How long do excited electrons live?

Relaxation of Hot Electrons in Noble Metals

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Lifetime of excited electrons

- Introduction
- Self-energy Formalism
- XC effects
- Role of d electrons.
- Conclusions

- Great importance for many physical and chemical phenomena
  - e.g. dynamical reactions a photon induces on a surface

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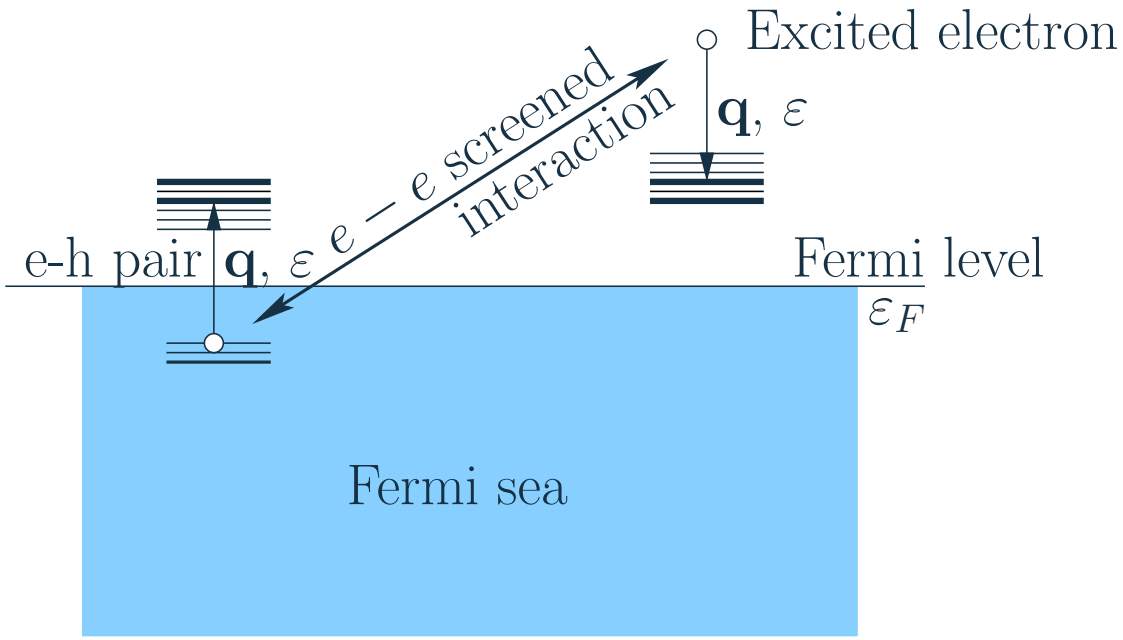

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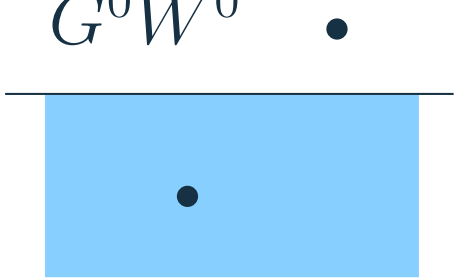

$e-e$ decay mechanism

- HEG: $\tau \sim (\varepsilon - \varepsilon_F)^{-2}$
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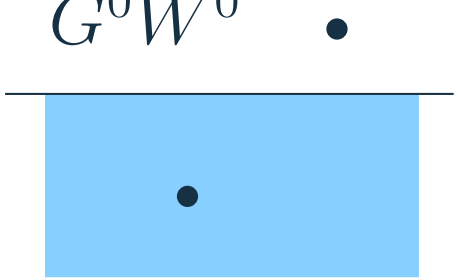

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$\rightarrow$ Beyond the G^0W^0: XC effects in the excited electron and in the screening electrons

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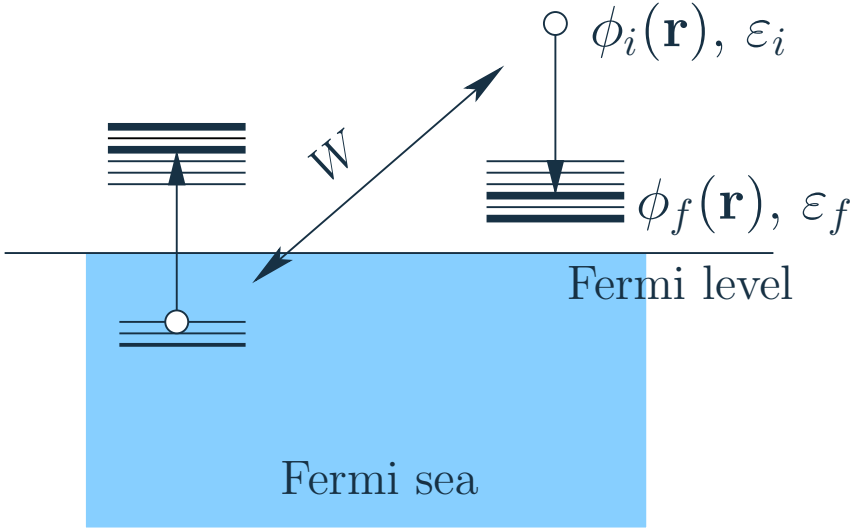
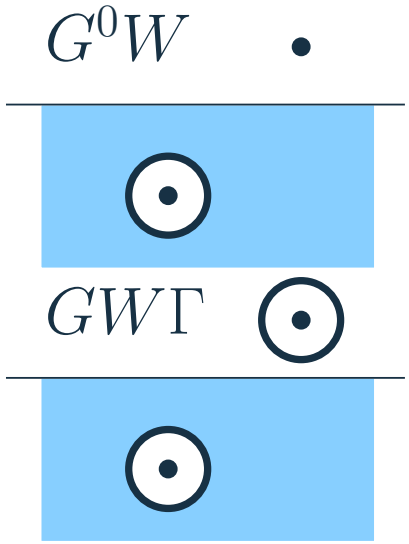
$$\tau_i^{-1} = -2 \sum_f \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \, \phi_i^*(\mathbf{r}) \, \phi_f^*(\mathbf{r}') \, \mathrm{Im}\, W(\mathbf{r}, \mathbf{r}'; \varepsilon_i - \varepsilon_f) \, \phi_i(\mathbf{r}') \, \phi_f(\mathbf{r})$$

