Compton Scattering and Warm Dense Matter Thermometry

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Thesis Defense
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Publication List

- *A plastic miniature x-ray emission spectrometer based on the cylindrical von Hamos geometry*
  B. A. Mattern, et al. Rev. of Sci. Inst. 83 (2), 023901-023901-9 (2012)
- *Real-space Green's function calculations of Compton profiles.*
  B. A. Mattern, et al. Phys. Rev. B 85 (11), 115135 (2012)
- *Theoretical treatments of the bound-free contribution and experimental best practice in X-ray Thomson scattering from warm dense matter*
  B. A. Mattern, G. T. Seidler. Phys. Plasmas 20, 022706 (2013)
- *Condensed phase effects on the electronic momentum distribution in the warm dense matter regime*
  B. A. Mattern, et al. *Submitted Phys. Rev. Lett. (Aug. 2013)*
- *Systematic errors in warm dense matter thermometry*
  B. A. Mattern, G. T. Seidler. *To be submitted Phys. Rev. E*

- *A miniature X-ray emission spectrometer (miniXES) for high-pressure studies in a diamond anvil cell*
  J. I. Pacold, et al. J. Synch. Rad. 19 (2), 245-251 (2012)
- *Recent tests of x-ray spectrometers using polycapillary optics*
  S. Heald, et al. SPIE Optical Engineering+ Applications 85020I-85020I-10 (2012)
- *Fast Detection Allowing Analysis of Metalloprotein Electronic Structure by X-ray Emission Spectroscopy at Room Temperature*
  K. M. Davis, et al. J. Phys. Chem. Lett. 3 (14), 1858-1864 (2012)
- *4f electron delocalization and volume collapse in praseodymium metal*
  J. A. Bradley, et al. Phys. Rev. B 85 (10), 100102 (2012)

