SAND2011-4936C

Strongly Coupled Coulomb Systems 2011

Budapest, July 24-28, 2011

XUV absorption in aluminum:

First-principles opacity calculations

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Acknowledgments

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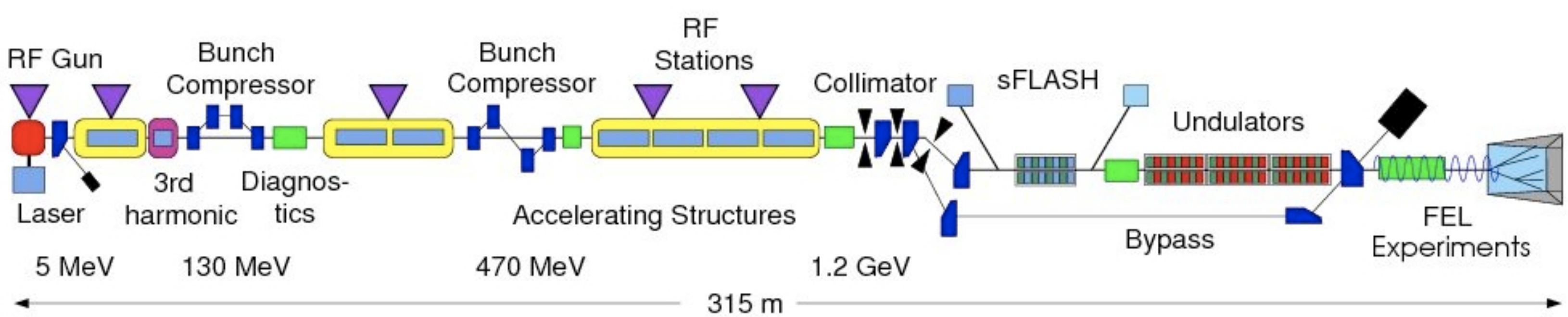
The XUV absorption of aluminum is of fundamental and practical interest

- A wide range of free-free dominated absorption
- Excellent test of electronic structure methods
- Practical applications for XUV lithography
- Routine use of Al filters between XUV lasers and spectrometers
- Several frequently cited data sets with unresolved discrepancies
- Well matched to new FEL XUV sources (FLASH at DESY)



Accurate optical properties in general are key to many approaches to temperature measurement

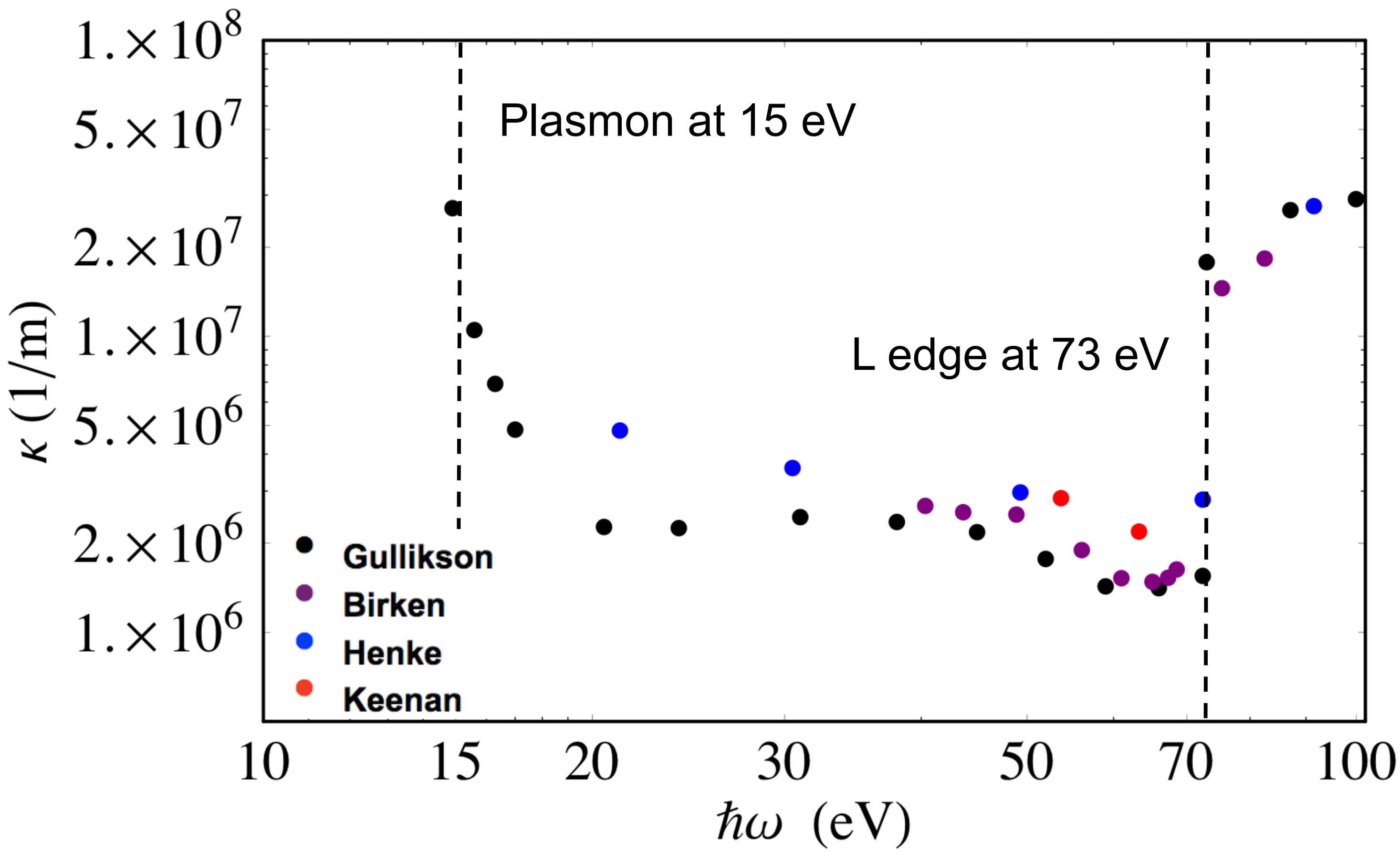
Several data sets have been generated for absorption in aluminum at ambient conditions

- **Gullikson** E.M. Gullikson, P. Denham, S. Mrowka, J. Underwood, Phys. Rev. B 49, 16283 (1994).
- **Birken** Birken, Jark, Kunz and Wolf, *Nucl. Instrum. Methods Phys. Res. A 253 166* (1986).
- **Henke** B.L. Henke, E.M. Gullikson, J.C. Davis, Atom. Data Nucl. Data Tables 54, 181 (1993).
- **Keenan** R. Keenan, C. Lewis, J. Wark, E. Wolfrum, J. Phys. B 35 L447 (2002).

Differences between the data sets are significant

Experiments must either carefully account for oxidation, or eliminate it

The data ranges from the plasmon energy to the L edge and beyond



Modest differences in absorption but large differences in transmission

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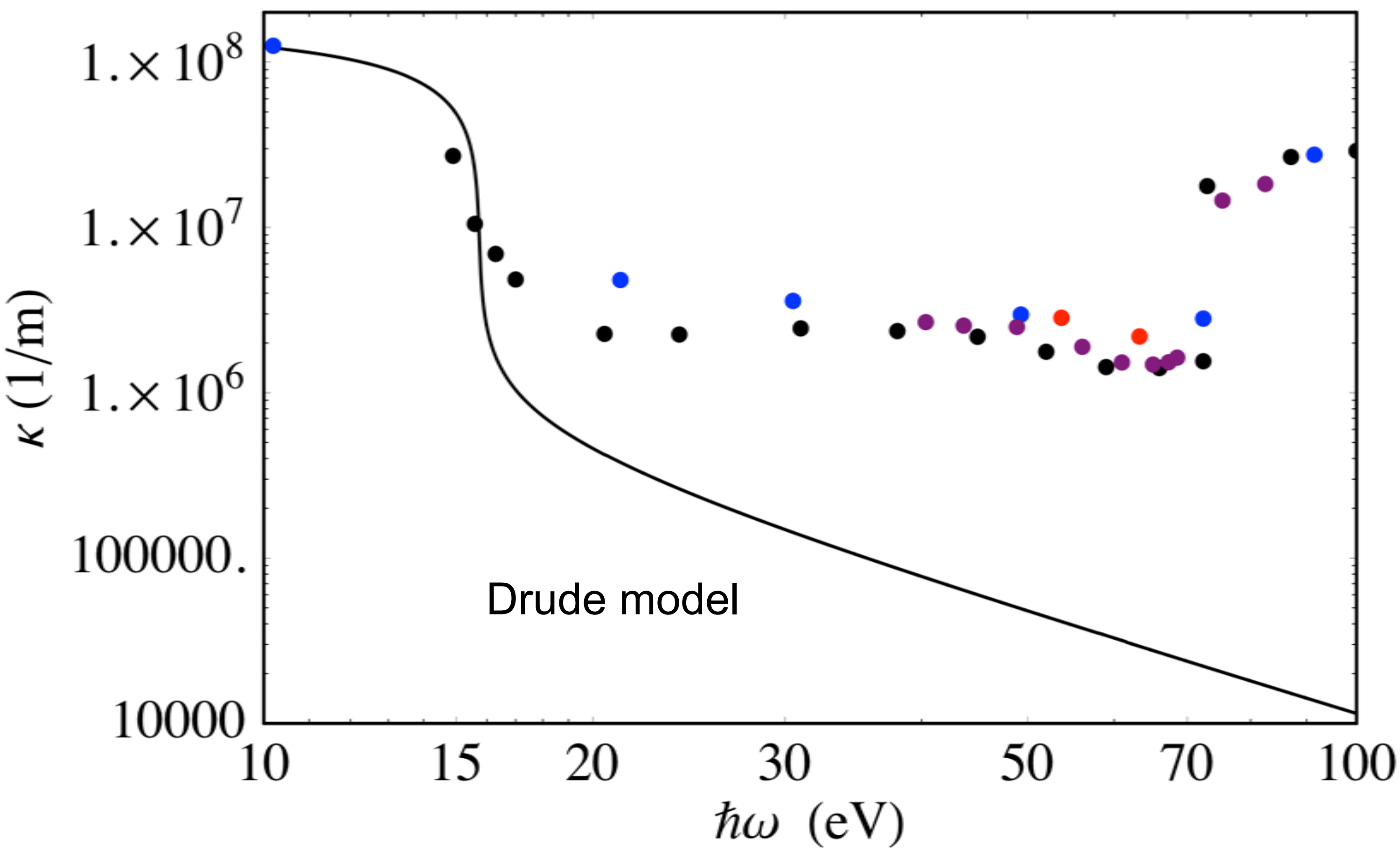
Although a free electron metal, the Drude model grossly underestimates the absorption in aluminum



Simple atomic cross section calculations do much better at higher energies

We calculate the absorption in fcc aluminum with electronic structure methods

- **Density functional theory (DFT)**
  - DFT calculations with VASP (Vienna *ab initio* simulation program)
    - Projector Augmented Wave (PAW) potentials
  - Kubo-Greenwood for transport properties (no local field corrections)
  - Full inverse dielectric calculations (local fields corrections included)
    - Adler (1962), Wiser (1963)

- ***GW* methods** (*G*: Green's function, *W*: Dynamically screened Coulomb operator; much better excited states; accurate band gaps in semiconductors)
  - Also with VASP, at the level of G_0W_0 (single pass, using DFT wavefunctions) and GW_0 (iterative convergence on *G*, no update on *W*)
  - With and without local field corrections

We first compute the dielectric and absorption properties without local field corrections

The usual approach (Kubo-Greenwood) to calculating the dielectric:

Assume $$\phi^{ext} = \phi^{ext}(\mathbf{q},\omega)\exp[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$$

