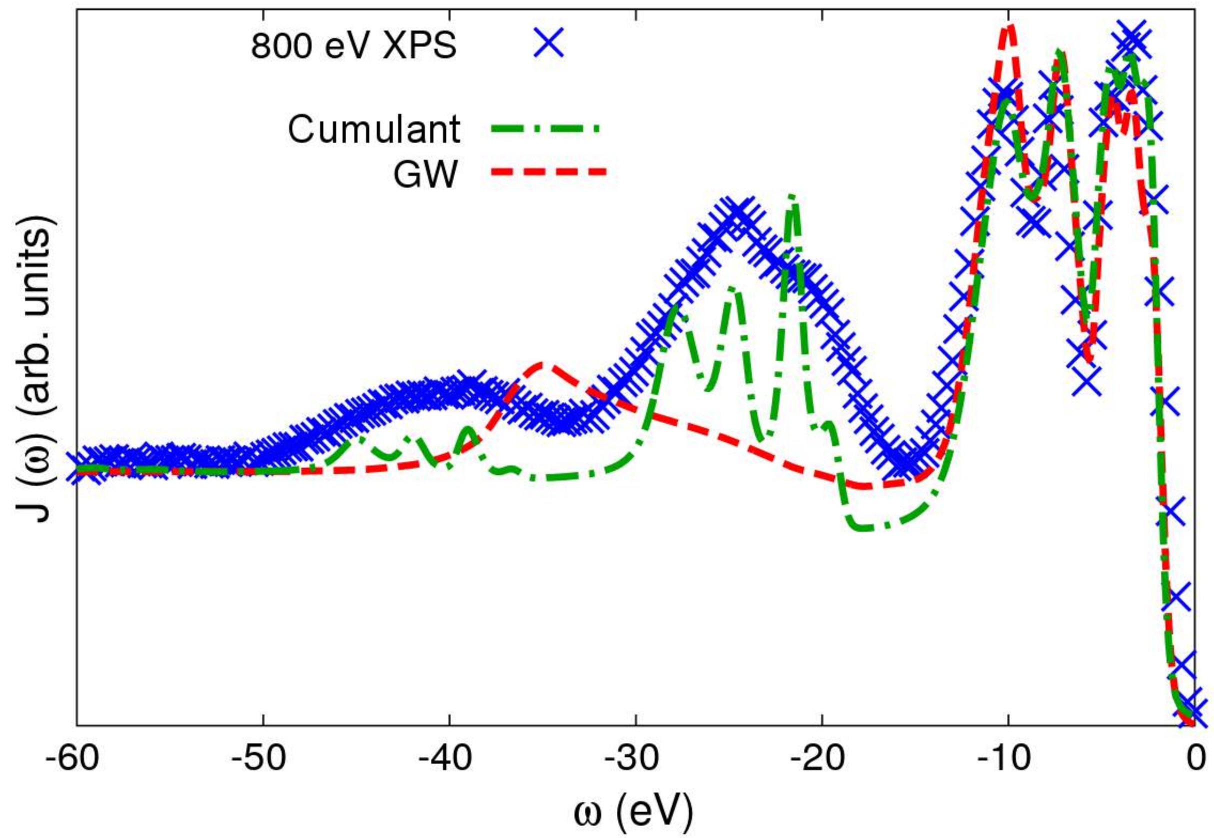
quasiparticle peak
$A(\omega)$
satellite
ϵ
E
ω

Photoemission of Silicon



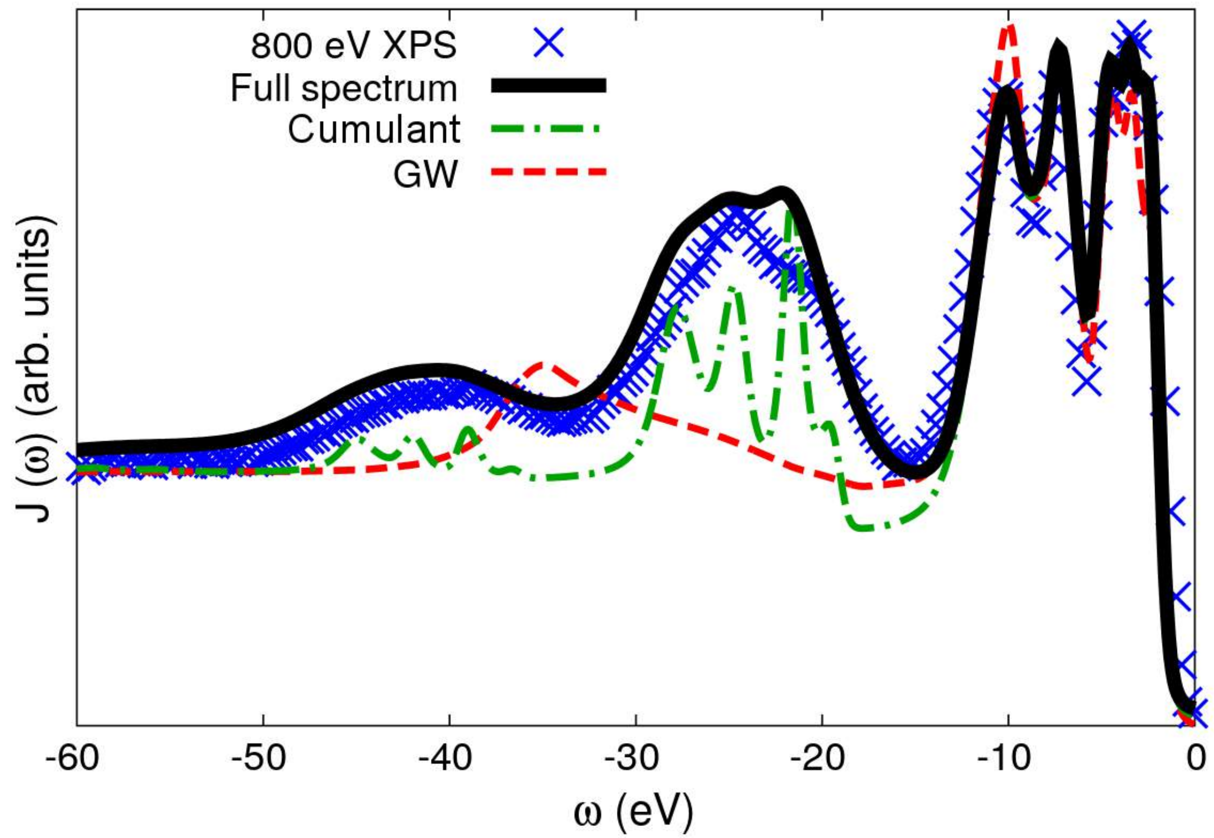
M. Guzzo et al. PRL **107**, 166401 (2011).

