Transport properties of dense plasmas within the PAW formalism

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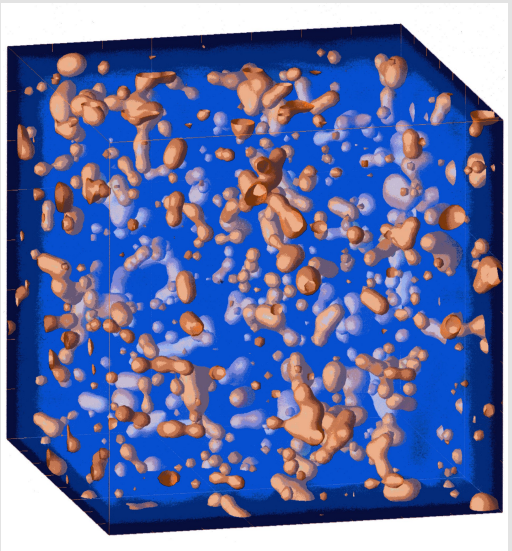
Matter under extreme density temperature conditions

Physical properties are necessary to the modeling of various systems in geophysics (earth interior), astrophysics (exoplanets, stellar atmospheres),...

Hydrogen, hydrogen-helium

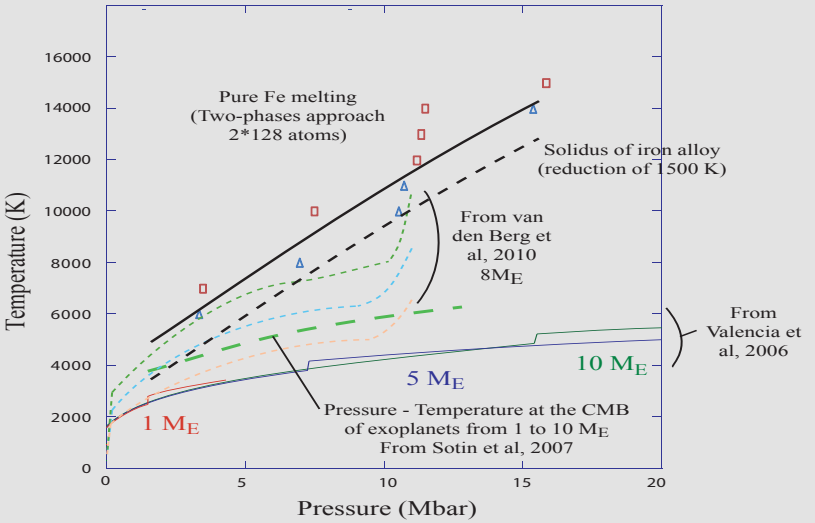
Inertial confinement fusion (ICF) and the interior of giant planets and exoplanets (*L. Caillabet et al. PRB 2011*)



Dense hydrogen at $\rho = 1\text{g/cm}^3$ and T=3eV

High pressure melting of Fe and Fe alloys

Largest uncertainty on earth and exoplanet modeling (*G. Morard, J. Bouchet et al., HEDP 2011*)



High pressure melting curve of iron

Motivations

- Regime of interest: $\rho_2/10 \leq \rho \leq 10\rho_o$ et $0K \leq T \leq 10eV$(1eV $\equiv$ 11604K)
- Difficult to characterize experimentally: conditions created using dynamical experiments shock or isentropic compression.
- High power lasers (GEKKO, LULI, OMEGA, NIF, LMJ,) continue to expend density-temperature domain reachable.
- Limited experimental data available.
- Ab initio Simulation Goals:
  - Obtain the physical properties (EOS, opacity,) of dense plasmas and solids at these extremes conditions.
  - Perform molecular dynamics simulations up to 1000 electrons at the Gamma point.
  - Consistent set of thermodynamical (EOS) and transport properties (Electrical and thermal conductivity, absorption,...).
  - Ab initio: parameter free approach validated on a limited set of experimental data but with predictive capabilities.
  - Use near edge absorption spectroscopy XANES to validate the approach and for diagnostic purposes.