Calculate the response $$\phi^{tot} = \phi^{ext} + \phi^{ind}$$

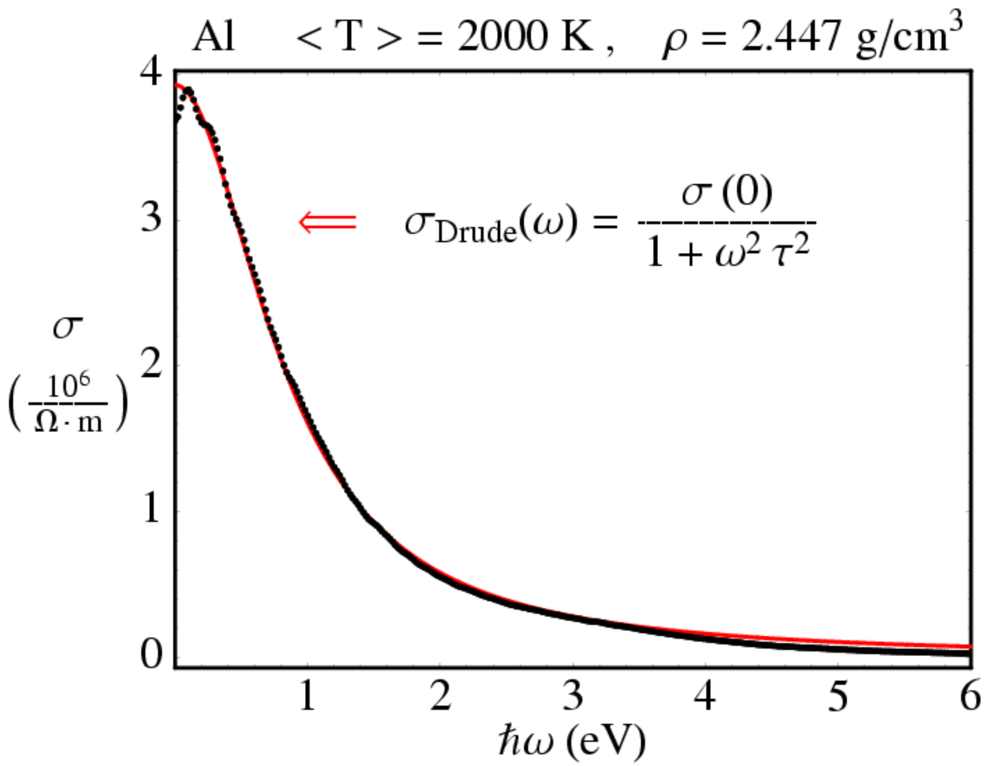
assuming $$\phi^{ind} = \phi^{ind}(\mathbf{q},\omega)\exp[i(\mathbf{q}\cdot\mathbf{r} - \omega t)]$$

For optical properties (**q** = 0)

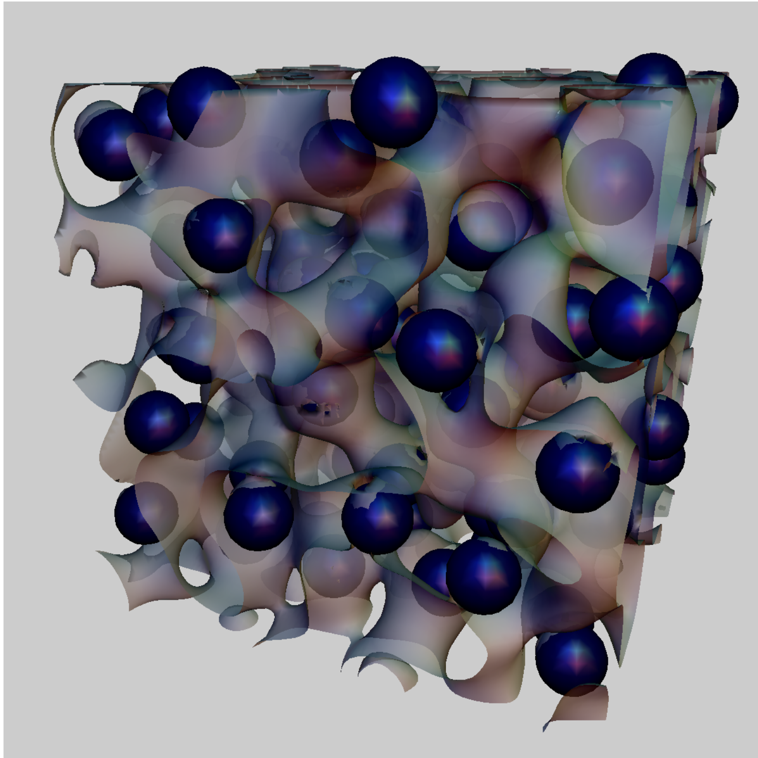
$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2\omega\Omega}\sum_{\alpha=1}^{3}\sum_{j=1}^{N}\sum_{i=1}^{N}(F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}}))\left|\left\langle\Psi_{j,\mathbf{k}}\middle|\nabla_\alpha\middle|\Psi_{i,\mathbf{k}}\right\rangle\right|^2\delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega),$$

with other optical properties derived through Kramers-Krönig relations

This approach has been very successful for dc and lower energy (visible light) optical properties in simple metals

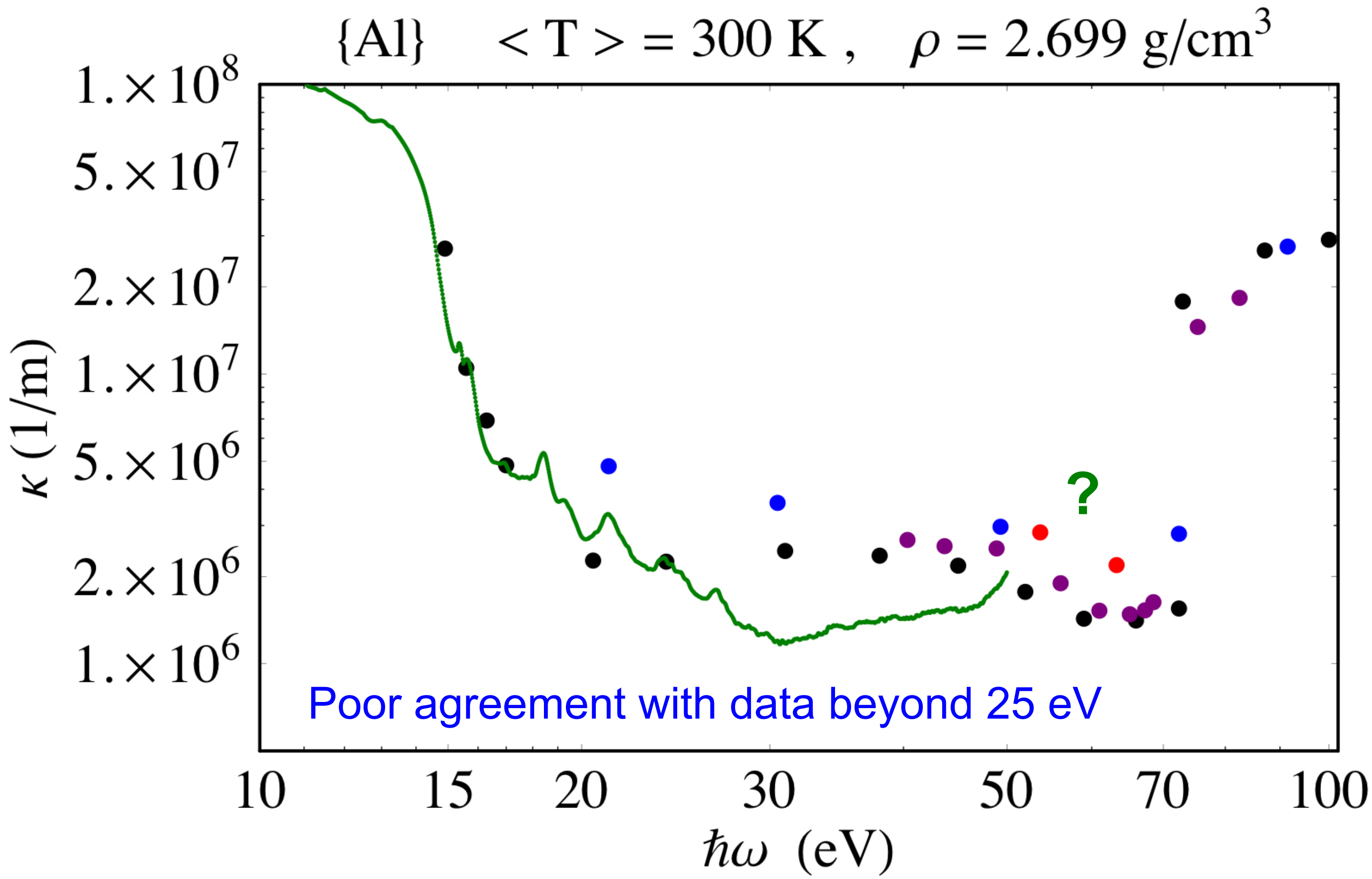


The agreement with the Drude model indicates 'nearly free' electrons



Ion cores displayed with iso-surfaces of the mean valence charge density

Our initial attempts to calculate the XUV absorption with DFT were disappointing



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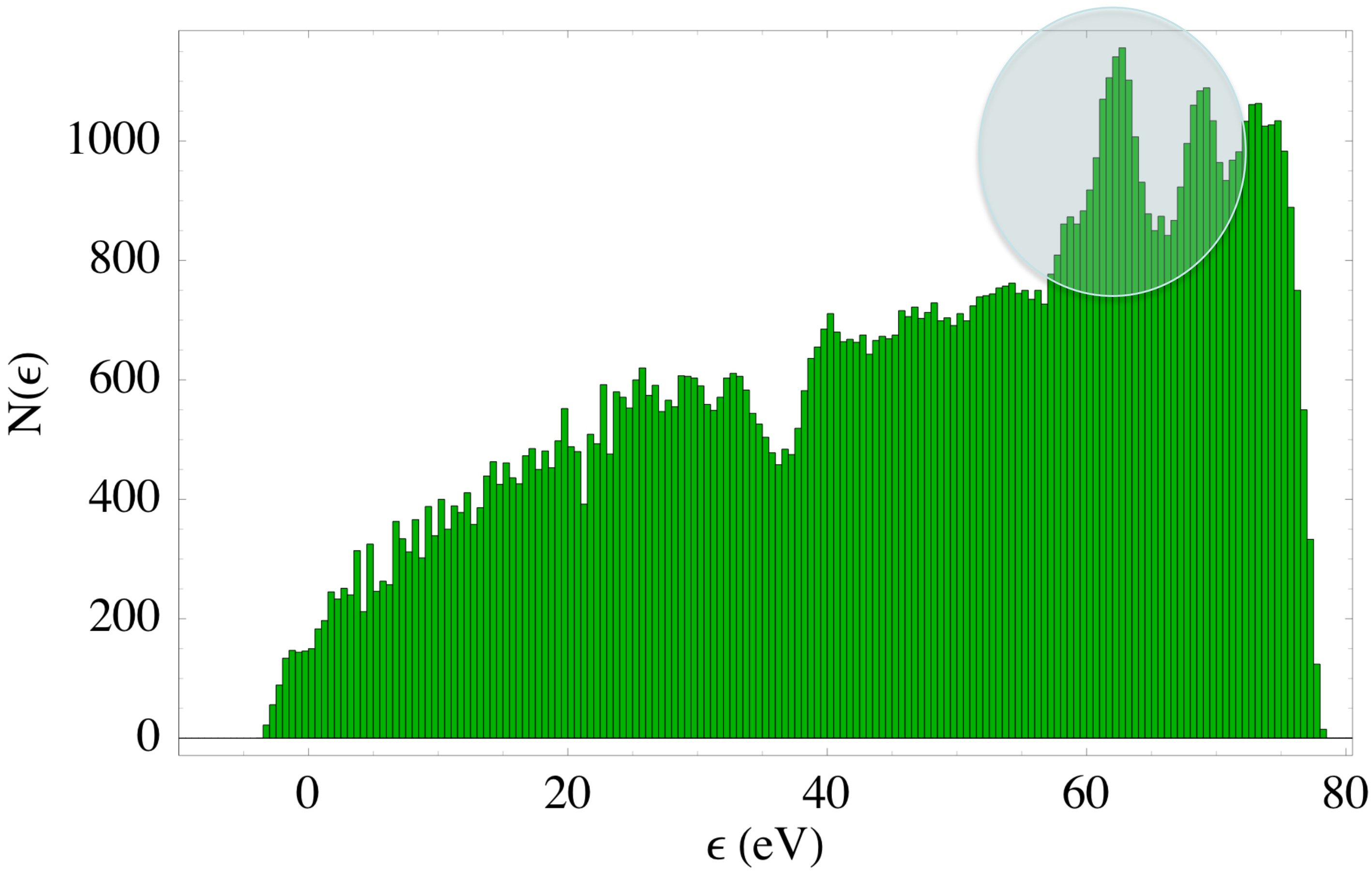
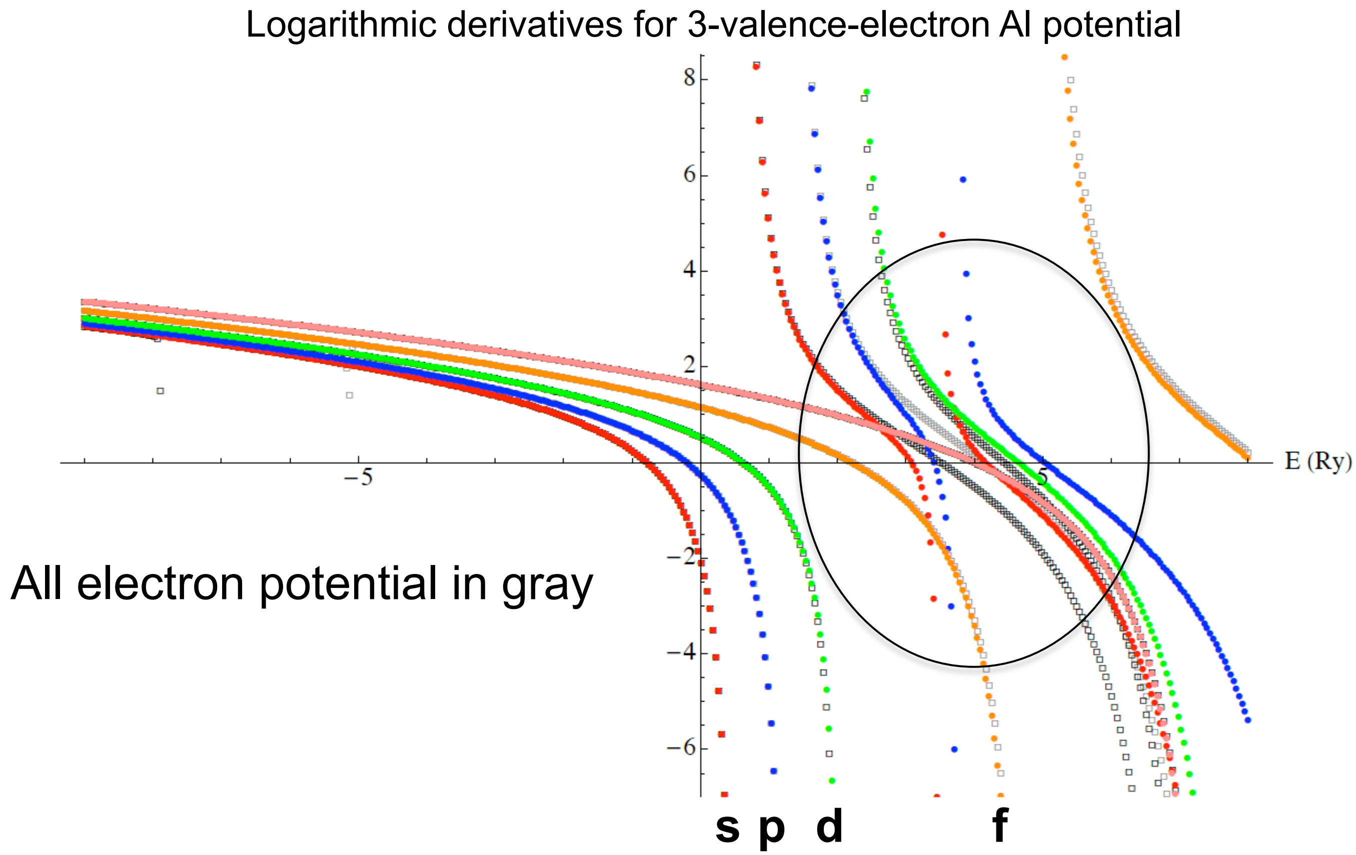
We truncated the higher energy absorption because of spurious features in the density of states