Photoemission of Silicon



M. Guzzo et al. PRL **107**, 166401 (2011).

Photoemission of Silicon

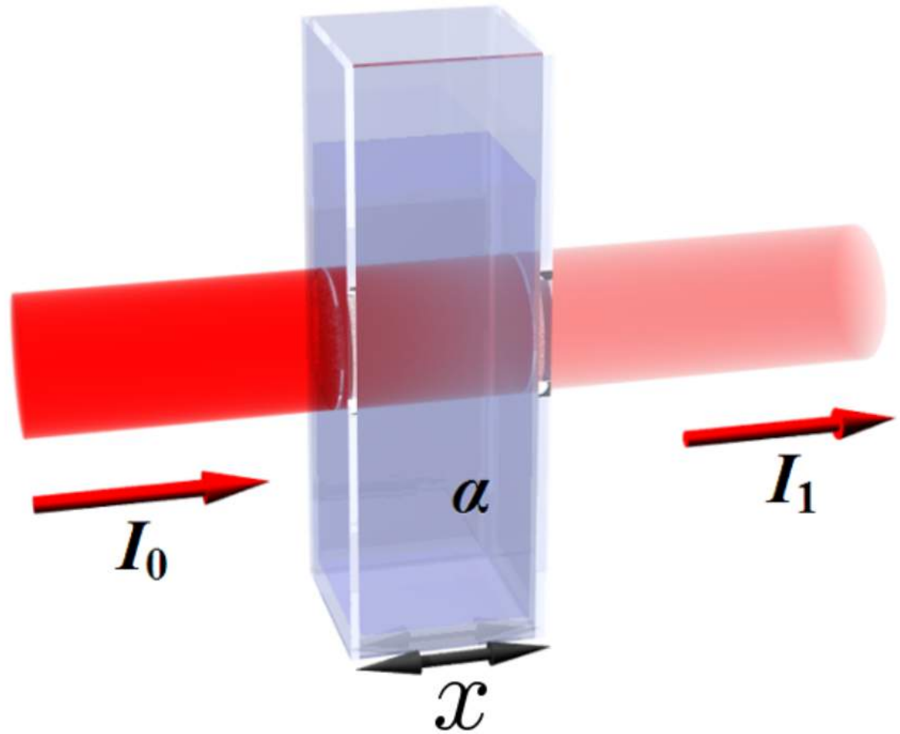


M. Guzzo et al. PRL **107**, 166401 (2011).

To know more about
PES satellites and
beyond GW ...
we need Sky!