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Kubo-Greenwood Formulation

Within the Kubo-Greenwood formulation, the real part of the conductivity is given by

$$\sigma_1(\mathbf{k},\omega) = \frac{\mathbf{2}\pi}{\mathbf{3}\omega\mathbf{\Omega}} \sum_{\mathbf{j=1}}^{\mathbf{n_b}} \sum_{\mathbf{i=1}}^{\mathbf{n_b}} \sum_{\alpha=\mathbf{1}}^{\mathbf{3}} (F(\epsilon_{i,\mathbf{k}}) - F(\epsilon_{j,\mathbf{k}})) \times |\langle \psi_{j,\mathbf{k}} | \nabla_\alpha | \psi_{i,\mathbf{k}} \rangle|^2 \delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \omega).$$

where

- m_e and e are the electron charge and the electron mass
- i and j are the sum over the n_b orbitals
- α stands for the 3 directions x, y, et z
- Ω is the volume of the simulation cell
- $\epsilon_{i,\mathbf{k}}$ and $\psi_{i,\mathbf{k}}$ are the i^{th} orbital for the k-point $\mathbf{k}$
- $F(\epsilon_{i,\mathbf{k}})$ are the occupations

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Dipole matrix elements within the PAW formalism

Within the PAW formalism, $|\psi_{i,\mathbf{k}}\rangle$ is connected to $|\tilde{\psi}_{i,\mathbf{k}}\rangle$ by the linear operator T:

$$|\psi_{i,\mathbf{k}}\rangle = |\tilde{\psi}_{i,\mathbf{k}}\rangle + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle \right) \langle \tilde{p}_{\mathbf{R},n} | \tilde{\psi}_{i,\mathbf{k}} \rangle .$$

In the PAW formulation, the dipole matrix elements become:

$$\begin{aligned} \langle \psi_{m,\mathbf{k}} | \vec{\nabla} | \psi_{n,\mathbf{k}} \rangle = \quad & \langle \tilde{\psi}_{m,\mathbf{k}} | \vec{\nabla} | \tilde{\psi}_{n,\mathbf{k}} \rangle \\ & + \sum_{i,j} \langle \tilde{\psi}_{m,\mathbf{k}} | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_{n,\mathbf{k}} \rangle \left(\langle \phi_i | \vec{\nabla} | \phi_j \rangle - \langle \tilde{\phi}_i | \vec{\nabla} | \tilde{\phi}_j \rangle \right) \end{aligned}$$

where i and j stand for the sum over $\{\mathbf{R}, n\}$. The first term is the "pseudo" contribution and the last two terms correct to reintroduce the natural atomic wave function

First term: plane wave contribution

We evaluate the first term in Cartesian coordinates using the plane wave expansion

$$\psi_{m,\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} C^m_{\vec{G}} e^{i(\vec{G}+\vec{k}).\vec{r}}$$

which leads to

$$\langle \tilde{\psi}_{m,\mathbf{k}} | \nabla_\alpha | \tilde{\psi}_{n,\mathbf{k}} \rangle = \sum_{\vec{G}} C^{*m}_{\vec{G}} C^n_{\vec{G}} (\vec{G}_\alpha + \vec{k}_\alpha).$$

"Pseudo" contribution to the matrix elements.

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Second and third terms: atomic contributions

We use the standard separation of an atomic orbital into a radial and an angular parts $\phi(\vec{r}) = \frac{u_{n,l}(r)}{r} S_{l,m}(\hat{r})$ where $S_{l,m}(\hat{r})$ are the real spherical harmonics, and express the gradient in spherical coordinates

$$\vec{\nabla} = \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r}\frac{\partial}{\partial \theta} \\ \frac{1}{rsin\theta}\frac{\partial}{\partial \phi} \end{pmatrix}, \qquad \begin{aligned} \hat{r} &= \sin\theta\cos\phi\vec{i} + \sin\theta\sin\phi\vec{j} + \cos\theta\vec{k}, \\ \hat{\theta} &= \cos\theta\cos\phi\vec{i} + \sin\phi\cos\phi\vec{j} - \sin\theta\vec{k}, \\ \hat{\phi} &= -\sin\phi\vec{i} + \cos\phi\vec{j}. \end{aligned}$$

We also use the expression of $\hat{r}$, $\hat{\theta}$, et $\hat{\phi}$ in Cartesian coordinates. This leads to 2 types of radial integrals and 8 angular integrals

$$f^1 = \int dr u_{n,l}(r)\frac{\partial}{\partial r}u_{n',l'}(r),$$
$$f^2 = \int dr \frac{1}{r}u_{n,l}(r)u_{n',l'}(r).$$