The aluminum potential exhibited poor scattering properties at higher energies

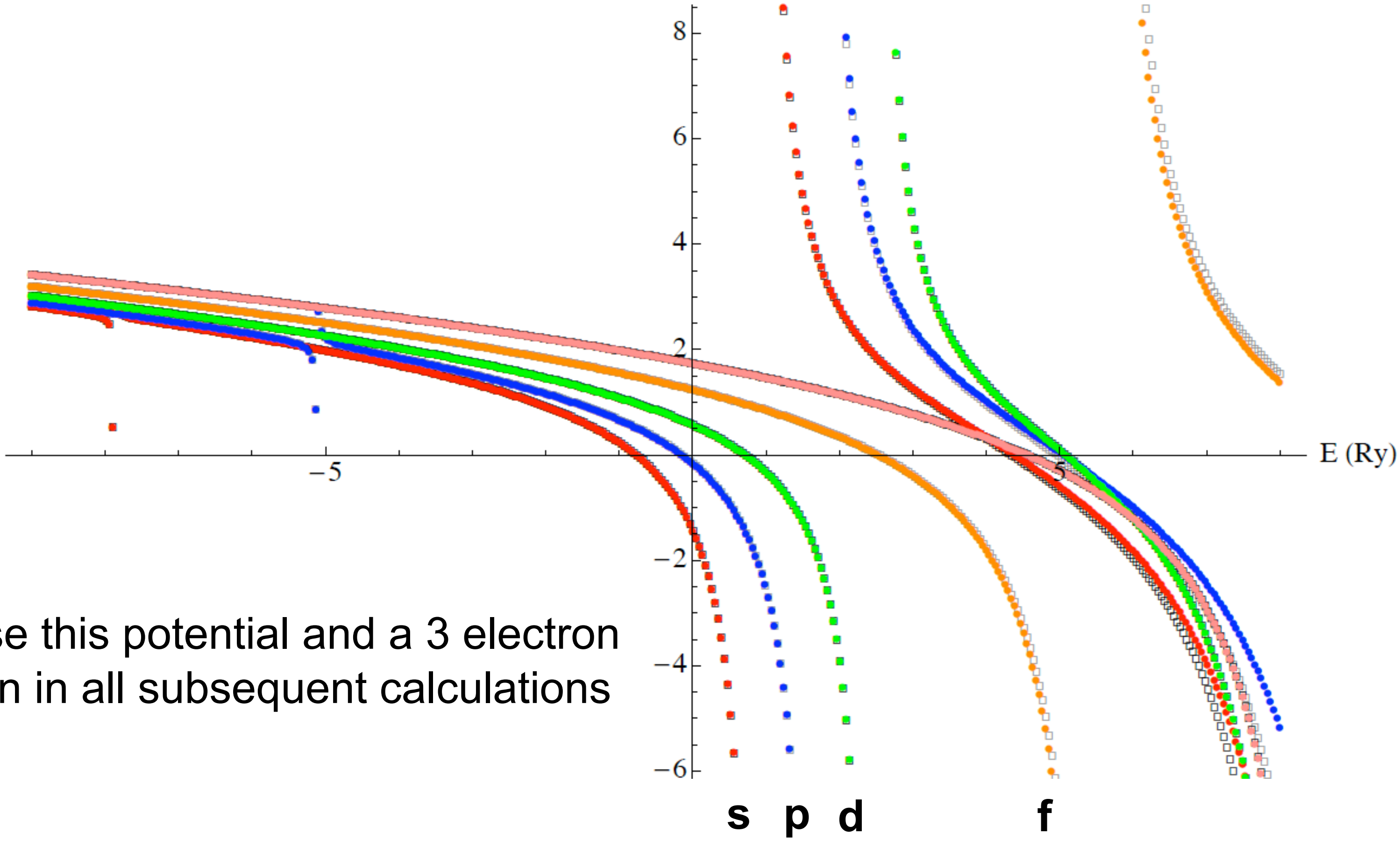


Nominal potentials supplied with condensed matter codes often have poor high-energy scattering properties

This 11 electron potential – $2s^2 2p^6 3s^2 3p^1$ – mimics the all electron results to high energies

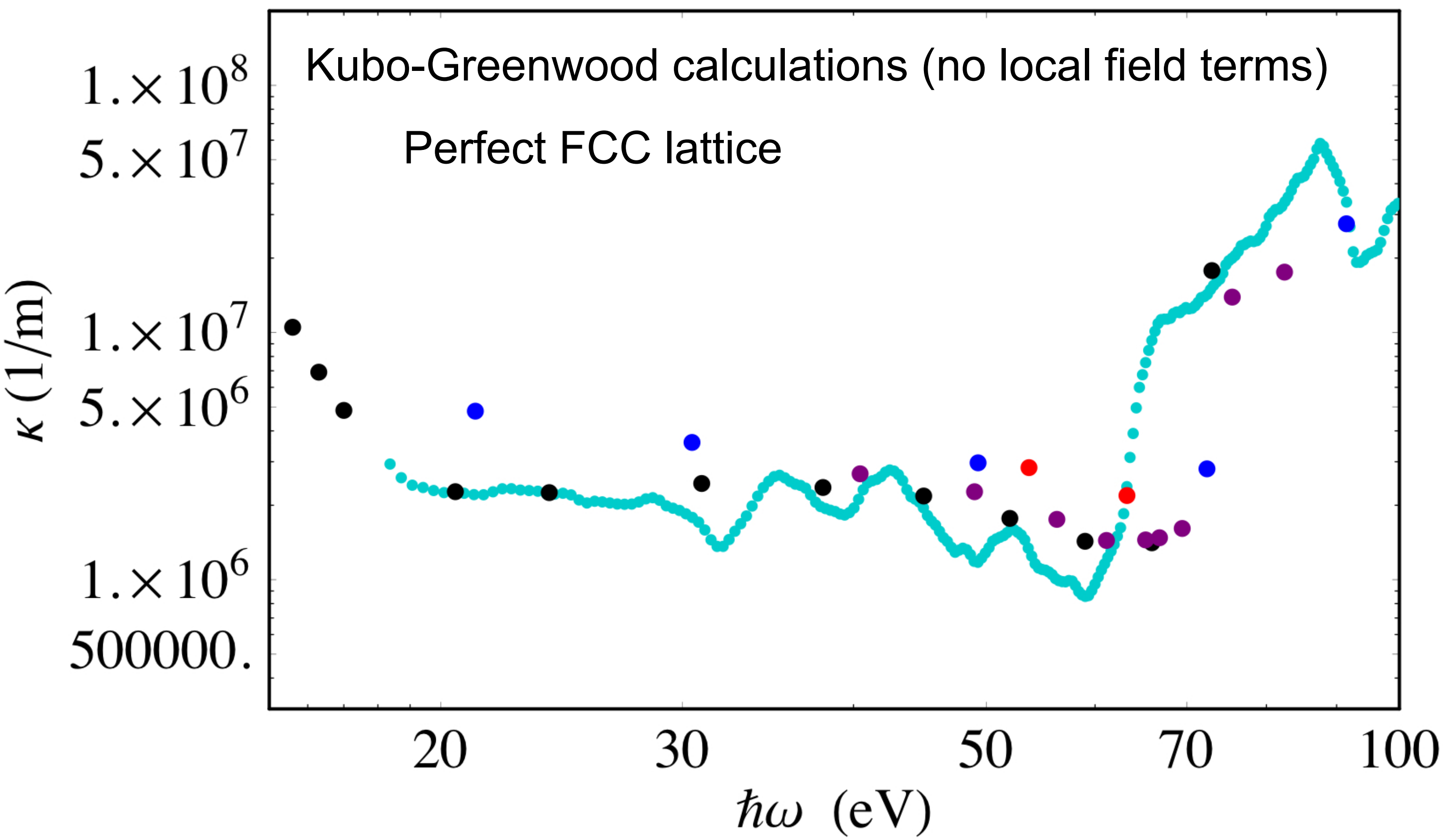
ℓ=s(red), p(blue), d(green), f(orange, local), 4(pink, local).

Logarithmic derivatives



We use this potential and a 3 electron version in all subsequent calculations

Density functional calculations of the XUV absorption lie below the data and give an L edge ~ 10 eV too low



Inaccurate prediction of the L edge is expected with DFT

Deriving the dielectric with local field effects included is considerably more involved

Recall that in periodic lattices (Bloch Theory), momentum conservation requires

$$\mathbf{k} \rightarrow \mathbf{k} + \mathbf{q} \qquad \textbf{OR} \qquad \mathbf{k} \rightarrow \mathbf{k} + \mathbf{q} \pm n\mathbf{K}$$

where **k** refers to the crystal momentum of an electron at point **k** in the first Brillouin zone and **K** is a reciprocal lattice vector (e.g. 2π/L).