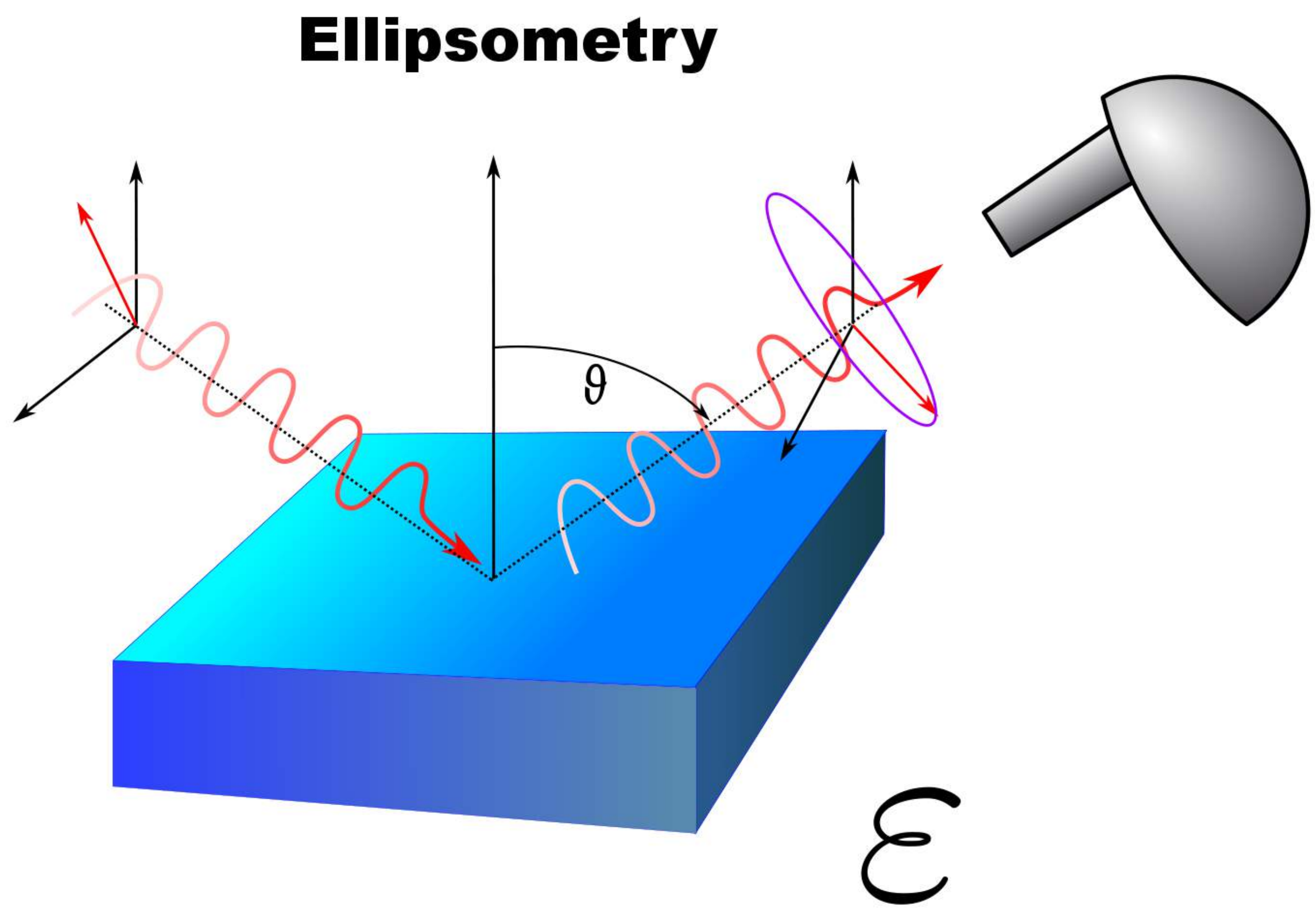
Absorption spectroscopy

Beer-Lambert regime



$$I = I_0 e^{-\alpha x}$$

$$\alpha = \frac{\omega \varepsilon_2}{\nu c}$$


Ellipsometry
ϑ
ε

$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | \ \Delta \ | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

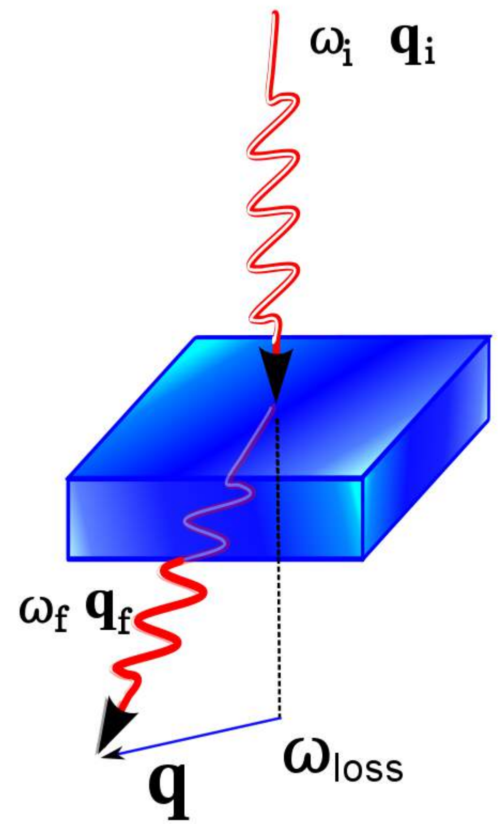
$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | \quad \mathbf{r} \quad | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | \quad \mathbf{r} \quad | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

IXS



$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | \quad \mathbf{r} \quad | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{Absorption} \propto \sum_f \left| \langle \Psi_f | \quad \mathbf{r} \quad | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{\displaystyle \mathrm{Im}\left[\sum_f \frac{\langle \Psi_i | \Delta | \Psi_f \rangle \ \langle \Psi_f | \Delta | \Psi_i \rangle}{\omega - E_f + E_i} \right]}$$

$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$\text{Im}\left[\sum_f \frac{\langle \Psi_i | \Delta | \Psi_f \rangle \; \langle \Psi_f | \Delta | \Psi_i \rangle}{\omega - E_f + E_i}\right]$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$\chi(\mathbf{r}, \mathbf{r}', t - t') = \langle \Psi_i | [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')] | \Psi_i \rangle$$

$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

$$\underbrace{}$$

$$\mathrm{Im}\left[\sum_f \frac{\langle \Psi_i | \Delta | \Psi_f \rangle \; \langle \Psi_f | \Delta | \Psi_i \rangle}{\omega - E_f + E_i}\right]$$

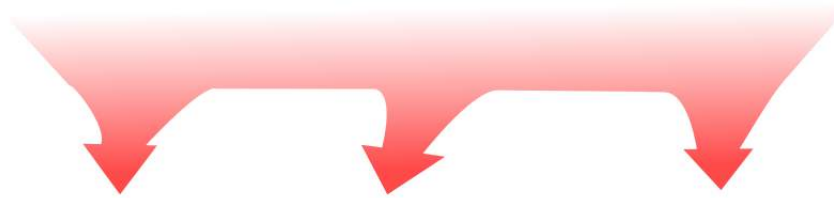
$$\underbrace{}$$

$$\chi(\mathbf{r}, \mathbf{r}', t - t') = \langle \Psi_i | [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')] | \Psi_i \rangle$$

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

$$\chi = \sum_f \frac{\langle \Psi_i | \mathbf{r} | \Psi_f \rangle \ \langle \Psi_f | \mathbf{r} | \Psi_i \rangle}{\omega - E_f + E_i}$$

$$|N\rangle \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(\mathbf{r}_1) & \psi_{\alpha_1}(\mathbf{r}_2) & .. & \psi_{\alpha_1}(\mathbf{r}_n) \\ \psi_{\alpha_2}(\mathbf{r}_1) & \psi_{\alpha_2}(\mathbf{r}_2) & .. & \psi_{\alpha_2}(\mathbf{r}_n) \\ .. & .. & .. & .. \\ \psi_{\alpha_n}(\mathbf{r}_1) & \psi_{\alpha_n}(\mathbf{r}_2) & .. & \psi_{\alpha_n}(\mathbf{r}_n) \end{vmatrix}$$



$$\chi = \sum_f \frac{\langle \Psi_i | \mathbf{r} | \Psi_f \rangle \, \langle \Psi_f | \mathbf{r} | \Psi_i \rangle}{\omega - E_f + E_i}$$

