Theoretical Spectroscopy via Green's functions and Density Functional Theory

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Blending the DFT-based multiple-scattering Greens' functional approach to spectroscopies with machine learning
Les Houches, 3 November 2023

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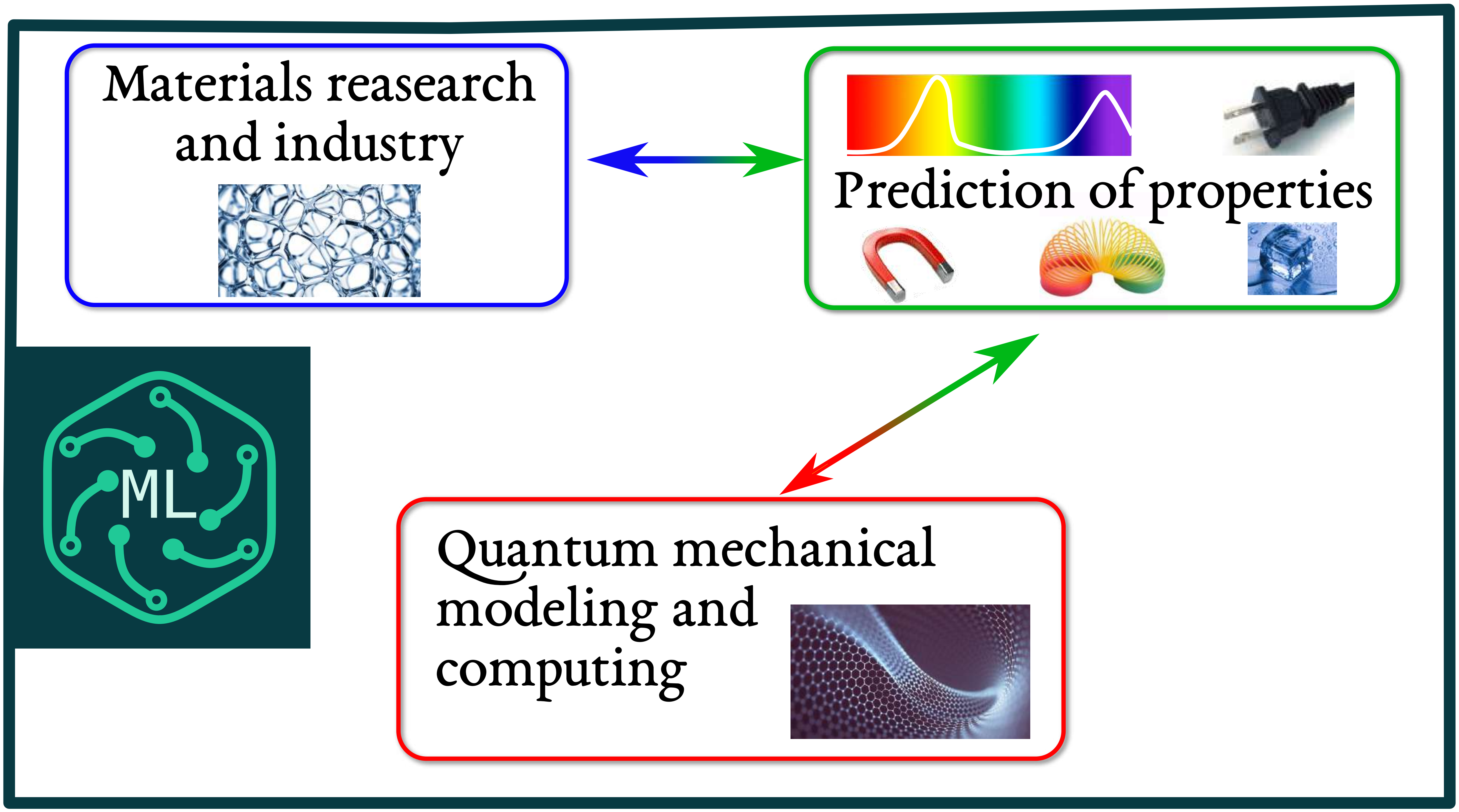


Materials reasearch and industry
Prediction of properties
ML
Quantum mechanical modeling and computing

Article | Open access | Published: 20 March 2023

A study on Shine-Muscat grape detection at maturity based on deep learning

Xinjie Wei, Fuxiang Xie, Kai Wang, Jian Song & Yang Bai

Scientific Reports **13**, Article number: 4587 (2023) | Cite this article

Abstract

Introduction

Related works

Results and analysis

Conclusion and future direction

Data availability

References

Funding

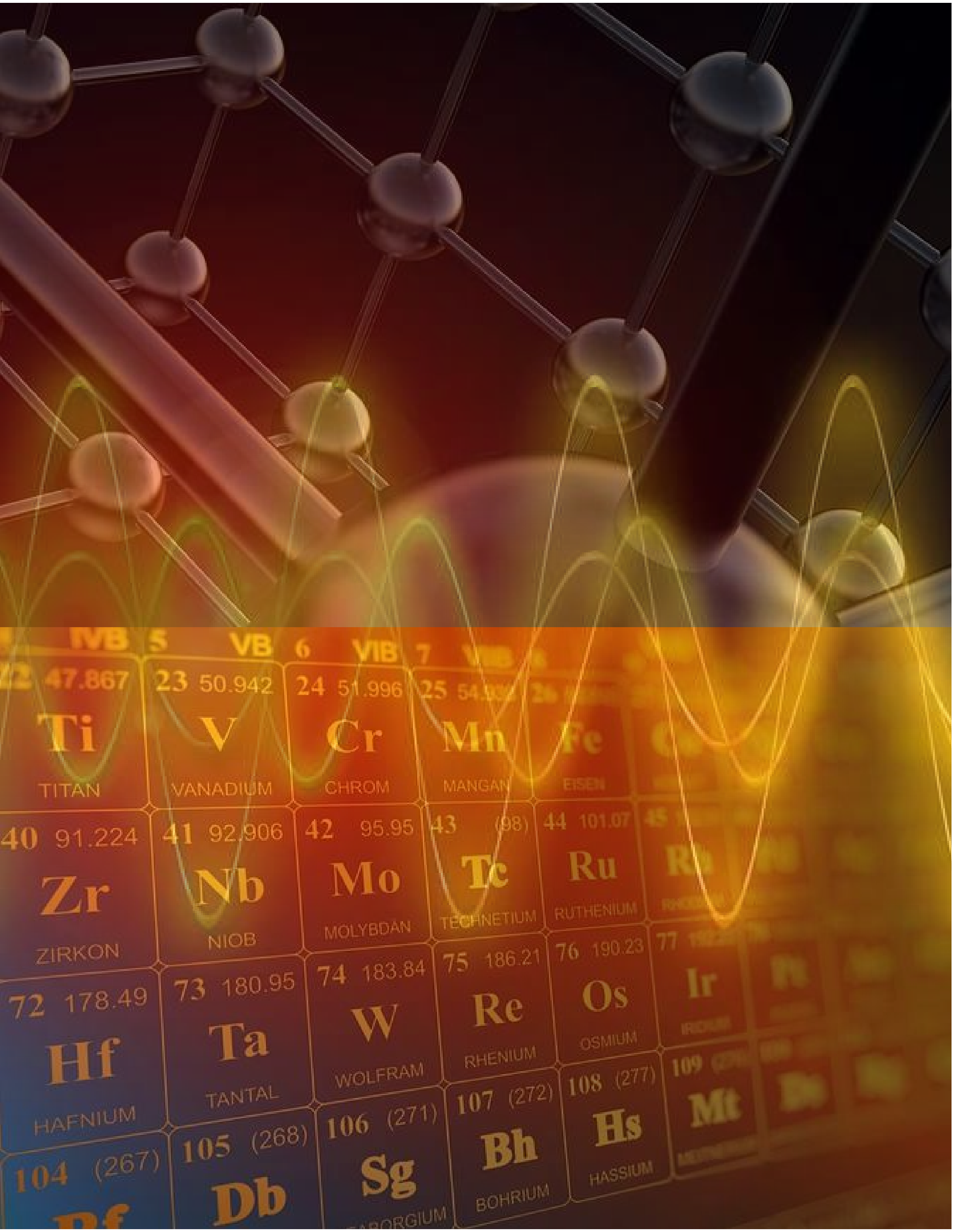
Author information

Abstract

The efficient detection of grapes is a crucial technology for fruit-picking robots. To better identify grapes from branch shading that is similar to the fruit color and improve the detection accuracy of green grapes due to cluster adhesion, this study proposes a Shine-Muscat Grape Detection Model (S-MGDM) based on improved YOLOv3 for the ripening stage. DenseNet is fused in the backbone feature

Variety of Machine Learning Approaches

- different Learning
  (supervised, unsupervised, active)
- different kind or function
  (regression, instance-based, tree, networks,..)
- different use



Variety of Machine Learning Approaches

- Machine Learning Approaches OK
- More data (even more)
- Better data (even better)

Absorption spectrum Electron Energy Loss

Surface differential reflectivity Compton Scattering

Refraction index

Photoemission

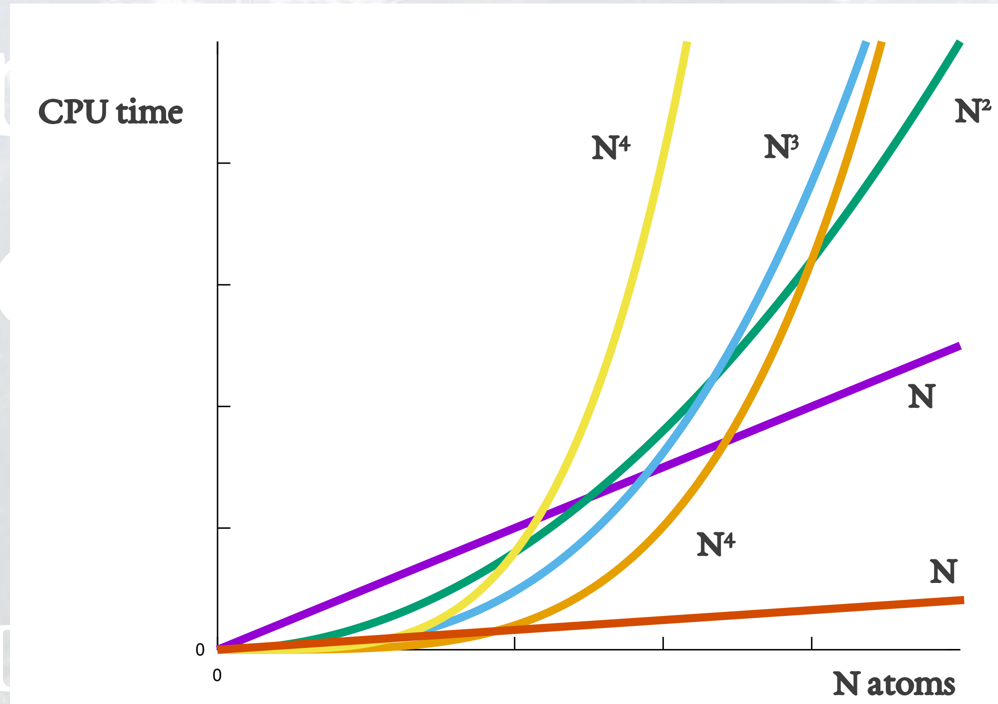
Reflectivity

Theor… scopy

via Gr… s and

Density … heory

Francesco Sottile, Ecole … (France)



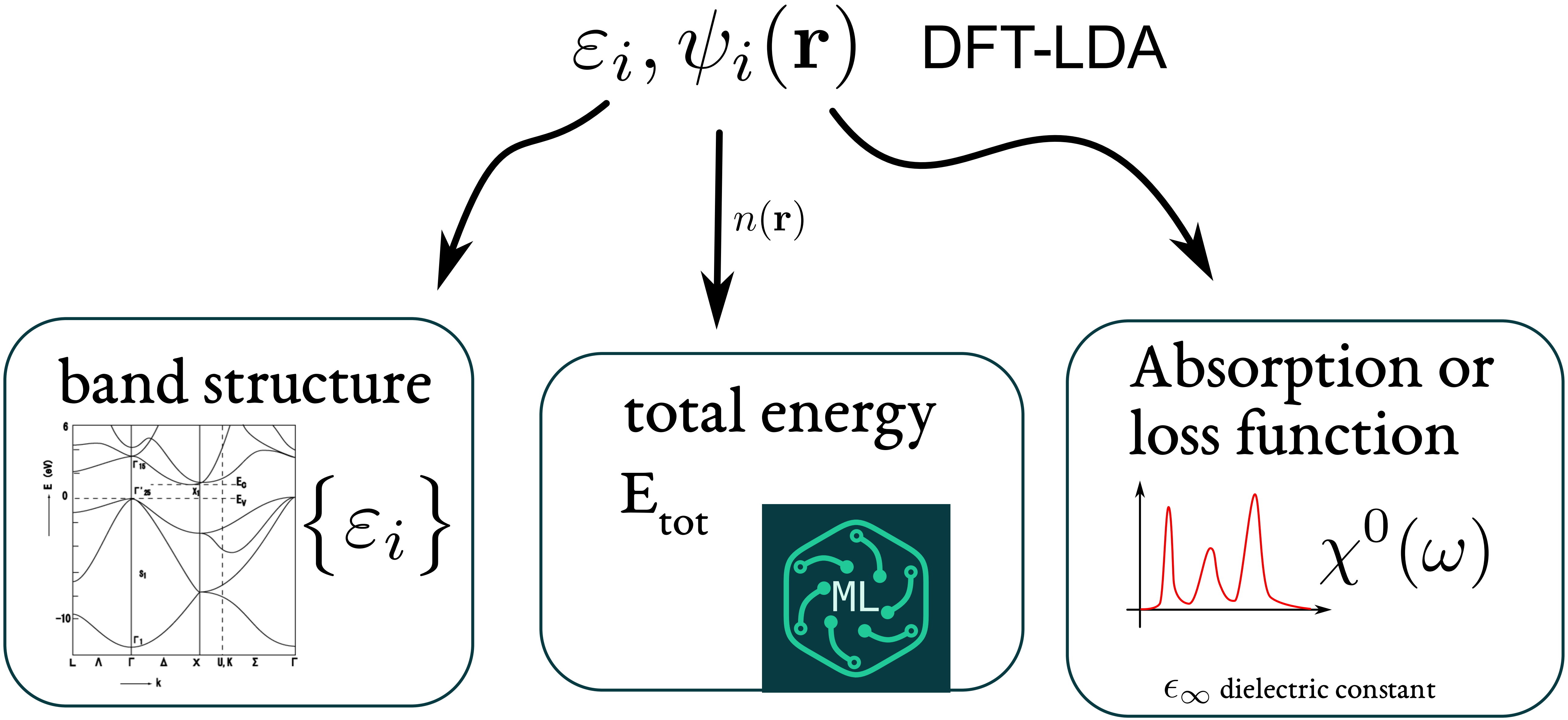
Reflectance Anisotropy spectroscopy

Blending the DFT-based multiple-scattering Greens' functional approach to spectroscopies with machine learning