In general then, an external field with wavevector **q** will induce

$$\phi^{ind} = \sum_{\mathbf{K}} \phi^{ind}(\mathbf{q},\mathbf{K},\omega)\exp[i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r} - i\omega t]$$

$$\rightarrow \quad \varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)$$

Local field contributions, Umklapp processes

A much more complicated object (Adler, Wiser)

The dielectric with local field corrections is the solution to an integral equation for 1/ε

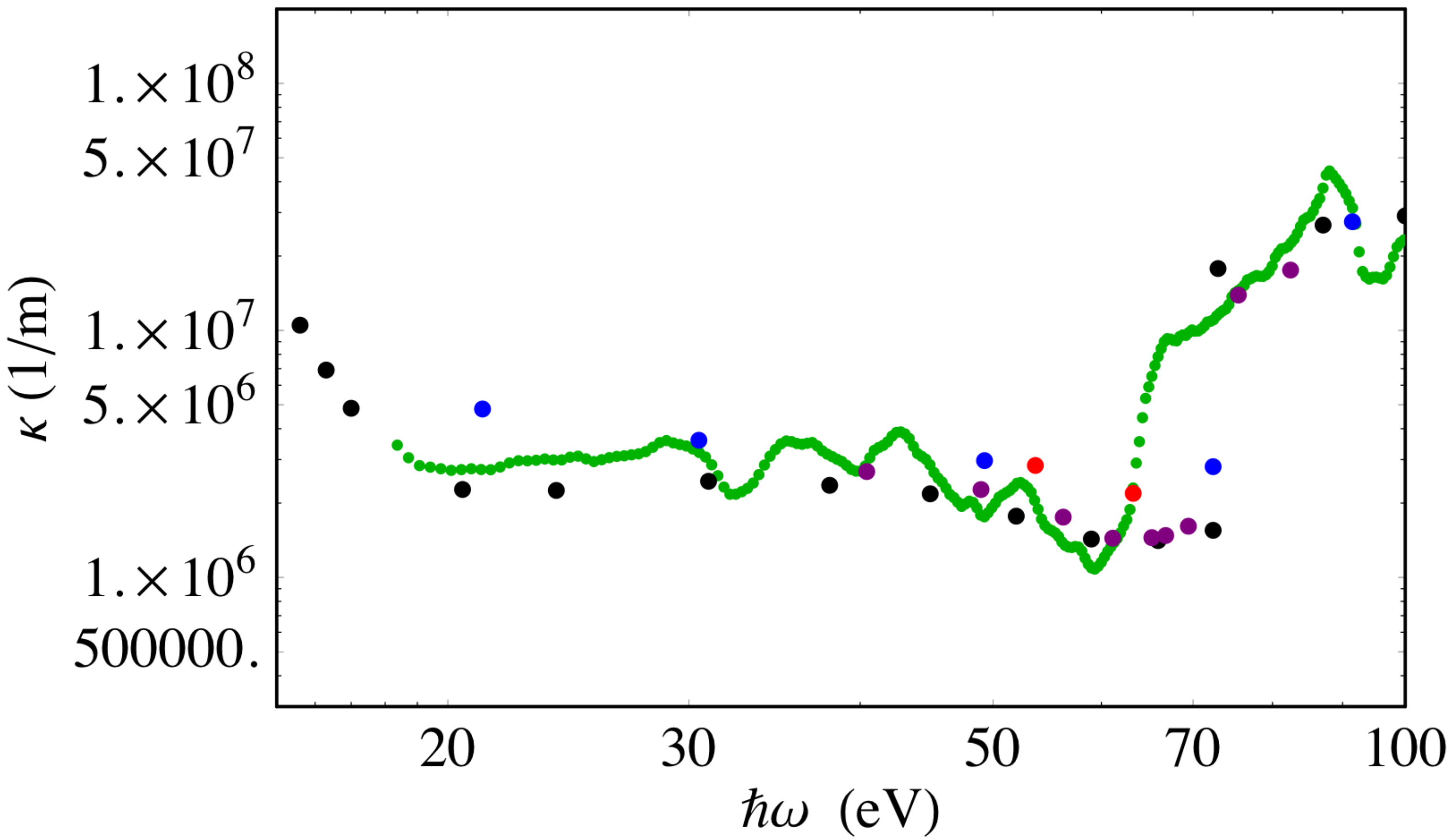
$$\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)=\delta_{\mathbf{K},\mathbf{K}'}+\sum_{\mathbf{K}''}\frac{G(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)}{\left|\mathbf{q}+\mathbf{K}''\right|^{2}}\varepsilon^{-1}(\mathbf{q}+\mathbf{K}'',\mathbf{q}+\mathbf{K}',\omega)$$

Where

$$G(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)=$$

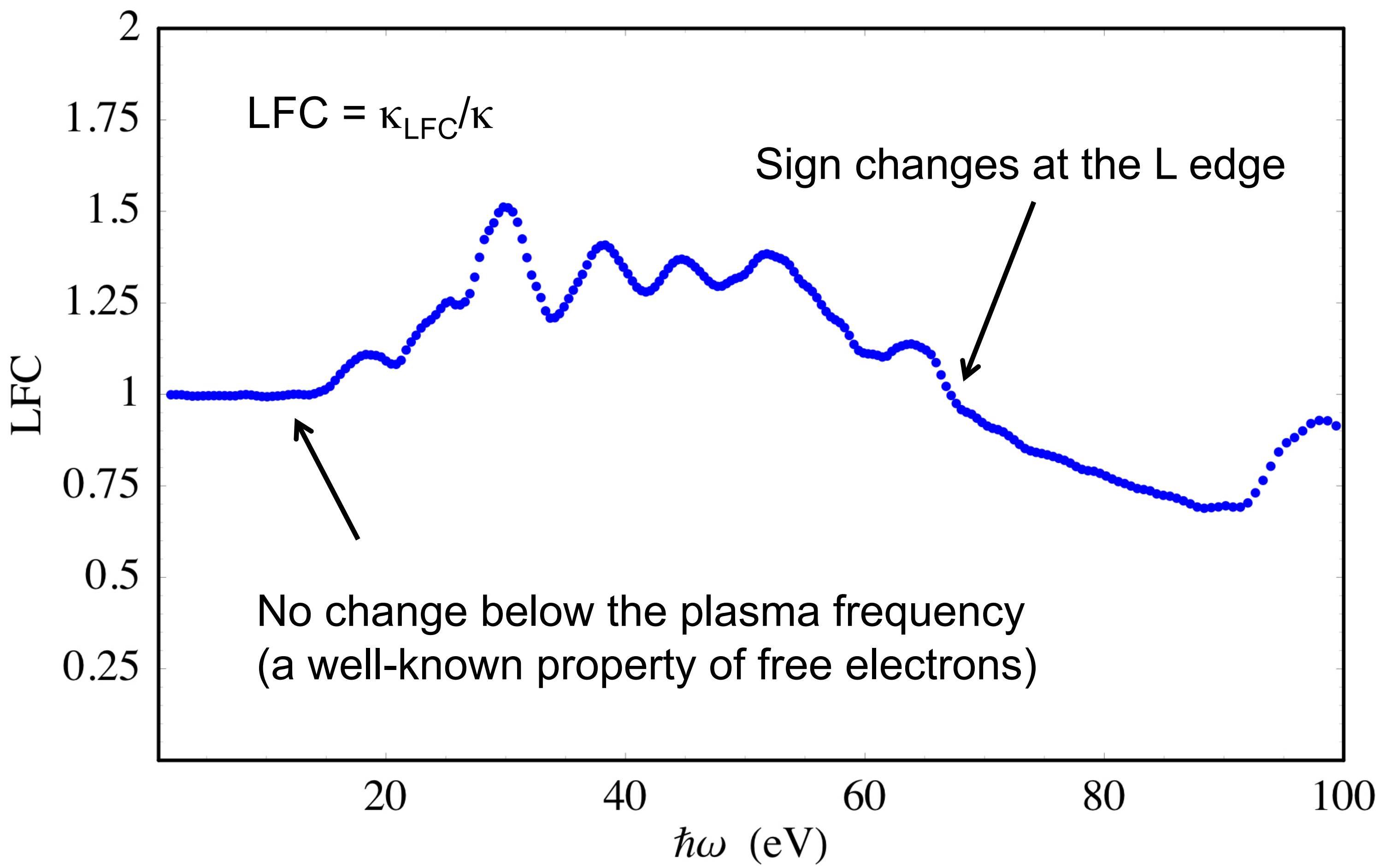
$$\frac{4\pi e^{2}}{V}\sum_{l\,l'\,\mathbf{k}}\frac{\langle l\mathbf{k}|\exp(-i\mathbf{K}\cdot\mathbf{r})|\,l'\mathbf{k}+\mathbf{q}\,\rangle\langle\,l'\mathbf{k}+\mathbf{q}|\exp(i\mathbf{K}''\cdot\mathbf{r})|\,l\mathbf{k}\rangle[F(\varepsilon_{l\mathbf{k}})-F(\varepsilon_{l'\mathbf{k}+\mathbf{q}})]}{\hbar\omega+\varepsilon_{l\mathbf{k}}-\varepsilon_{l'\mathbf{k}+\mathbf{q}}}$$

DFT with local field corrections improves the agreement with data but does nothing for the L edge

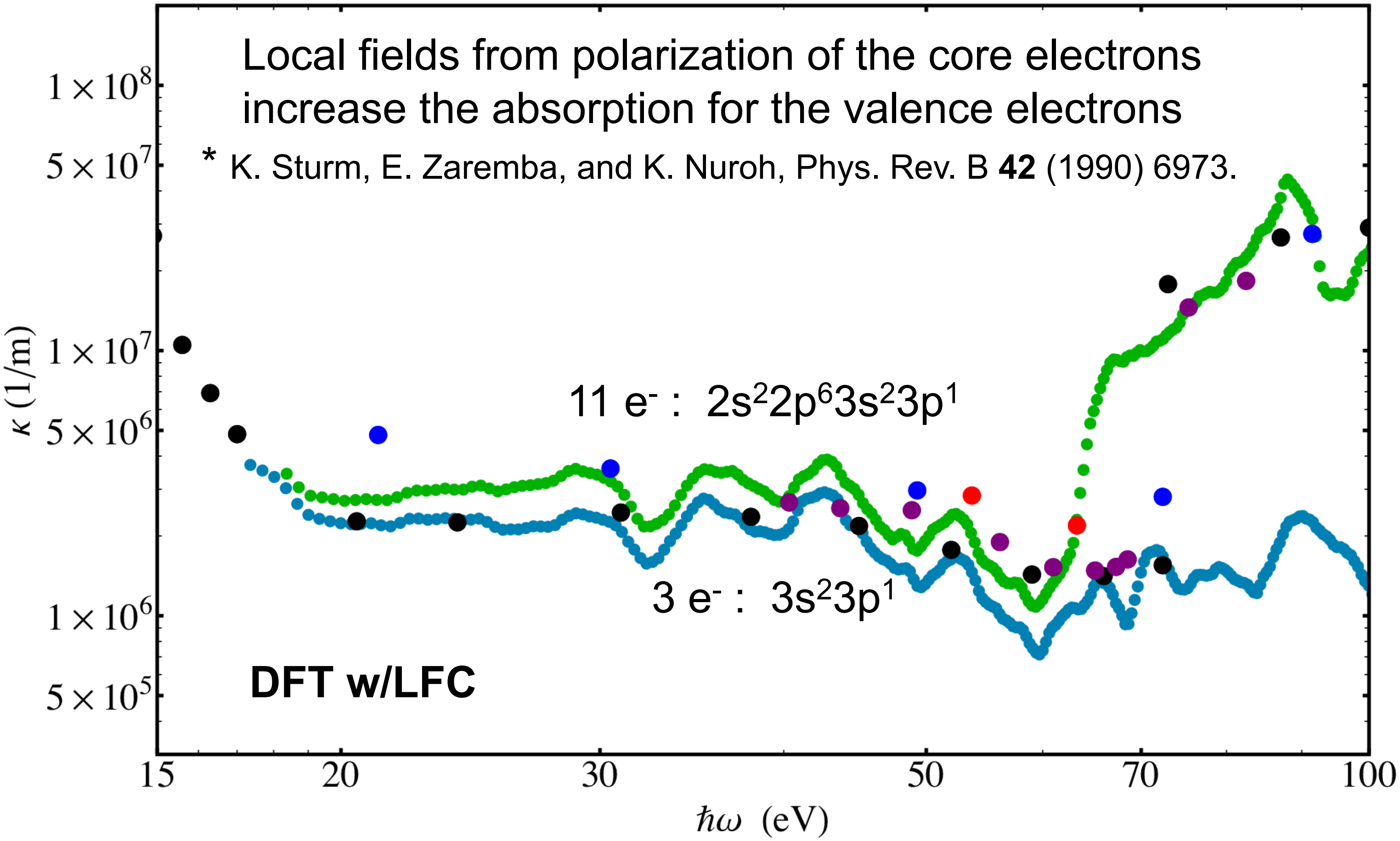


Much of the structure comes from the perfect FCC lattice and limited **k**-points