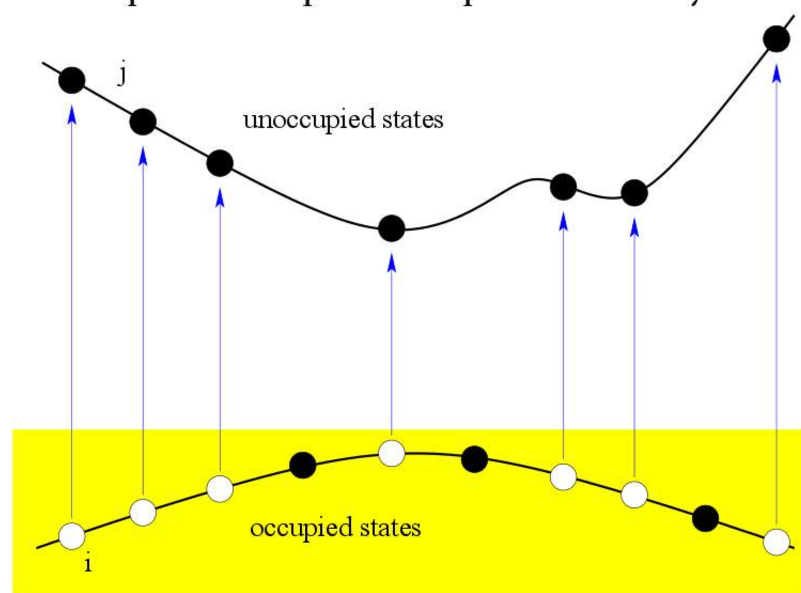
$$|N\rangle \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(\mathbf{r}_1) & \psi_{\alpha_1}(\mathbf{r}_2) & .. & \psi_{\alpha_1}(\mathbf{r}_n) \\ \psi_{\alpha_2}(\mathbf{r}_1) & \psi_{\alpha_2}(\mathbf{r}_2) & .. & \psi_{\alpha_2}(\mathbf{r}_n) \\ .. & .. & .. & .. \\ \psi_{\alpha_n}(\mathbf{r}_1) & \psi_{\alpha_n}(\mathbf{r}_2) & .. & \psi_{\alpha_n}(\mathbf{r}_n) \end{vmatrix}$$

$$\chi = \sum_f \frac{\langle \Psi_i | \mathbf{r} | \Psi_f \rangle \langle \Psi_f | \mathbf{r} | \Psi_i \rangle}{\omega - E_f + E_i}$$

$$\chi^0(\omega) = \sum_{ij} \frac{|\langle \psi_j | \mathbf{r} | \psi_i \rangle|^2}{\omega - \epsilon_j + \epsilon_i + i\eta}$$

$$\chi^0(\omega) = \sum_{ij} \frac{|\langle\psi_j|\mathbf{r}|\psi_i\rangle|^2}{\omega - \epsilon_j + \epsilon_i + i\eta}$$