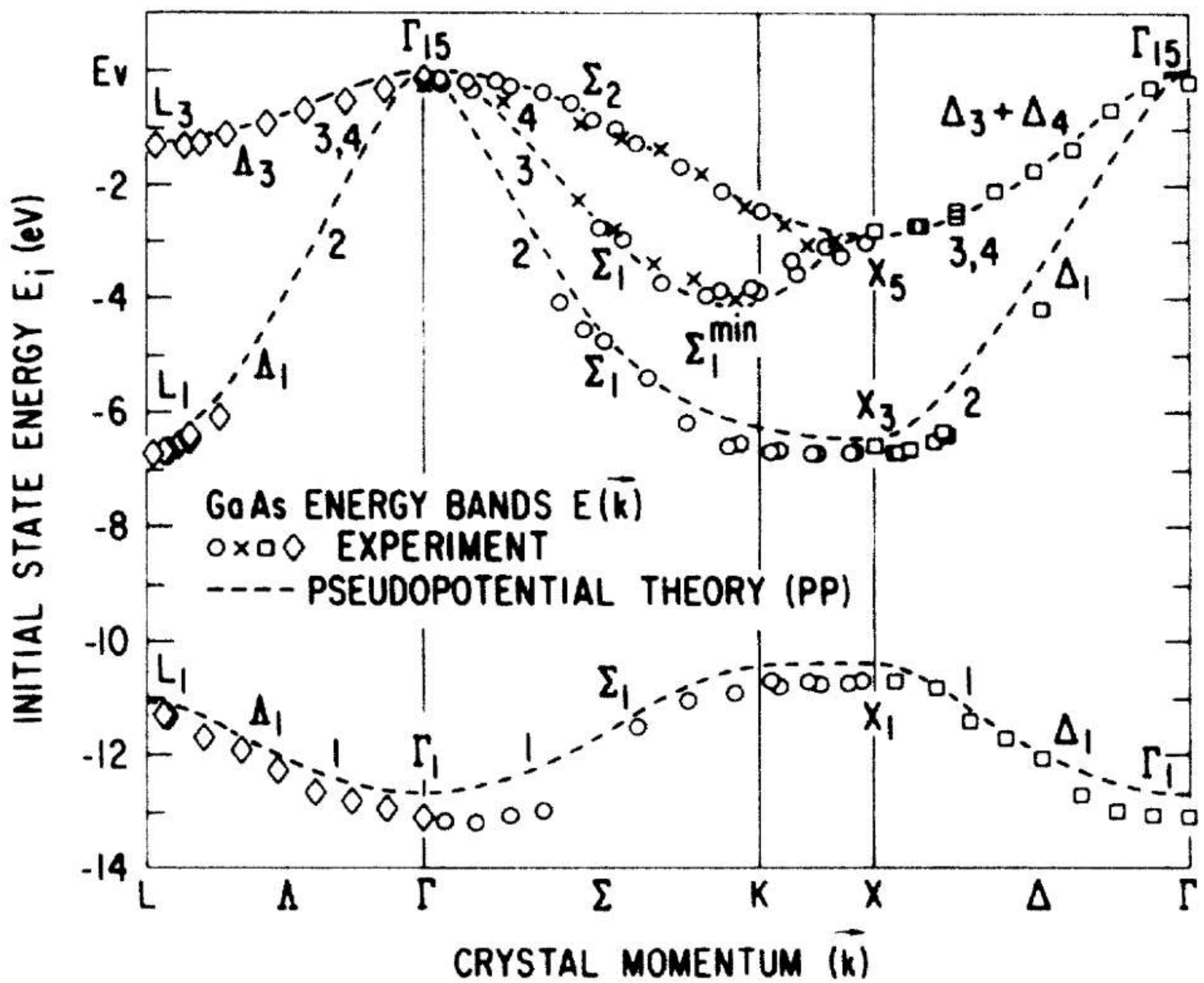
Les Houches, 2 October 2023

Inelastic X-ray Scattering

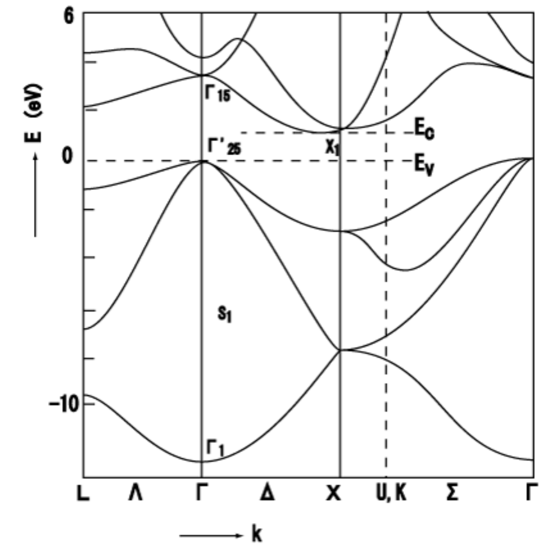
Spectroscopy with one-particle approach



Occupied states of GaAs



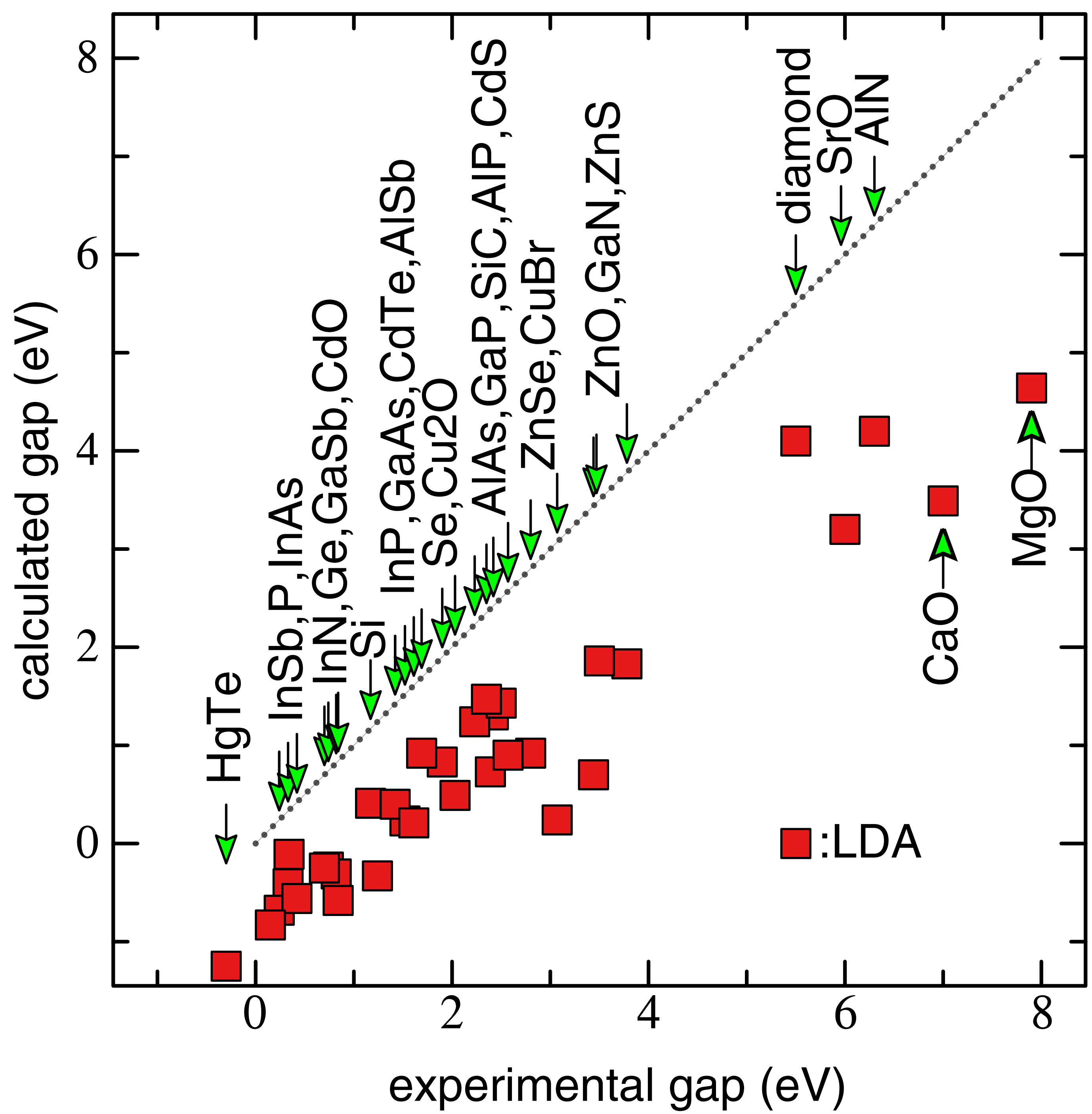
band structure



$$\{\varepsilon_i\}$$

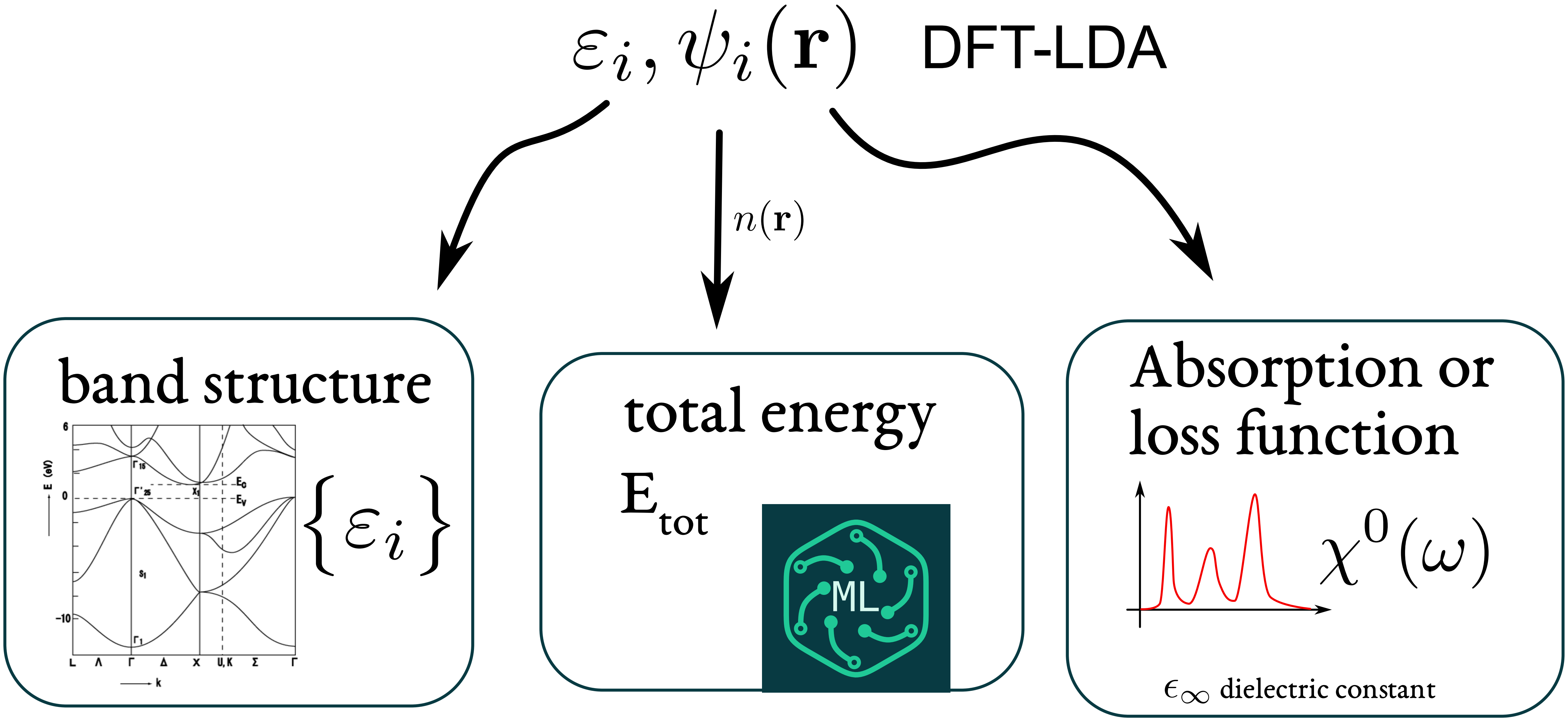
PRB **21**, 3513 (1980)

band-gap tipically underestimated



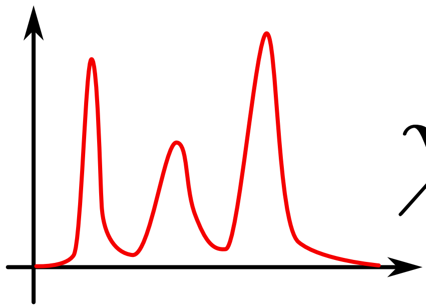
PRL **96**, 226402 (2006)

Spectroscopy with one-particle approach



Loss function of graphite

Absorption or loss function

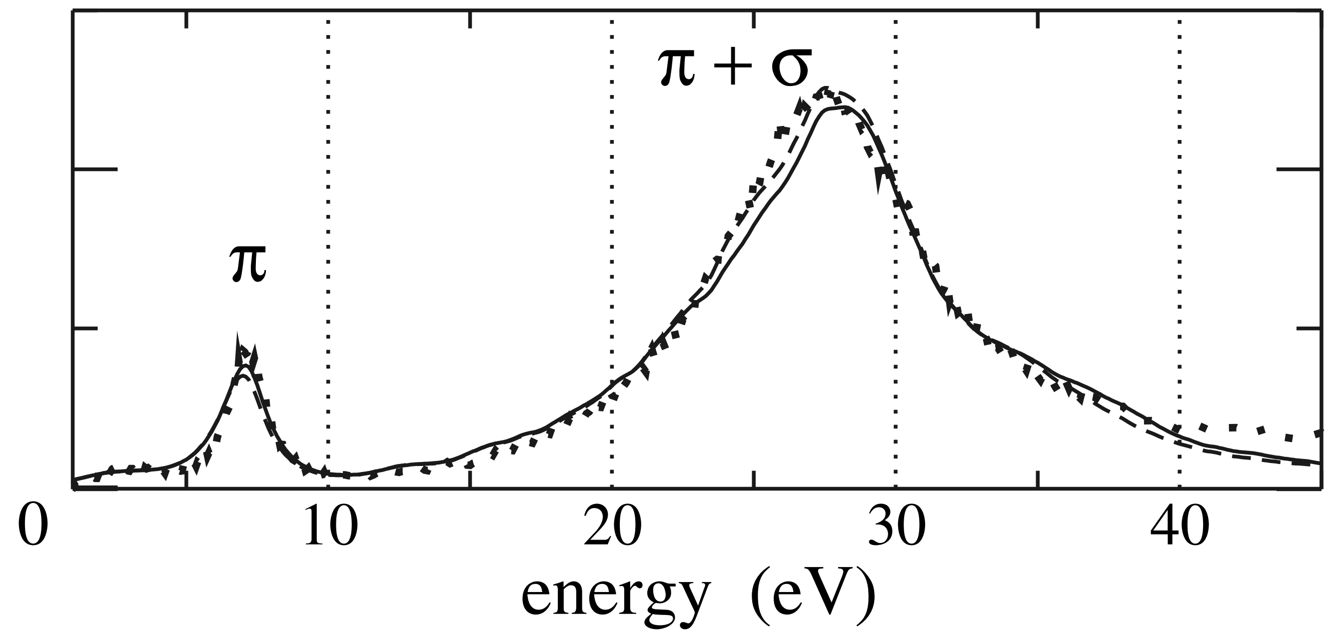


$$\chi^0(\omega)$$

ϵ_∞ dielectric constant

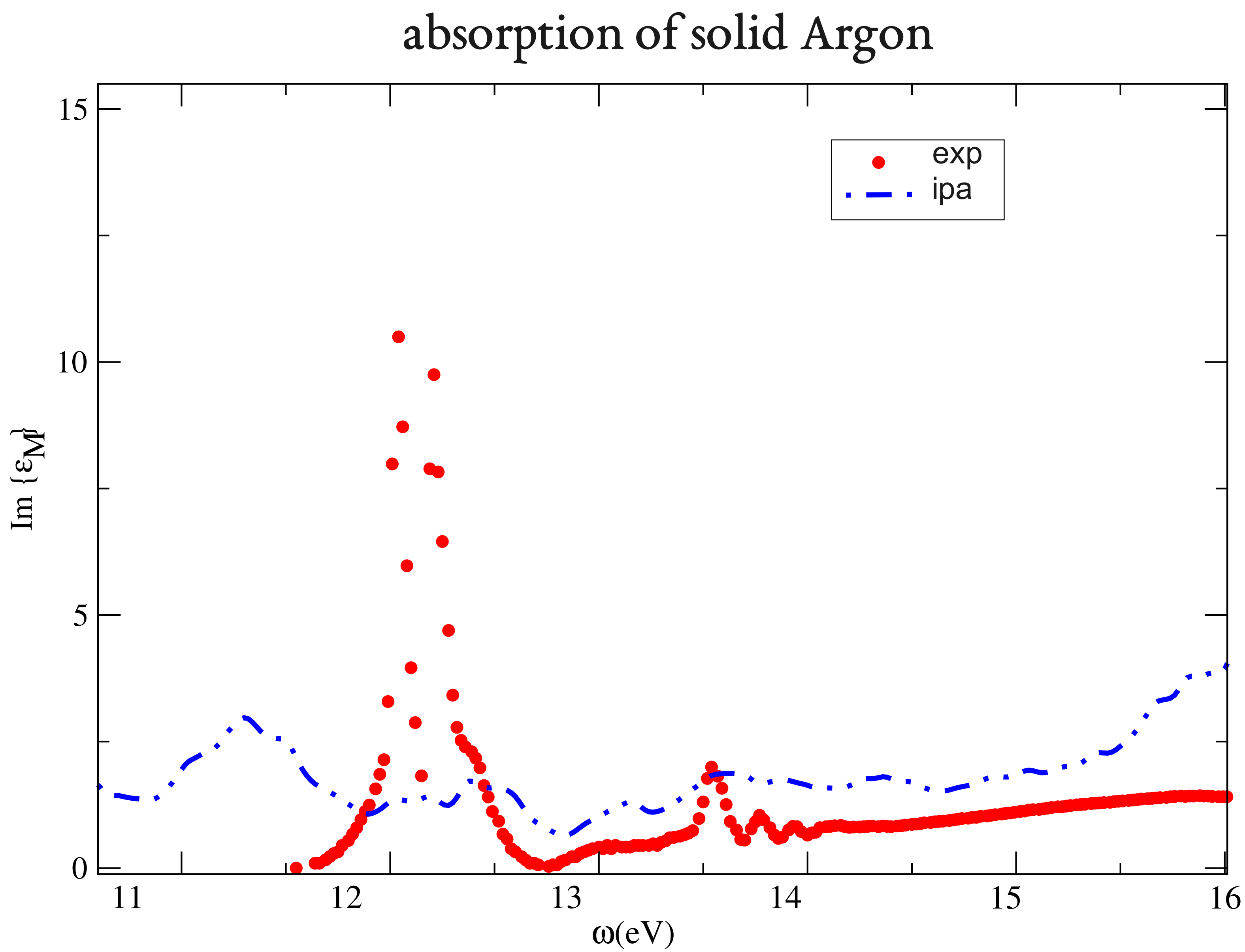
$$\chi^0(\omega) = \sum_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

$$-\operatorname{Im}\epsilon^{-1}(\omega) = -\operatorname{Im}\frac{1}{1 - v\chi^0(\omega)}$$

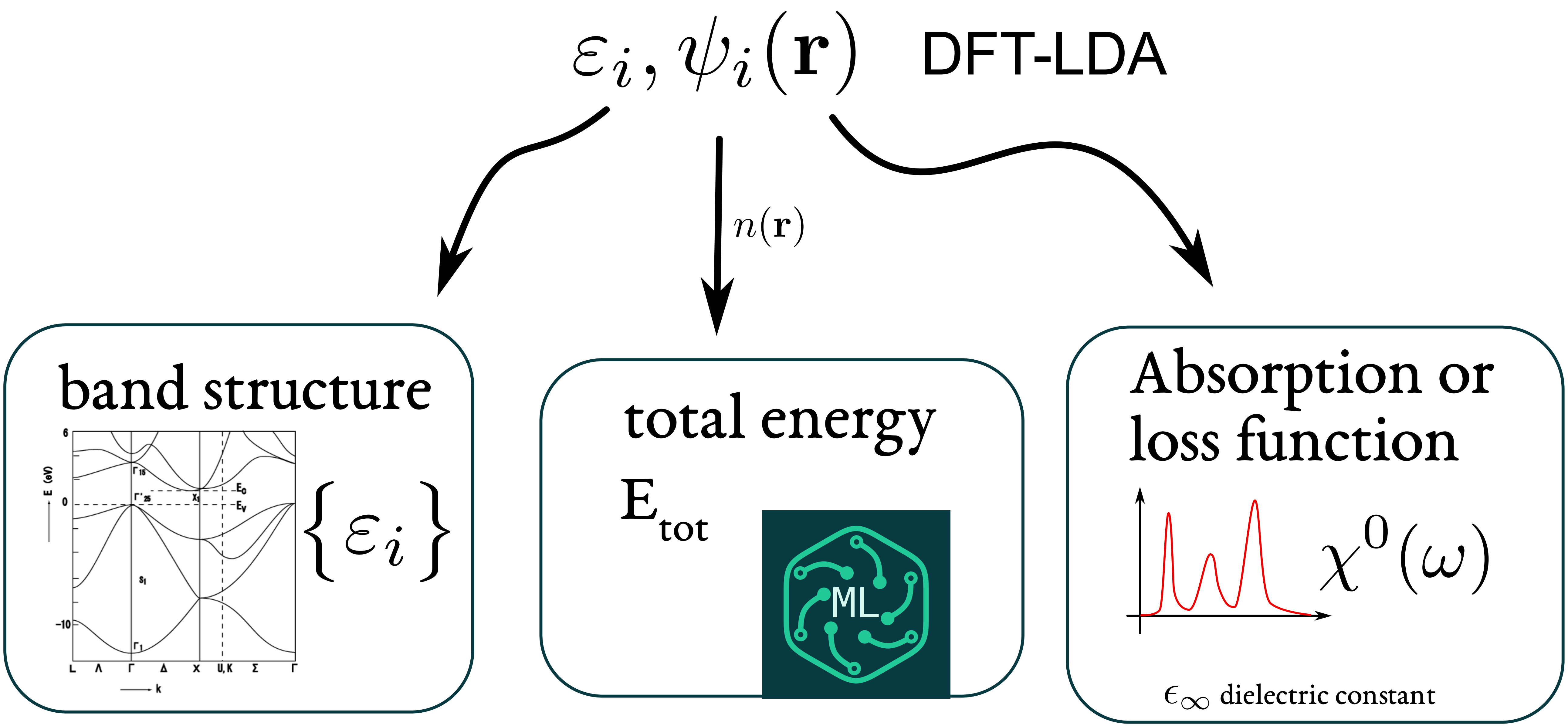


PRL **89**, 076402 (2002)

absorption tipically a disaster

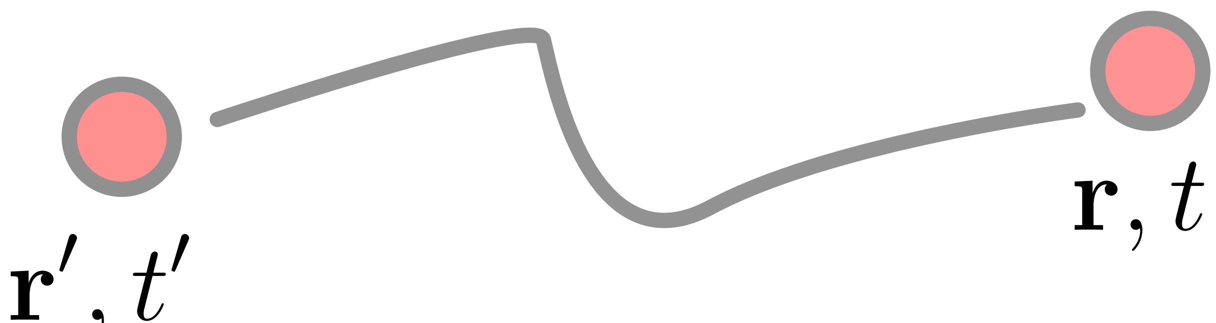


Spectroscopy beyond one-particle approach



Green's function definition

$$G(\mathbf{r}, t, \mathbf{r}', t') = -i \langle \Psi_0^N | \mathcal{T}[\hat{\psi}(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t')] | \Psi_0^N \rangle$$



Green's function definition

$$G(\mathbf{r}, t, \mathbf{r}', t') = -i \left\langle \Psi_0^N \middle| \mathcal{T}\left[\hat{\psi}(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t')\right] \middle| \Psi_0^N \right\rangle$$

$$G(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \to 0^+} \sum_n \frac{\left\langle \Psi_0^N \middle| \hat{\psi}(\mathbf{r}) \middle| \Psi_n^{N+1} \right\rangle \left\langle \Psi_n^{N+1} \middle| \hat{\psi}^\dagger(\mathbf{r}') \middle| \Psi_0^N \right\rangle}{\omega - (E_n^{N+1} - E_0^N) + i\eta} + \lim_{\eta \to 0^+} \sum_n \frac{\left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(\mathbf{r}) \middle| \Psi_n^{N-1} \right\rangle \left\langle \Psi_n^{N-1} \middle| \hat{\psi}(\mathbf{r}') \middle| \Psi_0^N \right\rangle}{\omega - (E_n^{N-1} - E_0^N) - i\eta}$$

$G^p(\mathbf{r}, \mathbf{r}', \omega)$

$G^h(\mathbf{r}, \mathbf{r}', \omega)$

poles of the Green's functions are the electron (and hole) energies $E_n^{N\pm1} - E_0^N$

Green's function definition

$$G(\mathbf{r}, t, \mathbf{r}', t') = -i \langle \Psi_0^N | \mathcal{T}[\hat{\psi}(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t')] | \Psi_0^N \rangle$$

peaks of the spectral functions are the electron (and hole) energies

$$A^p(\mathbf{r}, \mathbf{r}', \omega) = -\frac{1}{2\pi i} G^p(\mathbf{r}, \mathbf{r}', \omega) = \sum_n \left\langle \Psi_0^N \middle| \hat{\psi}(\mathbf{r}) \middle| \Psi_n^{N+1} \right\rangle \left\langle \Psi_n^{N+1} \middle| \hat{\psi}^\dagger(\mathbf{r}') \middle| \Psi_0^N \right\rangle \delta\Big(\omega - (E_n^{N+1} - E_0^N)\Big)$$

$$A^h(\mathbf{r}, \mathbf{r}', \omega) = -\frac{1}{2\pi i} G^h(\mathbf{r}, \mathbf{r}', \omega) = \sum_n \left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(\mathbf{r}) \middle| \Psi_n^{N-1} \right\rangle \left\langle \Psi_n^{N-1} \middle| \hat{\psi}(\mathbf{r}') \middle| \Psi_0^N \right\rangle \delta\Big(\omega + (E_n^{N-1} - E_0^N)\Big).$$

Green's function :: so what ?

density $$n(\mathbf{r}) = -i \lim_{t^+ \to t} G(\mathbf{r}, t, \mathbf{r}, t^+) = G(1, 1^+)$$

density matrix $$\rho(\mathbf{r}, \mathbf{r}') = -i \lim_{t^+ \to t} G(\mathbf{r}, t, \mathbf{r}', t^+)$$

$$\langle F \rangle = -i \int d\mathbf{r} \lim_{\mathbf{r}' \to \mathbf{r}} \lim_{t^+ \to t} F(\mathbf{r}) G(\mathbf{r}, t, \mathbf{r}', t^+)$$

observable of any one-body operator

Green's function of an independent particle system

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_s \frac{\phi_s^*(\mathbf{r}_1)\phi_s(\mathbf{r}_2)}{\omega - \epsilon_s \pm i\eta}$$

Koopmans' theorem

Green's function definition

$$G(\mathbf{r},t,\mathbf{r}',t') = -i\,\langle\Psi_0^N|\mathcal{T}[\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')]|\Psi_0^N\rangle$$

$$i\frac{\partial}{\partial t}G(1,2) = \ldots..$$

Green's function equation of motion

$$G(1,2) = G^0(1,2) + G^0(1,3)v_c(3,4)G^{(2)}(3,4,2,4^+)$$

$$G^{(2)}(1,2,3,4) = -\left\langle \Psi_0^N \middle| \mathcal{T}[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3)] \middle| \Psi_0^N \right\rangle$$

2-particle Green's function

Green's function equation of motion

$$G^{(2)}(1,3,2,4) = G(1,2)G(3,4) - \frac{\delta G(1,2)}{\delta V_{ext}(4,3)}$$

$$G(1,2) = G^0(1,2) + G^0(1,3)v_c(3,4)G(4,2)G(4,4^+) + G^0(1,3)v_c(3,4)\frac{\delta G(3,2)}{\delta V_{ext}(4,4^+)}$$

Green's function equation of motion

$$G^{(2)}(1,3,2,4) = G(1,2)G(3,4) - \frac{\delta G(1,2)}{\delta V_{ext}(4,3)}$$

$$G(1,2) = G^0(1,2) + G^0(1,3)\boldsymbol{v_c(3,4)}G(4,2)\boldsymbol{G(4,4^+)}$$ ← **Hartree GF**

$$G(1,2) = G^0(1,2) + G^0(1,3)V_H(3)\delta(3,4)G(4,2) + G^0(1,3)v_c(3,4)G(3,5)\frac{\delta G^{-1}(5,6)}{\delta V_{ext}(4,4^+)}G(6,2)$$

Hartree-Fock $G(1,2) = G^0(1,2) + G^0(1,3)V_H(3)G(3,2) + G^0(1,3)v_c(3,4)G(3,4)G(4,2)$