The local field effects make a significant contribution to the absorption

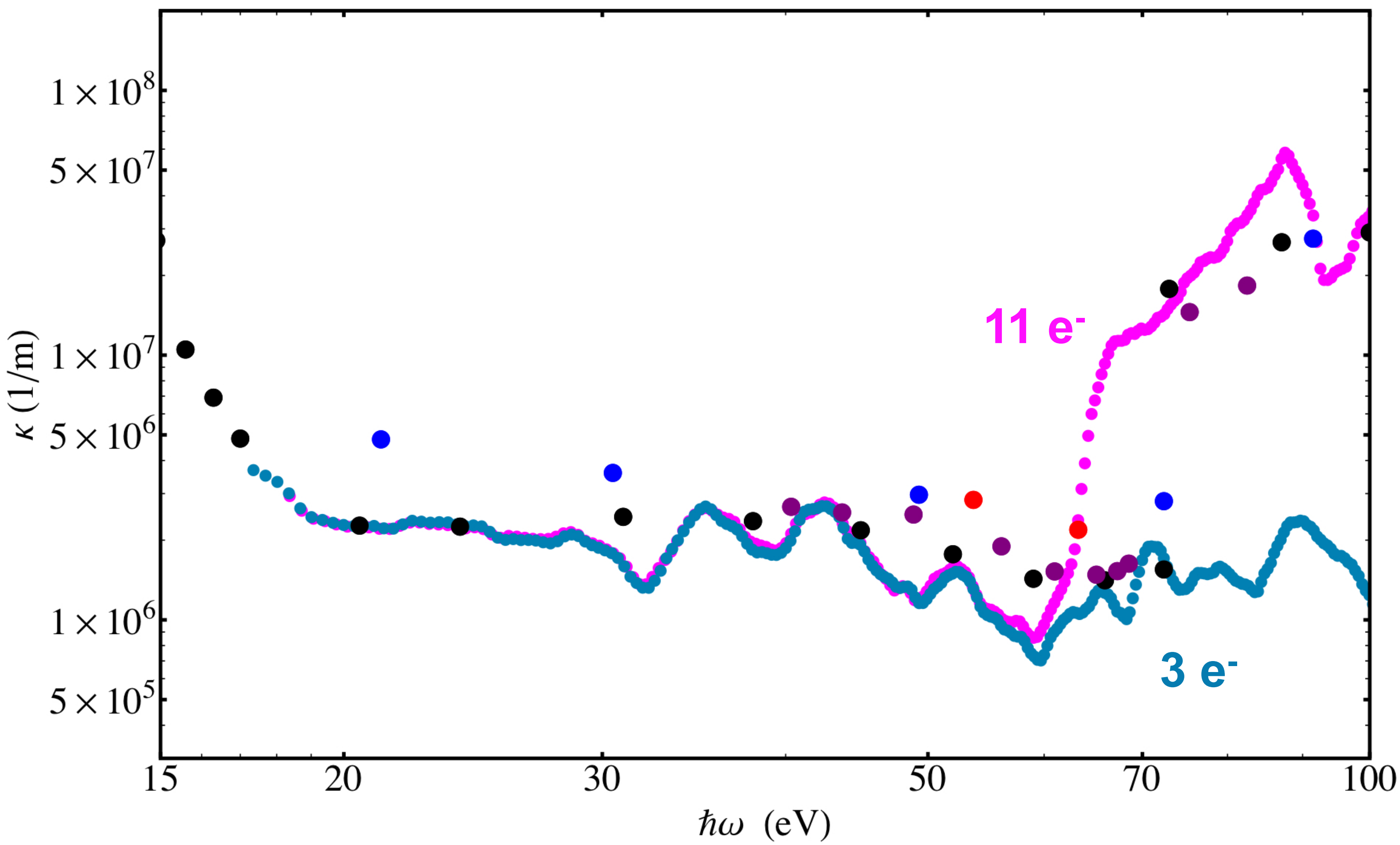


Core electrons are important when local fields are included*



There are local field contributions from the *3s3p* electrons above the plasma frequency, but they are much smaller

If we ignore the local field corrections, the core electrons play no role below the L edge



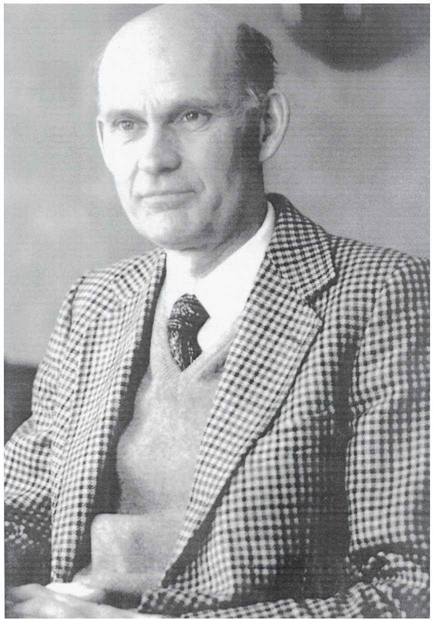
Fixing the L edge: Hedin's *GW* approximation

$$(T + V - \varepsilon_{l\mathbf{k}})\psi_{l\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}' \, \Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{l\mathbf{k}})\psi_{l\mathbf{k}}(\mathbf{r}') = 0$$

where the self energy operator **Σ** is given by

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{4\pi}\int_{-\infty}^{\infty} e^{i\omega'\delta} G(\mathbf{r},\mathbf{r}',\omega+\omega') W(\mathbf{r},\mathbf{r}',\omega') d\omega'$$

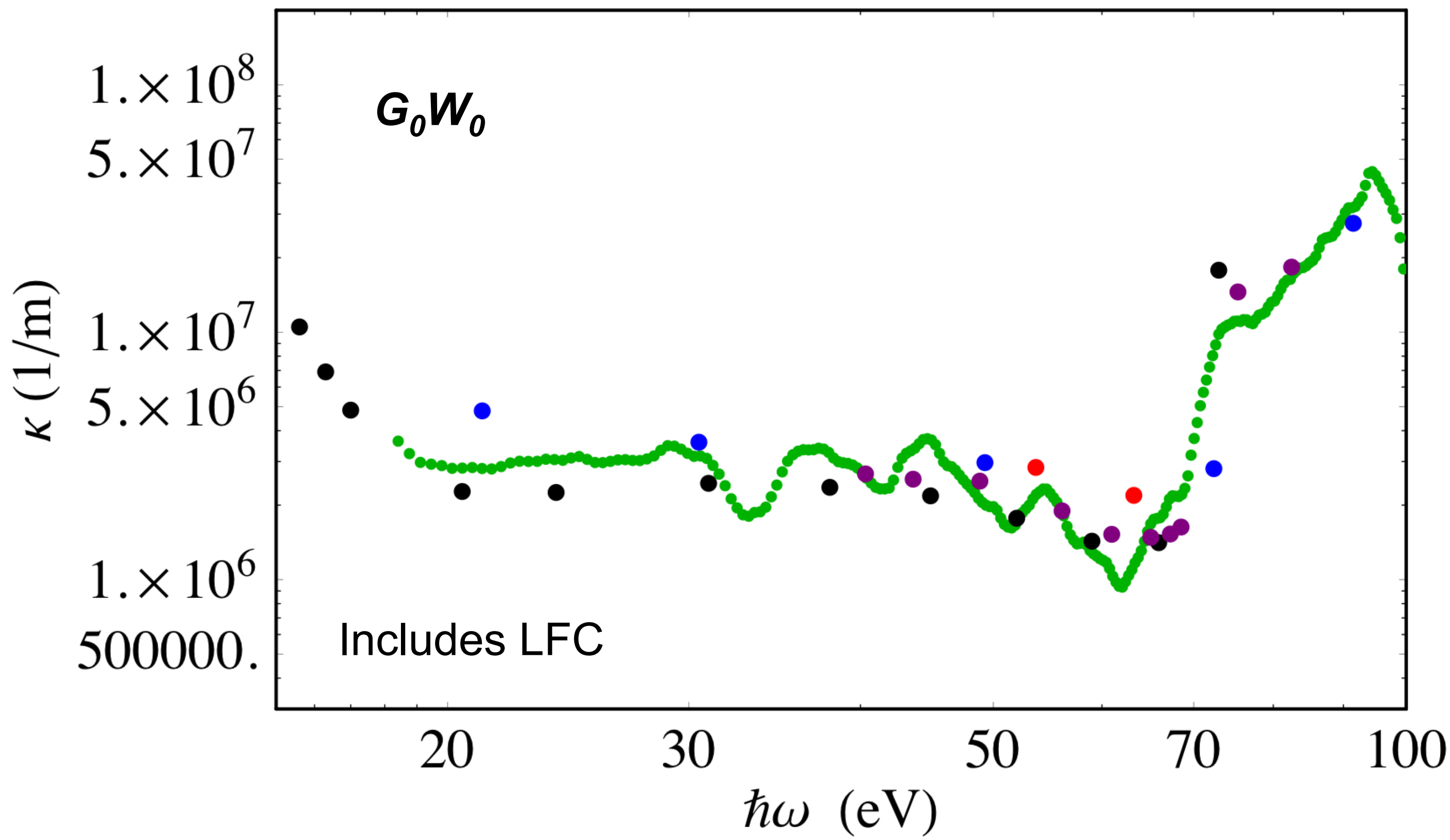
and where ***G*** is the single particle Green's function
and ***W*** is the dynamically screened Coulomb interaction.



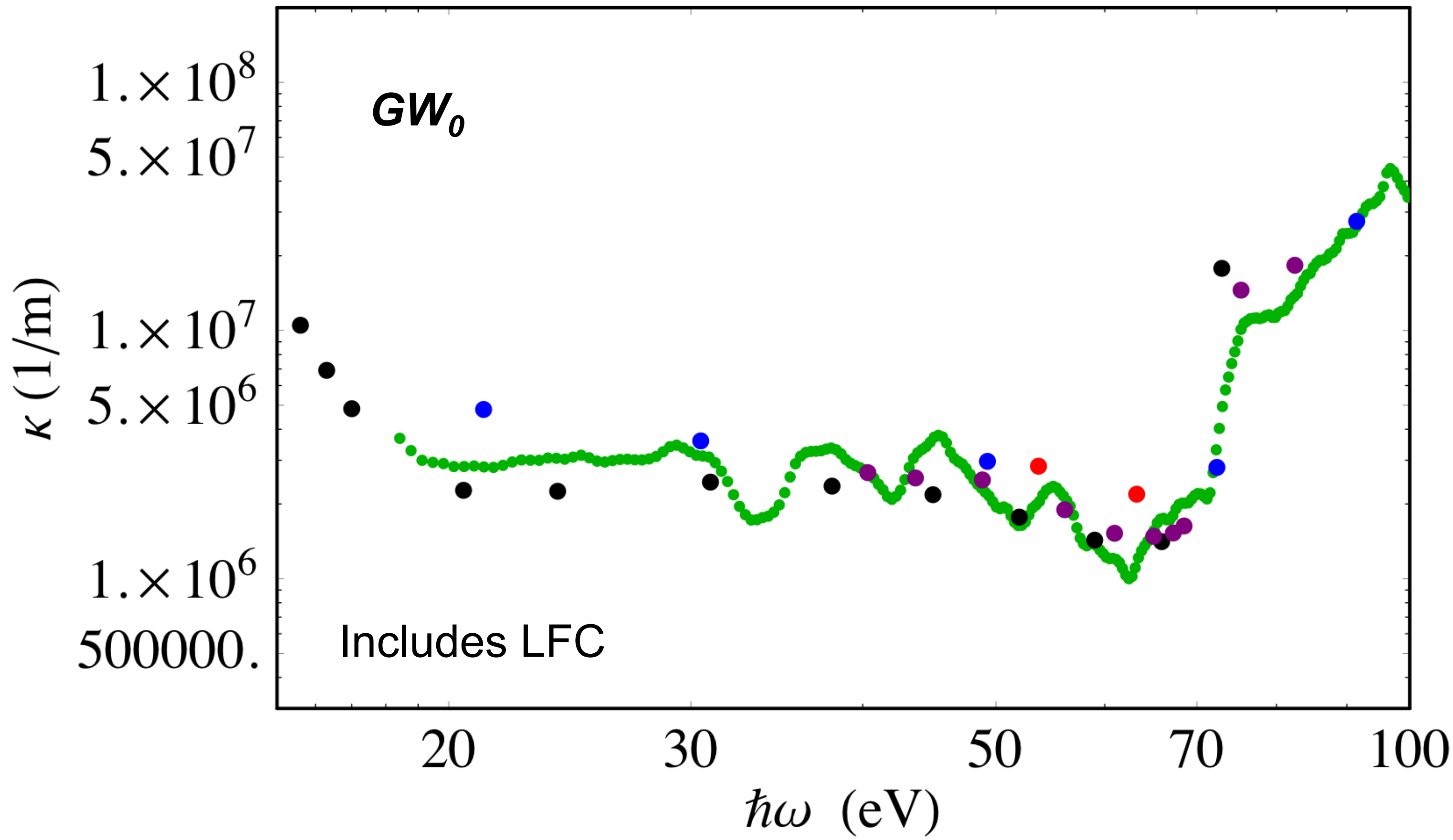
Lars Hedin

This dramatically improves over DFT in the calculation of
band gaps and band widths (much more expensive)