Implementation in Abinit

- Ground state calculation with prtnabla=1 and prtwfk=1: call to optics_paw.F90 from outscfcv.F90 (in /src/95_drive)
  - Subroutine optics_paw.F90 (in src/66_paw)
    - calculate the radial integrals f_1 and f_2 for $u_{n,l}(r)$ and $\tilde{u}_{n,l}(r)$
    - call to int_ang.F90 calculate the angular integrals
    - write the matrix elements in the file filename_OPT
  - Parallel band/fft (paral_kgb=1) since abinit_6.0
- Postprocessing of the dipole matrix elements using conducti (/src/98_main/conducti.F90)
- execution: conducti <filename.files
  - filename.in:
    2 ! call PAW version in /src/67_common/conducti_paw.F90
    filename_OPT ! optics filename
    0.073119 0.0000001 5.00 1000 !width, ω_{min}, ω_{max}, nbr pts
- calculate the electrical and thermal conductivities
- **new in version abinit_6.5: temperature and K-points read from filename_OPT**

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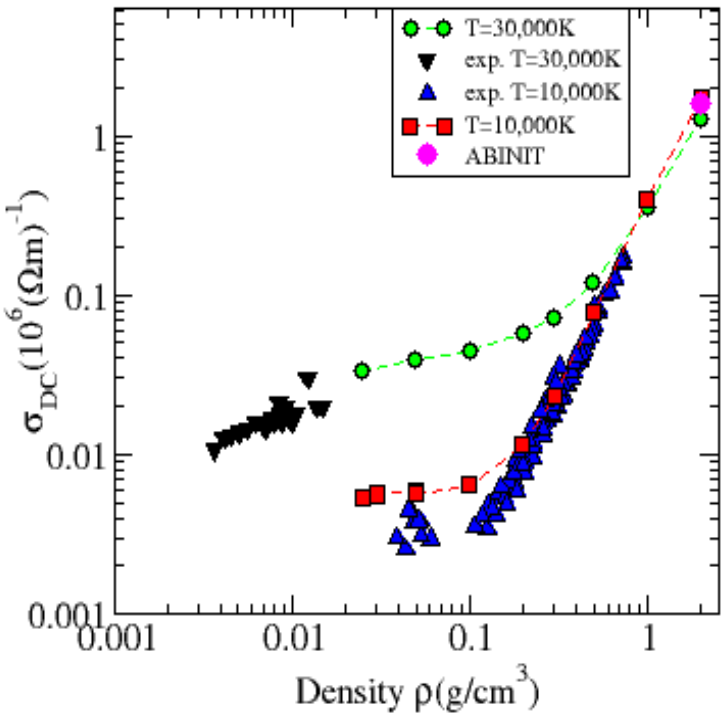
Validation of the Aluminum conductivity



Aluminum optical properties S. Mazevet *et al.* PRE 2005

- MD at 1.5eV and 2g with E_{cut} =15eV
- GGA-PBE pseudo with *atompaw* N. Holzwarth, Comp.Phys.Comm. (2001).
- $r_c = 1.7a_B$ $3s^2 3p^1$ with two projectors per angular momentum
- $V_0 = 16.98\mathring{A}^3/atm$ and $B_0 = 81.5$GPa
- all electron $V_0 = 16.48\mathring{A}^3/atm$ and $B_0 = 75$GPa
- $\sigma_1(\omega)$ leads to all the optical quantities for frequencies below 100eV, i.e where valence electrons contribute

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Transport properties I

- Other properties follow from the real part of the optical conductivity The imaginary part arises from the application of a Kramers-Kronig relation as

$$\sigma_2(\omega) = -\frac{2}{\pi} P \int \frac{\sigma_1(\nu)\omega}{(\nu^2 - \omega^2)} d\nu, \tag{1}$$

  where P stands for the principal value of the integral.
- The dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + \epsilon_2(\omega)$:

$$\epsilon_1(\omega) = 1 - \frac{4\pi}{\omega}\sigma_2(\omega), \tag{2}$$

$$\epsilon_2(\omega) = \frac{4\pi}{\omega}\sigma_1(\omega). \tag{3}$$

- The index of refraction

$$n(\omega) = \sqrt{\frac{1}{2}[|\epsilon(\omega)| + \epsilon_1(\omega)]}, \tag{4}$$

$$k(\omega) = \sqrt{\frac{1}{2}[|\epsilon(\omega)| - \epsilon_1(\omega)]}. \tag{5}$$