Green's function equation of motion

$$G^{(2)}(1,3,2,4) = G(1,2)G(3,4) - \frac{\delta G(1,2)}{\delta V_{ext}(4,3)}$$

$$G = G^0 + G^0[V_H + \Sigma]G$$

$$\Sigma(1,2) = v_c(1,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta V_{ext}(3,3^+)}$$

Self-Energy

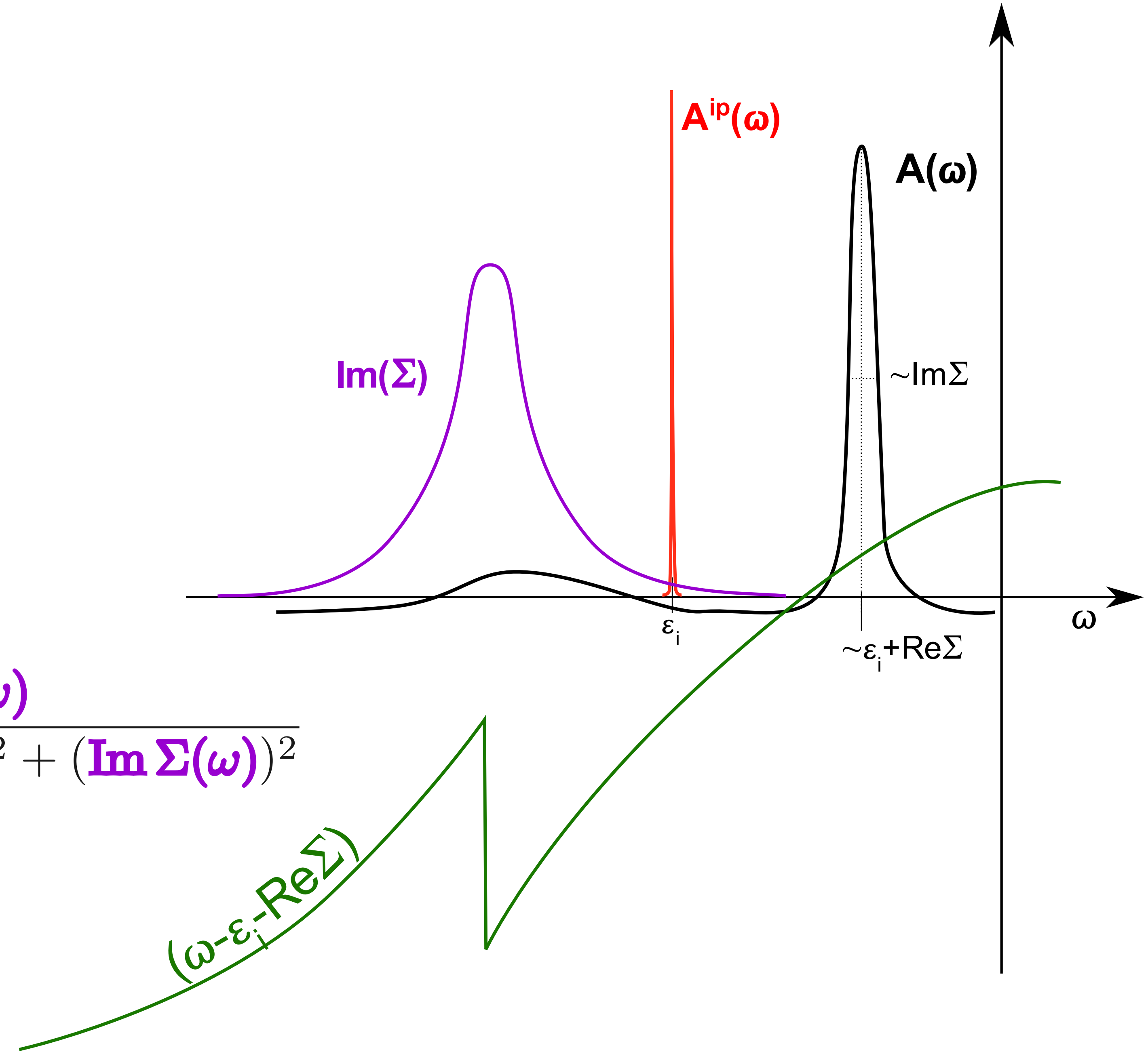
Dyson equation for the Green's function :: what's new ?

$$G = G^0 + G^0[V_H + \Sigma]G$$

$$G = G^0_H + G^0_H \Sigma G$$

$$A^{ip}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G^H(\omega) = \frac{1}{\pi}\delta(\omega - \varepsilon_i)$$

$$A(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G(\omega) = \frac{1}{\pi}\frac{\mathbf{Im}\,\boldsymbol{\Sigma}(\boldsymbol{\omega})}{(\boldsymbol{\omega} - \boldsymbol{\varepsilon_i} - \mathbf{Re}\,\boldsymbol{\Sigma}(\boldsymbol{\omega}))^2 + (\mathbf{Im}\,\boldsymbol{\Sigma}(\boldsymbol{\omega}))^2}$$



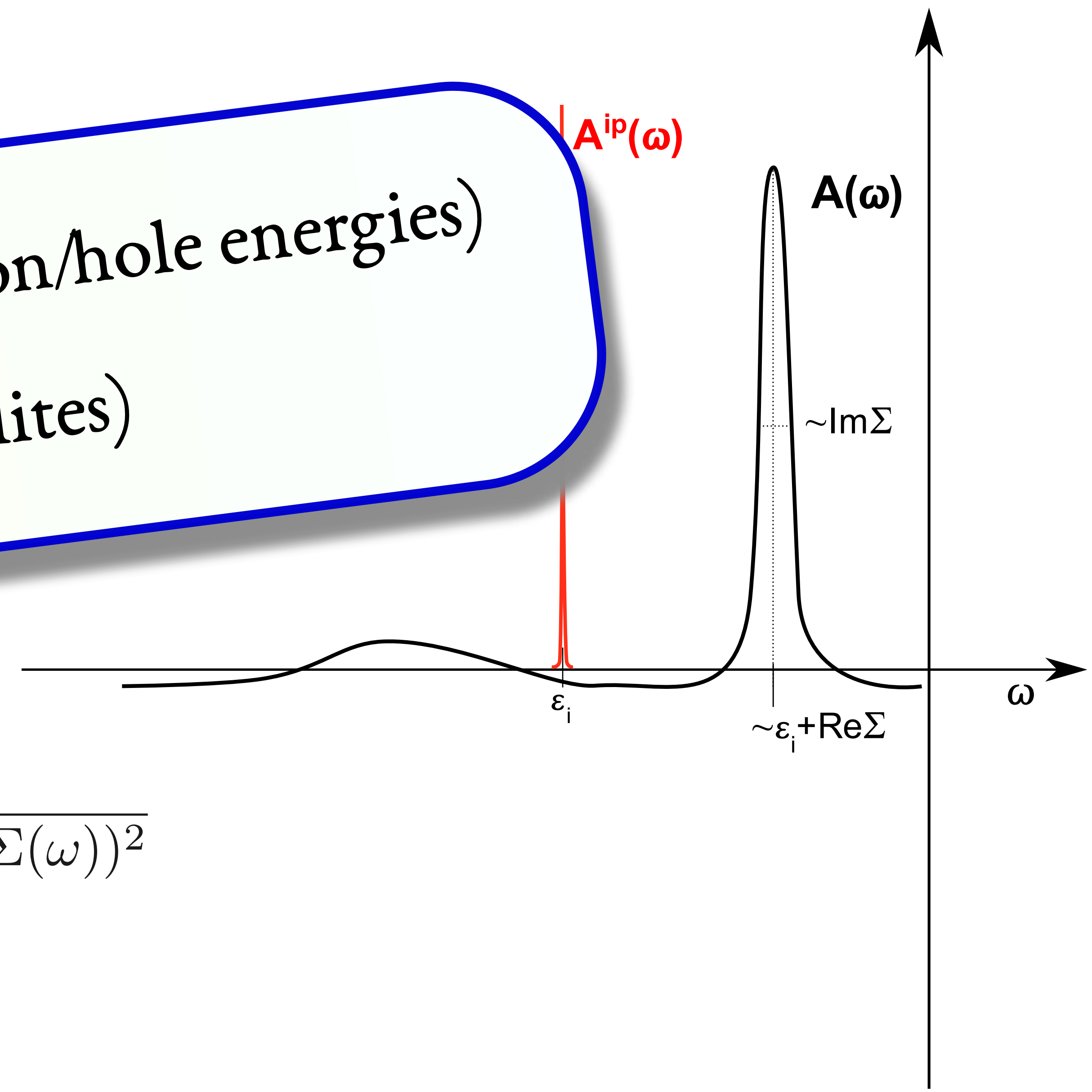
Dyson equation for the Green's function :: what's new ?

$$G = G^0 + G^0[V_H + \Sigma]G$$

$G = G^0 + G^0 \ldots$

- G has new poles (new electron/hole energies)
- G has a new structure (satellites)

$A^{ip}(\ldots$



$$A(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G(\omega) = \frac{1}{\pi}\,\frac{\mathrm{Im}\,\Sigma(\omega)}{(\omega - \varepsilon_i - \mathrm{Re}\,\Sigma(\omega))^2 + (\mathrm{Im}\,\Sigma(\omega))^2}$$

Green's function and self-energy

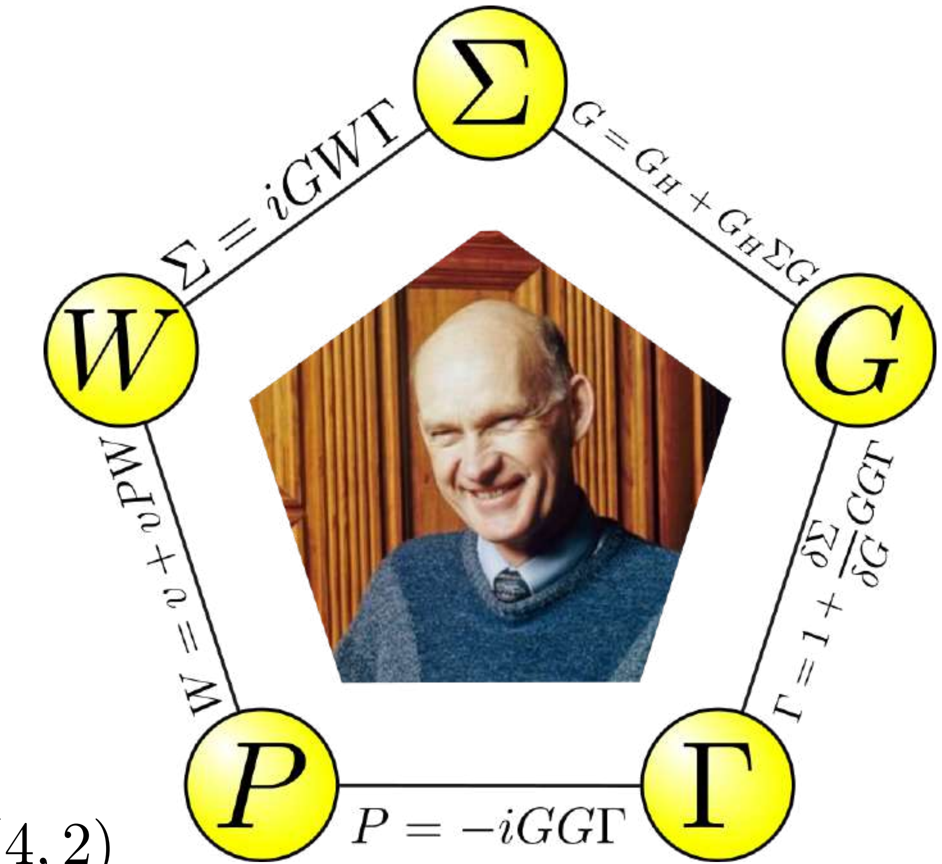
$$G = G^0 + G^0[V_H + \Sigma]G$$

$$\Sigma(1,2) = v_c(1,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta V_{ext}(3,3^+)} = v_c G \frac{\delta G^{-1}}{\delta V_{tot}}\frac{\delta V_{tot}}{\delta V_{ext}}$$

$$= \boldsymbol{v_c} G \boldsymbol{\epsilon^{-1}} \frac{\boldsymbol{\delta G^{-1}}}{\boldsymbol{\delta V_{tot}}}$$

$$= G(1,3)\boldsymbol{W(4,1)}\Gamma(3,2,4)$$

Hedin's equations



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

$$G(1,2) = G_0(1,2) + \int d(34)\, G_0(1,3) \left[V_H(3) + \Sigma(3,4) \right] G(4,2)$$

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

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

$$W(1,2) = v_c(1,2) + \int d(45) v_c(1,4) P(4,5) W(5,2),$$

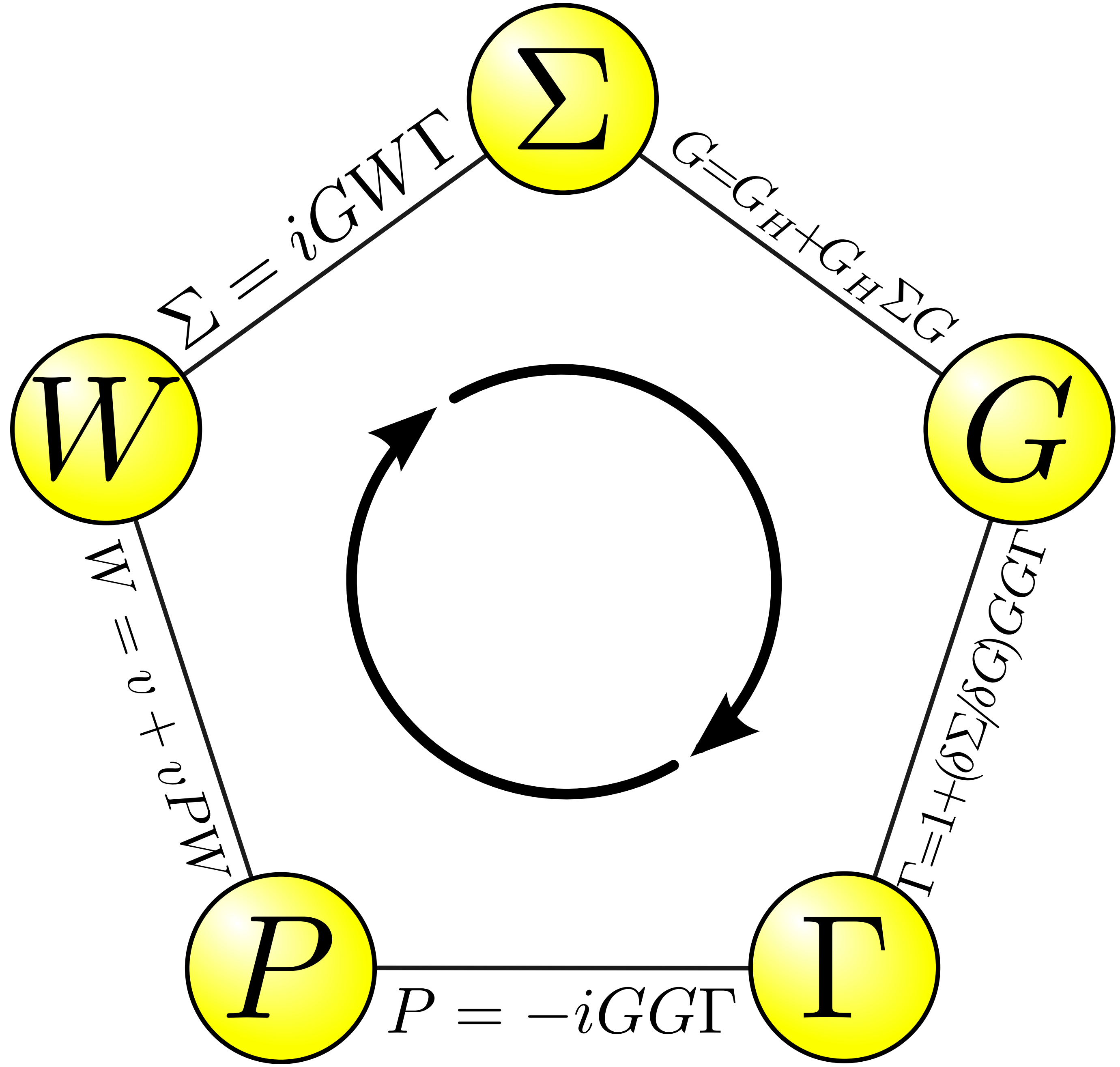
$$\Sigma = GW\Gamma$$

$$G = G_H + G_H \Sigma G$$

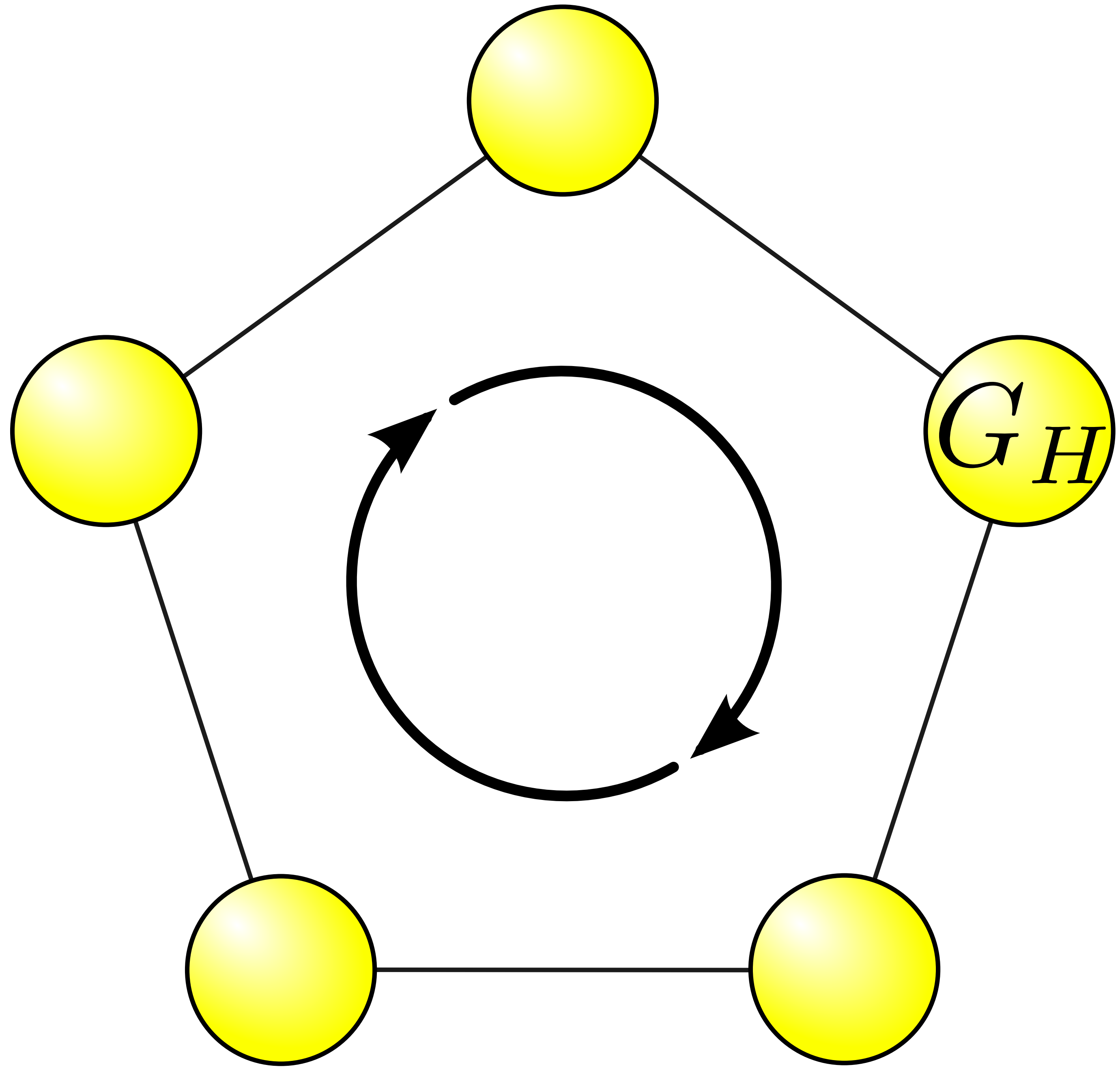
$$\Gamma = 1 + \frac{\delta \Sigma}{\delta G} GG\Gamma$$