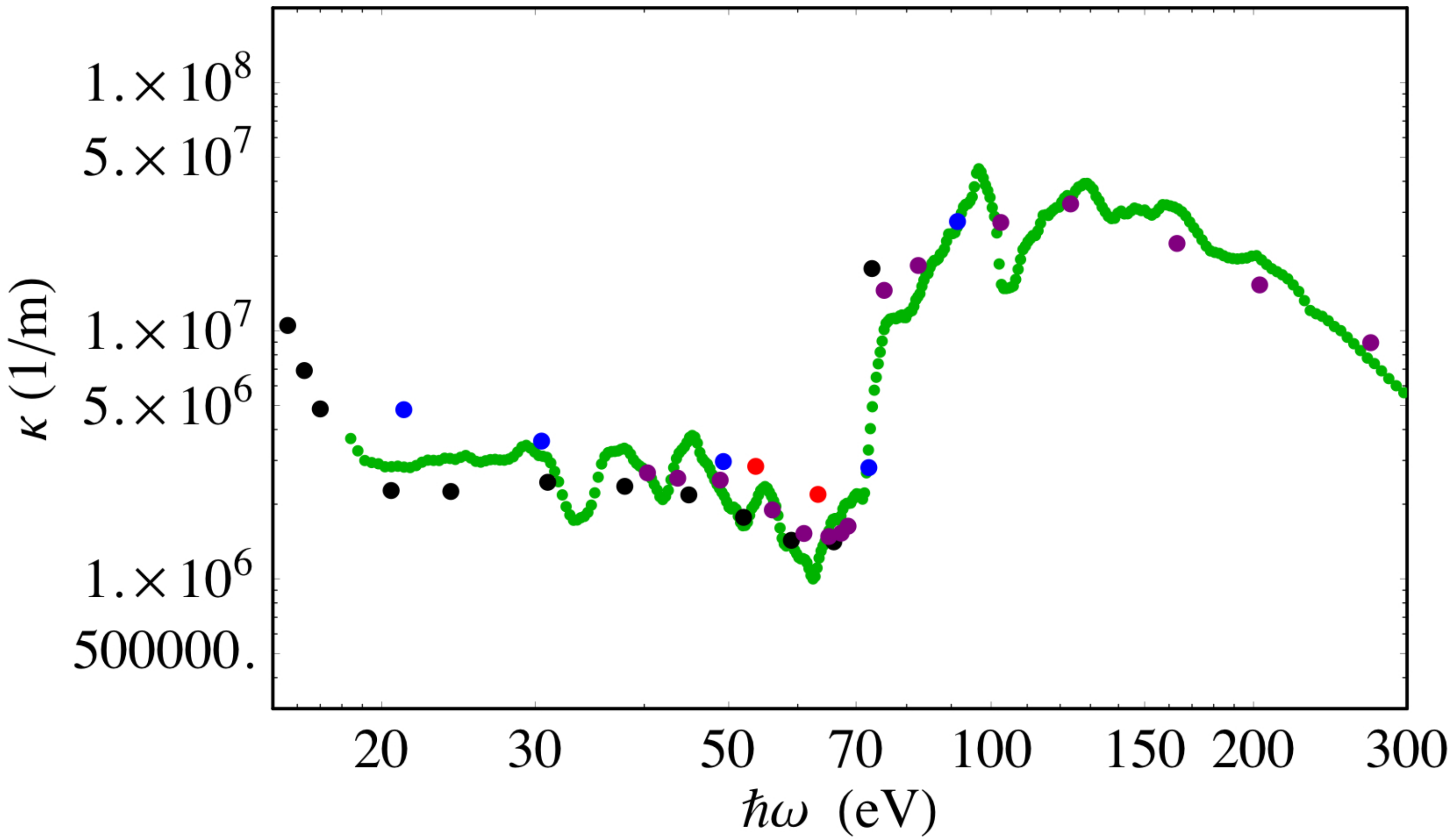
In the G_0W_0 approximation, DFT eigenvalues and eigenfunctions are used to construct G and W



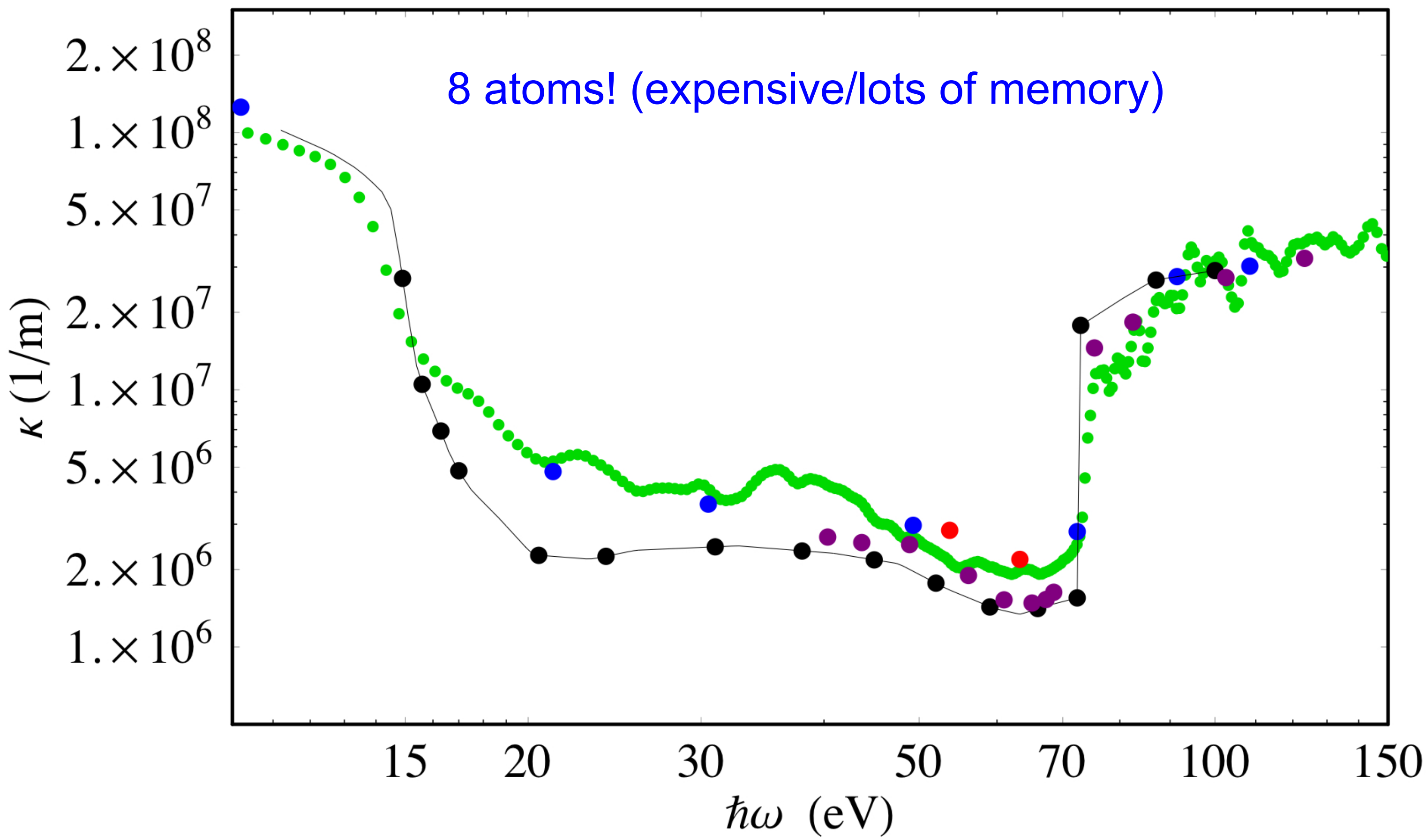
Iterating on the eigenvalues and eigenfunctions in *G* converges to the measured L edge



We find good agreement with absorption data out to 300 eV

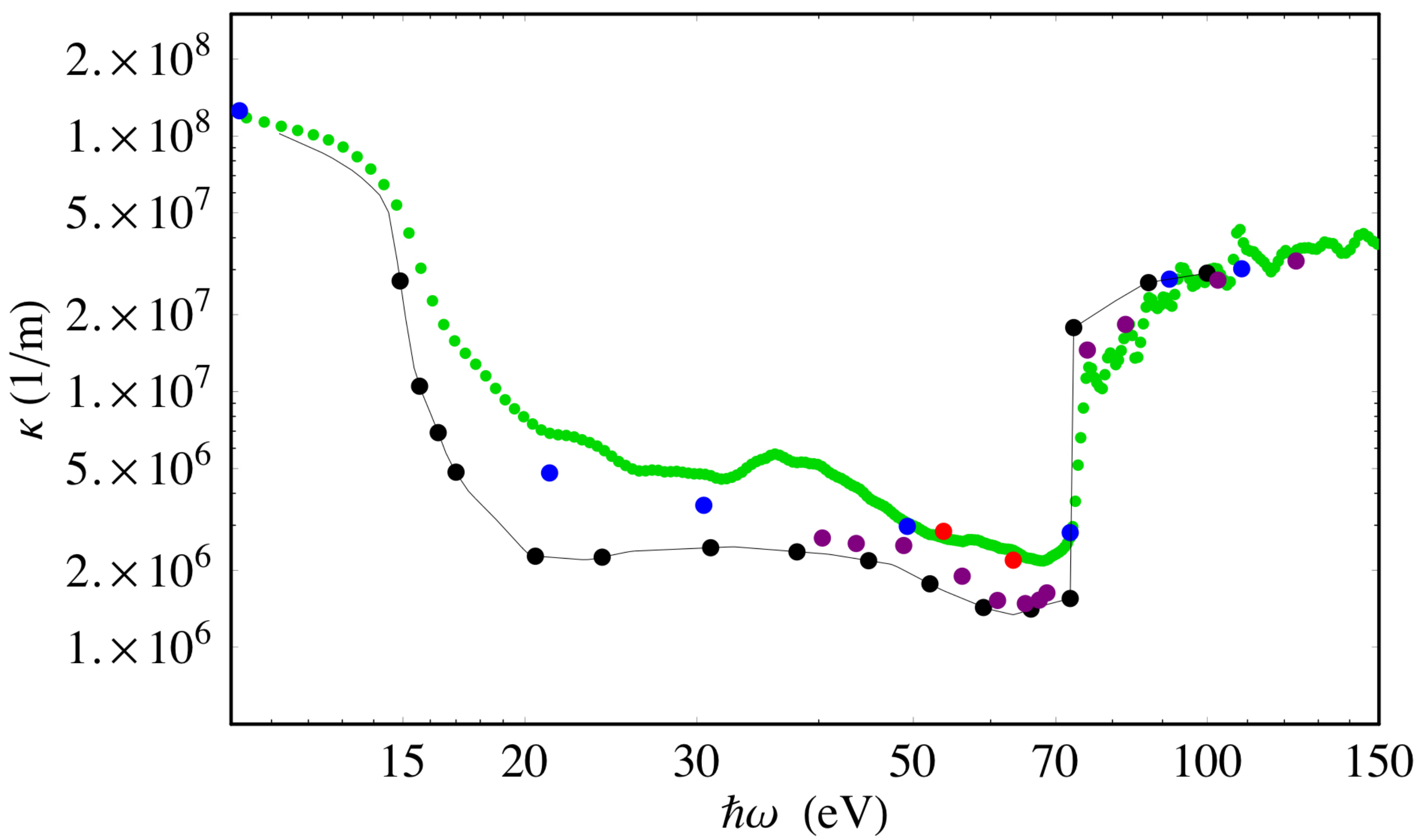


We now turn to thermal FCC configurations for the GW calculations

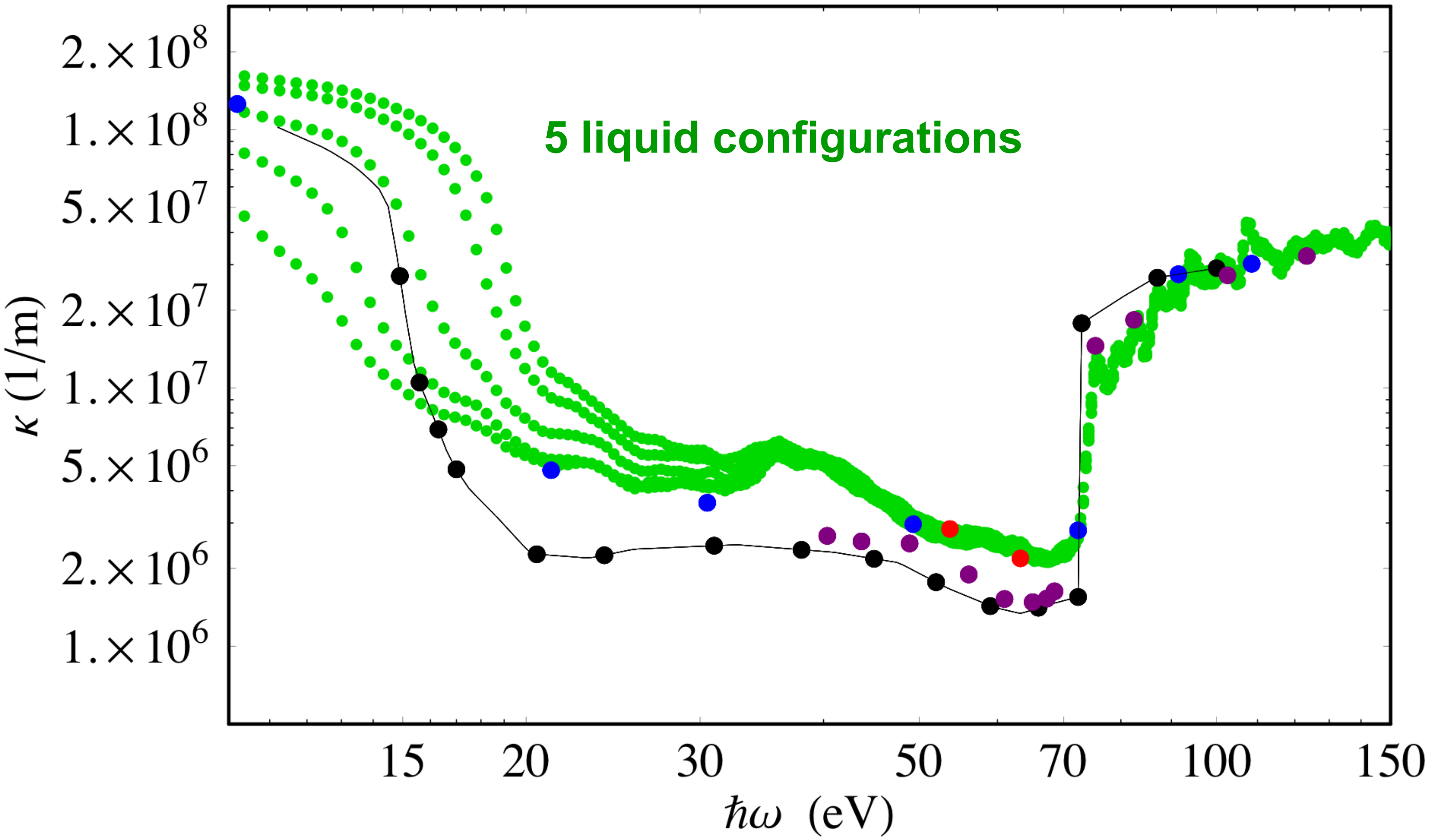


GW calculations with thermal configurations show enhanced lower energy absorption