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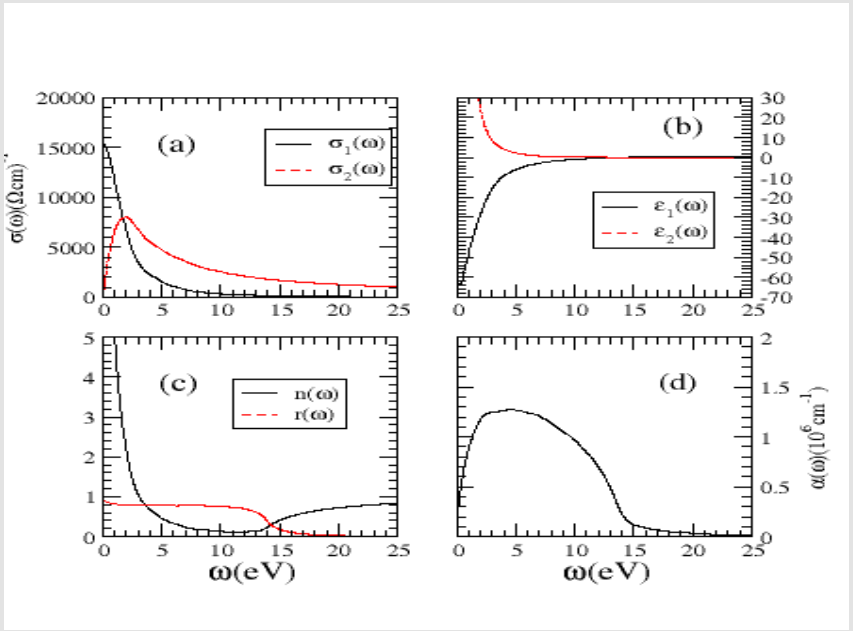
Transport properties II



Aluminum optical properties at 2g/cm^3 and T=1.5eV

- The reflectivity, $r(\omega)$ and absorption coefficient $\alpha(\omega)$ are defined as

$$r(\omega) = \frac{[1-n(\omega)]^2 + k(\omega)^2}{[1+n(\omega)]^2 + k(\omega)^2} \tag{6}$$

$$\alpha(\omega) = \frac{4\pi}{n(\omega)c}\sigma_1(\omega). \tag{7}$$

These propertied are calculated by default using conducti

- filename_abs: energy(eV), $n(\omega)$, $k(\omega)$, $r(\omega)$, $a(\omega)$
- filename_eps: energy(eV) $\sigma_1(\omega)$,$\sigma_2(\omega)$, $\epsilon_1(\omega)$,$\epsilon_2(\omega)$

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Transport properties III

- The linear response of a system to an electrical field $\mathbf{E}$ and temperature gradient ∇T is characterized by the electrical and heat current densities

$$< j >= \frac{1}{e}\left(e\mathcal{L}_{11}\mathbf{E} - \frac{\mathcal{L}_{12}\nabla T}{T}\right), \tag{8}$$

and

$$< j_q >= \frac{1}{e^2}\left(e\mathcal{L}_{21}\mathbf{E} - \frac{\mathcal{L}_{22}\nabla T}{T}\right), \tag{9}$$

where e is electron charge.

- In the Chester-Tellung-Kubo-Greenwood formulation

$$\mathcal{L}_{ij} = (-1)^{(i+j)}\int d\epsilon\hat{\sigma}_1(\epsilon)(\epsilon-\mu)^{(i+j-2)}\left(-\frac{\partial F(\epsilon)}{\partial\epsilon}\right), \tag{10}$$

Transport properties IV

- Implementation in abinit:

$$\mathcal{L}_{ij}(\omega) = (-1)^{(i+j)} \frac{2\pi}{3\omega\Omega} \sum_{n,m,\mathbf{k},\alpha} |\langle\psi_{n,\mathbf{k}}|\nabla_\alpha|\psi_{m,\mathbf{k}}\rangle|^2 \quad (11)$$
$$\times(\epsilon_{m,\mathbf{k}}-\mu)^{i-1}(\epsilon_{n,\mathbf{k}}-\mu)^{j-1}\left(F(\epsilon_{m,\mathbf{k}})-F(\epsilon_{n,\mathbf{k}})\right)\delta(\epsilon_{n,\mathbf{k}}-\epsilon_{m,\mathbf{k}}-\omega).$$