Outline

- Warm Dense Matter
- Thermometry
- X-ray based diagnostics
  - Heavier elements: X-ray Absorption and Emission
  - Light elements: Non-resonant Inelastic X-ray Scattering (NIXS)
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- Valence contribution to NIXS
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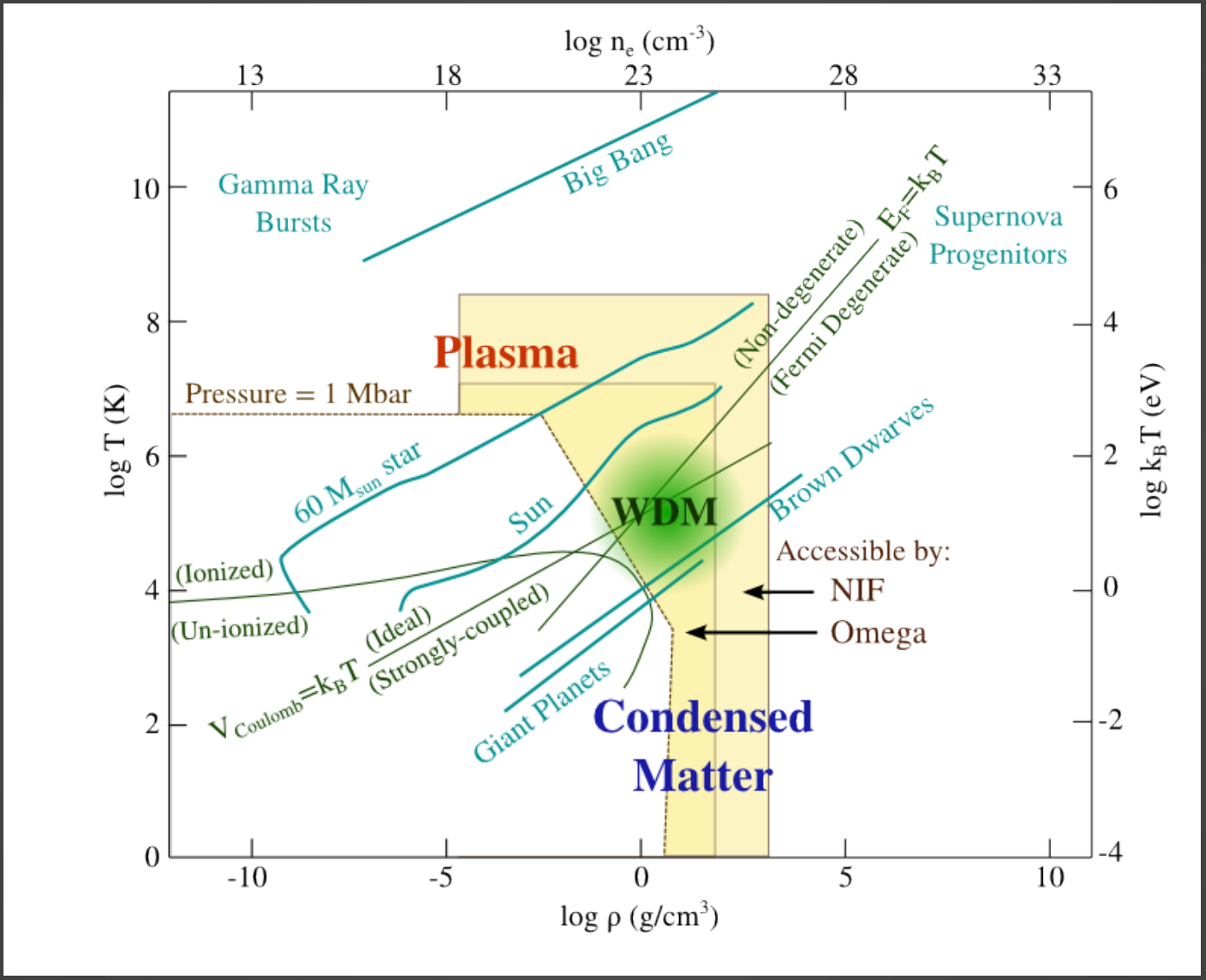
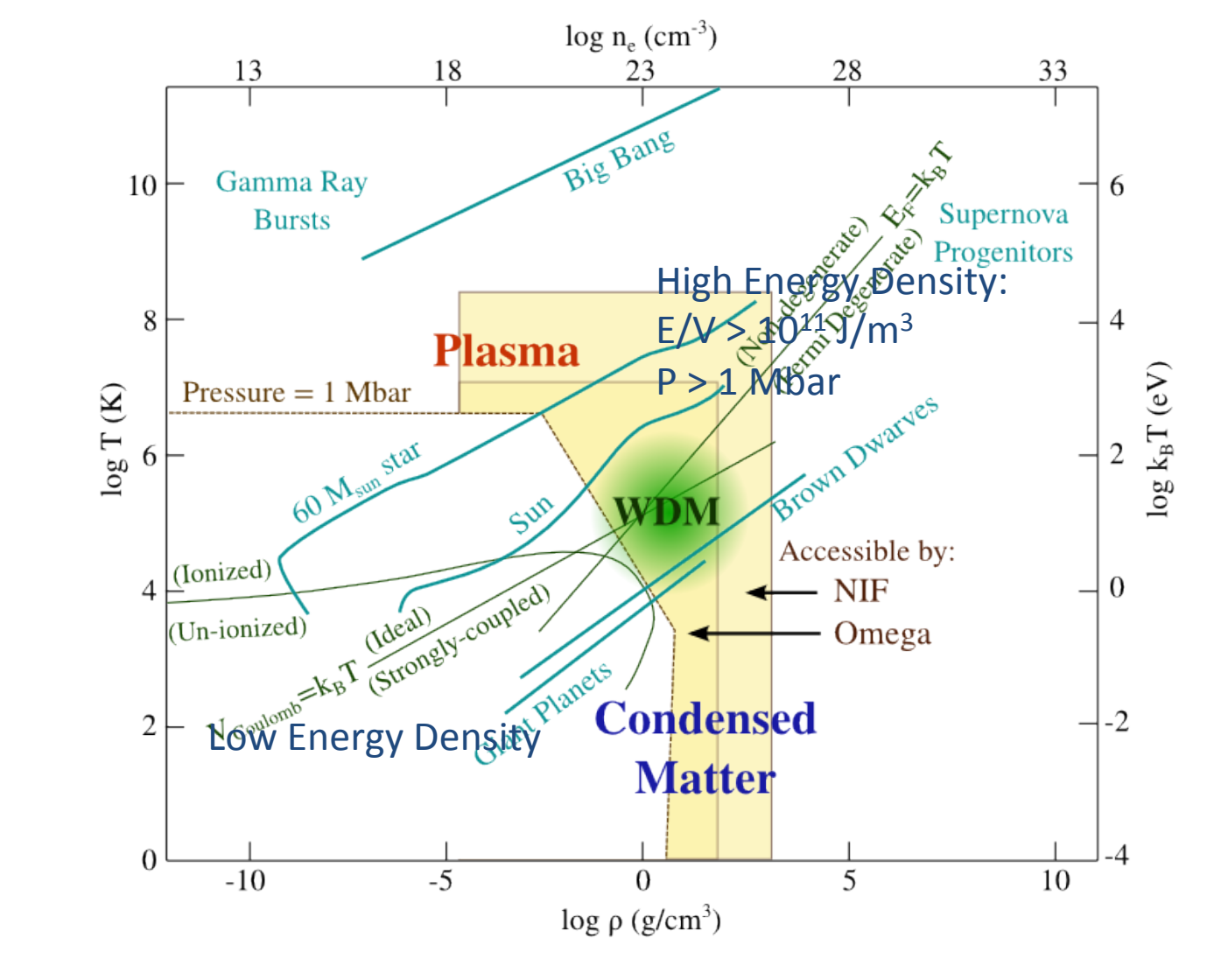
  - Psuedopotentials and the nearly-free-electron approximation
  - Effect of orthogonalization on the momentum distribution
- Conclusions