$$W \rightarrow \tilde{W}$$





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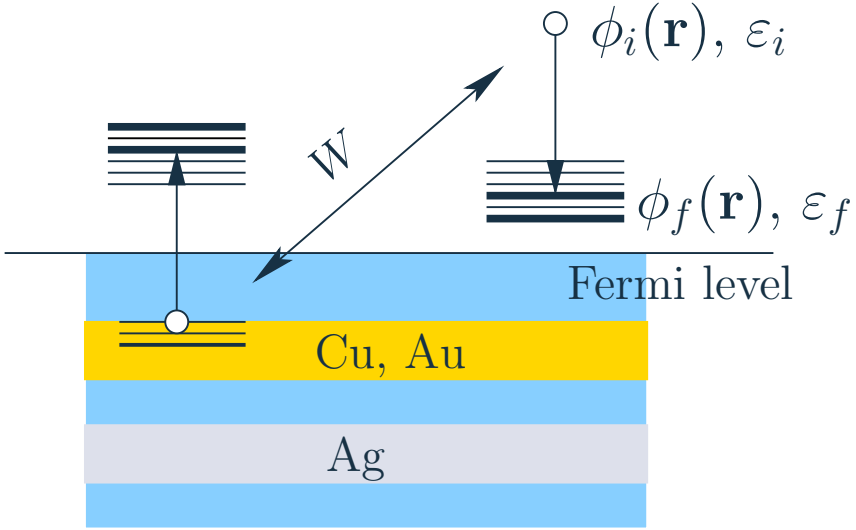

NOBLE METALS

- filled d bands: $nd^{10}\,(n+1)s^1$
  - Cu, Au $\sim$2 eV below ε_F
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- PW + Pseudopotentials
  - Full calculation: $nd^{10}\,(n+1)s^1$ as valence electrons
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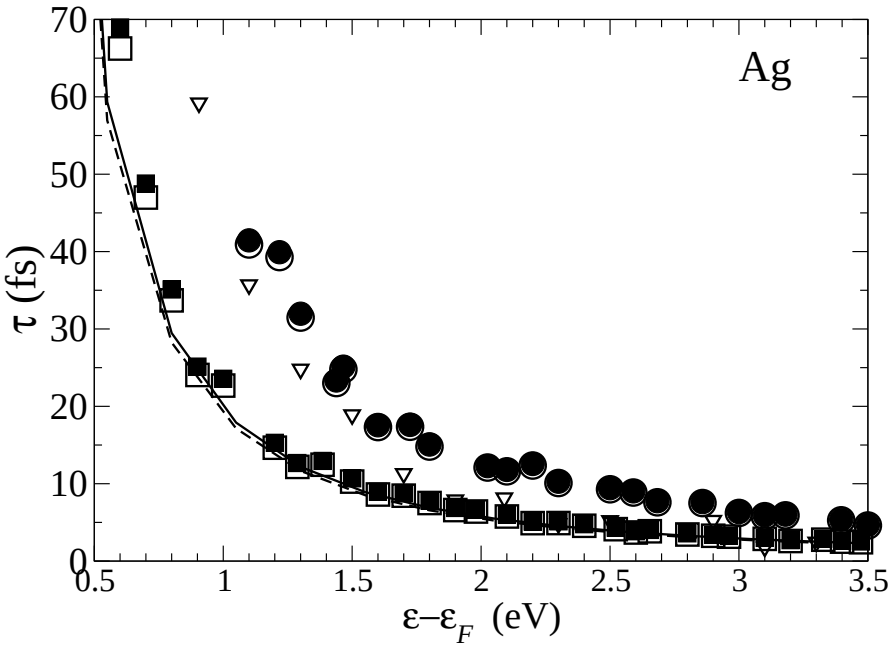

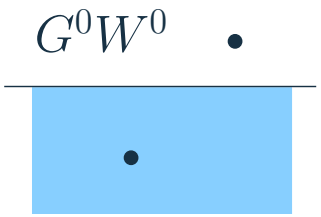

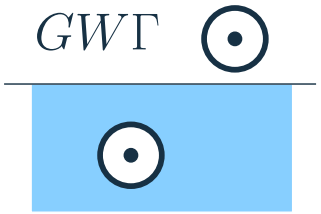

▽ M. Bauer and M. Aeschlimann (2002)

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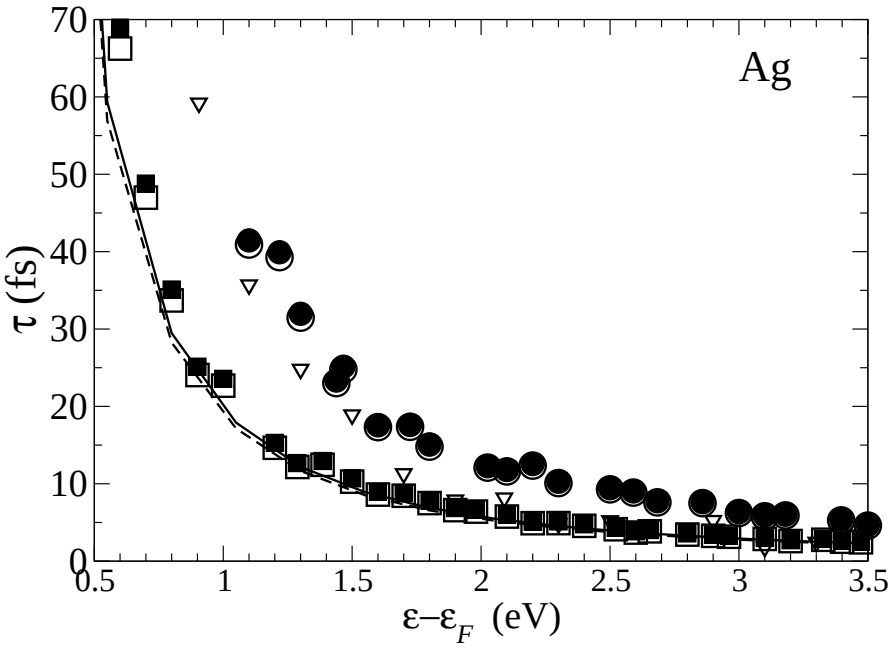