- Thermal conductivity $K_c = \frac{1}{e^2T}\left(\mathcal{L}_{22} - \frac{\mathcal{L}_{12}^2}{\mathcal{L}_{11}}\right)$
- thermopower $S = \frac{\mathcal{L}_{12}}{|e|TL_{11}}$
- Lorenz number $L = \frac{K}{\sigma T}$
- Calculated by default using conducti
  - filename_kth: ω(au) $\hbar\omega$ K_{th}(W/m/K), $S(\omega)$, $L(\omega)$
  - filename_Lij: ω(au) $L_{11}(\omega)$ $L_{12}(\omega)$ $L_{21}(\omega)$ $L_{22}(\omega)$

Properties limited to $\hbar\omega < 100$eV i.e. involving valence electrons

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X-ray absorption: Theory

- $\alpha(\omega)$ is directly related to the real part of the electrical conductivity $\alpha(\omega) = \sigma_1(\omega)/n(\omega)$ where $n(\omega)$ is the index of refraction.
- Include frozen orbitals ϕ_c in $\sigma_1^{\mathbf{k}}(\omega)$.

$$\langle\psi_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle = \langle\tilde{\psi}_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle + \sum_i \langle\tilde{\psi}_{m,\mathbf{k}}|\tilde{p}_i\rangle \left(\langle\phi_i|\vec{\nabla}|\phi_c\rangle - \langle\tilde{\phi}_i|\vec{\nabla}|\phi_c\rangle\right).$$

- when $\phi_c = 0$ for $r > \Omega_{\mathbf{R}}$ the dipole matrix elements become

$$\langle\psi_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle = \sum_i \langle\tilde{\psi}_{m,\mathbf{k}}|\tilde{p}_i\rangle\langle\phi_i|\vec{\nabla}|\phi_c\rangle.$$

where we use the fact that $\{|\tilde{\phi}\rangle\}$ represent a complete basis for $|\tilde{\psi}\rangle$ inside $\Omega_{\mathbf{R}}$

- Average on the different atomic sites **R**

Implementation in Abinit

- N.A. Holzwarth PAW pseudopotential generator
- Save the core WF when producing the PAW pseudopotential
- New feature in atompaw3.0 **prtcorewf**
- Ground state calculation with prtnabla=2: call to optics_paw_core.F90 from outscfcv.F90
- Subroutine optics_paw_core.F90 (in /src/66_paw)
  - similar functions as optics_paw.F90
  - calculate the additional matrix elements including the core states
  - write the matrix elements in the file filename_OPT2
  - read in core wavefunctions in corewf.dat
  - Compatible paral_kgb=1 since version abinit_6.5
- Postprocessing of the dipole matrix elements using conducti
  - 4 in conducti.in: calculate conducti and X-ray absorption
  - 5 in conducti.in: calculate X-ray absorption only

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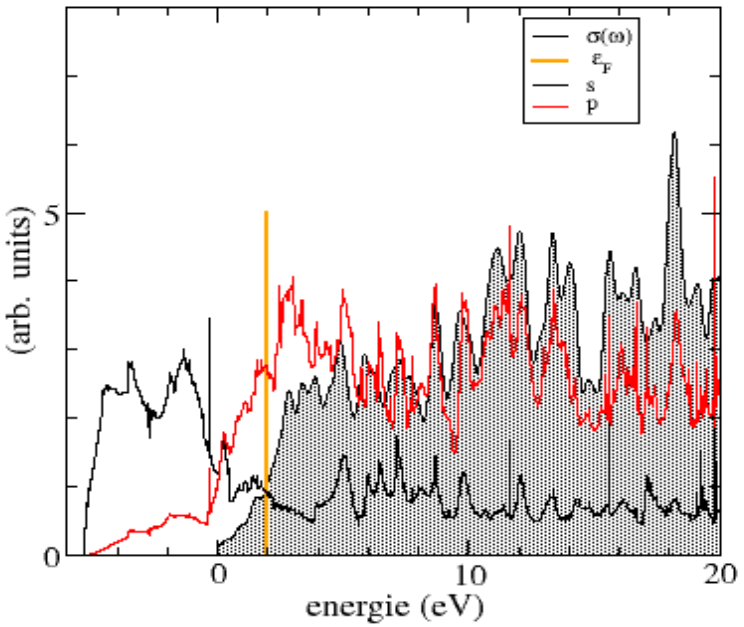
Validation using the projected DOS