The universe of high-energy-density physics



Adapted from “Frontiers in High Energy Density Physics: The X-Games of Contemporary Science” (2003)

The universe of high-energy-density physics



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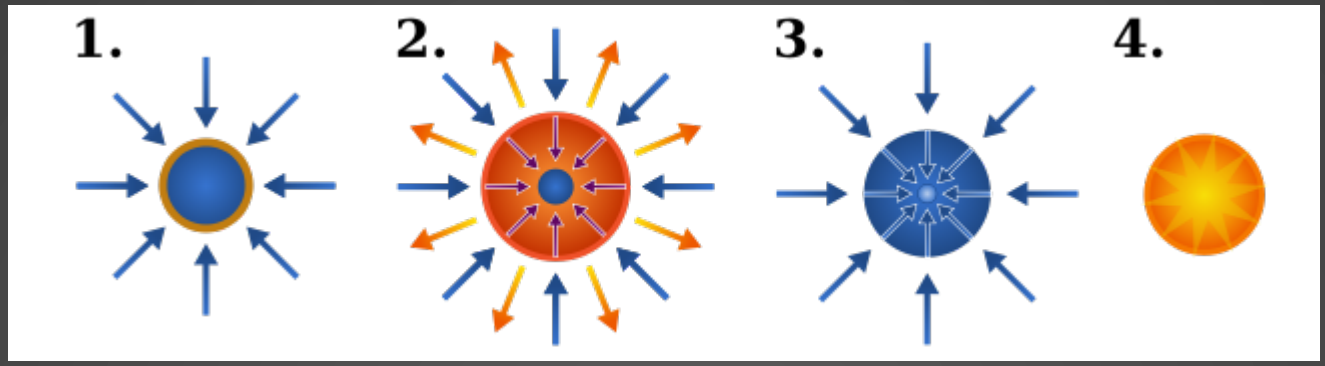
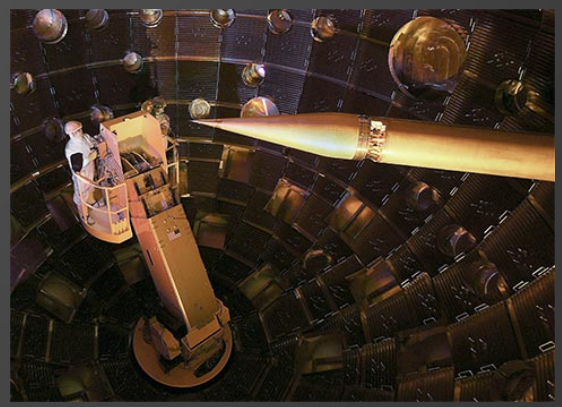
Inertial Confinement Fusion (ICF)