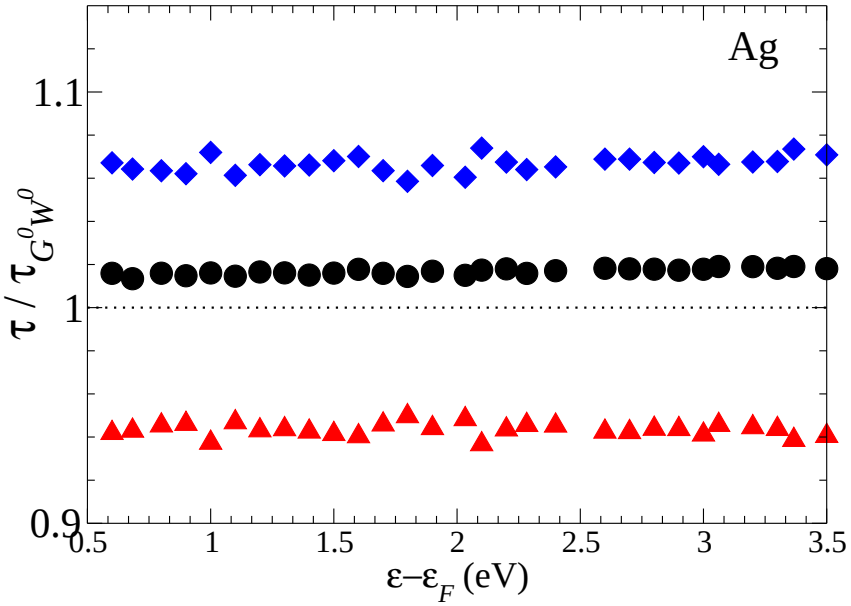

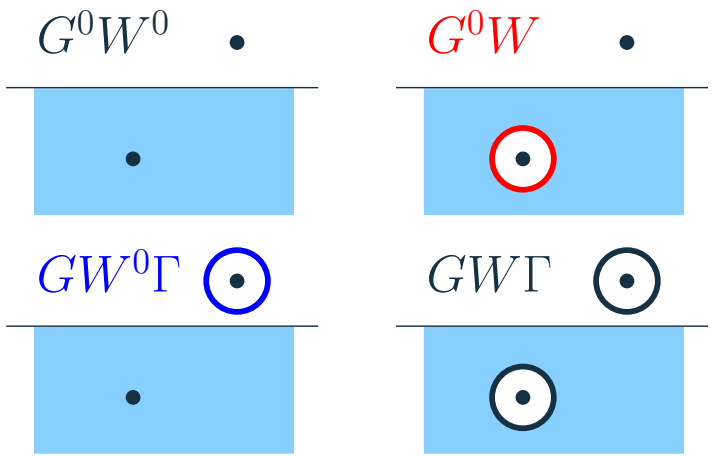

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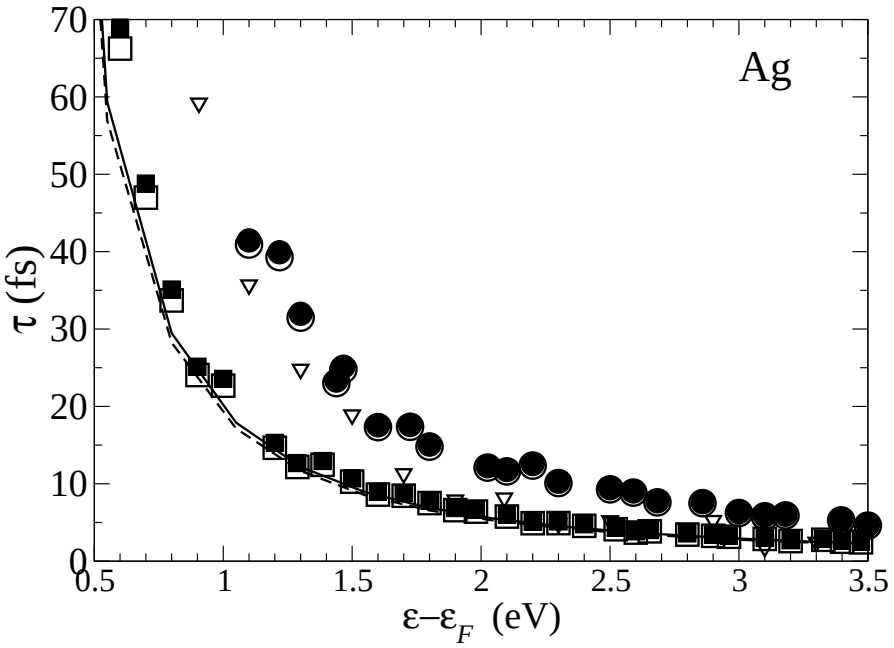
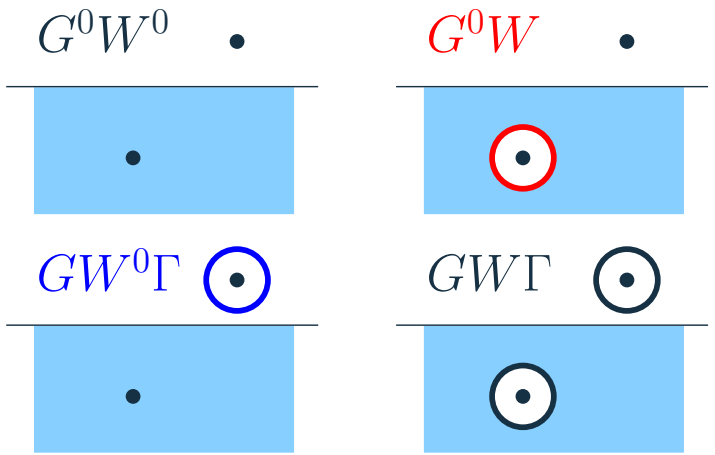
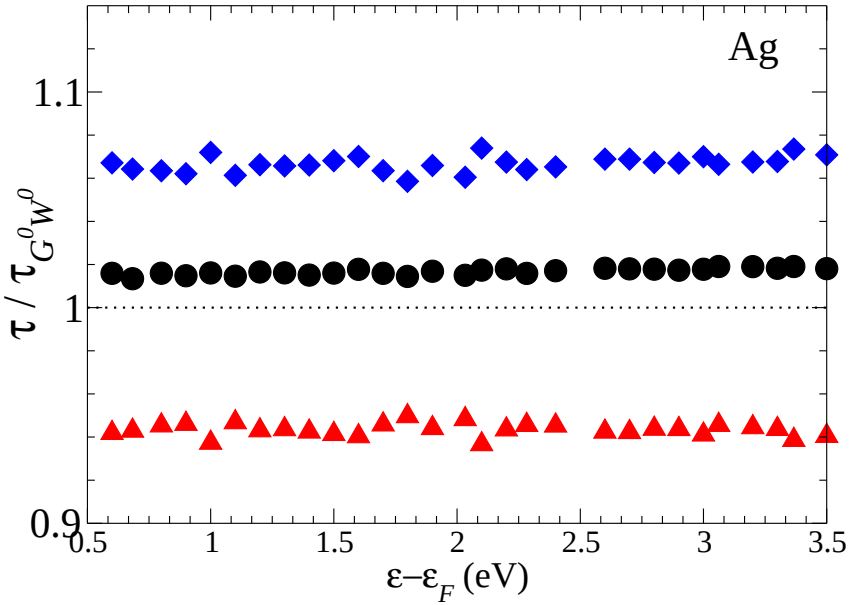
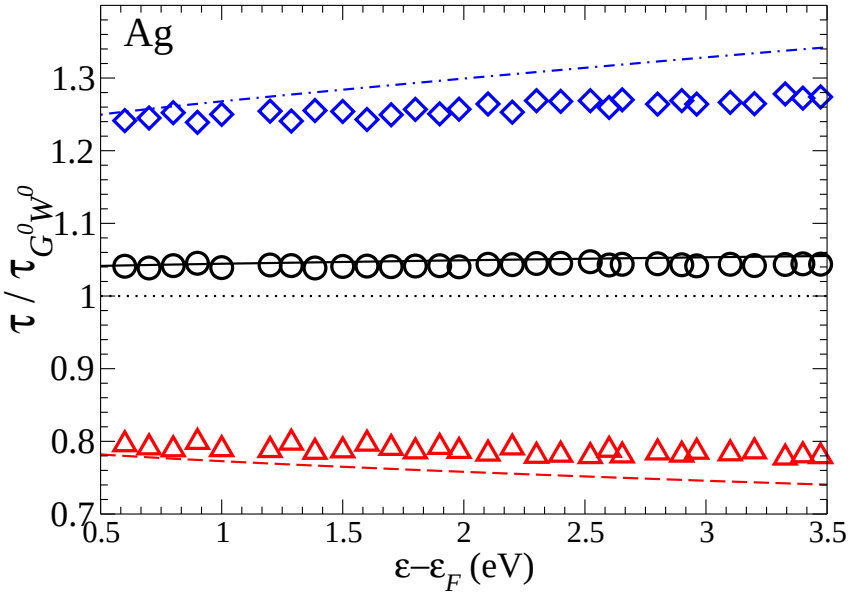