2 atoms at 1.3g/cm^3 10x10x10 kpoints T=1eV

- The same decomposition holds for the projected DOS and the X-ray cross section
- $n_l^\alpha(\epsilon) = \tilde{n}_l^\alpha(\epsilon) + n_l^{\alpha,1}(\epsilon) - \tilde{n}_l^{\alpha,1}(\epsilon)$
- The K-edge cross section is proportional to the p component
- Higher l contributions are not corrected by the PAW transformation when the pseudopotential contains only $l \leq 1$ components
- 1s wave function ϕ_{1s} and ϵ_{1s} obtained at the PAW pseudo calculation.

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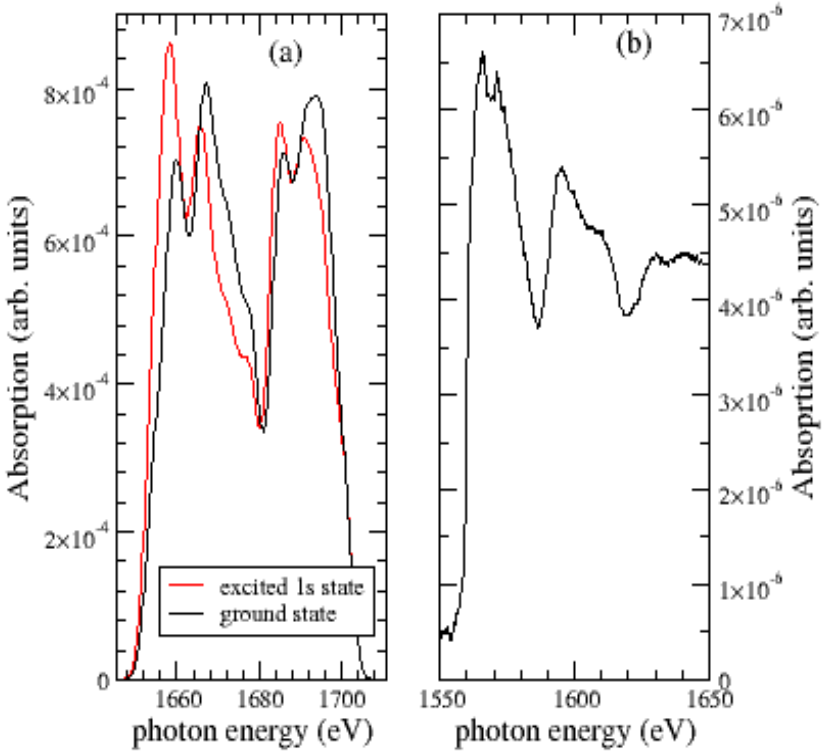
Validation against experimental measurements



(a)300K Al Xanes Spectra (b)experimental measurements F. Dorchies et al. Appl. Phys. Lett 2008

- 108 atoms, Γ point, 2000 bands
- Converged 50eV above the edge
- XANES calculated over each atoms "ground"
- Impurity model: the absorbing atom has a pseudo-potential created with a hole in the 1s shell "Excited". C. Pickard et al. 1998.
- The 1s orbital is consistent with the pseudo-potential used
- The position of the edge is not correct
- The second maximum requires bigger cell and a larger number of bands