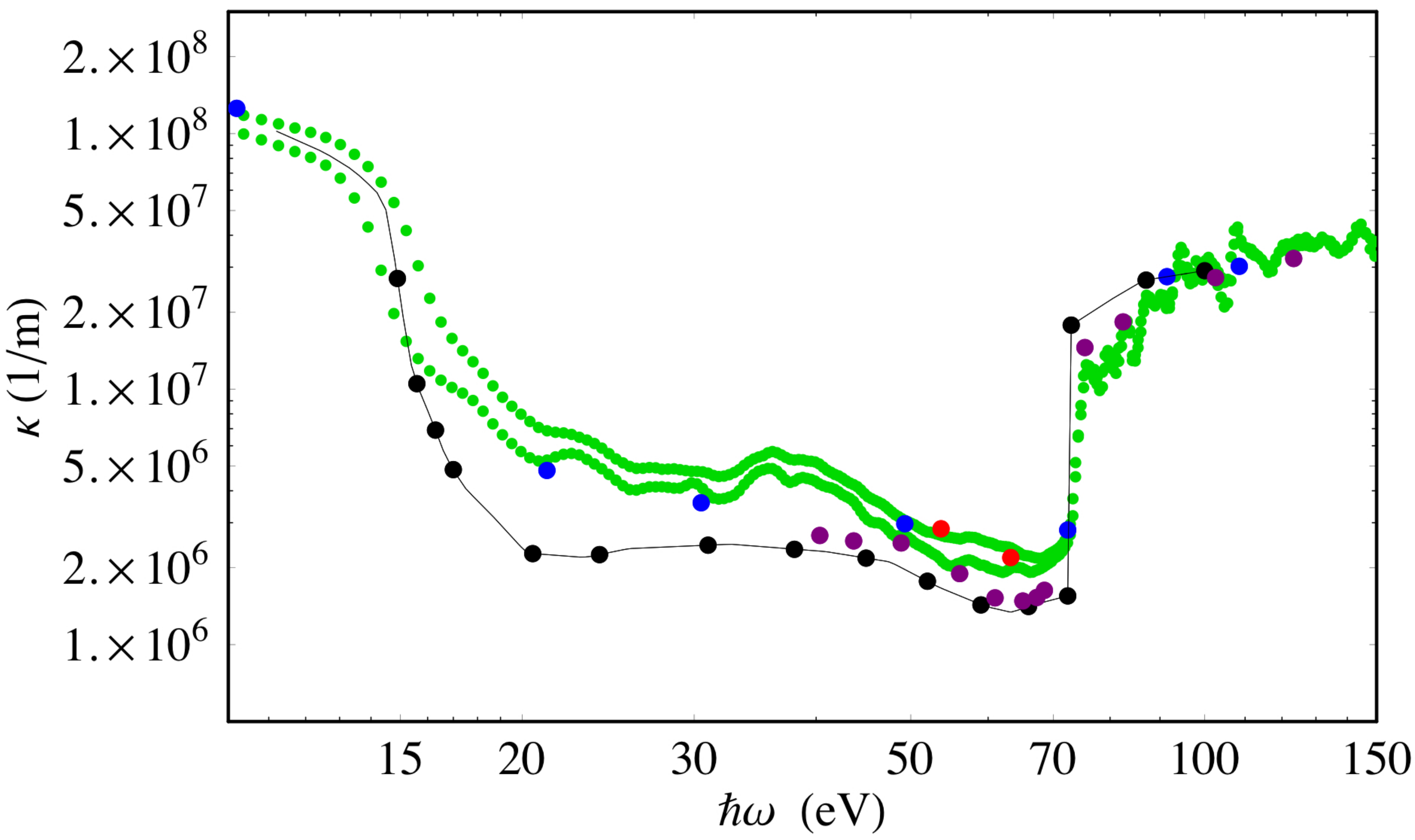
The absorptions for liquid aluminum configurations are slightly higher still



The specific thermal configurations matter little beyond 40 eV

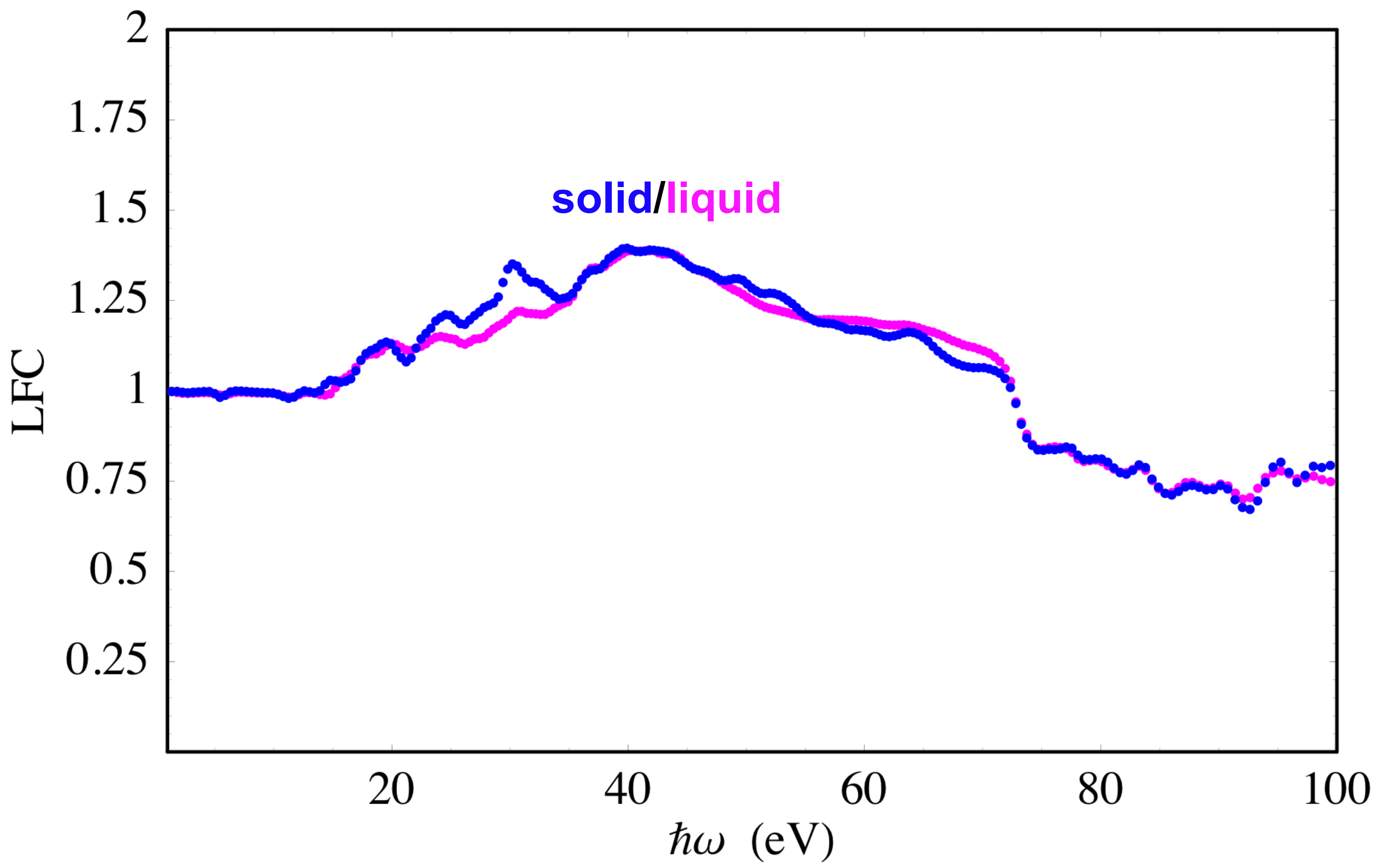


But there remains a persistent difference between the averages for solid and liquid configurations