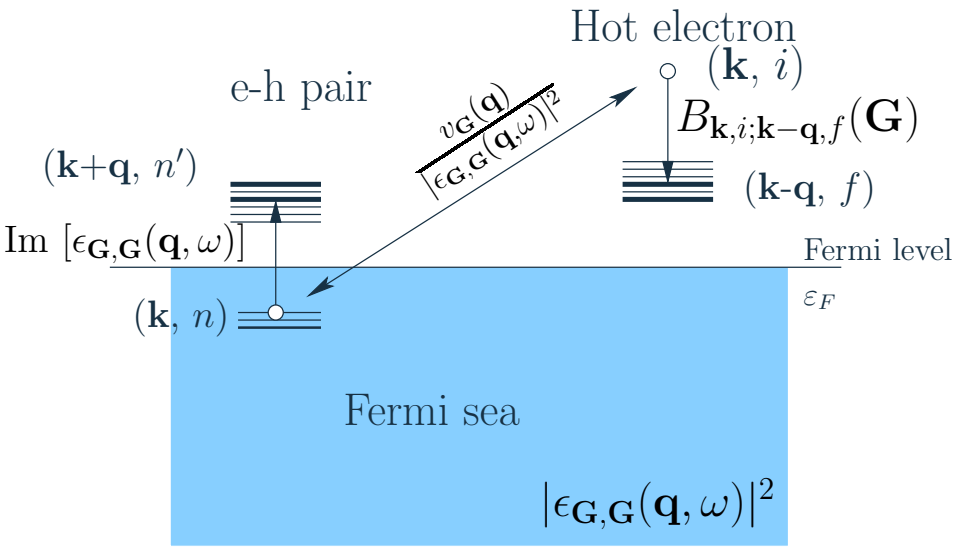


Role of d electrons

Large differences between first principles (and experimental) and HEG lifetimes are due to the presence of d states.

- Neglecting LFE ($\tau^{\mathrm{LFE}} < \tau^{\mathrm{noLFE}}$)
- Neglecting XC ($\tau^{\mathrm{XC}} > \tau^{\mathrm{noXC}}$)

$$\tau^{-1}_{\mathbf{k},i} = \frac{1}{\pi^2} \sum_f \int_{\mathrm{BZ}} \mathrm{d}\mathbf{q} \sum_{\mathbf{G}} \frac{\left|B_{\mathbf{k},i;\mathbf{k}-\mathbf{q},f}(\mathbf{G})\right|^2}{\left|\mathbf{q}+\mathbf{G}\right|^2} \frac{\mathrm{Im}\left[\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q}, \varepsilon_{\mathbf{k},i} - \varepsilon_{\mathbf{k}-\mathbf{q},f})\right]}{\left|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q}, \varepsilon_{\mathbf{k},i} - \varepsilon_{\mathbf{k}-\mathbf{q},f})\right|^2}.$$



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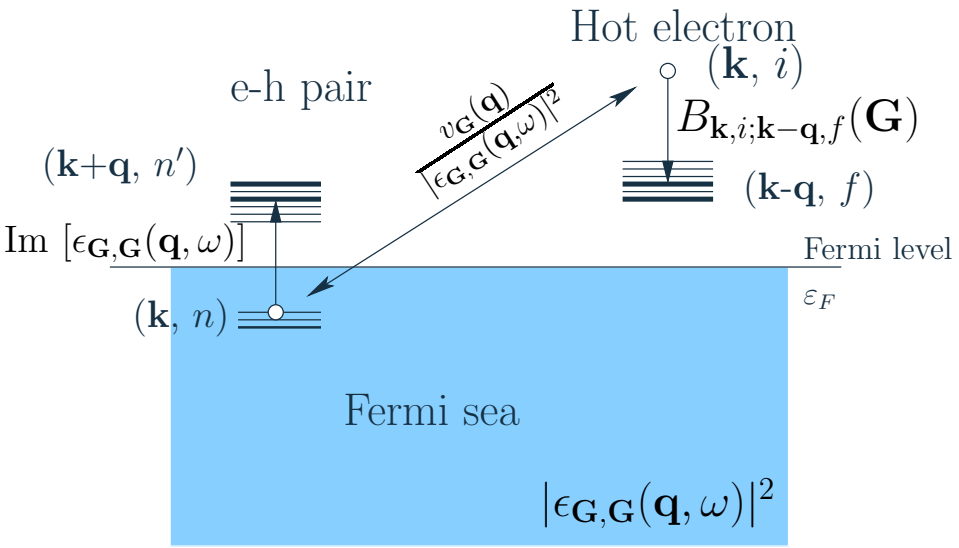