1. Rapidly heat outer layer of target (Be or C-H plastic coating) using 500 TW, 20 ns laser pulse (1000 x total US power output!)
2. Outer layer *ablates* (is ejected)
3. Interior (hydrogen/deuterium) implodes
4. Goal: get target hot and dense enough for fusion to occur



Where does WDM come in?

- Energy supplied by lasers gets distributed between
  - Compression
  - Heating
  - Ionization
- Dependent on shape of laser pulse and *equation of state* (EOS) of material
- **But,** EOS is difficult to model in WDM regime (created in early stages of compresion).
- Need to know EOS to plan shots. So, *measure* it!
- Need method for determining thermodynamic state of WDM:
  - density
  - temperature
  - ionization

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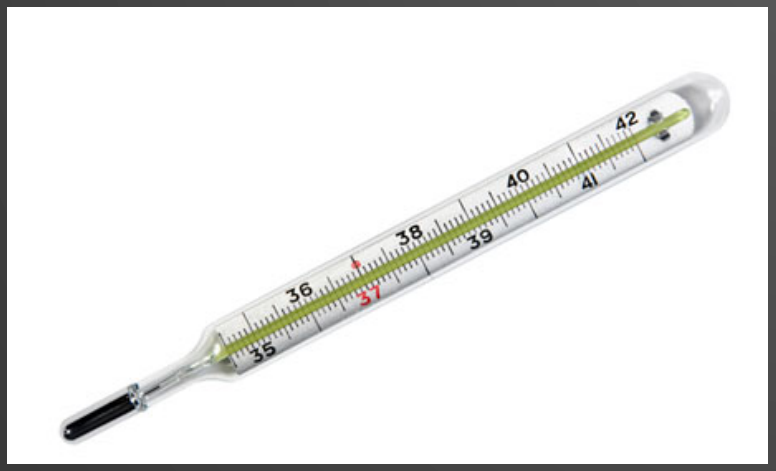
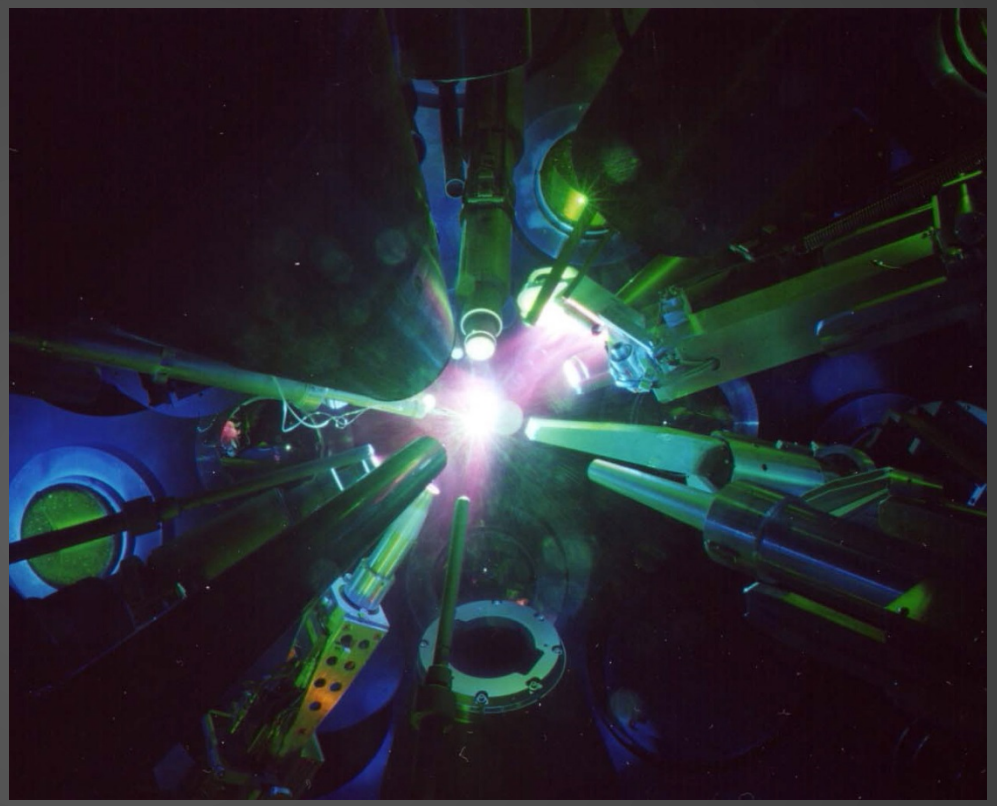
What is a thermometer?