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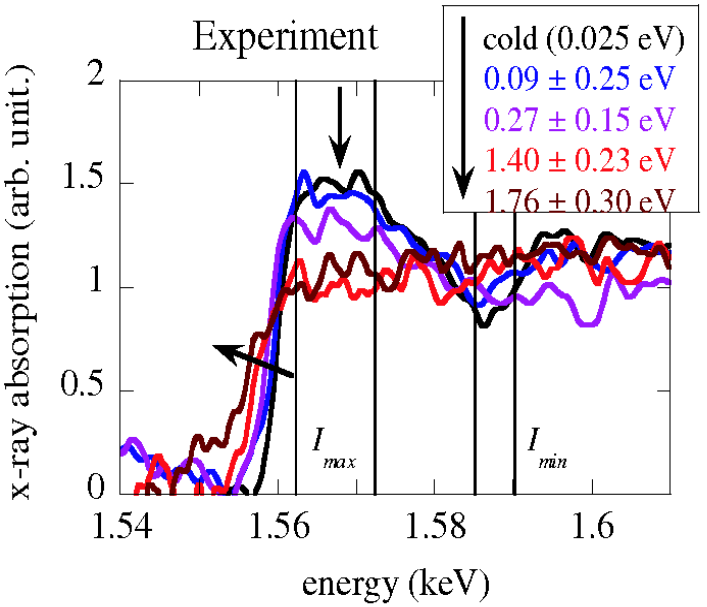
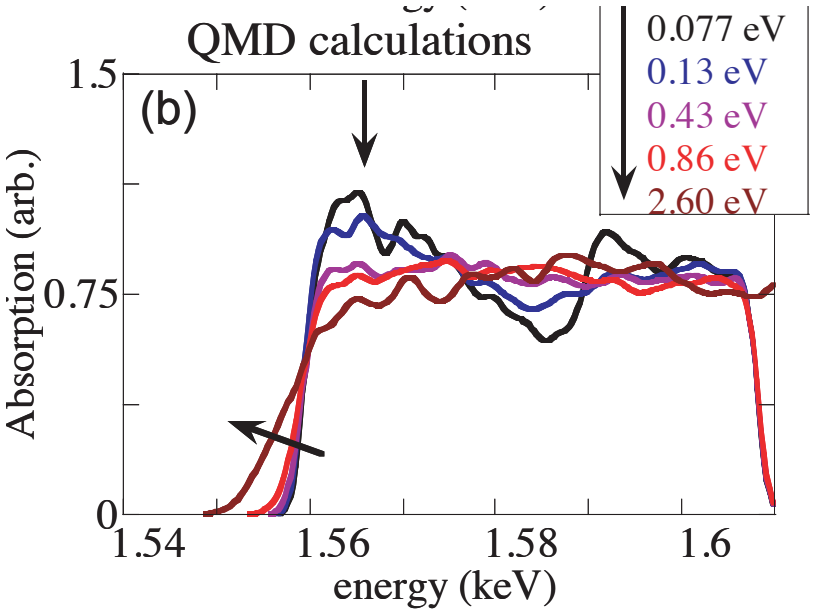
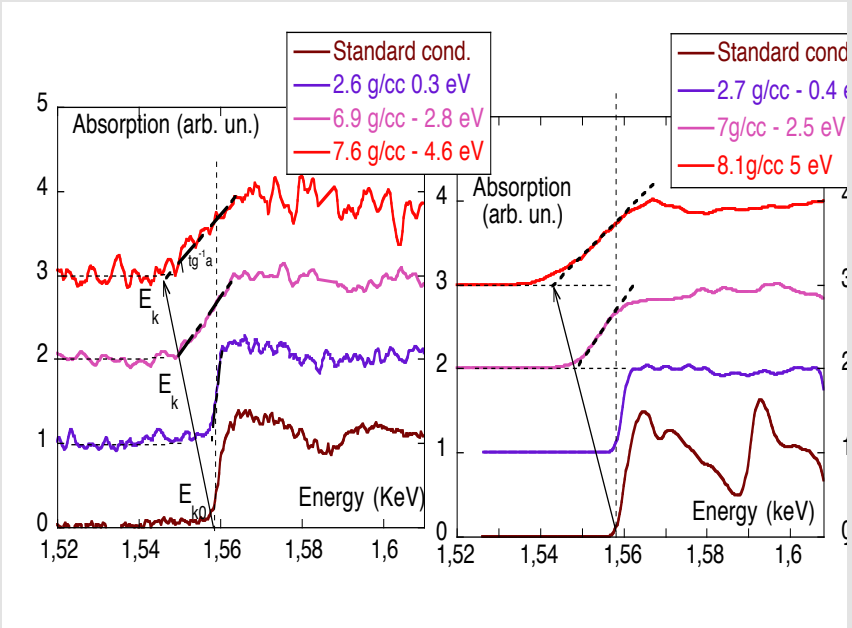
Temperature effects: proton heating of Al foil *A. Mancic et al. PRL 2010*





- Average over 5 configurations of 108 atoms, $2 \times 2 \times 2$ kpoints
- Follow the evolution of the XANES spectrum in temperature
- Loss of correlation $\equiv$ loss of structure
- Brut force: 2000 bands ($2/3$ are empty bands)
- Impurity model: requires an " excited " pseudopotential with p-projectors up to 5Ha
- Pseudo-potential is difficult to optimize as Al^+ structure.