$$P = -iGG\Gamma$$

$$W = v_c + v_c PW$$

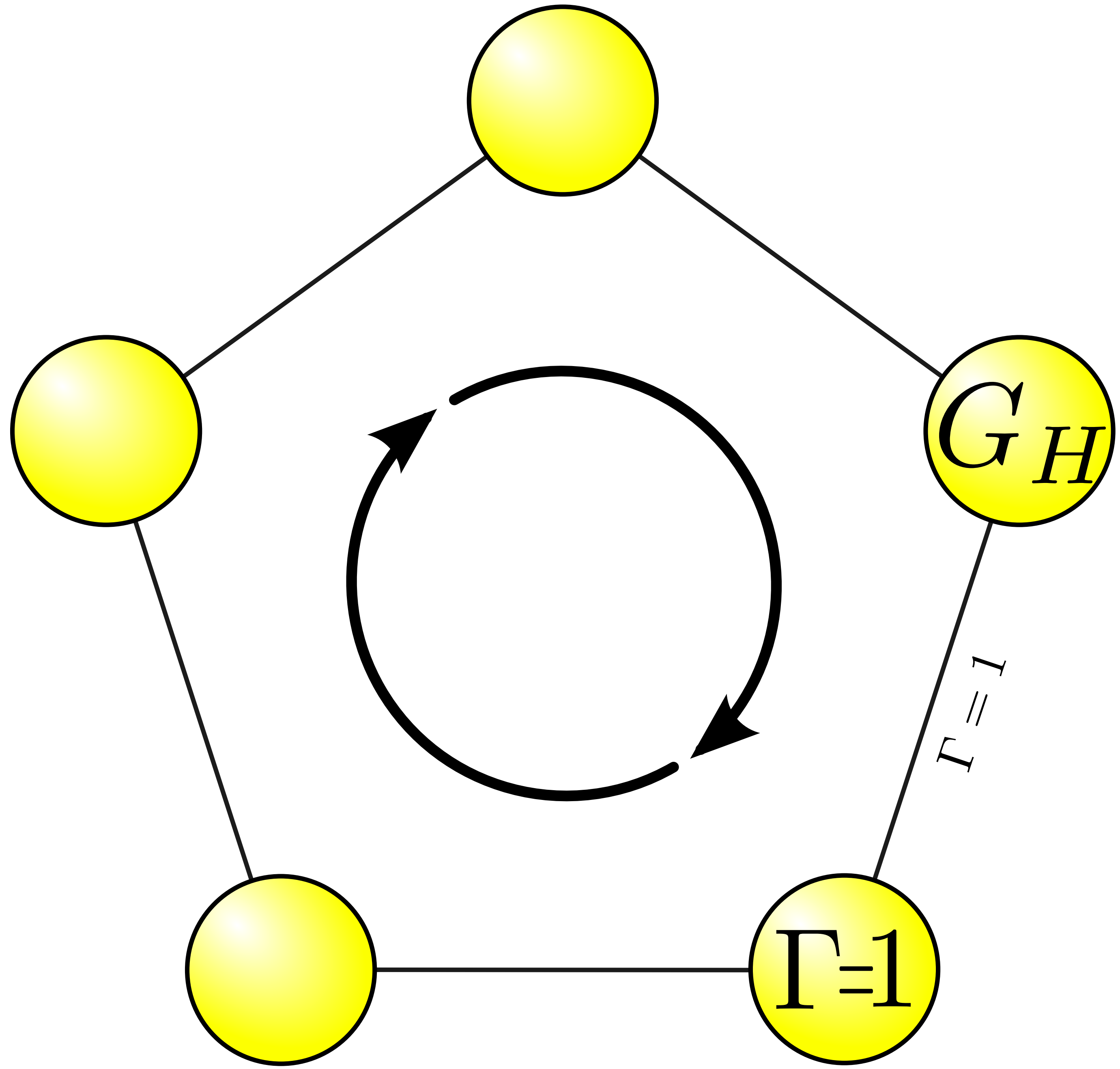


$$G = G_H$$

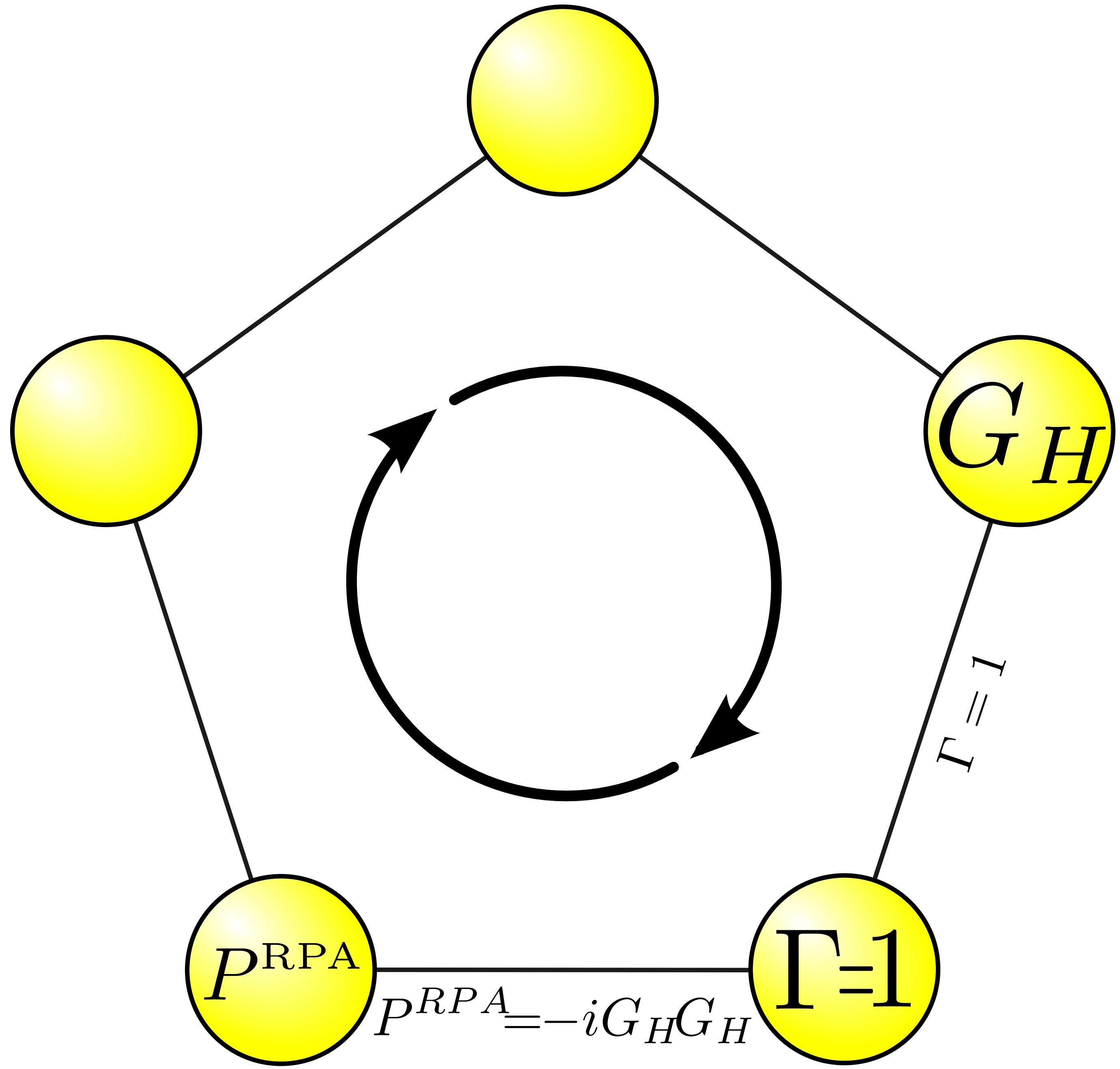


$G = G_H$

$\Gamma = 1$



$$G = G_H$$
$$\Gamma = 1$$
$$P^{RPA} = -iG_H G_H$$

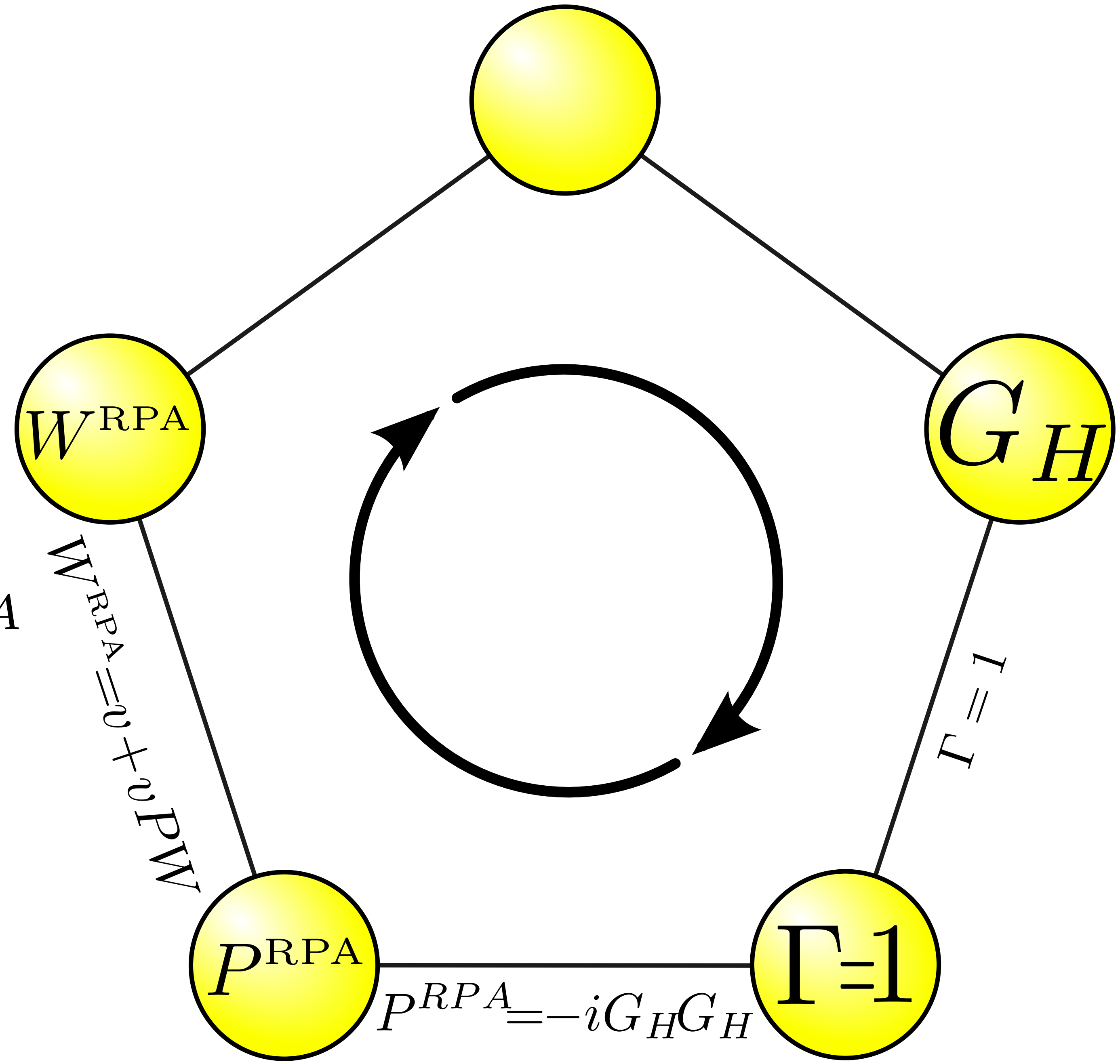


$$G = G_H$$

$$\Gamma = 1$$

$$P^{RPA} = -iG_H G_H$$

$$W^{RPA} = v_c + v_c P^{RPA} W^{RPA}$$



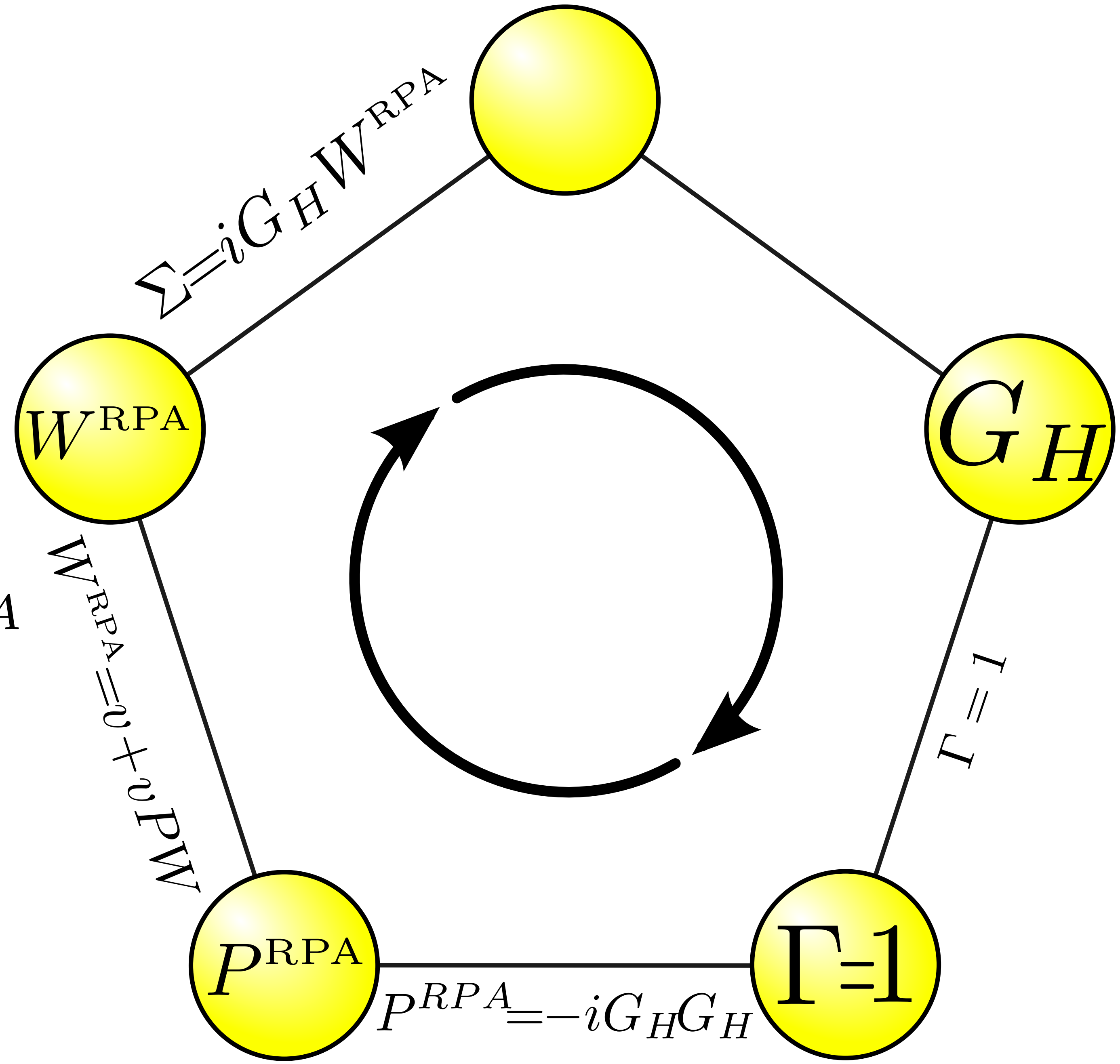
$$G = G_H$$

$$\Gamma = 1$$

$$P^{RPA} = -iG_H G_H$$

$$W^{RPA} = v_c + v_c P^{RPA} W^{RPA}$$

$$\Sigma = G_H W^{RPA}$$



$$G = G_H$$

$$\Gamma = 1$$

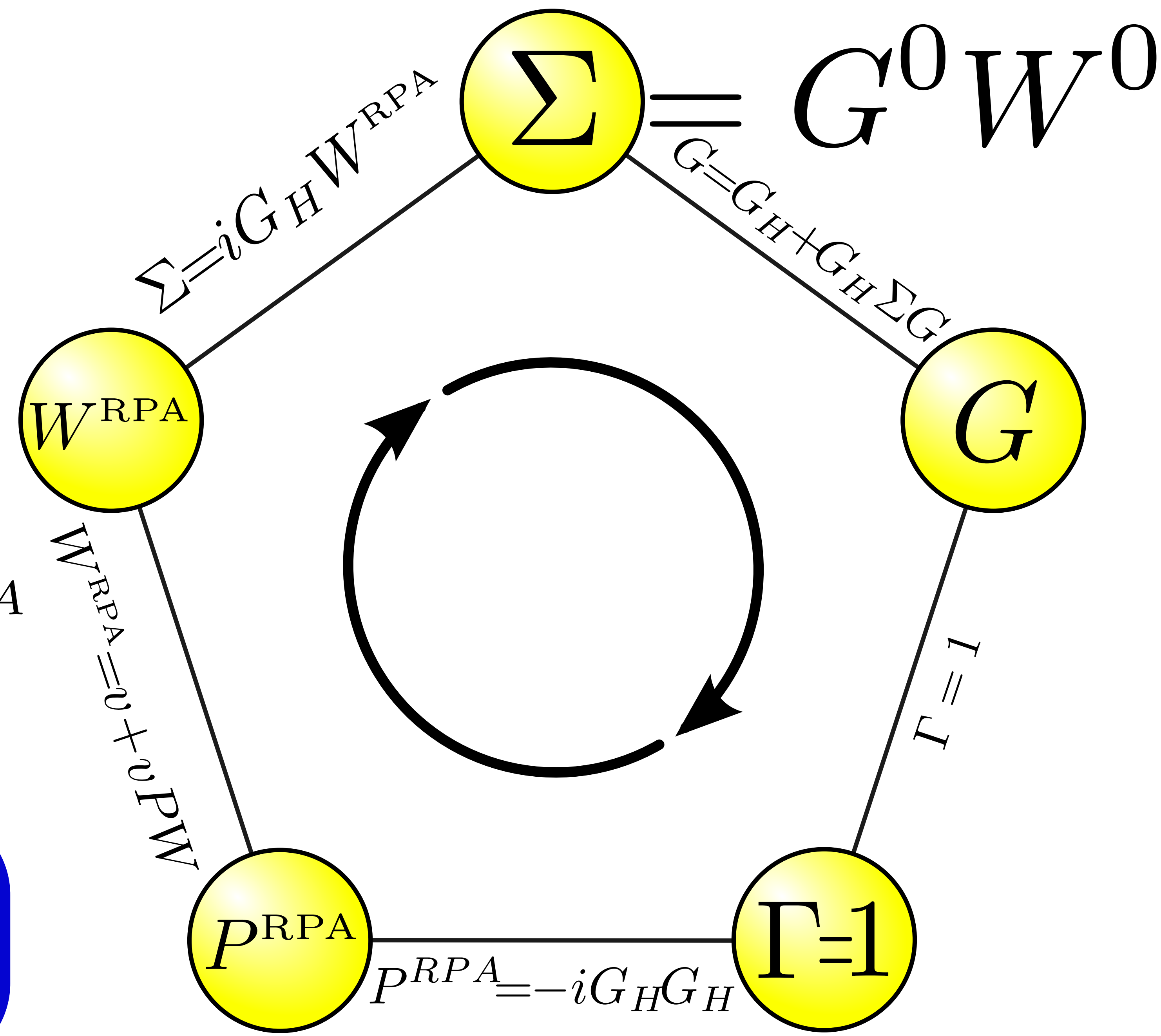
$$P^{RPA} = -iG_H G_H$$

$$W^{RPA} = v_c + v_c P^{RPA} W^{RPA}$$

$$\Sigma = G_H W^{RPA}$$

$$\Sigma = G^0 W^0$$

GW approximation



GW approximation = dynamically screened Hartree-Fock

$$\Sigma = GW = G\epsilon^{-1}v_c$$

quasi-particle approximation for GW

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

Hartree-Fock equations

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\phi_i(\mathbf{r}) + \int d\mathbf{r}' \sum_{j\neq i} \frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}') = \varepsilon_i\phi_i(\mathbf{r})$$

GW approximation = dynamically screened Hartree-Fock

$$\Sigma = GW = G\epsilon^{-1}v_c$$

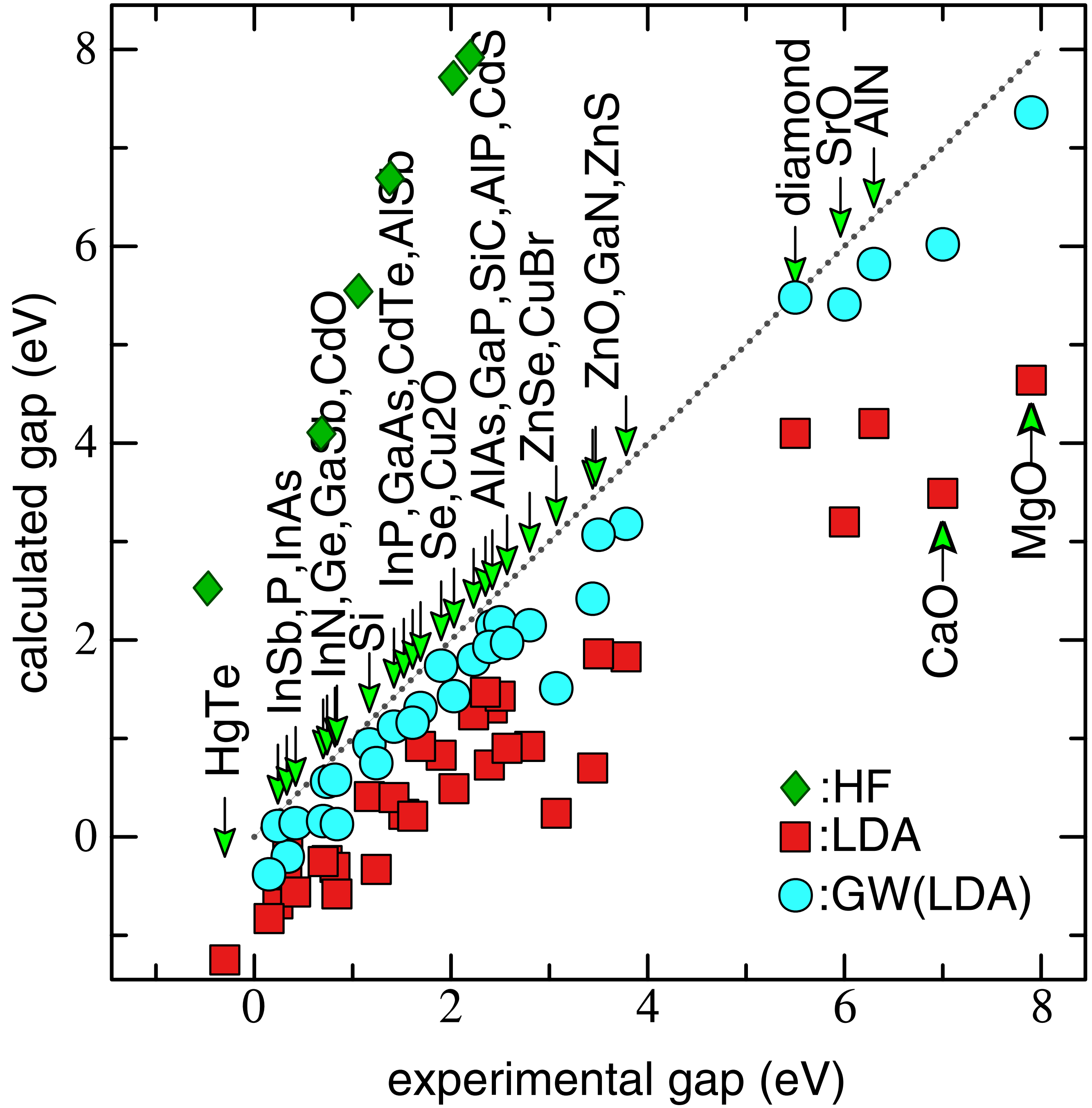
quasi-particle approximation for GW

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

Hartree-Fock equations

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

GW approximation some results

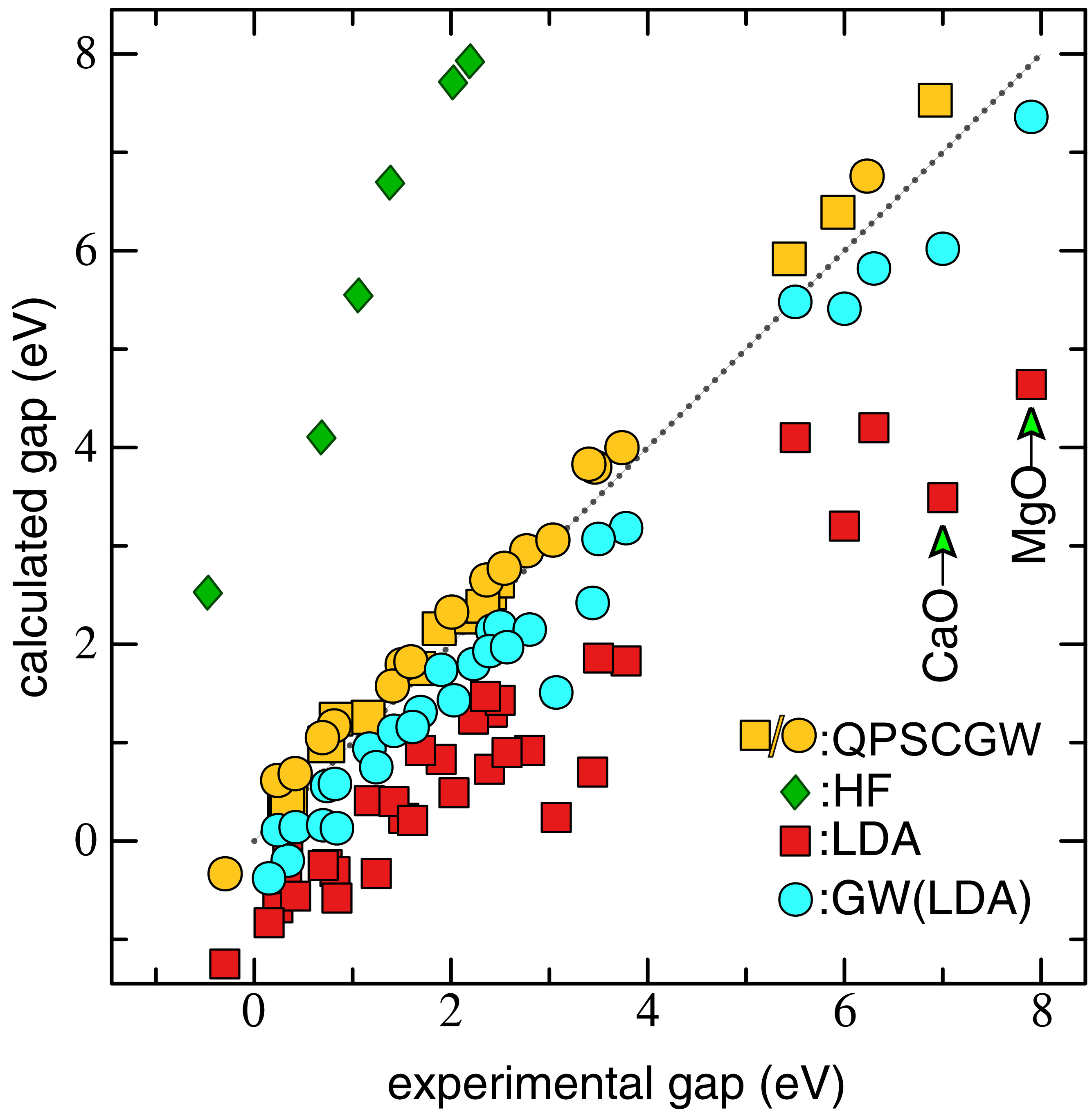


PRL **96**, 226402 (2006)