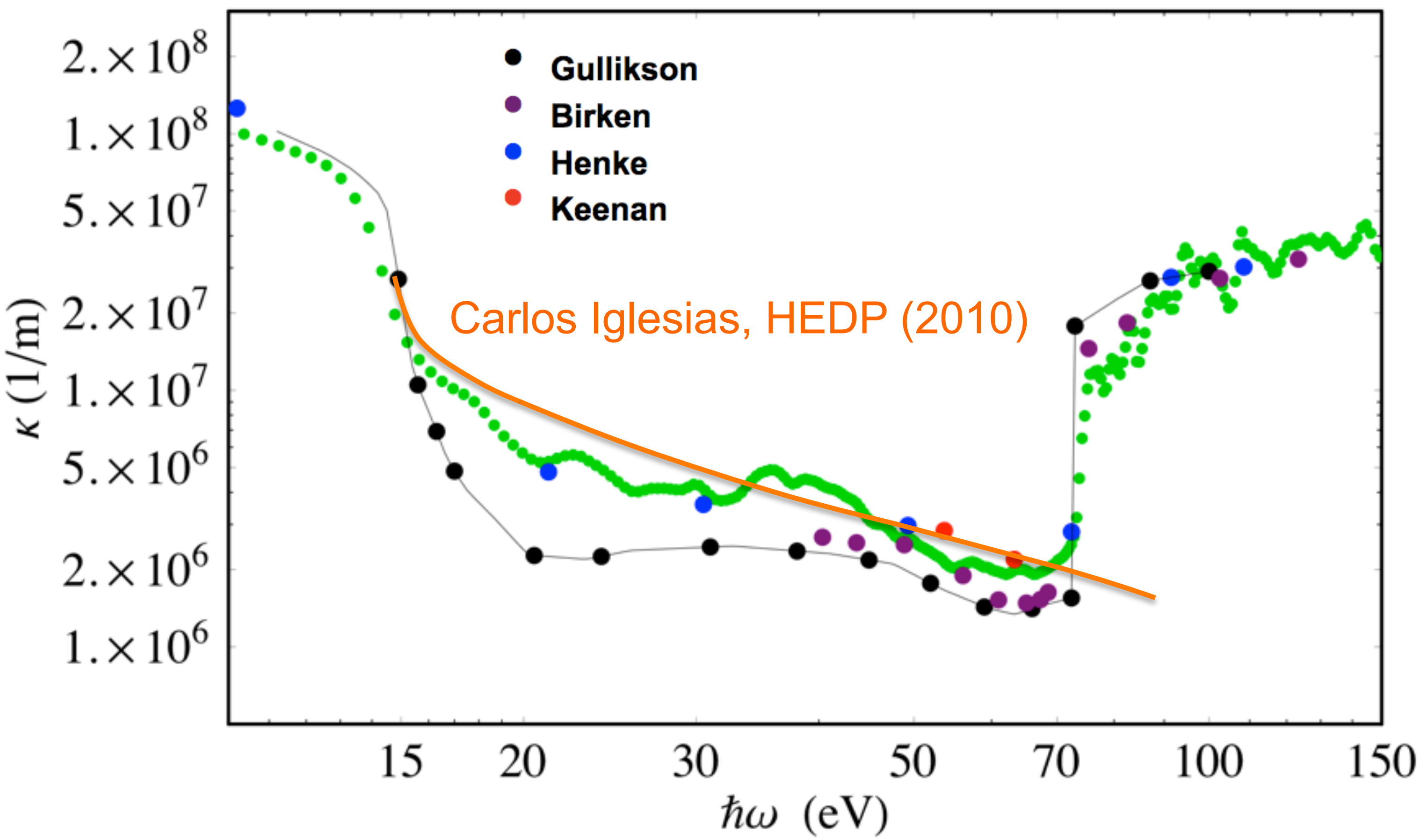


Both calculations have the same electron thermal spread

It is not related to the local field corrections

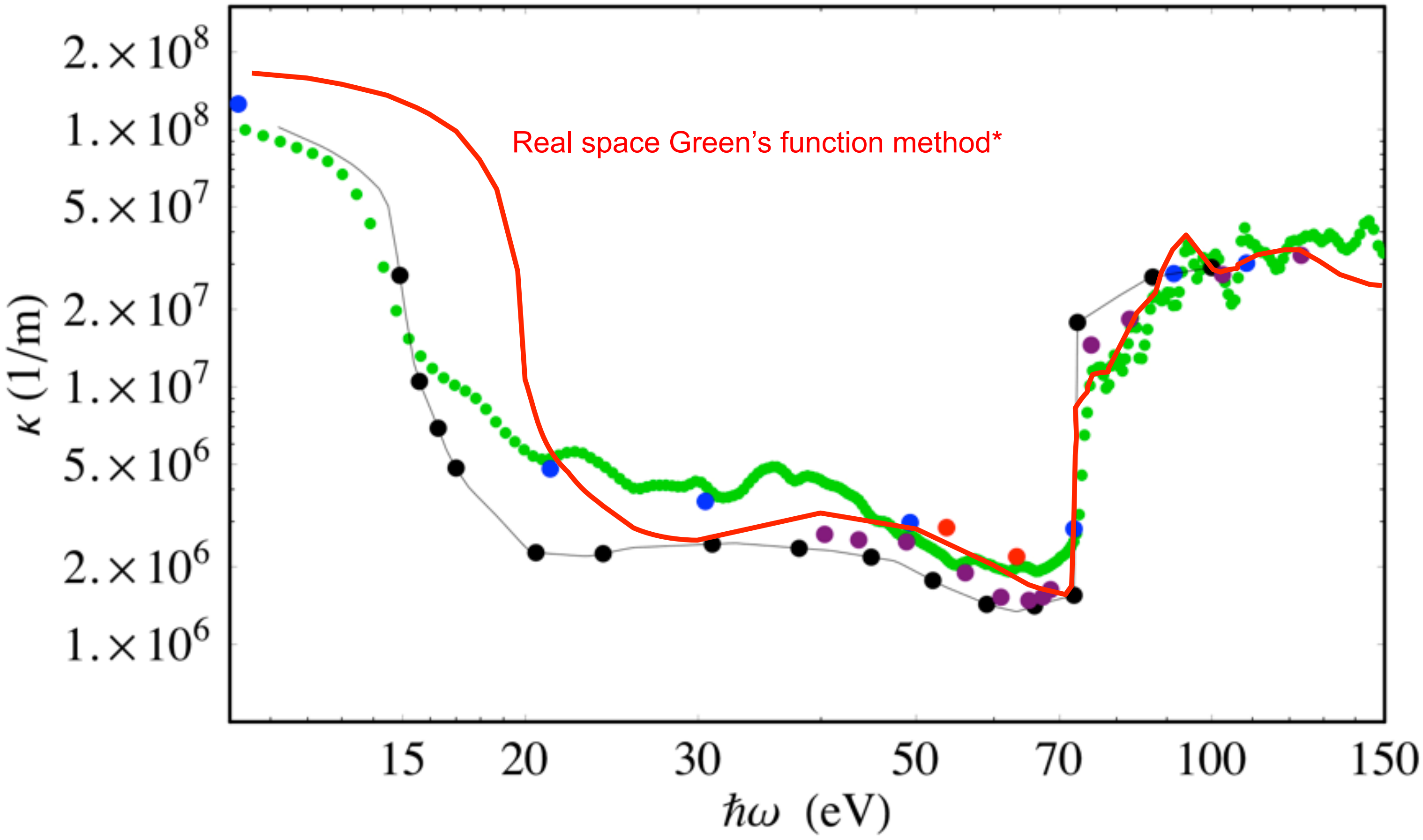


These results are consistent with recent results using traditional opacity methods and an *ad hoc* potential



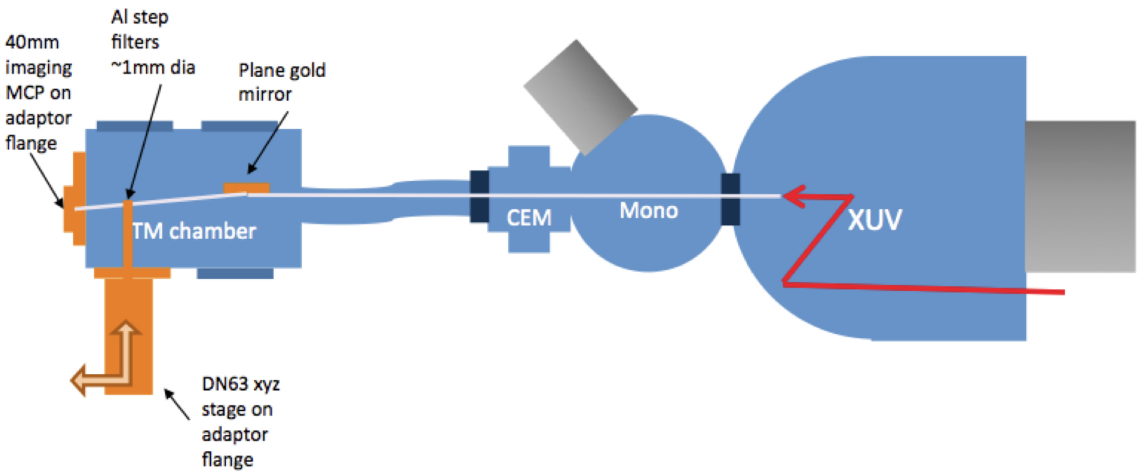
Note that the Iglesias model assumes no ion-ion correlations (S(q)=1) and a frozen core potential (no core polarization effects).

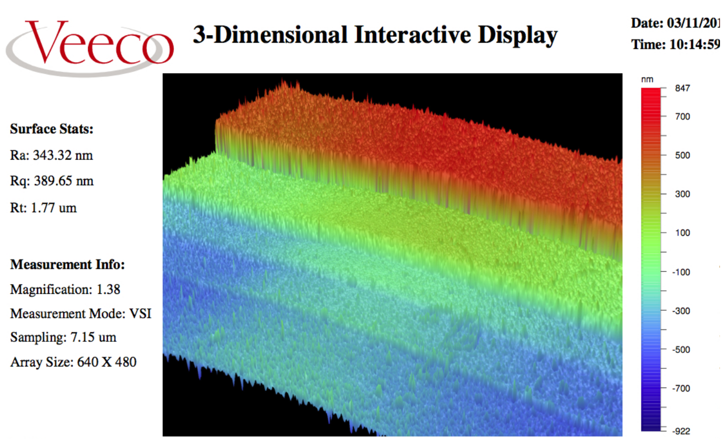
This approach improves over RSGF calculations in the condensed matter range (below 40 eV)



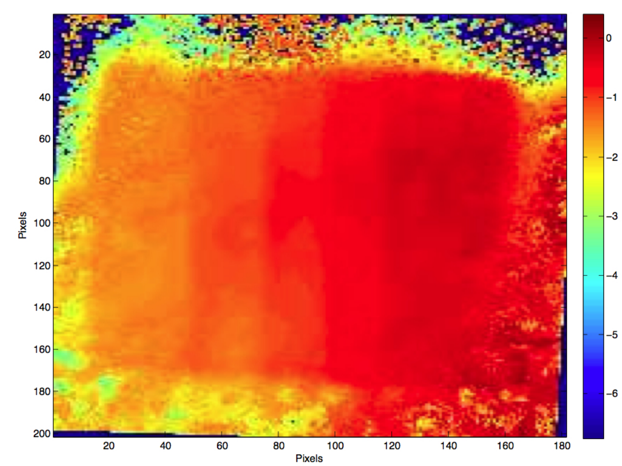
*M. P. Prange, J. J. Rehr, G. Rivas, J. J. Kas, and J. W. Lawson, Phys. Rev. B 80, 155110 (2010).
See also http://leonardo.phys.washington.edu/feff/opcons/

We have performed XUV absorption experiments* on the Artemis Facility at Rutherford Appleton Laboratory



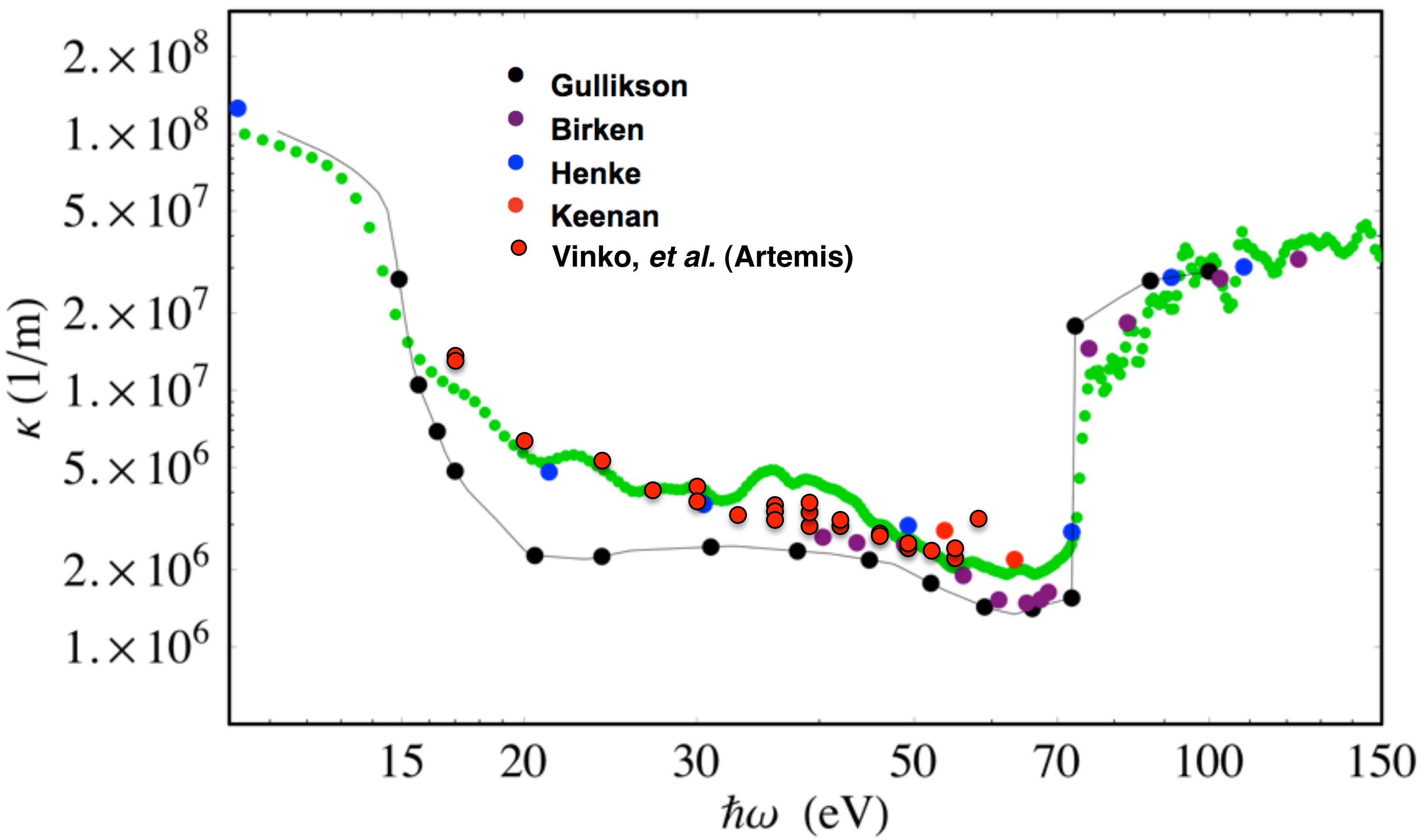


Transmission grid



***Sam Vinko is the PI on these experiments**

The Artemis data compares well to the Henke and Keenan data sets, and with our *ab initio* calculations



Summary

- **The XUV absorption of aluminum has been calculated with electronic structure methods of varying complexity.**

- **Several deficiencies, both practical and formal, of standard DFT/Kubo-Greenwood calculations were demonstrated.**

- **Local field corrections, resulting from the polarization of core electrons, are an essential component of accurate XUV absorptions.**

- ***GW* methods provide for a very good prediction of the L edge in aluminum.**

- **Thermal configurations are most important for energies below 40 eV, but differences between fcc and liquid persist to the L edge.**