- An object which:
  - Is in *thermal equilibrium* with the system of interest
  - Undergoes a T-dependent *physical change* (e.g. density, electrical resistance)
  - Has known *material properties (e.g., expansivity)*
  - Or has been *calibrated* with another thermometer



What if the system of interest:

- Exists for ~1 ns
- Has T > 10,000 K?



Hard to equilibrate with a standard thermometer…
Measure a physical property of the system itself!

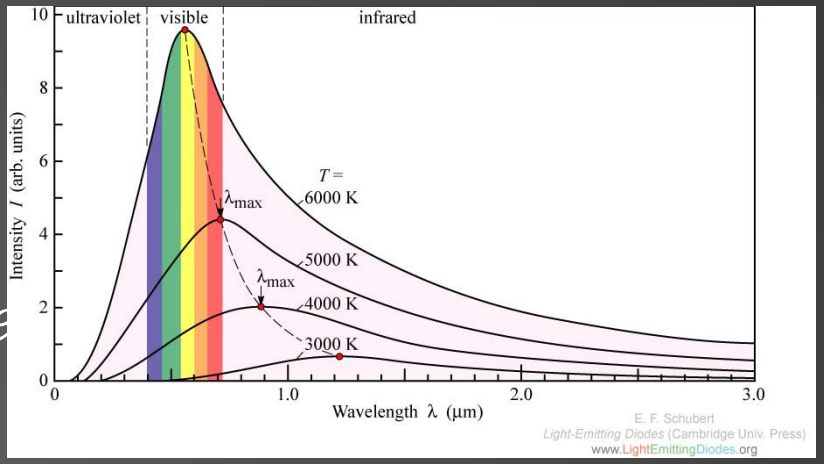
Non-contact Thermometry

- Black-body radiation (Pyrometry):
  - Stefan-Boltzmann Law:

$$P = \epsilon \sigma T^4$$

  - Black-body spectrum:

$$P(\omega) d\omega = \hbar / 4\pi^2 c^2 \ \omega^3 \ d\omega / e$$

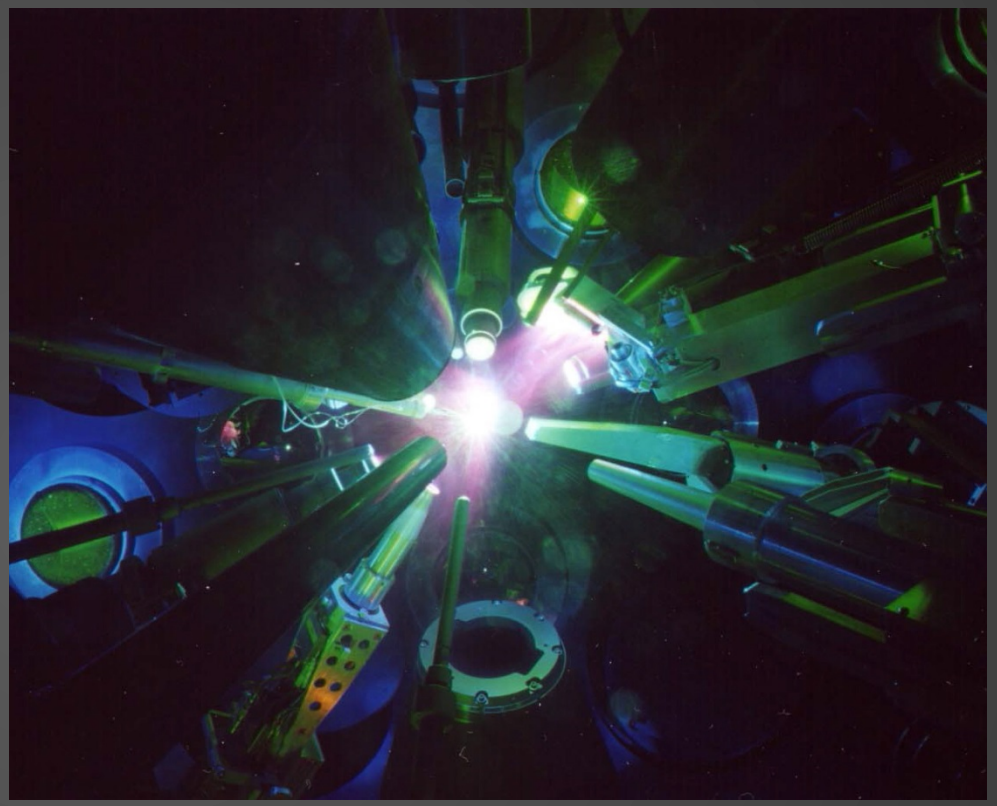


Need to know material property: emissivity ϵ

- Optical Thomson Scattering
  - Scatter optical laser light off of a plasma
  - Observe Doppler broadening of elastic scatter
  - For ideal plasmas: Boltzmann velocity distribution => T
    (material properties happen to be very simple in this case)

What if the system of interest:

- Exists for ~1 ns
- Has T > 10,000 K
- Is denser than a typical solid?



Low energy (optical) probes can neither penetrate into nor escape from sample.
Need more penetrating probe => **X rays**