V. Olevano courtesy

GW approximation some results

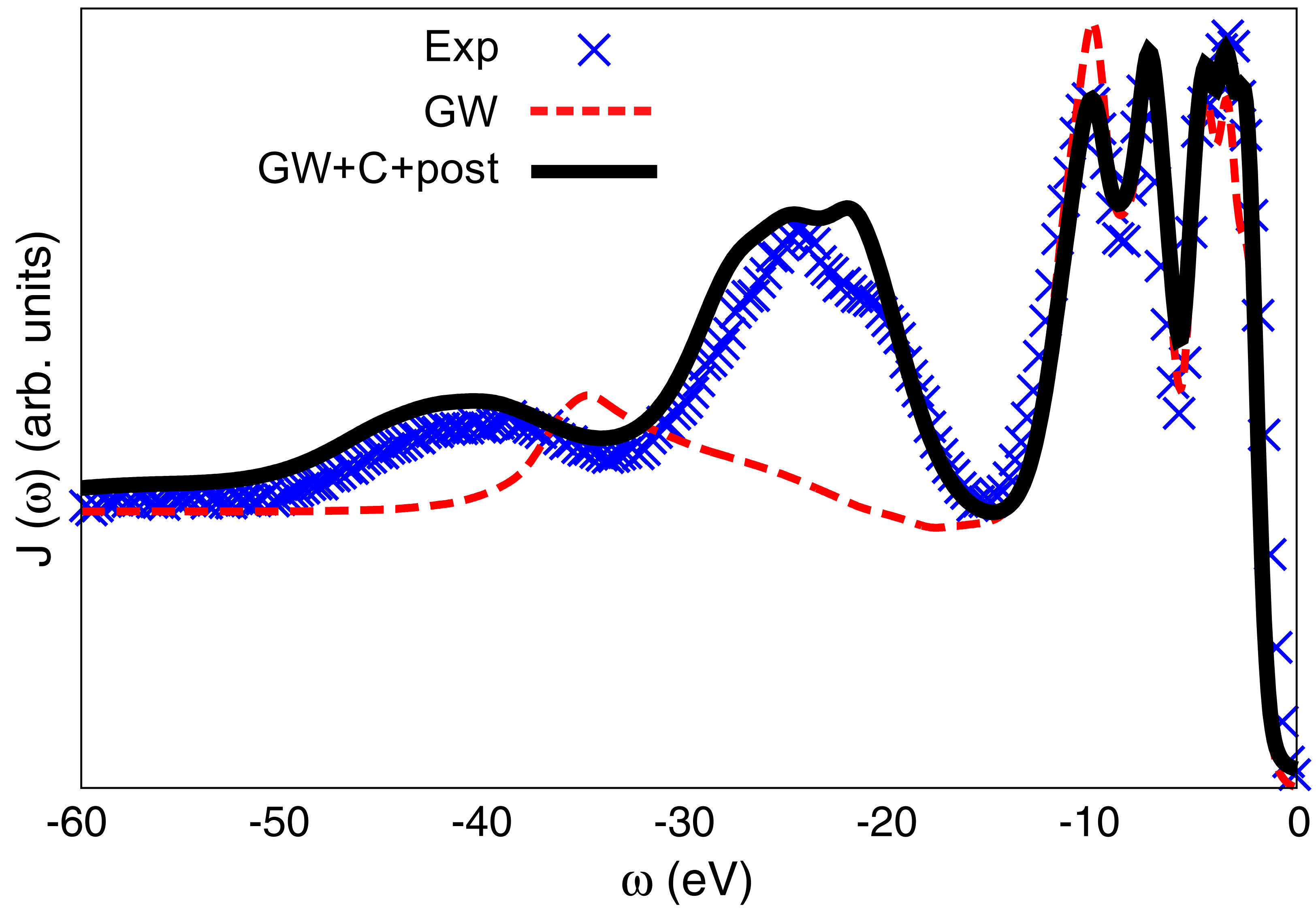
GW systematically improve band-gap



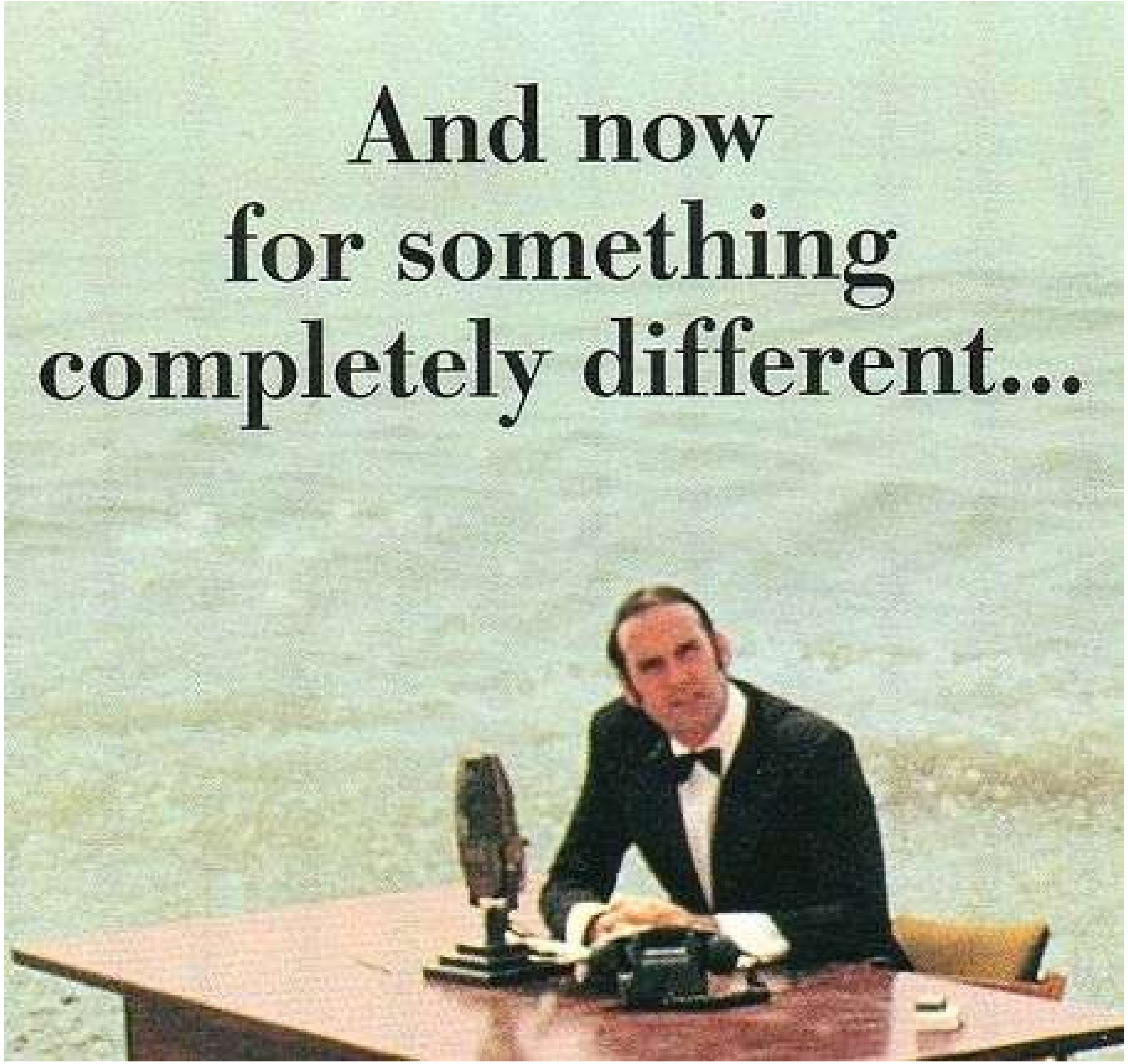
PRL **96**, 226402 (2006)

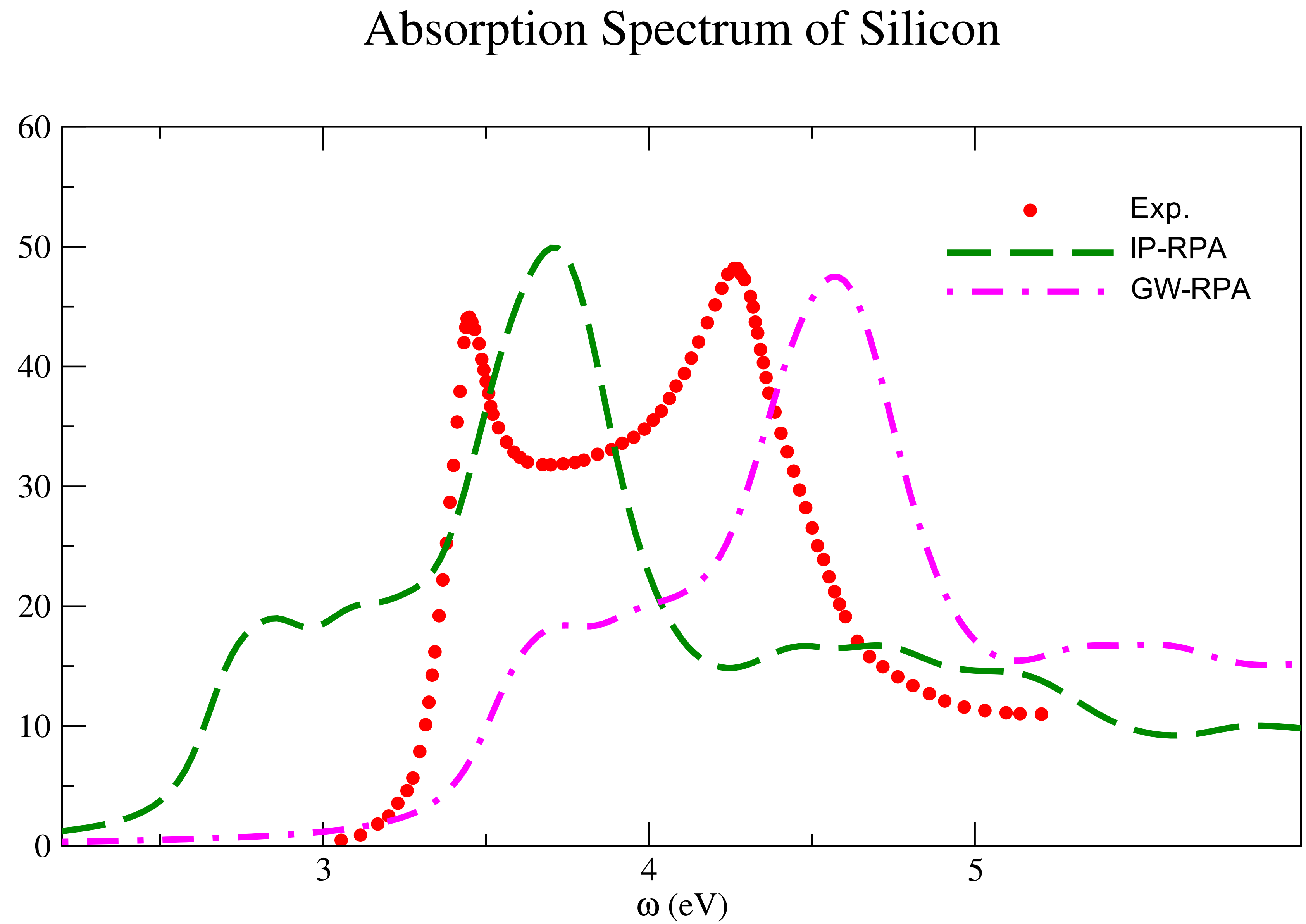
V. Olevano courtesy

Photo-emission spectrum of bulk silicon

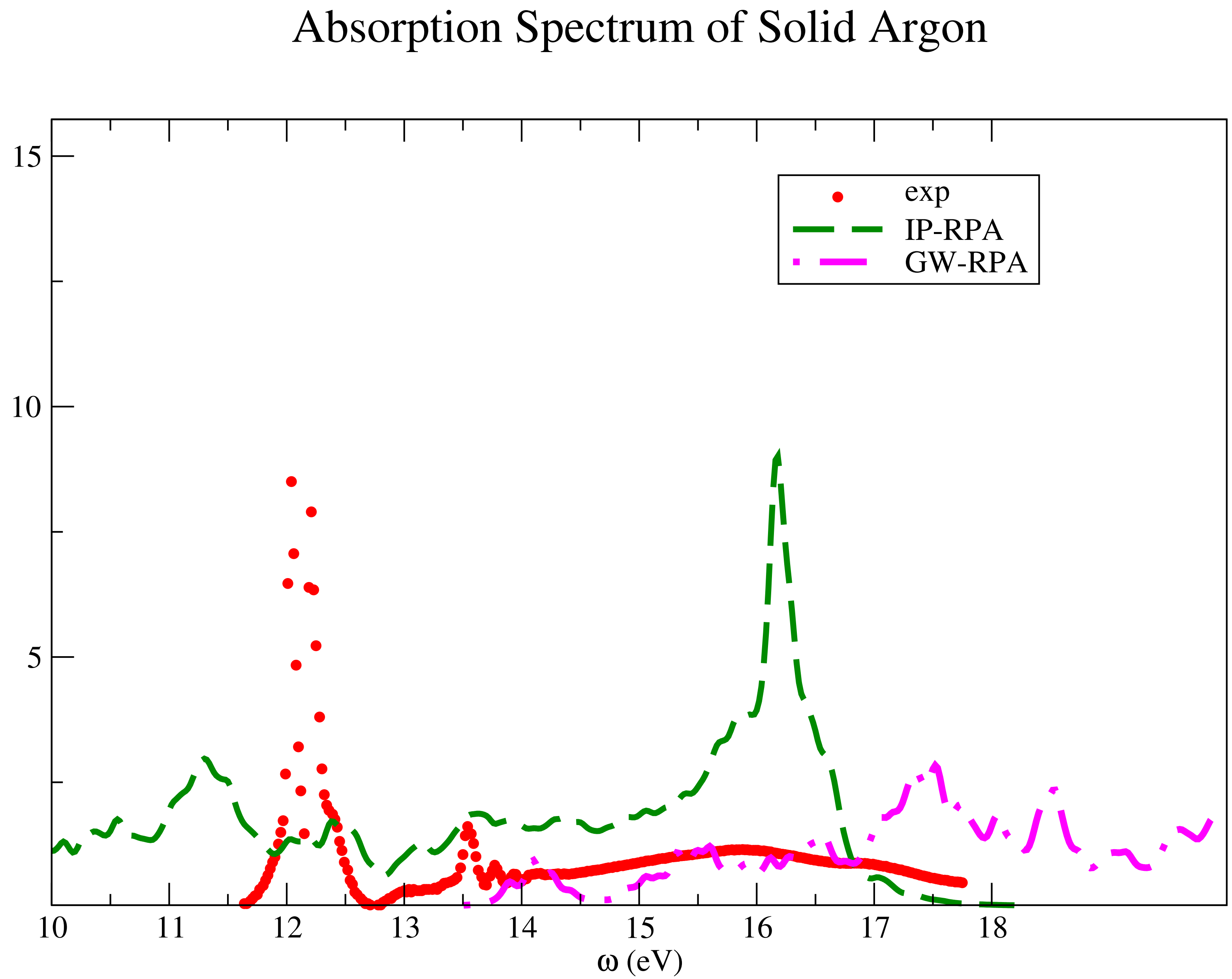


PRL **107**, 166401 (2011)


And now
for something
completely different...

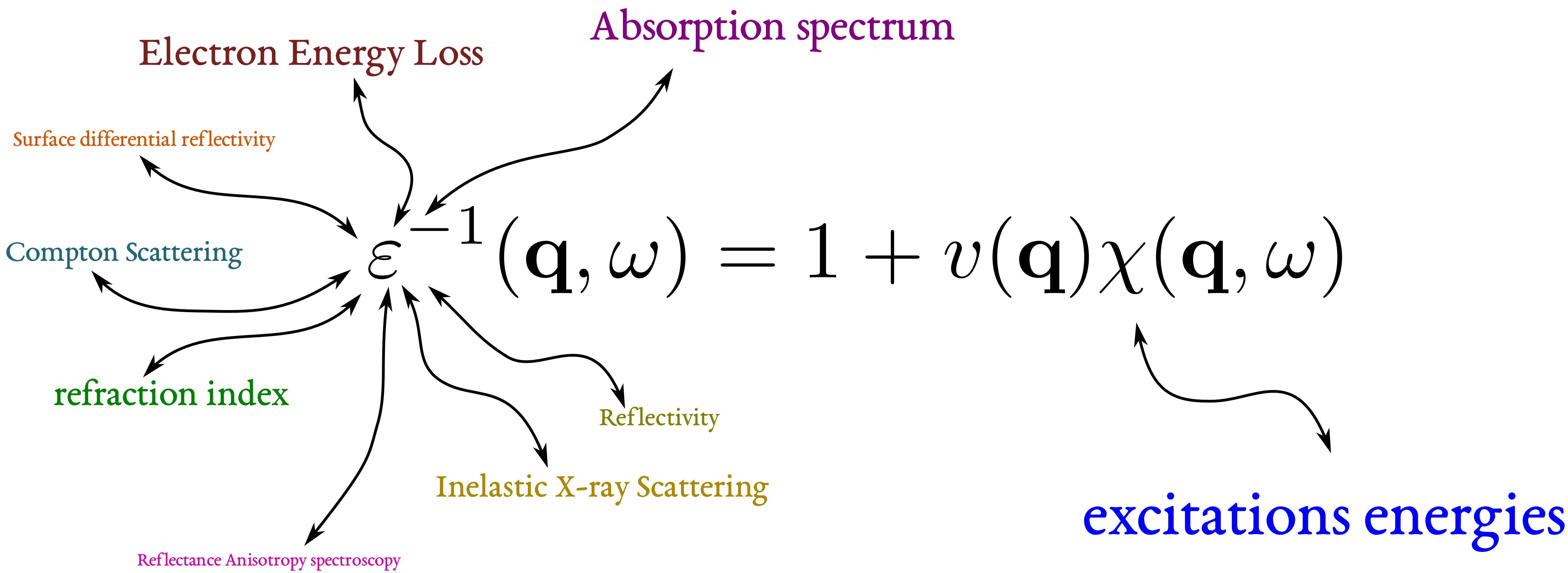


$$\chi_0^{\mathrm{GW}}(\mathbf{r},\mathbf{r}',\omega) = \sum_{ij}(f_i - f_j)\frac{\tilde{\psi}_j^*(\mathbf{r}')\tilde{\psi}_i^*(\mathbf{r}')\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_j(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_i + \Delta_{ij}) + i\eta}$$



Absorption Spectrum of Solid Argon
15
10
5
exp
IP-RPA
GW-RPA
10
11
12
13
14
15
16
17
18
ω (eV)

Dielectric function or polarizability



$$\chi(1,2) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

Polarizability

$$\epsilon^{-1}(1,2) = \frac{\delta V_{tot}(1)}{\delta V_{ext}(2)}$$

Inverse dielectric function

Green's functions approach

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

$$G(1,2) = G_0(1,2) + \int d(34)\, G_0(1,3) \big[V_H(3) + \Sigma(3,4)\big] G(4,2)$$