Independent-particle polarizability χ^0

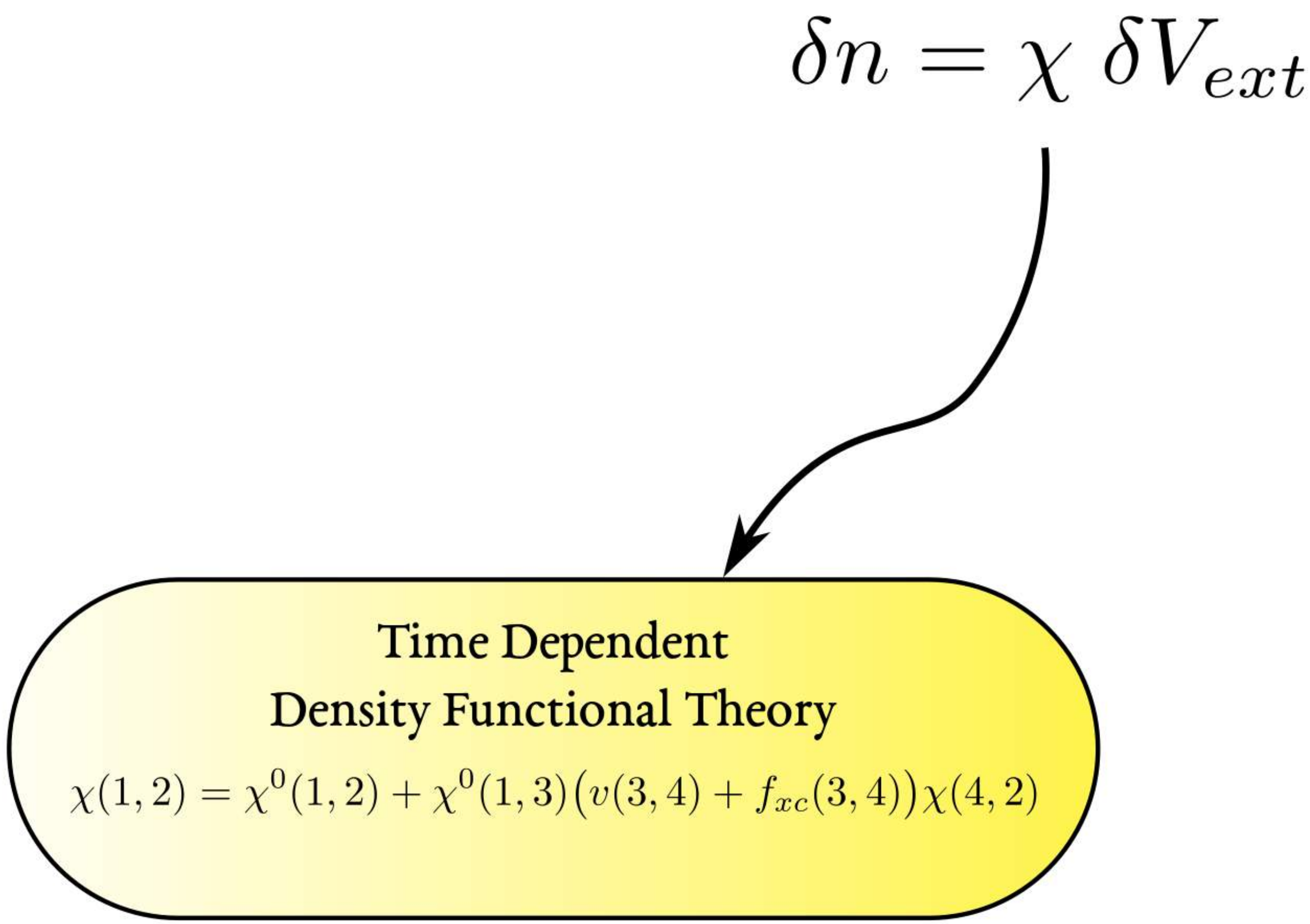


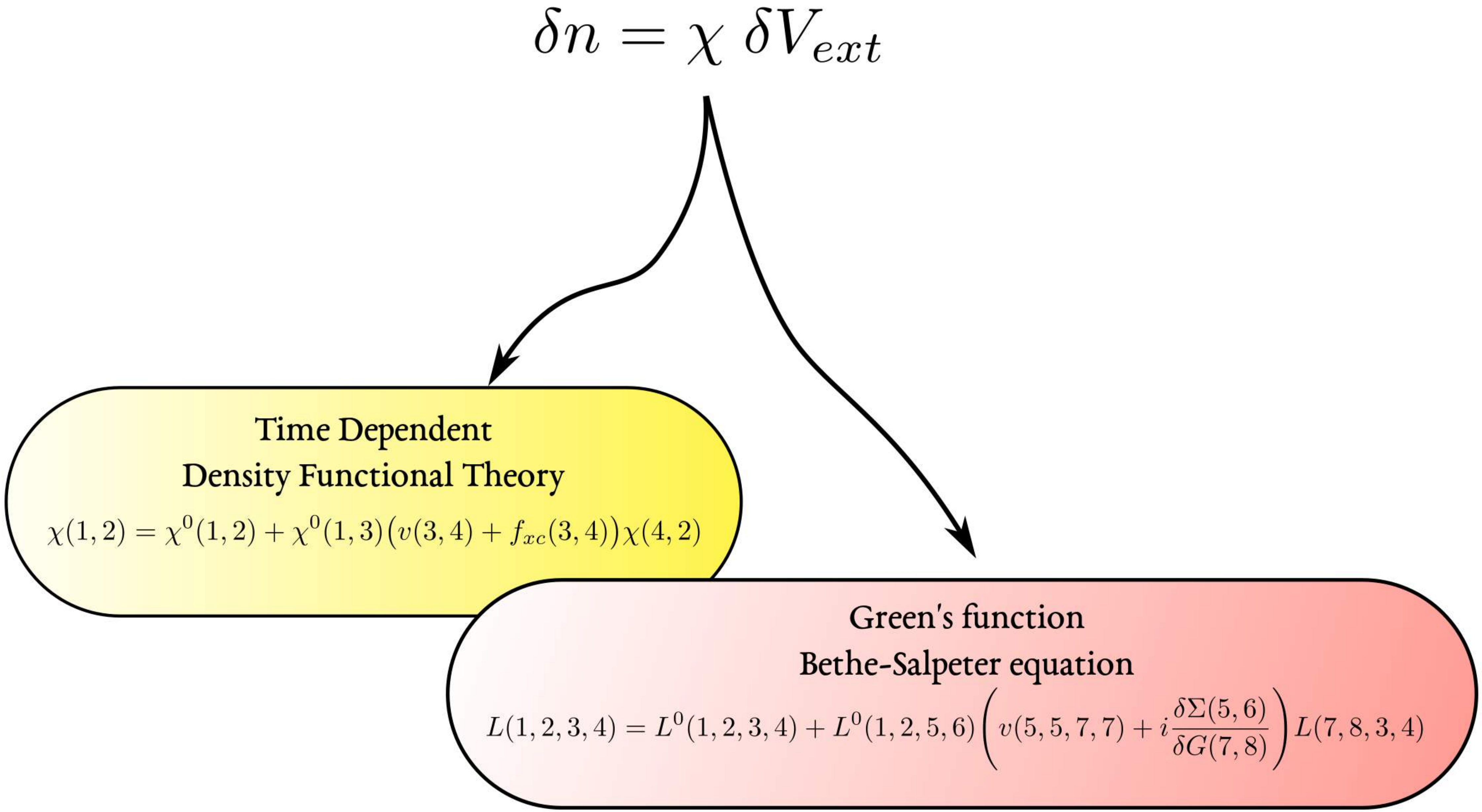
$$\text{NIXS, EELS} \propto \sum_f \left| \langle \Psi_f | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi_i \rangle \right|^2 \delta(\omega - E_f + E_i)$$

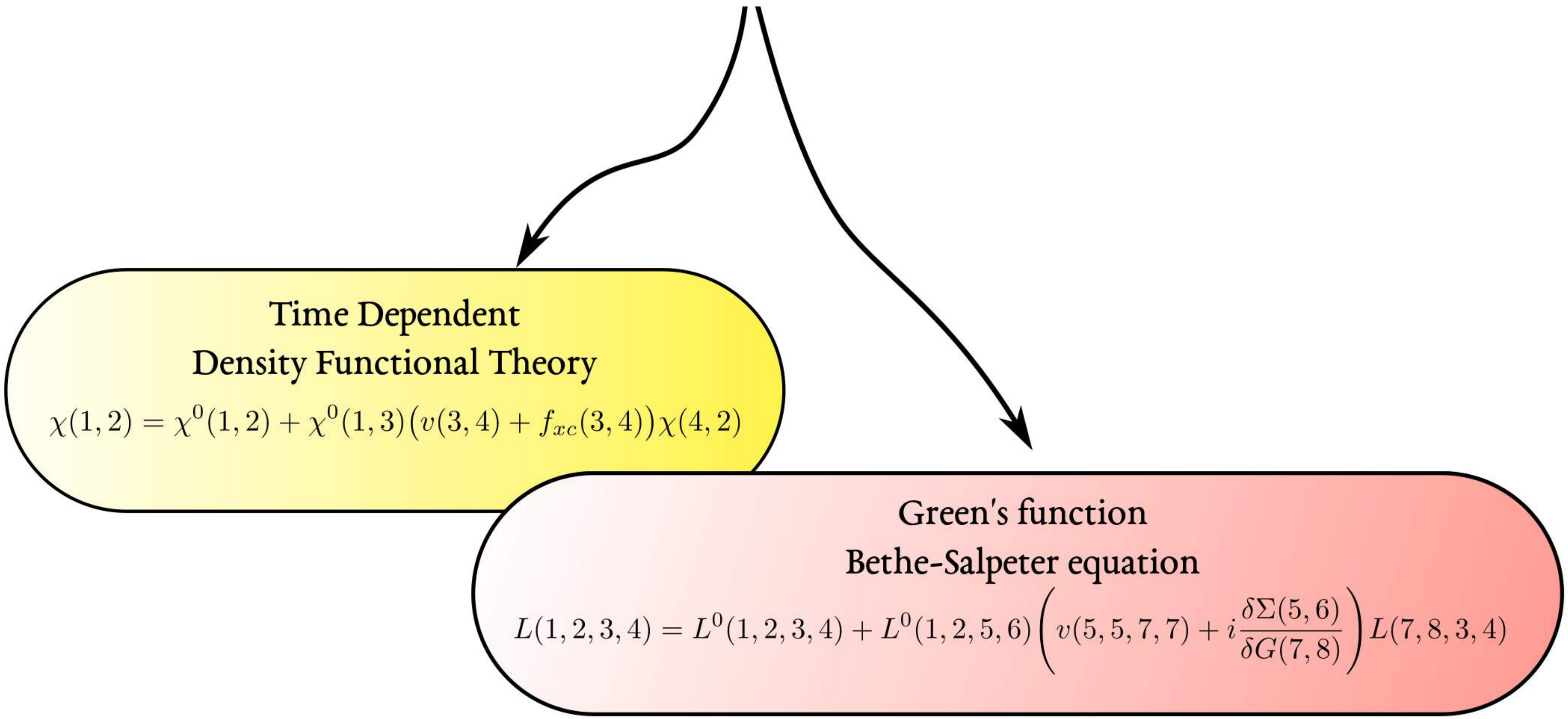
$$\overbrace{\mathrm{Im}\left[\sum_f \frac{\langle \Psi_i | \Delta | \Psi_f \rangle \ \langle \Psi_f | \Delta | \Psi_i \rangle}{\omega - E_f + E_i} \right]}$$