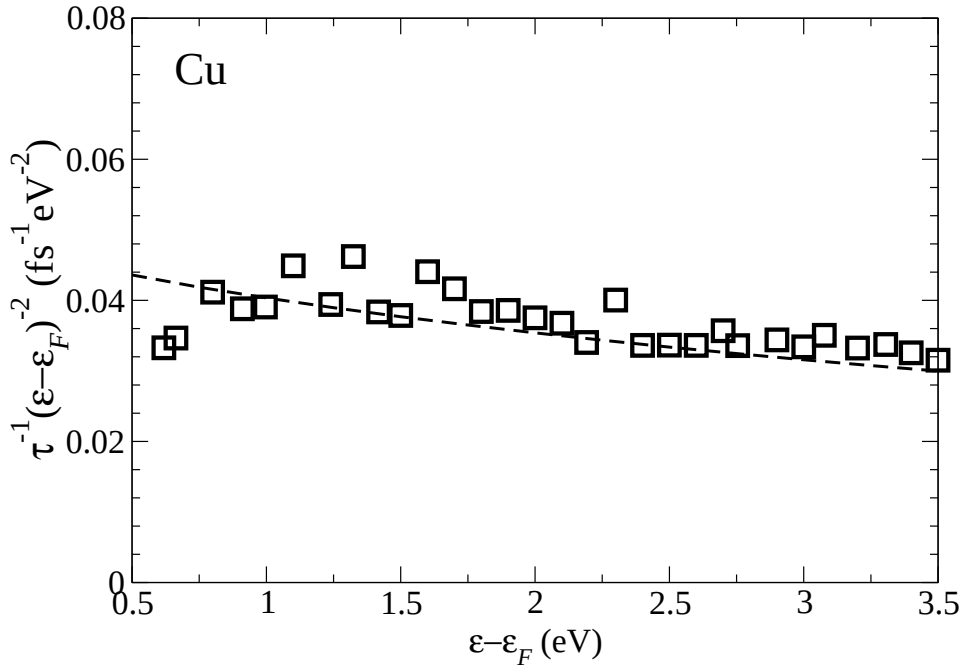

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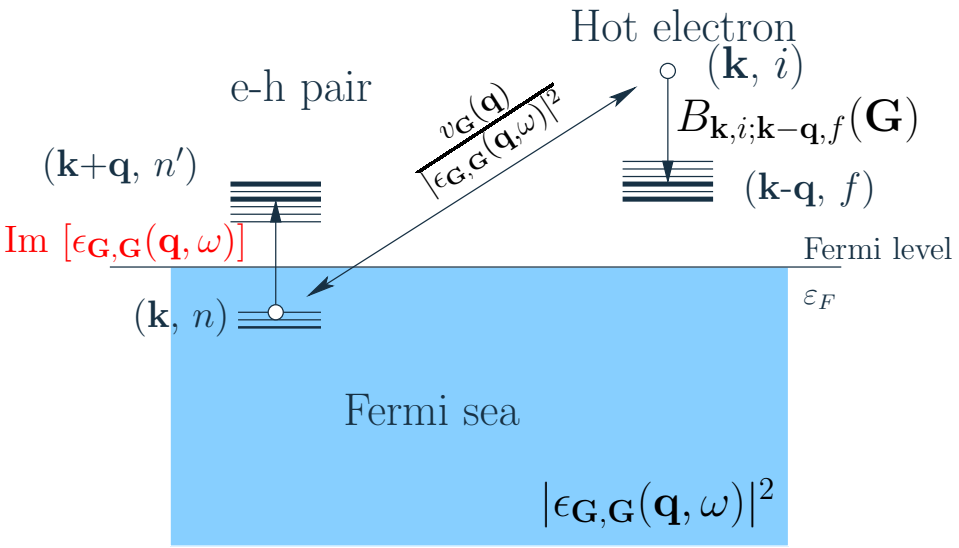