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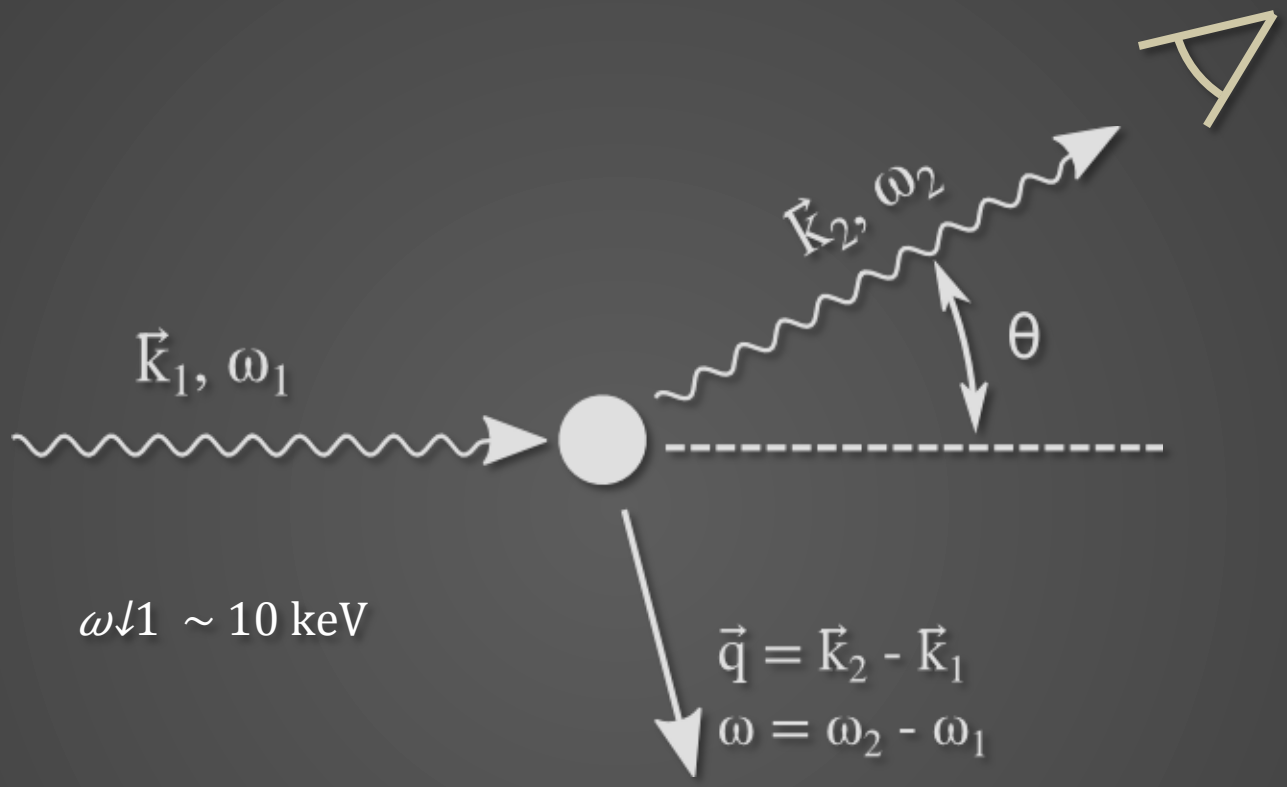
X-ray based diagnostics

- For heavier elements ($Z \gtrapprox 10$), binding energies are > 1 keV. Can directly probe using a variety of techniques:
  - X-ray absorption spectroscopy (XAS)
    - Measure absorption as a function of incident photon energy near core-shell binding energy
    - Cho, et al. PRL **106**, 167601 (2011) Cu L-edge XAS
      - Extracted temperature from shape of the edge (using MD-DFT calculations)
  - Resonant inelastic x-ray scattering (RIXS)
    - Measure fluorescence spectra as a function of excitation energy near an absorption edge
    - Ciricosta, et al. PRL **109**, 065002 (2012) Ionized Al Kα RIXS
      - Determined ionization-state dependence of core-shell binding energy (*continuum lowering)*
  - X-ray fluorescence (XRF)
    - Measure presence / absence of x-ray emission lines
    - Hoarty, et al. PRL 110, 265003 (2013) Ionized Al Kβ XRF
      - Observed delocalization of 3p states as density increases (continuum lowering)

- For lighter elements (H, Li, Be, C), binding energies are too small:
  - Probe *indirectly* using Non-resonant inelastic x-ray scattering (NIXS)