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

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

$$W(1,2) = V(1,2) + \int d(45) V(1,4) P(4,5) W(5,2)$$

$$\chi(1,2) = \frac{\delta n(1)}{\delta V_{ext}(2)} = -i\frac{\delta G(1,1)}{\delta V_{ext}(2,2)}$$ **Polarizability (2-point)**

$$L(1,2,3,4) = -i\frac{\delta G(1,2)}{\delta V_{\text{ext}}(3,4)}$$ **4-point Polarizability**

$$L(1,1,3,3) \rightarrow \chi(1,3)$$

$$\chi(1,2) = \frac{\delta n(1)}{\delta V_{ext}(2)} = -i\frac{\delta G(}{\delta V_{ext}}$$

$$iG(1,2)G(3,4) - G^{(2)}(1,2,3,4) = \boxed{L(1,2,3,4) = -i\frac{\delta G(1,2)}{\delta V_{\text{ext}}(3,4)}}$$

$$L(1,1,3,$$

$$G = G_0 + G_0(V_H + \Sigma)G = \Big[1 - G_0(V_H + \Sigma)\Big]^{-1} G_0$$

$$G^{-1} = G_0^{-1} - V_H - \Sigma$$

$$L(1,2,3,4) = -i \frac{\delta G(1,2)}{\delta V_{\text{ext}}(3,4)} = i \int d(56) G(1,5) \frac{\delta G^{-1}(5,6)}{\delta V_{\text{ext}}(3,4)} G(6,2),$$

$$\begin{aligned}
L(1,2,3,4) &= i \int d(56) G(1,5) \left[\frac{\delta G_0^{-1}(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta V_H(5)\delta(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta \Sigma(5,6)}{\delta V_{\text{ext}}(3,4)} \right] G(6,2) \\
&= i \int d(56) G(1,5) \left[-\delta(5,3)\delta(6,4) - \frac{\delta V_H(5)\delta(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta \Sigma(5,6)}{\delta V_{\text{ext}}(3,4)} \right] G(6,2) \\
&= -iG(1,3)G(4,2) - \int d(5678) G(1,5) \left[\frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)} + \frac{\delta \Sigma(5,6)}{\delta G(7,8)} \right] \frac{\delta G(7,8)}{\delta V_{\text{ext}}(3,4)} G(6,2) \\
&= -iG(1,3)G(4,2) + \\
&\quad - \int d(5678) G(1,5) \left[-iv(5,7)\delta(5,6)\delta(7,8) + \frac{\delta \Sigma(5,6)}{\delta G(7,8)} \right] G(6,2) L(7,8,3,4)
\end{aligned}$$

$$
\begin{aligned}
L(1,2,3,4) &= i\int d(56)G(1,5)\left[\frac{\delta G_0^{-1}(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta V_H(5)\delta(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta\Sigma(5,6)}{\delta V_{\text{ext}}(3,4)}\right]G(6,2) \\
&= i\int d(56)G(1,5)\left[-\delta(5,3)\delta(6,4) - \frac{\delta V_H(5)\delta(5,6)}{\delta V_{\text{ext}}(3,4)} - \frac{\delta\Sigma(5,6)}{\delta V_{\text{ext}}(3,4)}\right]G(6,2) \\
&= -iG(1,3)G(4,2) - \int d(5678)G(1,5)\left[\frac{\delta V_H(5)\delta(5,6)}{\delta G(7,8)} + \frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right]\frac{\delta G(7,8)}{\delta V_{\text{ext}}(3,4)}G(6,2) \\
&= -iG(1,3)G(4,2) + \\
&\quad - \int d(5678)G(1,5)\left[-iv(5,7)\delta(5,6)\delta(7,8) + \frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right]G(6,2)L(7,8,3,4)
\end{aligned}
$$

$$
\boxed{L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678)L_0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) + \Xi(5,6,7,8)\right]L(7,8,3,4)}
$$

$$
L_0(1,2,3,4) = -iG(1,3)G(4,2) \qquad \Xi(5,6,7,8) = i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}
$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) + \Xi(5,6,7,8) \right] L(7,8,3,4)$$

$$L_0(1,2,3,4) = -iG(1,3)G(4,2)$$

$$\Xi(5,6,7,8) = i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}$$

$$L = L_0 + L_0(v + \Xi)L$$

BSE

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) + \Xi(5,6,7,8)\right] L(7,8,3,4)$$

GW approximation

$$\begin{aligned}\Xi(5,6,7,8) &= i\frac{\delta\Sigma(5,6)}{\delta G(7,8)} = \\ &= -\frac{\delta[G(5,6)W(5,6)]}{\delta G(7,8)} = -W(5,6)\delta(5,7)\delta(6,8) - \underbrace{\cancel{G(5,6)\frac{\delta W(5,6)}{\delta G(7,8)}}}_{\text{second order in } W} \\ &\approx -W(5,6)\delta(5,7)\delta(6,8).\end{aligned}$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8)\right] L(7,8,3,4)$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8) \right] L(7,8,3,4)$$

static (W) approximation

$$W(1,2) \approx W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)\delta(t_1 - t_2),$$

$$\begin{aligned} L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) &= L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) + \\ &+ \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_5, \mathbf{r}_6, \omega) \Big[v(\mathbf{r}_5 - \mathbf{r}_7)\delta(\mathbf{r}_5 - \mathbf{r}_6)\delta(\mathbf{r}_7 - \mathbf{r}_8) + \\ &\qquad - W(\mathbf{r}_5, \mathbf{r}_6)\delta(\mathbf{r}_5 - \mathbf{r}_7)\delta(\mathbf{r}_7 - \mathbf{r}_8) \Big] L(\mathbf{r}_7, \mathbf{r}_8, \mathbf{r}_3, \mathbf{r}_4, \omega) \end{aligned}$$

$$L(1,2,3,4;\omega) = L_0(1,2,3,4;\omega) + L_0(1,2,5,6;\omega) \left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8) \right] L(7,8,3,4;\omega)$$

$$L(1,2,3,4;\omega) = L_0(1,2,3,4;\omega) + L_0(1,2,5,6;\omega)\left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8)\right] L(7,8,3,4;\omega)$$

independent propagation L_0

$$L_0 = -iG_0^{GW} G_0^{GW} = \chi_0^{\mathrm{GW}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_j^*(\mathbf{r}_3)\psi_i^*(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (\epsilon_j - \epsilon_i + \Delta_{ij}) + i\eta}$$

- **GW approximation**
- **static (W) approximation**
- **independent propagation** L_0

$$L_0 = -iG_0^{GW} G_0^{GW} = \chi_0^{\mathrm{GW}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_j^*(\mathbf{r}_3)\psi_i^*(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (\epsilon_j - \epsilon_i + \Delta_{ij}) + i\eta}$$

and now ??

$$L(1,2,3,4;\omega) = L_0(1,2,3,4;\omega) + L_0(1,2,5,6;\omega)\left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8)\right]L(7,8,3,4;\omega)$$

really invert 4-point function for each frequency ??

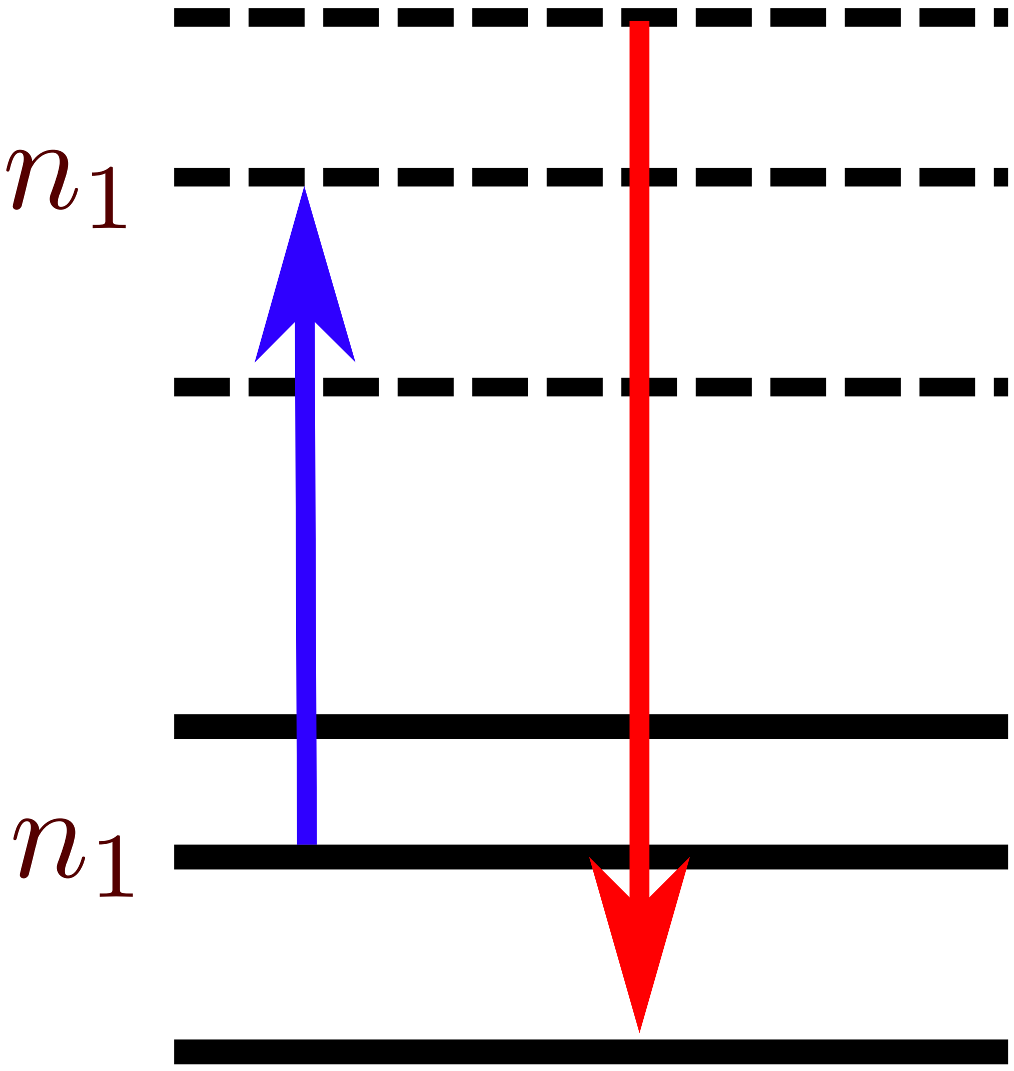
let's define a basis

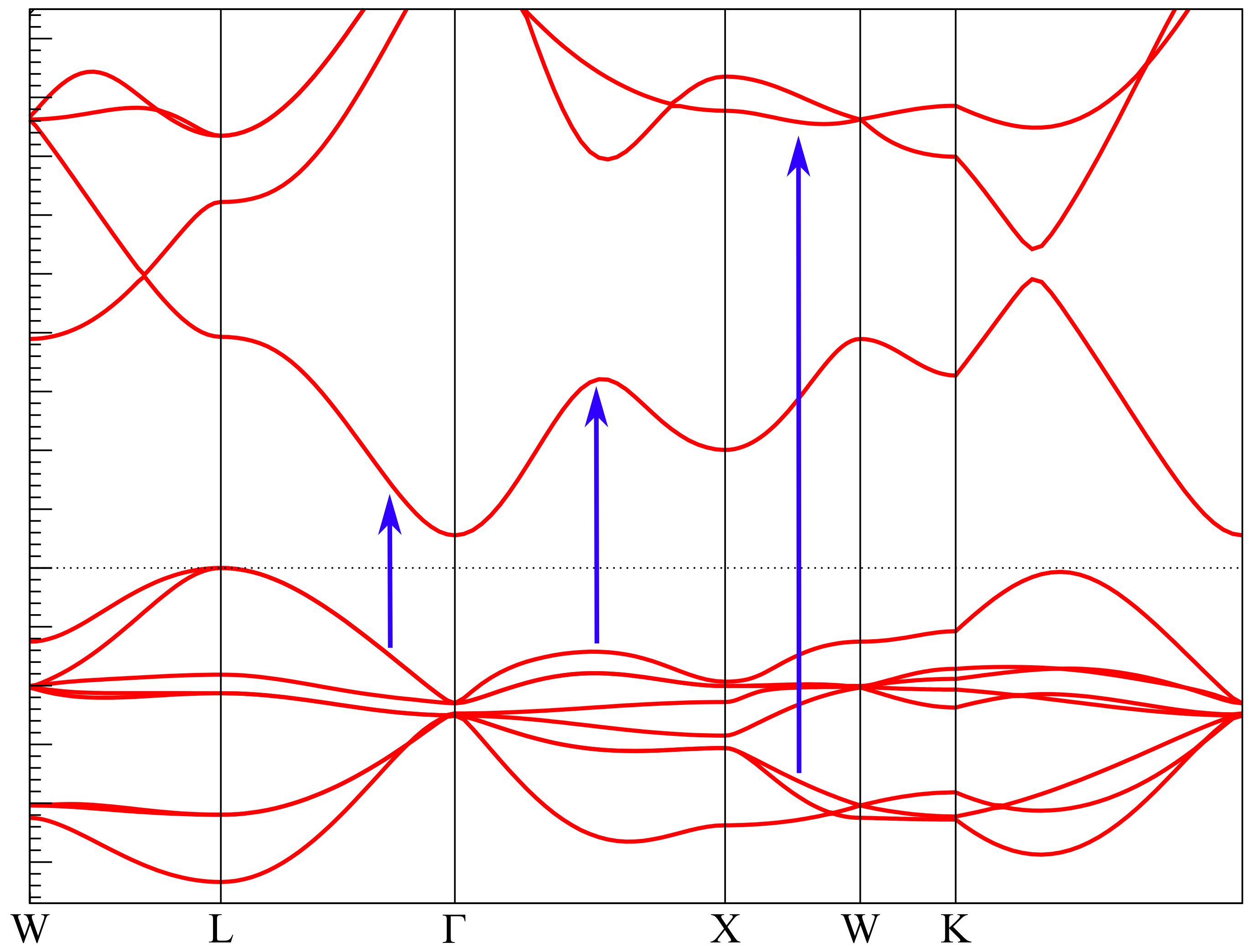
$$\psi_{n_1}^*(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$$

orbital basis

transition basis

transition space $t = n_1 \to n_2$





let's define a basis $\psi^*_{n_1}(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$ *orbital basis*

transition basis

diagonalizes the independent-particle L

$$L_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\omega)=\sum_{ij}(f_i-f_j)\frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega-(E_j-E_i)+i\eta}$$

$$L_0{}^{(n_3n_4)}_{(n_1n_2)}=\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\ \sum_{ij}(f_i-f_j)\frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega-(E_j-E_i)+i\eta}\psi^*_{n_1}(\mathbf{r}_1)\psi^*_{n_2}(\mathbf{r}_2)\psi_{n_3}(\mathbf{r}_3)\psi_{n_4}(\mathbf{r}_4)$$

let's define a basis $\psi^*_{n_1}(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$

orbital basis

transition basis

diagonalizes the independent-particle L

$$L_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\omega) = \sum_{ij}(f_i - f_j)\frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta}$$

$$L_{0\,(n_1 n_2)}^{\,(n_3 n_4)} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \sum_{ij}(f_i - f_j)\frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\boldsymbol{\psi_i(\mathbf{r}_1)}\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta}\boldsymbol{\psi^*_{n_1}(\mathbf{r}_1)}\psi^*_{n_2}(\mathbf{r}_2)\psi_{n_3}(\mathbf{r}_3)\psi_{n_4}(\mathbf{r}_4)$$

δ_{i,n_1}

let's define a basis

$\psi^*_{n_1}(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$

orbital basis

transition basis

diagonalizes the independent-particle L

$$L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij}(f_i - f_j)\frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta}$$

$$L_0{}^{(n_3 n_4)}_{(n_1 n_2)} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \boldsymbol{d\mathbf{r}_4} \sum_{ij}(f_i - f_j)\frac{\psi^*_j(\mathbf{r}_3)\boldsymbol{\psi^*_i(\mathbf{r}_4)}\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta}\psi^*_{n_1}(\mathbf{r}_1)\psi^*_{n_2}(\mathbf{r}_2)\psi_{n_3}(\mathbf{r}_3)\boldsymbol{\psi_{n_4}(\mathbf{r}_4)}$$

δ_{i,n_4}

let's define a basis $\psi^*_{n_1}(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$ ***orbital basis***

transition basis

diagonalizes the independent-particle L

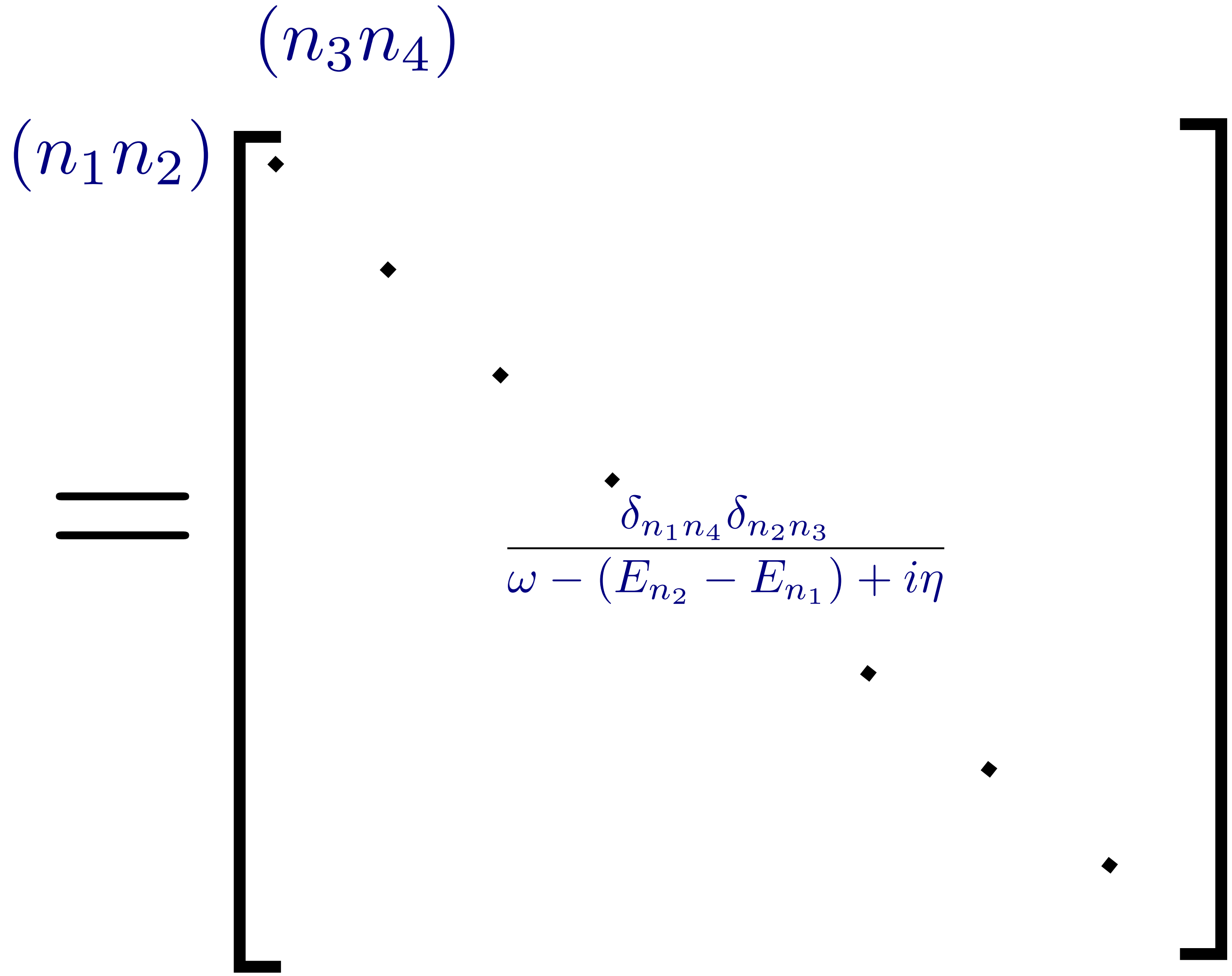
$$L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij} (f_i - f_j) \frac{\psi^*_j(\mathbf{r}_3)\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta}$$

$$L_0{}^{(n_3 n_4)}_{(n_1 n_2)} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \sum_{ij} (f_i - f_j) \frac{\psi^*_j(\mathbf{r}_3)\boldsymbol{\psi^*_i(\mathbf{r}_4)\psi_i(\mathbf{r}_1)}\psi_j(\mathbf{r}_2)}{\omega - (E_j - E_i) + i\eta} \boldsymbol{\psi^*_{n_1}(\mathbf{r}_1)}\psi^*_{n_2}(\mathbf{r}_2)\psi_{n_3}(\mathbf{r}_3)\boldsymbol{\psi_{n_4}(\mathbf{r}_4)}$$

$$\sum_i \delta_{i,n_1} f(i) \delta_{i,n_4} = f(n_1)\delta_{n_1 n_4}$$

$$L_0{}^{(n_3 n_4)}_{(n_1 n_2)} = \frac{(f_{n_1} - f_{n_2})\delta_{n_1,n_4}\delta_{n_2,n_3}}{\omega - (E_{n_2} - E_{n_1}) + i\eta}$$