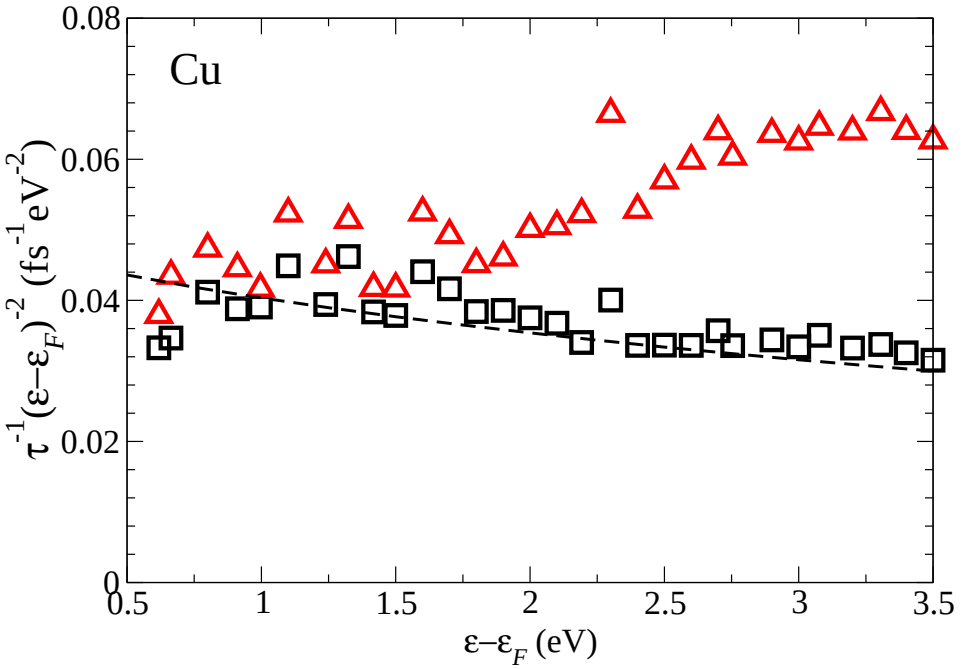

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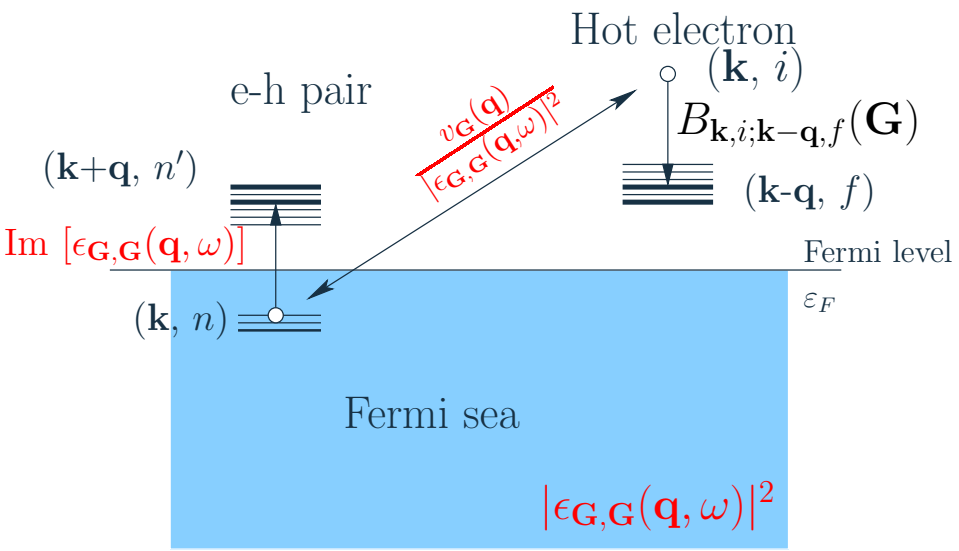

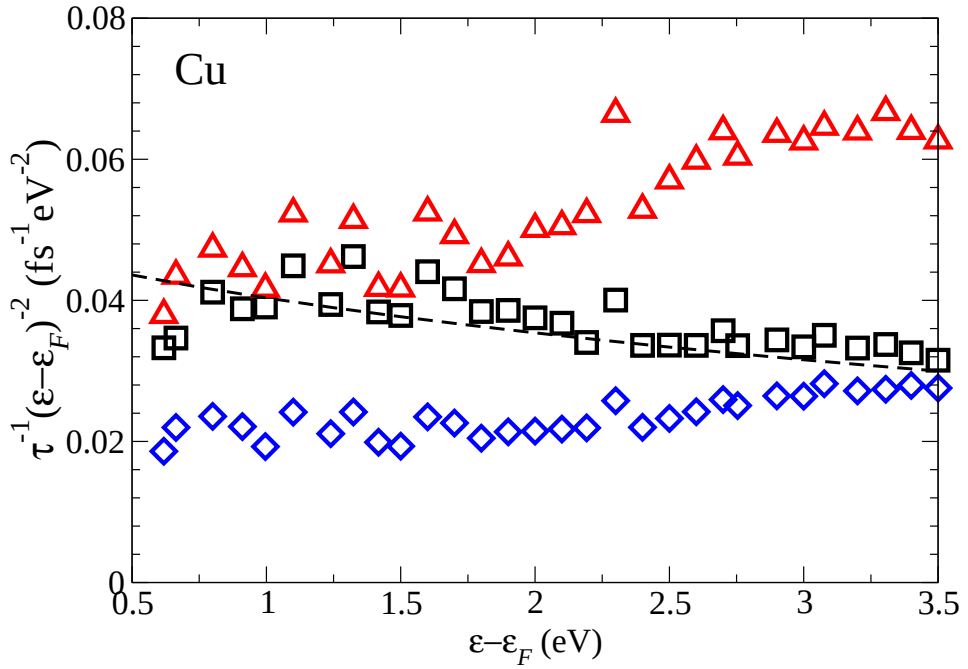

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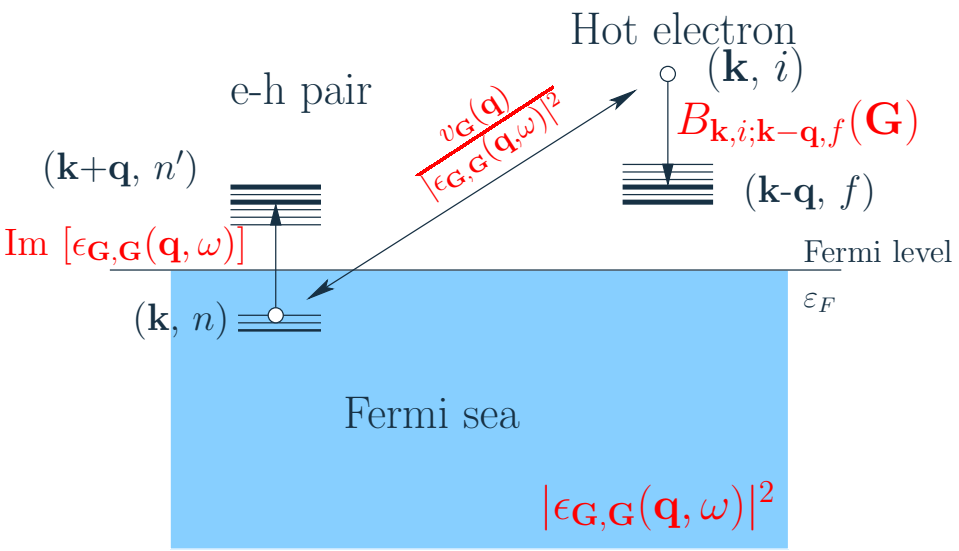