$$\overbrace{\chi(\mathbf{r}, \mathbf{r}', t - t') = \ \langle \Psi_i | [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')] | \Psi_i \rangle}$$

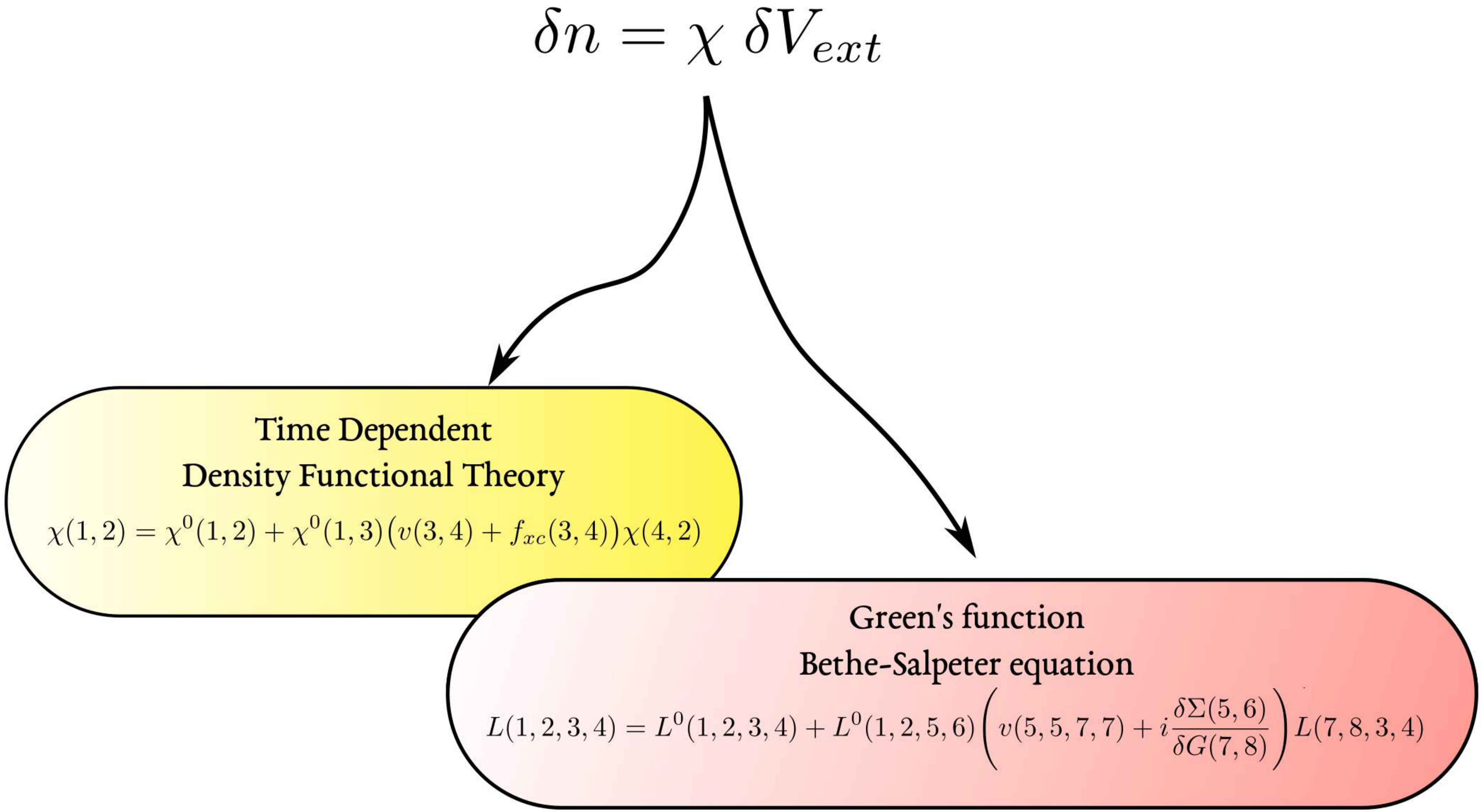
$$\delta n = \chi \, \delta V_{ext}$$

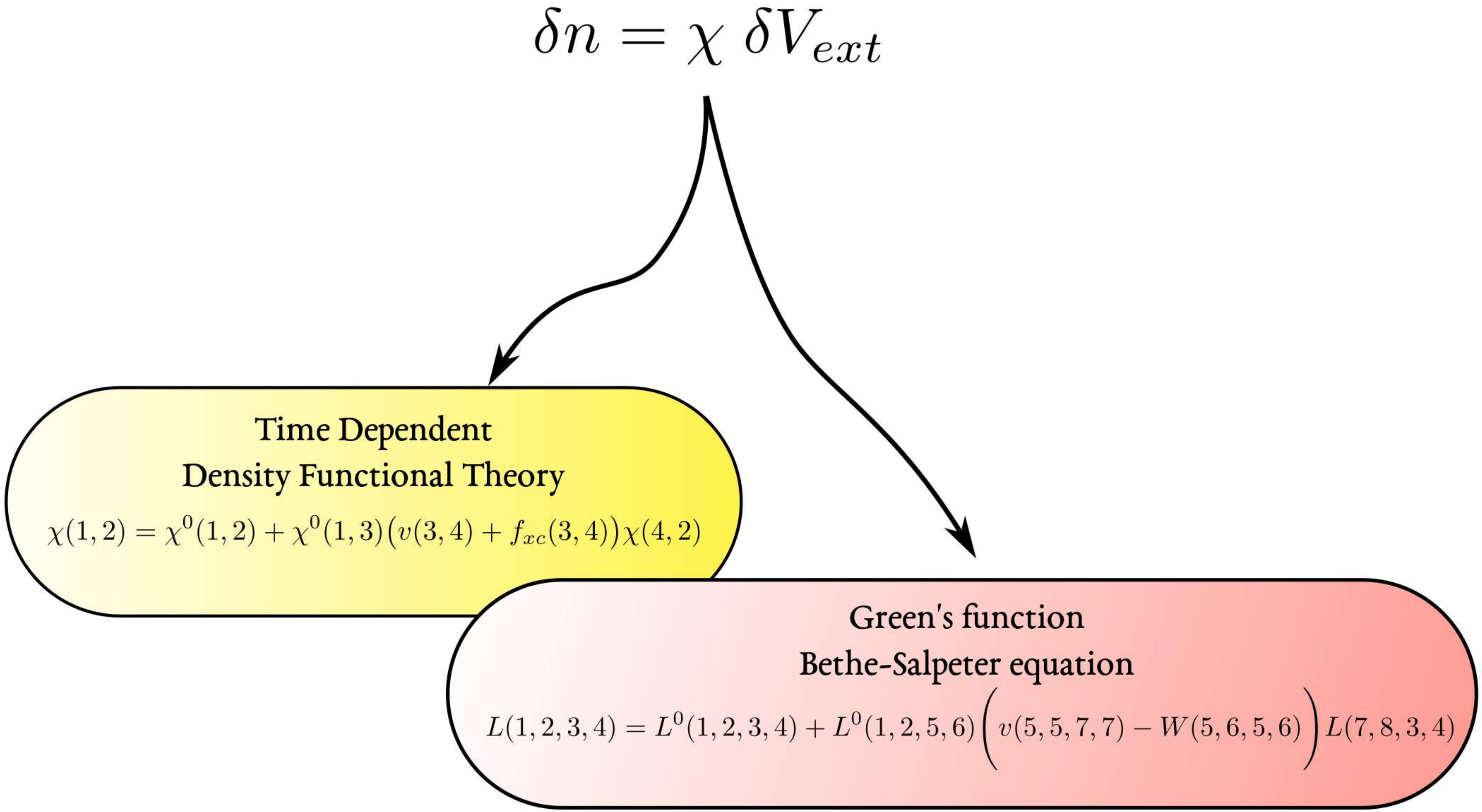

$\delta n = \chi \, \delta V_{ext}$
Time Dependent
Density Functional Theory
$\chi(1,2) = \chi^0(1,2) + \chi^0(1,3)\big(v(3,4) + f_{xc}(3,4)\big)\chi(4,2)$