$$[L^0]^{n_3 n_4}_{n_1 n_2} =$$



$$L = L_0 + L_0(v - W)L$$

Exercise

$$L = \left[(L_0)^{-1} - (v - W)\right]^{-1}$$

$$L = \left[(L_0)^{-1} - (v - W) \right]^{-1}$$

$$L_{n_2 n_2}^{n_3 n_4}$$

$$\omega - (E_{n_2} - E_{n_1}) \delta_{n_1 n_4} \delta_{n_2 n_3}$$

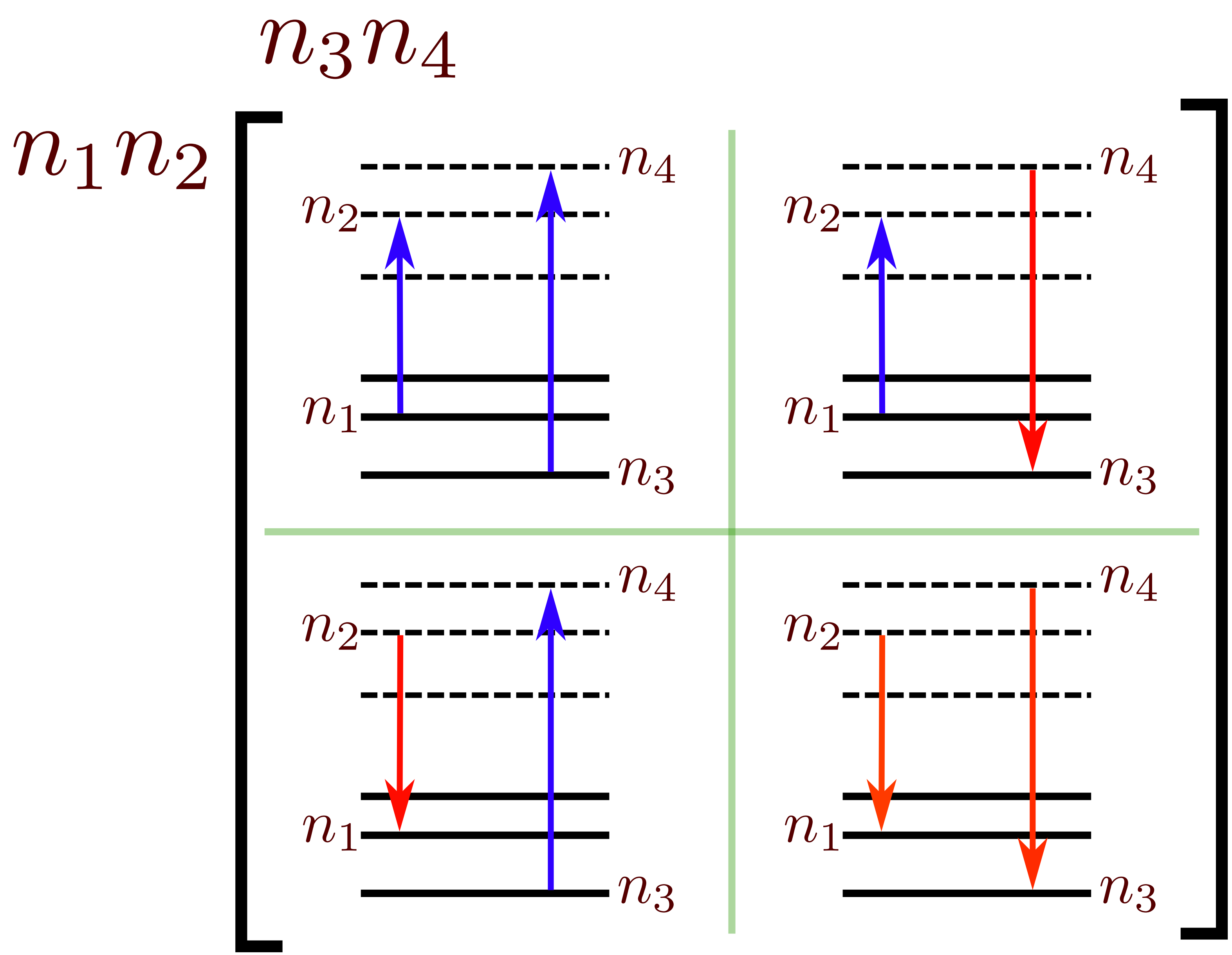
$$v_{n_1 n_2}^{n_3 n_4} = \iint \psi_{n_1}^{*}(\mathbf{r}) \psi_{n_2}^{*}(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \, \psi_{n_3}(\mathbf{r}) \psi_{n_4}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$W_{n_1 n_2}^{n_3 n_4} = \iint \psi_{n_1}^{*}(\mathbf{r}) \psi_{n_2}^{*}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \, \psi_{n_3}(\mathbf{r}') \psi_{n_4}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

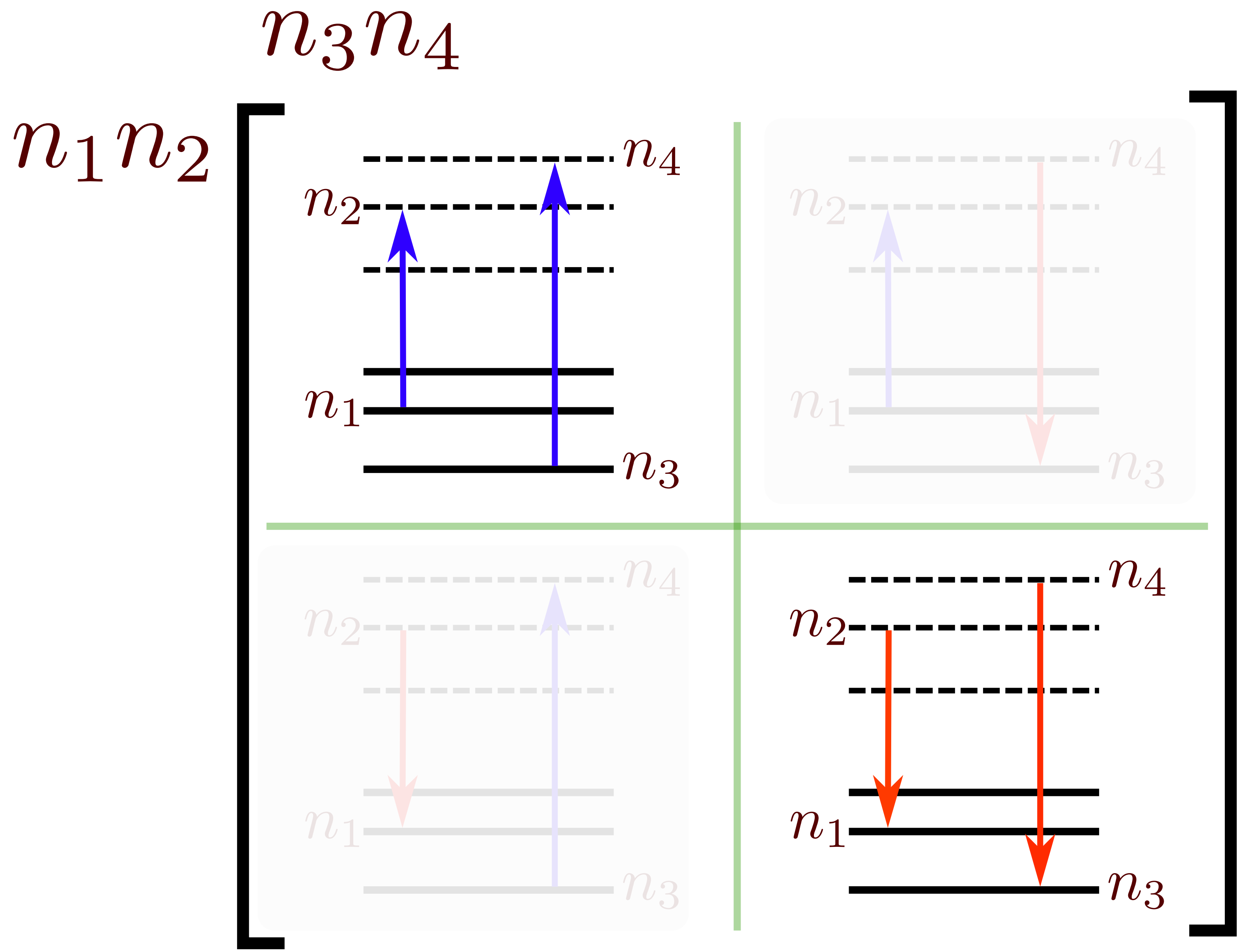
$$L = \frac{1}{\omega - H^{exc}}$$

$$H^{exc} = (E_{n_2} - E_{n_1}) \delta_{n_1 n_4} \delta_{n_2 n_3} + v_{n_1 n_2}^{n_3 n_4} - W_{n_1 n_2}^{n_3 n_4}$$

$$H^{exc} =$$



$$H^{exc} =$$



Tamm-Dancoff approx

Tamm-Dancoff approx

$$\begin{bmatrix} \mathbf{A} & \\ & \mathbf{-A^*} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = E_\lambda \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$|\lambda\rangle = \begin{bmatrix} \mathrm{X} \\ \mathrm{Y} \end{bmatrix}$$

$$\left[\begin{array}{c|c} \mathbf{A} & \mathbf{B} \\ \hline -\mathbf{B}^* & -\mathbf{A}^* \end{array}\right]\begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = E_\lambda \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$|\lambda\rangle = \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$\left[\begin{array}{c|c} \mathbf{A} & \mathbf{B} \\ \hline \mathbf{B}^* & -\mathbf{A}^* \end{array}\right]\left[\begin{array}{c} \mathbf{X} \\ \mathbf{Y} \end{array}\right] = E_\lambda \left[\begin{array}{c|c} 1 & 0 \\ \hline 0 & -1 \end{array}\right]\left[\begin{array}{c} \mathbf{X} \\ \mathbf{Y} \end{array}\right]$$

$$|\lambda\rangle = \left[\begin{array}{c} \mathrm{X} \\ \mathrm{Y} \end{array}\right]$$

$$L = \frac{1}{\omega - H^{exc}} = \sum_{\lambda} \frac{|\lambda\rangle \langle\lambda|}{\omega - E_\lambda}$$

Tamm-Dancoff approx

$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda\lambda'} \left[\sum_{(n_1 n_2)} \langle n_1 | e^{-i\mathbf{q}\cdot\mathbf{r}} | n_2 \rangle \frac{A_\lambda^{(n_1 n_2)}}{E_\lambda^{exc} - \omega - i\eta} \times \right.$$

$$\left. \times S_{\lambda\lambda'}^{-1} \sum_{(n_3 n_4)} \left\langle n_4 | e^{i\mathbf{q}\cdot\mathbf{r}'} | n_3 \right\rangle A_\lambda^{*(n_3 n_4)} \left(f_{n_4} - f_{n_3} \right) \right]$$

$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{(n_1 n_2)} \langle n_1 | e^{-i\mathbf{q}\cdot\mathbf{r}} | n_2 \rangle A_\lambda^{(n_1 n_2)} \right|^2}{E_\lambda^{exc} - \omega - i\eta}$$

Tamm-Dancoff approx

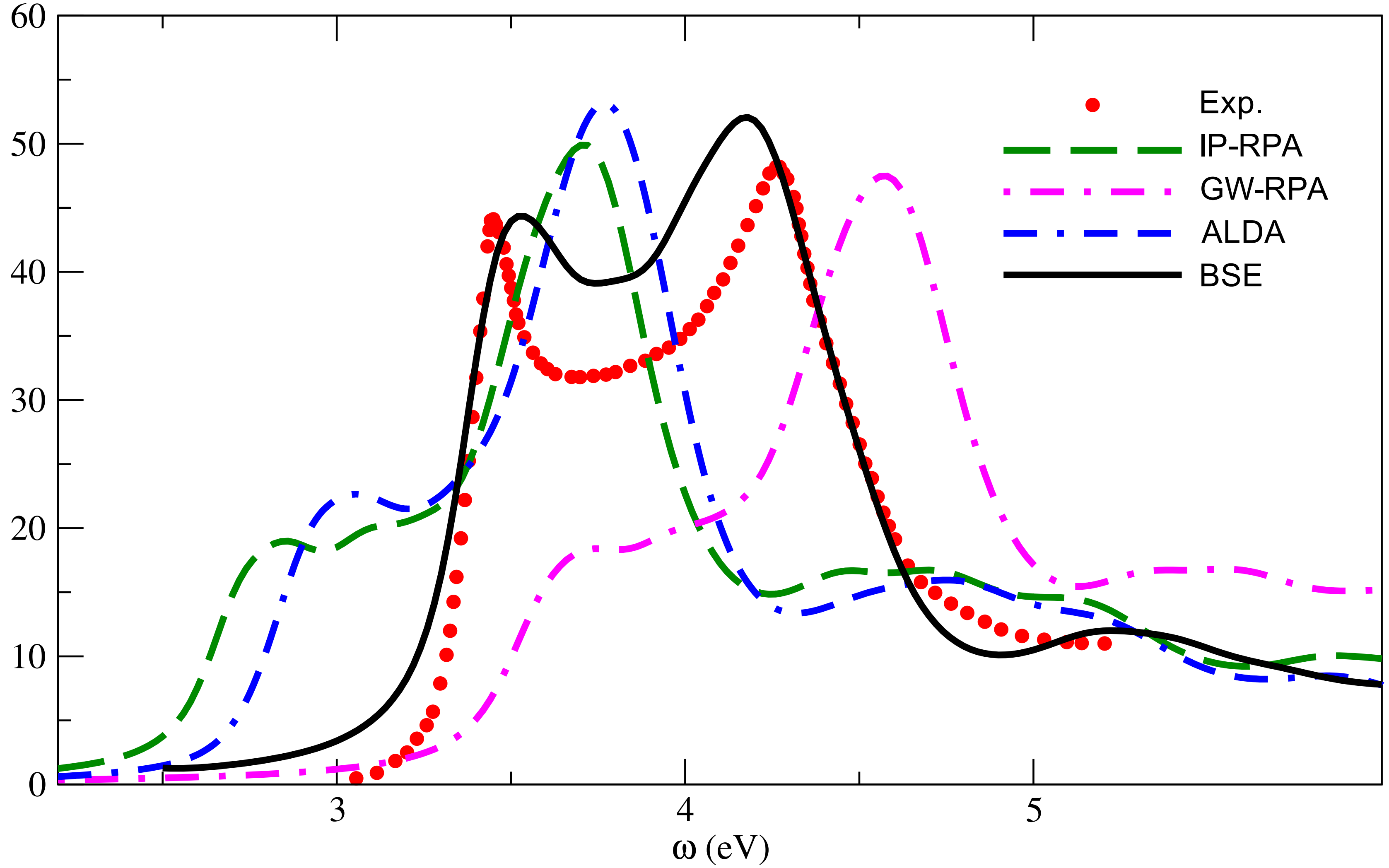
$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{vc} \langle c | e^{-i\mathbf{q}\cdot\mathbf{r}} | v \rangle \, A_{\lambda}^{vc} \right|^2}{E_{\lambda}^{exc} - \omega - i\eta}$$

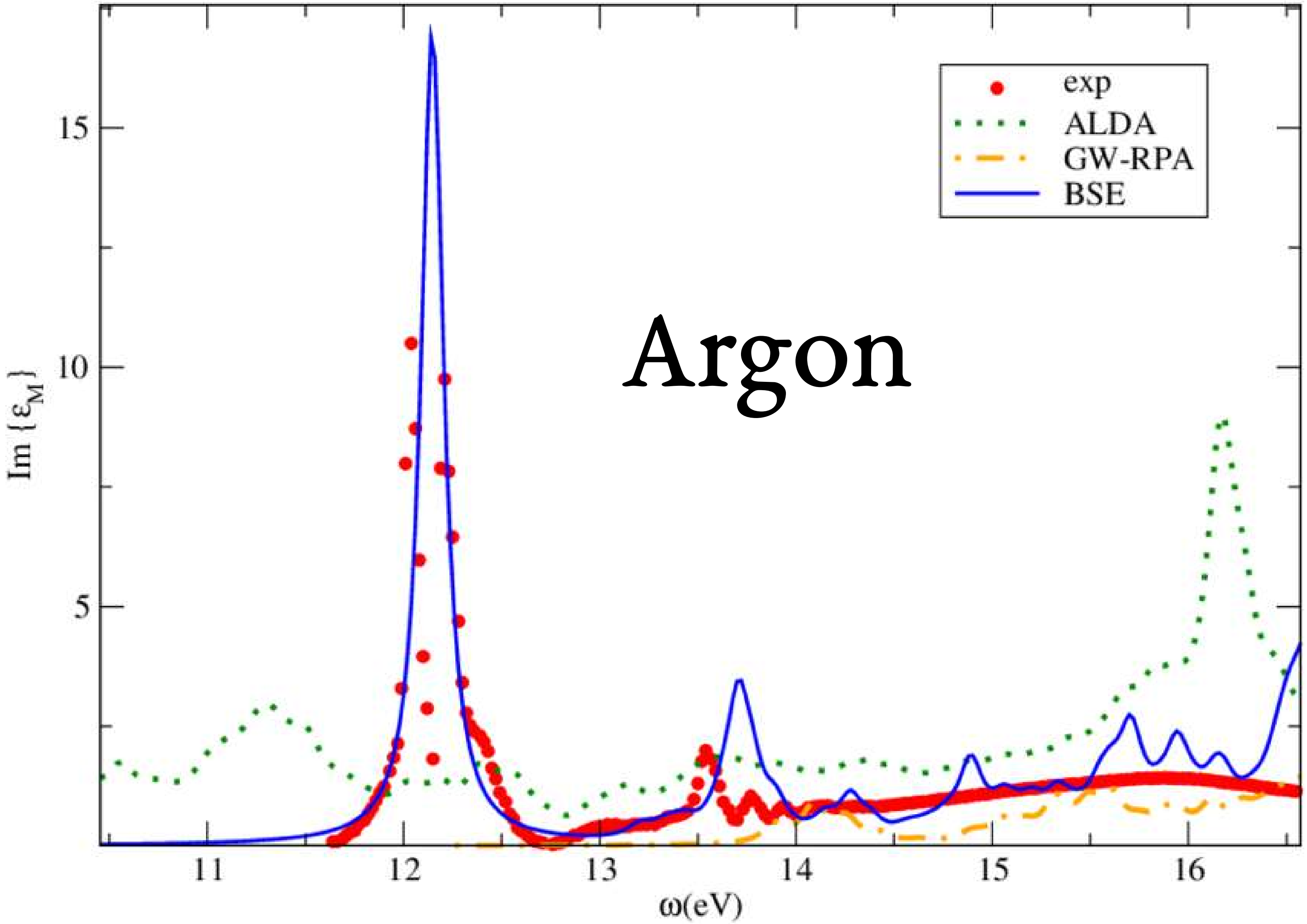
BSE

$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{vc} \frac{\left| \langle c | e^{-i\mathbf{q}\cdot\mathbf{r}} | v \rangle \right|^2}{(\epsilon_c - \epsilon_v) - \omega - i\eta}$$

IP

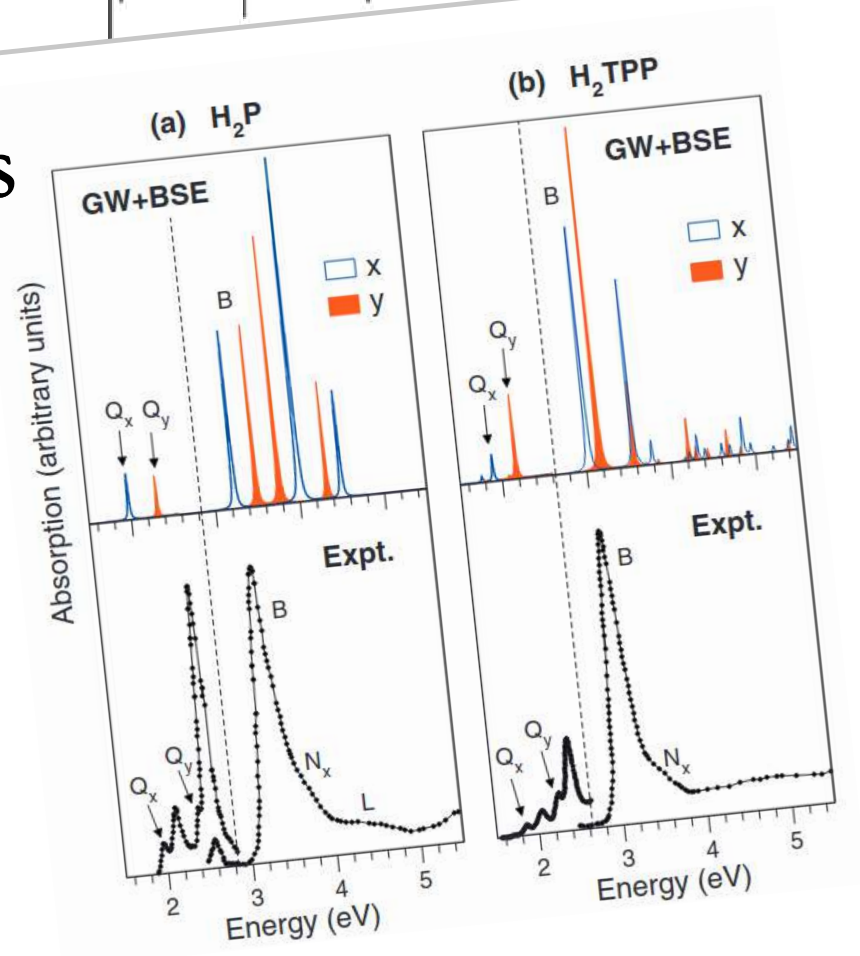
Optical absorption of Silicon





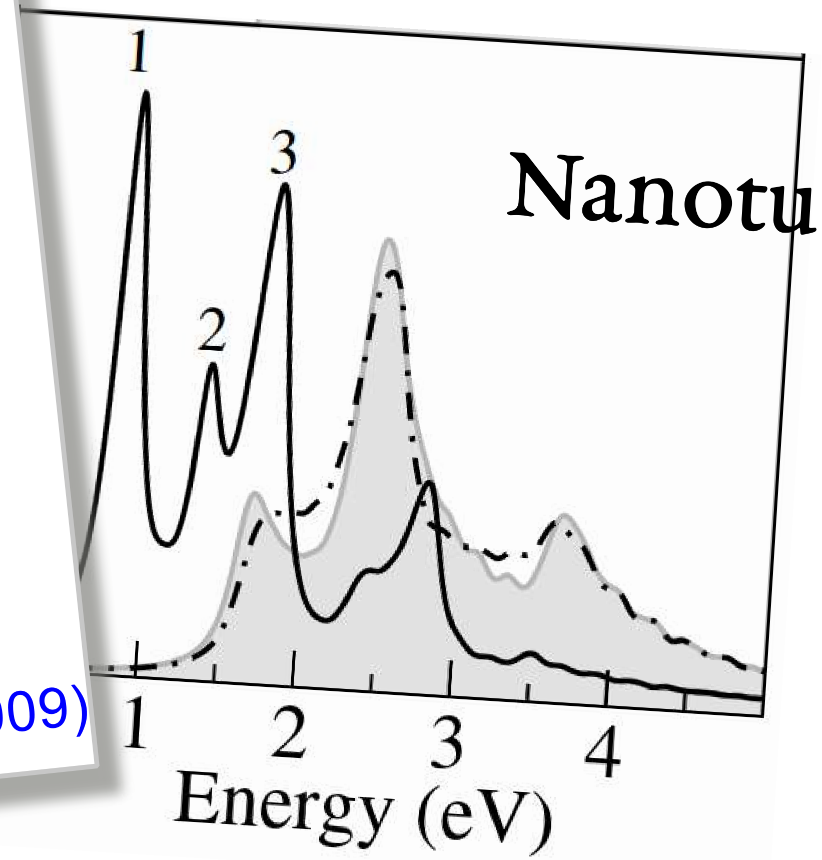
Phys. Rev. B **76** 161103 (2007)