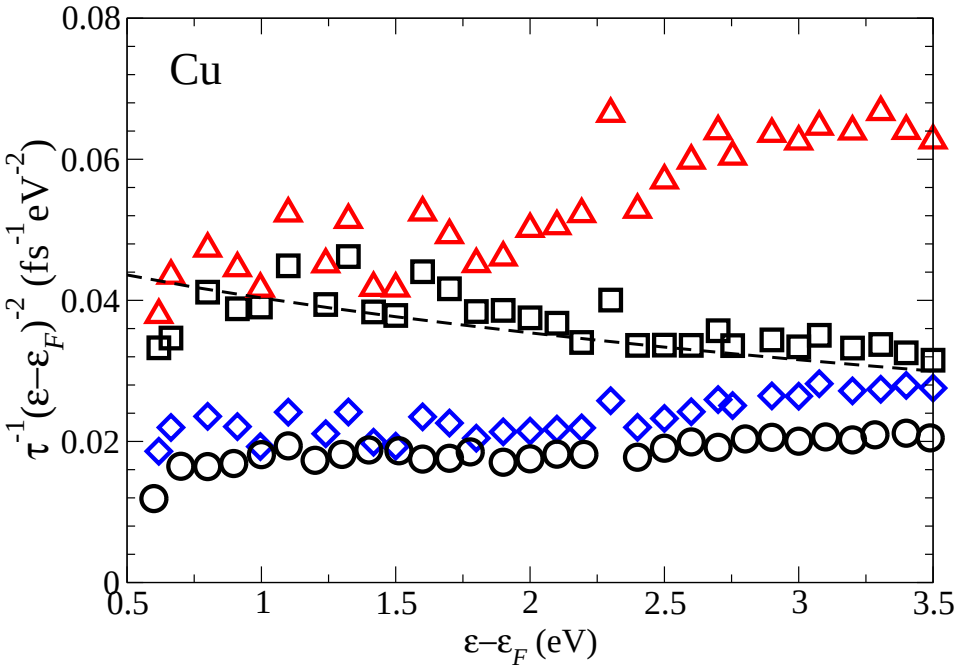

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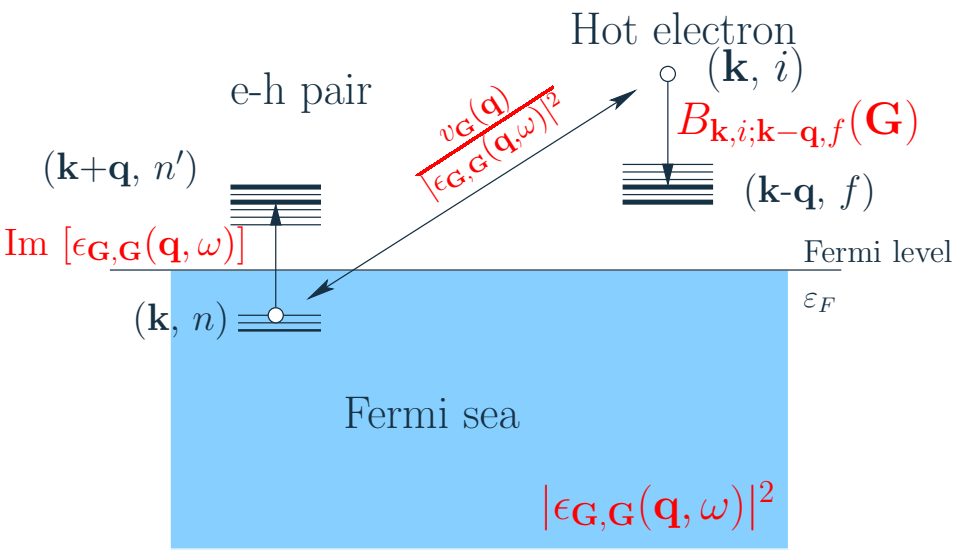

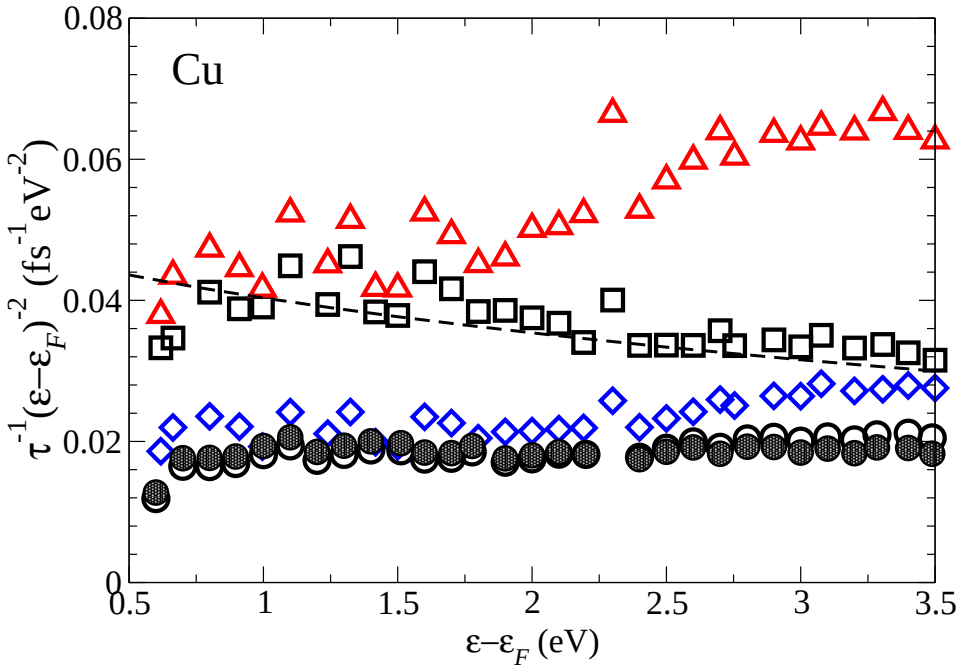

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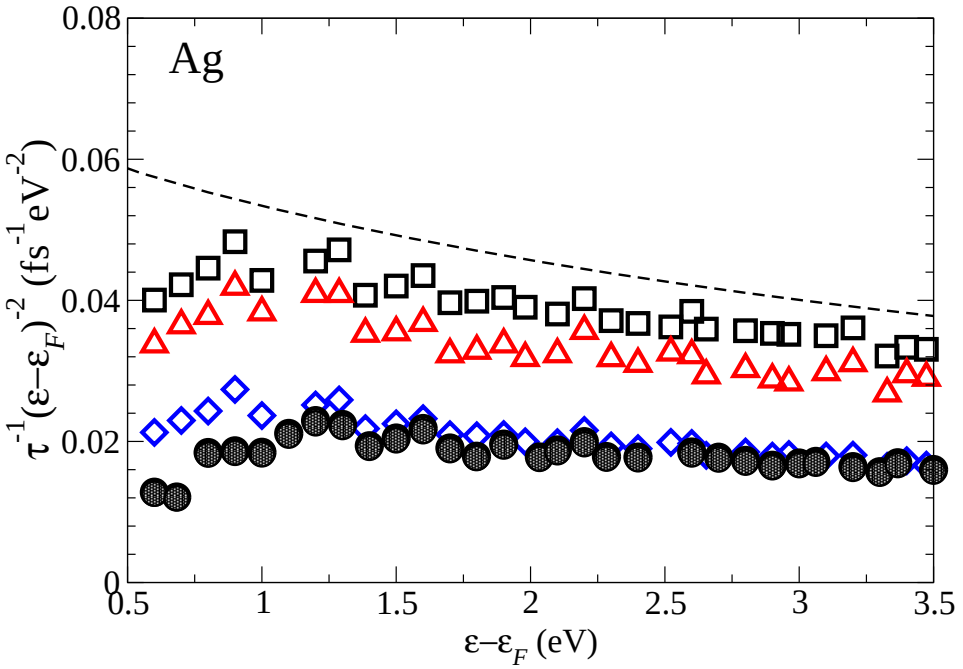