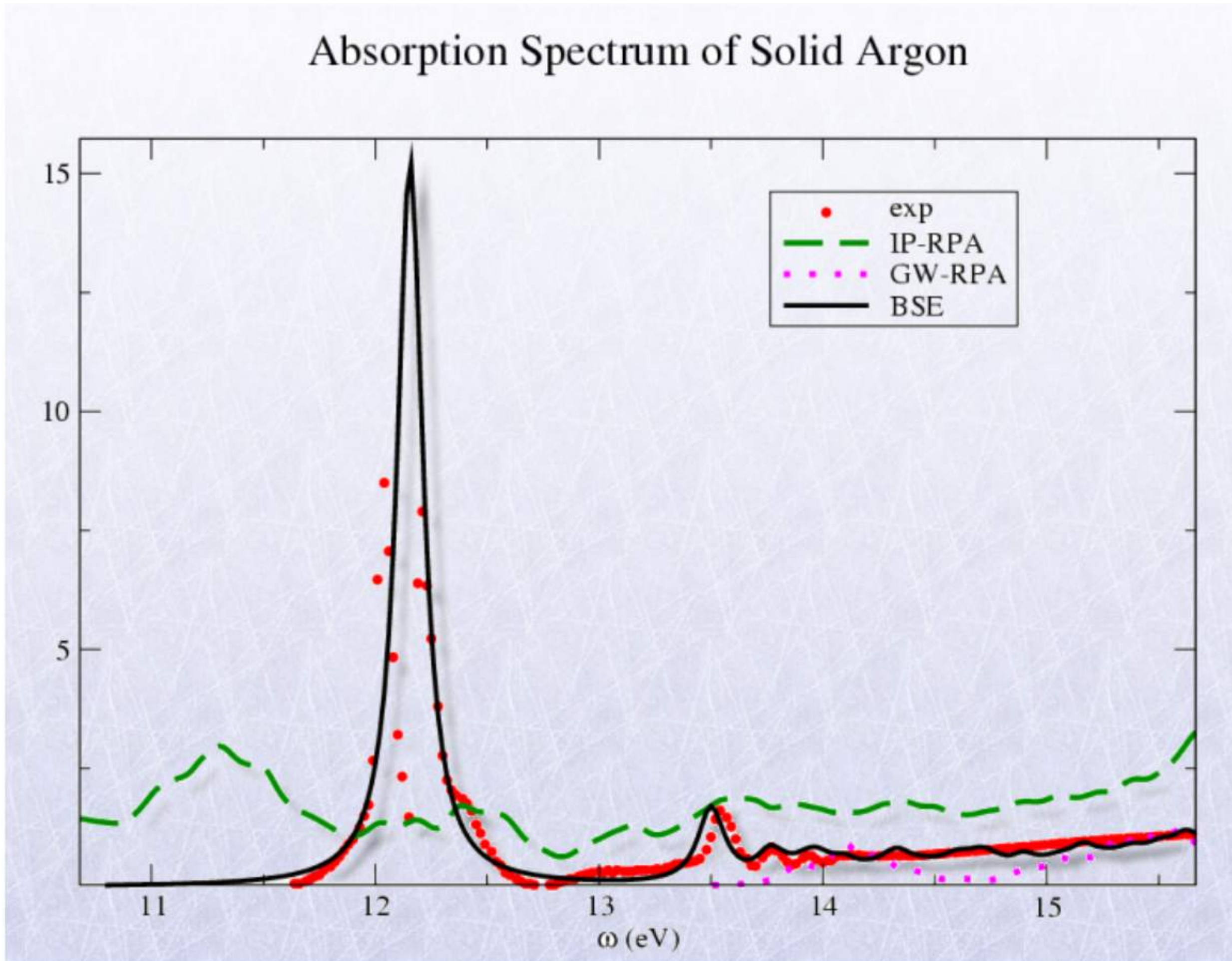

$\delta n = \chi \, \delta V_{ext}$
Time Dependent
Density Functional Theory
$\chi(1,2) = \chi^0(1,2) + \chi^0(1,3)\big(v(3,4) + f_{xc}(3,4)\big)\chi(4,2)$
Green's function
Bethe-Salpeter equation
$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\left(v(5,5,7,7) + i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right)L(7,8,3,4)$



$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4567)\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7,3)$$

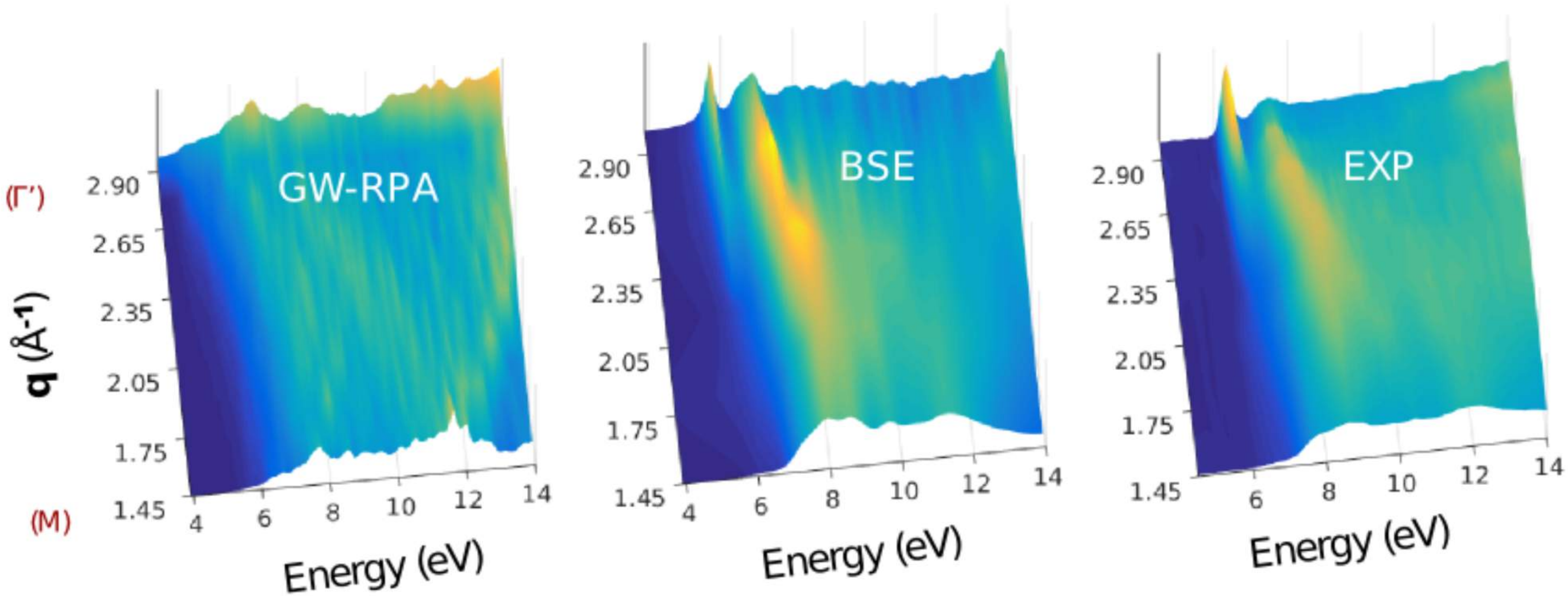

$\delta n = \chi \, \delta V_{ext}$
Time Dependent
Density Functional Theory
$\chi(1,2) = \chi^0(1,2) + \chi^0(1,3)\big(v(3,4) + f_{xc}(3,4)\big)\chi(4,2)$
Green's function
Bethe-Salpeter equation
$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\left(v(5,5,7,7) + i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right)L(7,8,3,4)$


$\delta n = \chi \, \delta V_{ext}$
Time Dependent
Density Functional Theory
$\chi(1,2) = \chi^0(1,2) + \chi^0(1,3)\big(v(3,4) + f_{xc}(3,4)\big)\chi(4,2)$
Green's function
Bethe-Salpeter equation
$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\Bigg(v(5,5,7,7) - W(5,6,5,6)\Bigg)L(7,8,3,4)$



F. Sottile *et al.*, PRB **76**, 116103 (2007).

Exciton dispersion of h BN



ID20 beamline 5/2015

G. Fugallo et al. Phys. Rev. B **92**, 165122 (2015)

To know more about
new challenges beyond
static BSE...

we need Pierluigi!

Core and valence spectroscopy

- Same theory

Core and valence spectroscopy

- Same theory
- Different point of view

Core and valence spectroscopy

- Same theory
- Different point of view
- Mutual gain

Core and valence spectroscopy

- Same theory
- Different point of view
- Mutual gain

→ core states == localized states (correlated)

→ non linearity, dynamics

→ Green's functions for several core spectroscopies