Porphyrins



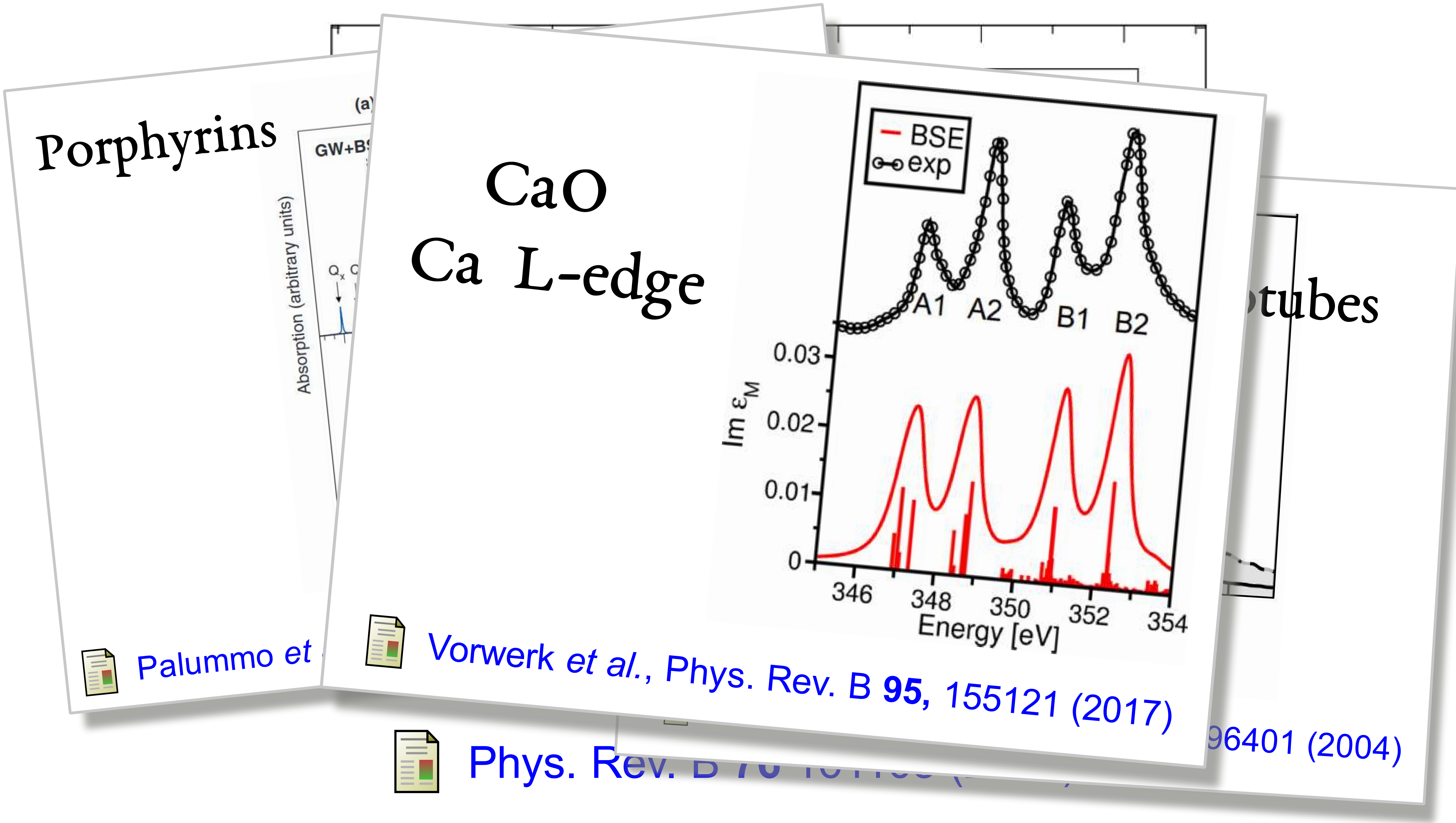
Palummo *et al.*, J. Chem. Phys. **131** 084102 (2009)

Nanotubes



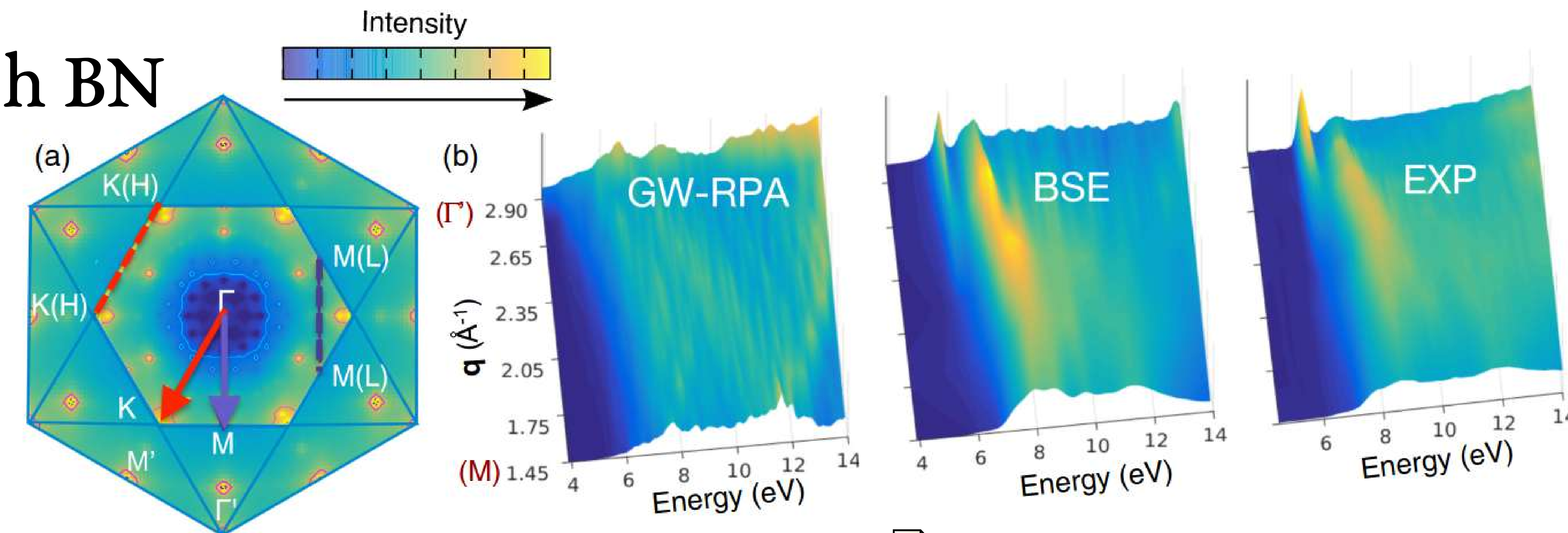
Chang *et al.*, Phys. Rev. Lett. **92** 196401 (2004)

Phys. Rev. B 70


Porphyrins
GW+BS
Absorption (arbitrary units)
Palummo et
CaO
Ca L-edge
BSE
exp
A1
A2
B1
B2
Im ε_M
0.03
0.02
0.01
0
346
348
350
352
354
Energy [eV]
Vorwerk *et al.*, Phys. Rev. B **95**, 155121 (2017)
tubes
96401 (2004)
Phys. Rev. B 70

Bethe-Salpeter Equation - finite momentum transfer

$$S(\mathbf{q},\omega) \propto \chi_M(\mathbf{q},\omega) = \sum_\lambda \frac{\left|\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{i\mathbf{q}\cdot\mathbf{r}}|v\rangle\right|^2}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

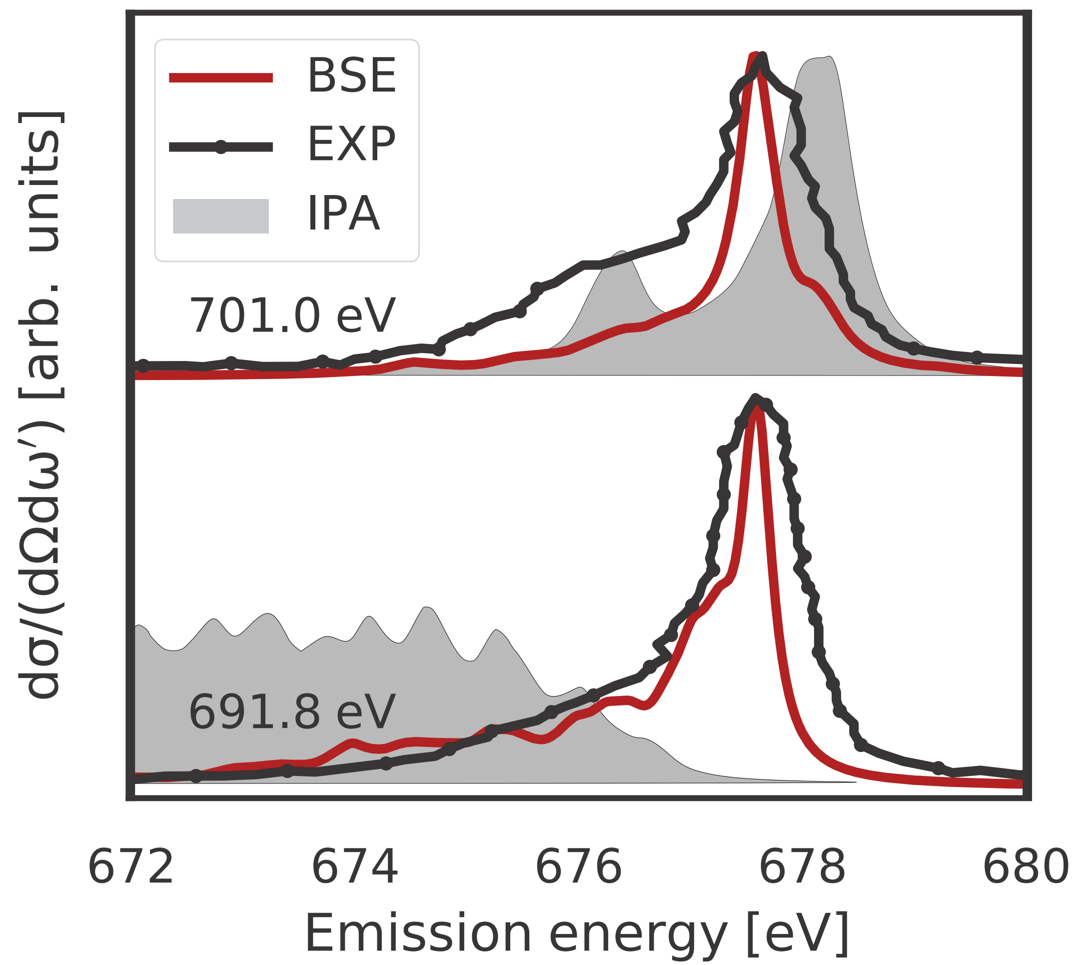


Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

Resonant Inelastic X-ray Scattering (RIXS)

$$\frac{d^2\sigma}{d\Omega_2 d\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

2 BSE calculations (valence and core)

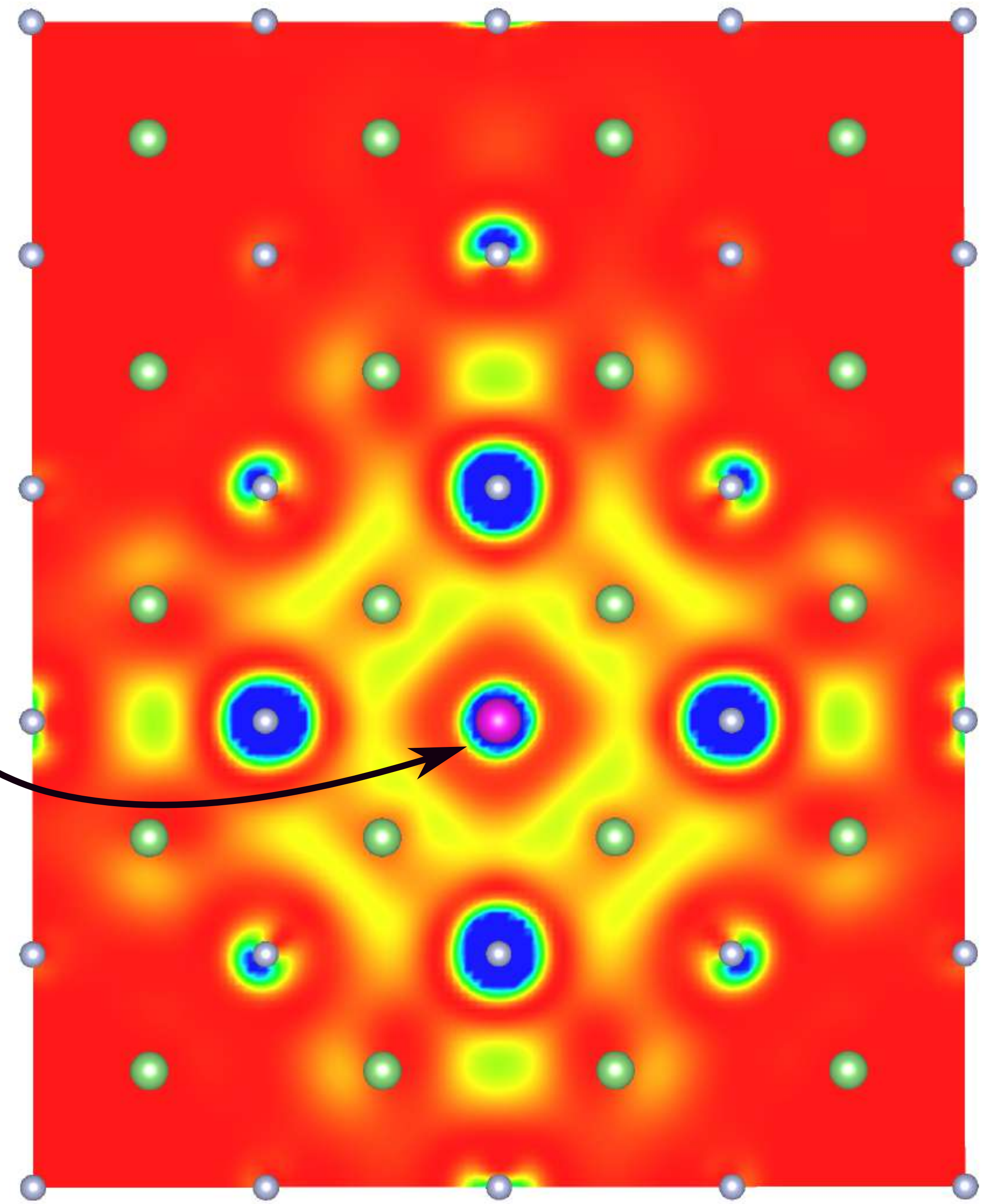


Phys. Rev. Research **2**, 042003(R) (2020)

Excitonic wavefunction of LiF

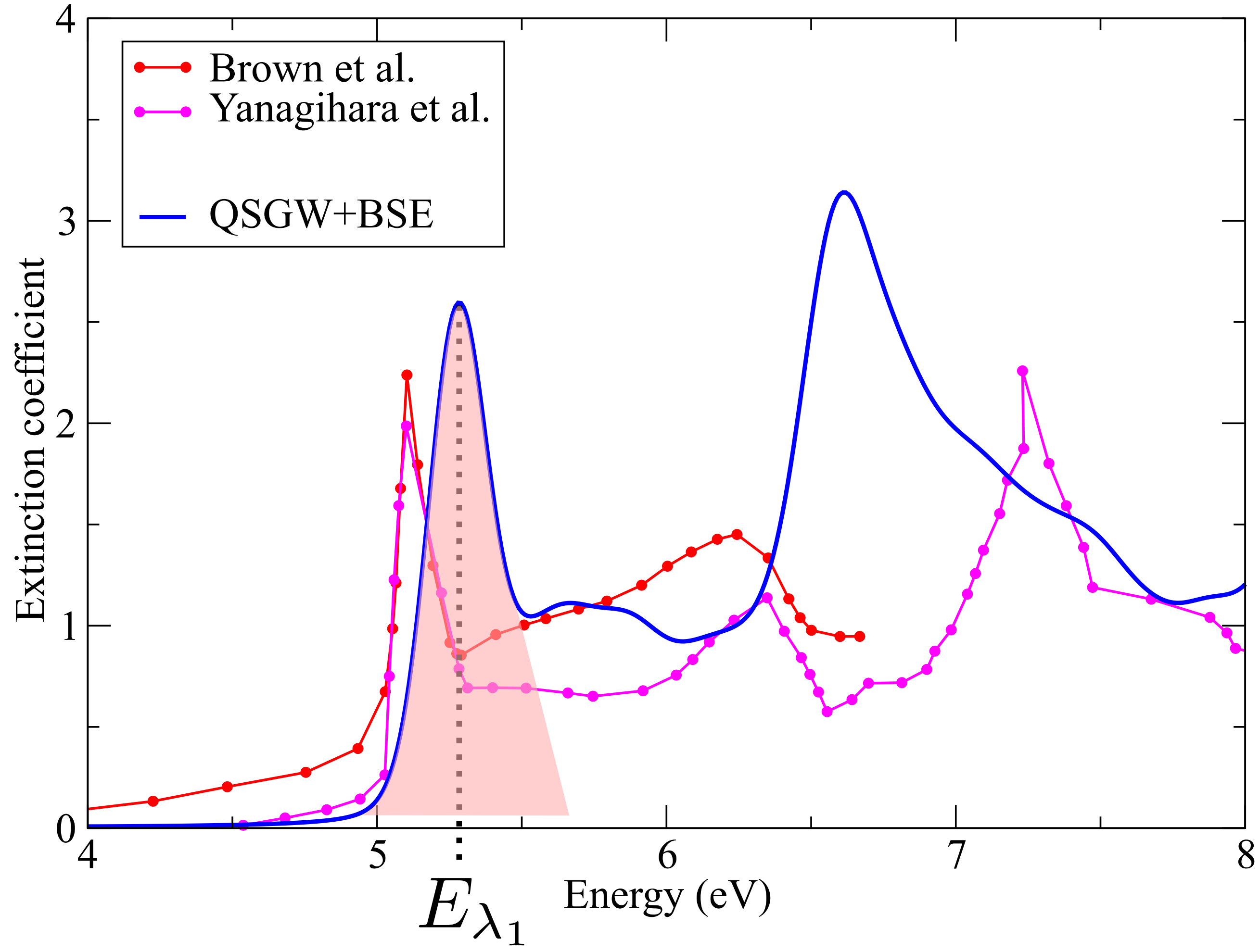
$$|\Psi_\lambda(\mathbf{r}_e,\mathbf{r}_h)|^2 = \left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi^*_{c\mathbf{k}}(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)\right|^2$$

- where is the exciton localised ?
- how much ?

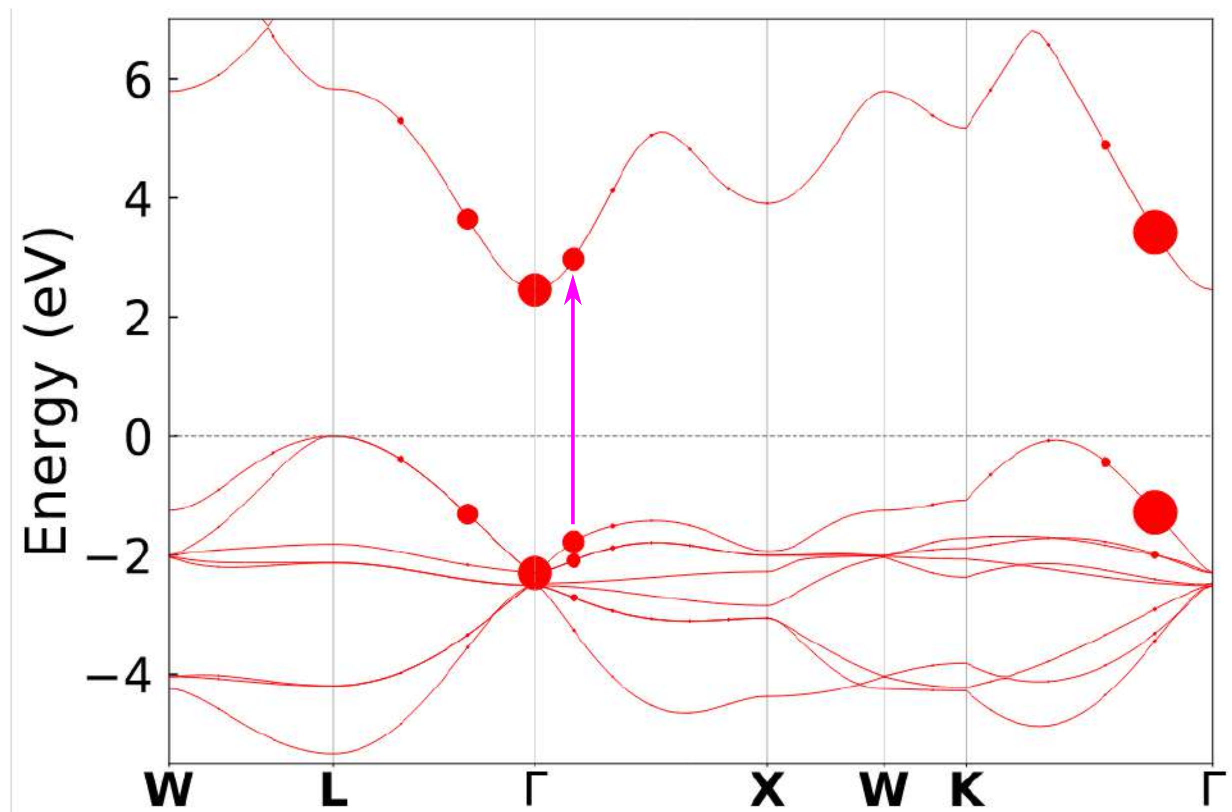


Gatti and Sottile, Phys. Rev. B **98**, 155113 (2013)

AgCl absorption



$$\chi_M = \sum_{\lambda} \frac{\left| \sum_{vc\mathbf{k}} A_{\lambda_1}^{vc\mathbf{k}} \langle c\mathbf{k} | \hat{\mathbf{d}} | v\mathbf{k} \rangle \right|^2}{\omega - E_\lambda + i\eta}$$



Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)