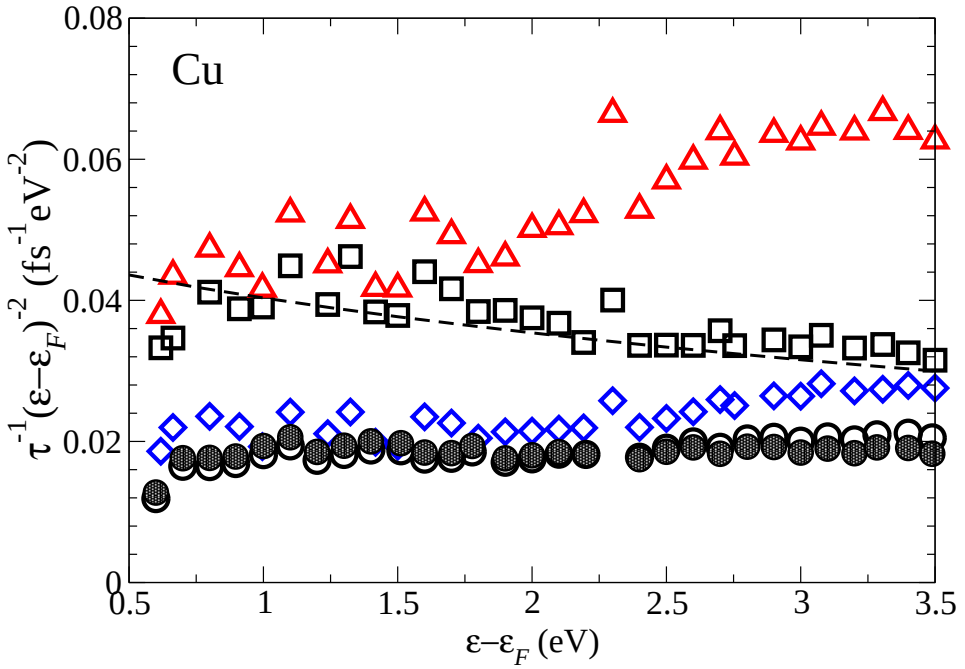

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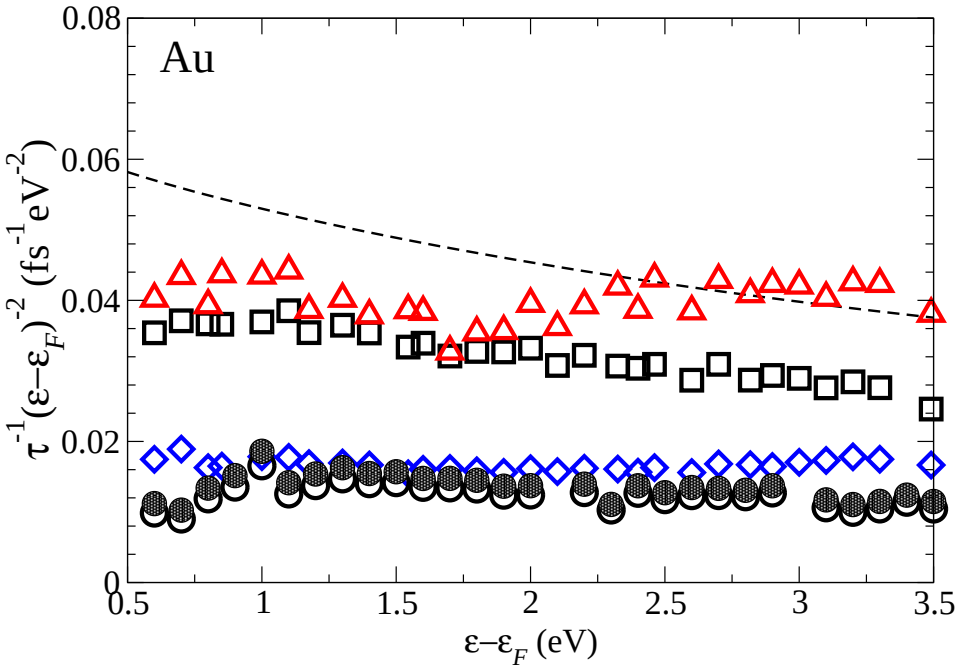

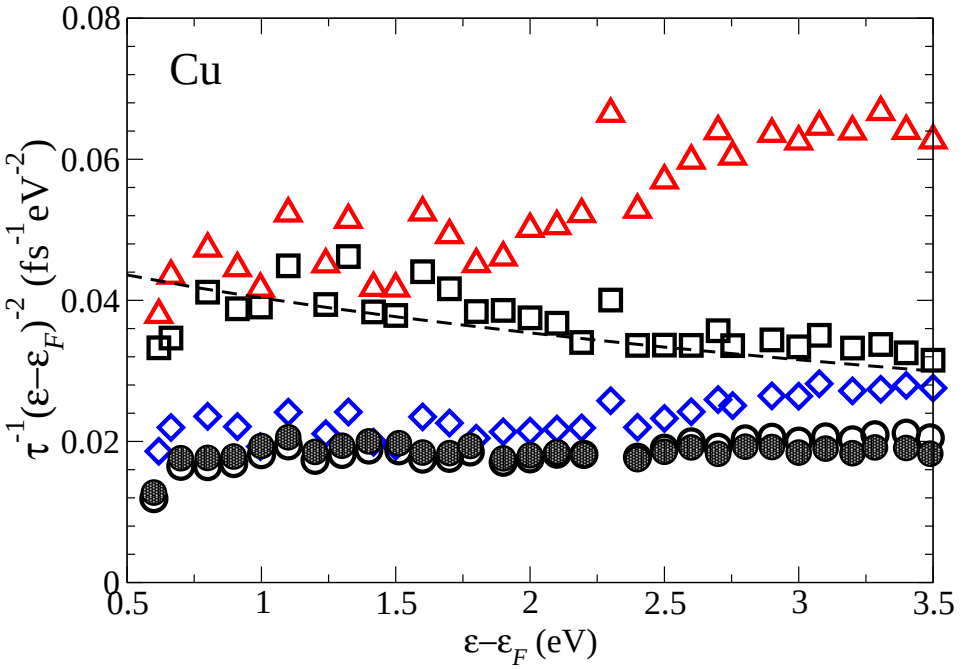

Quasiparticle Lifetimes. Conclusions

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- Extensive first-principles calculations of the inelastic lifetime of low-energy electrons in noble metals in the $GW\Gamma$ approximation

$$\text{Same footing XC of} \begin{cases} \text{screening of the interaction} \\ \text{interaction itself} \end{cases}$$

  - Both contributions nearly compensate
    impact of XC hole in the excited electron dominates
    $GW\Gamma$ lifetimes slighty larger than G^0W^0 lifetimes

- Effect of d electrons
  - Main role: participate in the screening
  - Cu, Au: opening a scattering band at $\varepsilon - \varepsilon_F$ $\sim$2 eV