Density effect in shocked Al. *S. Mazevet et al. PRL 2008; V. Recoules et al. PRB 2009*



Al XANES spectra along the shock Hugoniot to be submitted

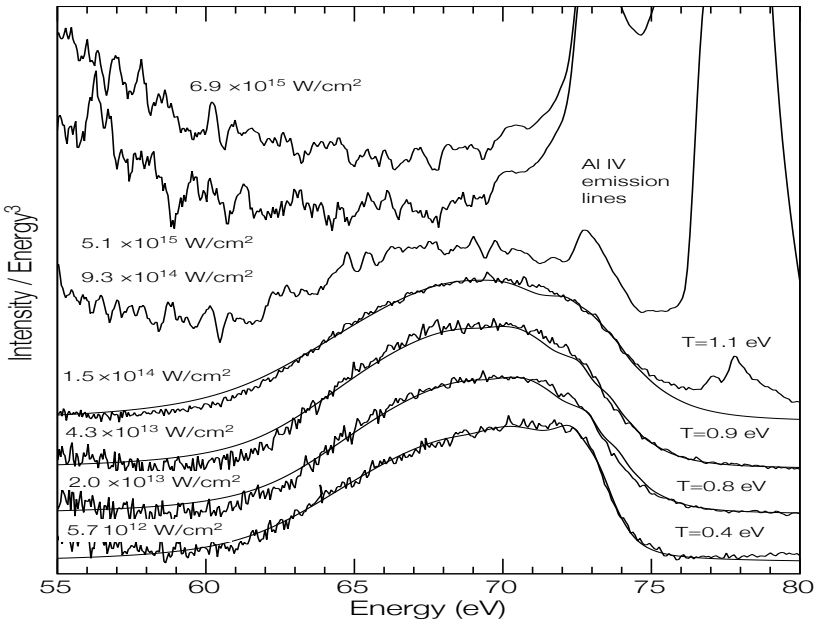
- 108 atoms, $2 \times 2 \times 2$ k-points, 2000 bands
- Transition between the 1s and E_F
- As density increases E_F increases
- Not red but blue shift!!
- ϵ_{1s} corresponds to the isolated atom

- Agreement obtained by correcting the isolated atom $1s$ energy
- Unit cell with an all electron Al pseudo-potential
- Not consistent with the impurity model
- Requires to relax the core orbital for a self consistent model

Emission spectrum of Al sample illuminated by XFEL *S. Vinko et al PRL 2010*

X-ray emission radiated power

$$I(E) \propto E^2 \sum_{n,k} |\langle \psi_{2p}|\nabla|\varphi_{nk}\rangle|^2 \delta(E - E_{2p} + \varepsilon_{nk}), \qquad (12)$$



Emission in solid Al as a function of XFEL intensity

- Al atoms excited above E_f decay toward 2p core state
- Pseudo potential with a hole in the 2p state and d projector
- two types of transition d→p and s→p
- Same matrix elements as for conductivity and X-ray spectra
- Not very sensitive to the impurity model
- option 5 in conducti

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Summary and outlook

- Implement the calculation of transport properties
- Extensions to x-ray absorption and emission also available
- S. Mazevet, V. Recoules, M. Torrent, et al HEDP 2010
- One particule description appears sufficient for dense plasmas
- Efficiency and accuracy can be improved by
  - Considering an alternative for empty states: Lanczos,....
  - This will remove issues with pseudo potentials with high energy projectors
  - Relaxed core would improve the description in the impurity model: this requires to recalculate the pseudo potential on the fly
- Warning: it is sometimes difficult to perform this type of data with Abinit (over the past 8 months:)
  - change in atompaw
  - change in reading of wavefunction cores
  - change in writing optics
  - change in parallelization
- Lost backward compatibility
- acknowledgement: M. Torrent for his constant help in developping and tracking the abinit changes.

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