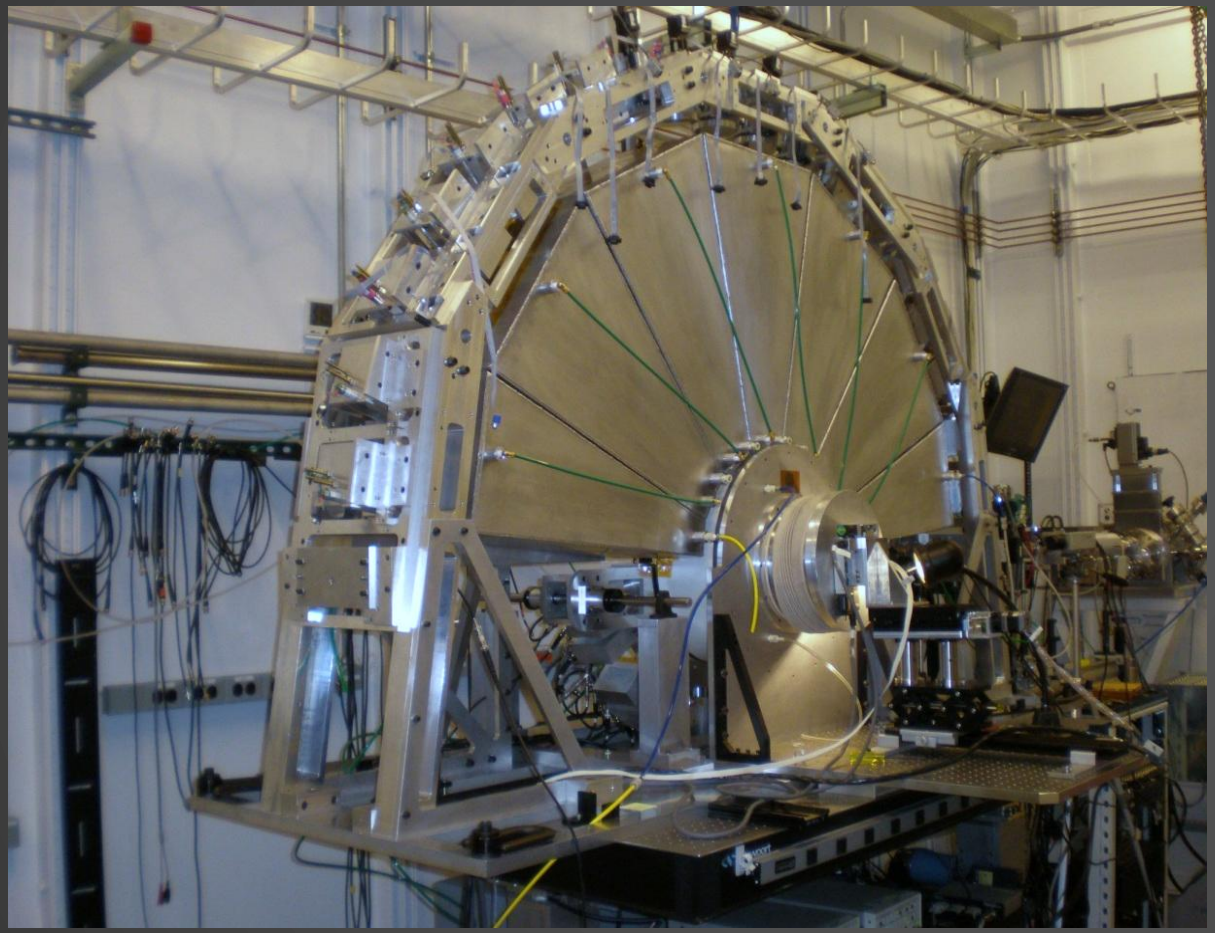
Non-resonant Inelastic X-ray Scattering (NIXS)



Observable: Dynamic Structure Factor

$$S(q,\omega) = \sum_I \rho_I \sum_F |\langle F|e^{iq\cdot r}|I\rangle|^2 \, \delta(E_F - E_I - \omega)$$

NIXS has a long history of use in condensed matter studies



Allows probing:

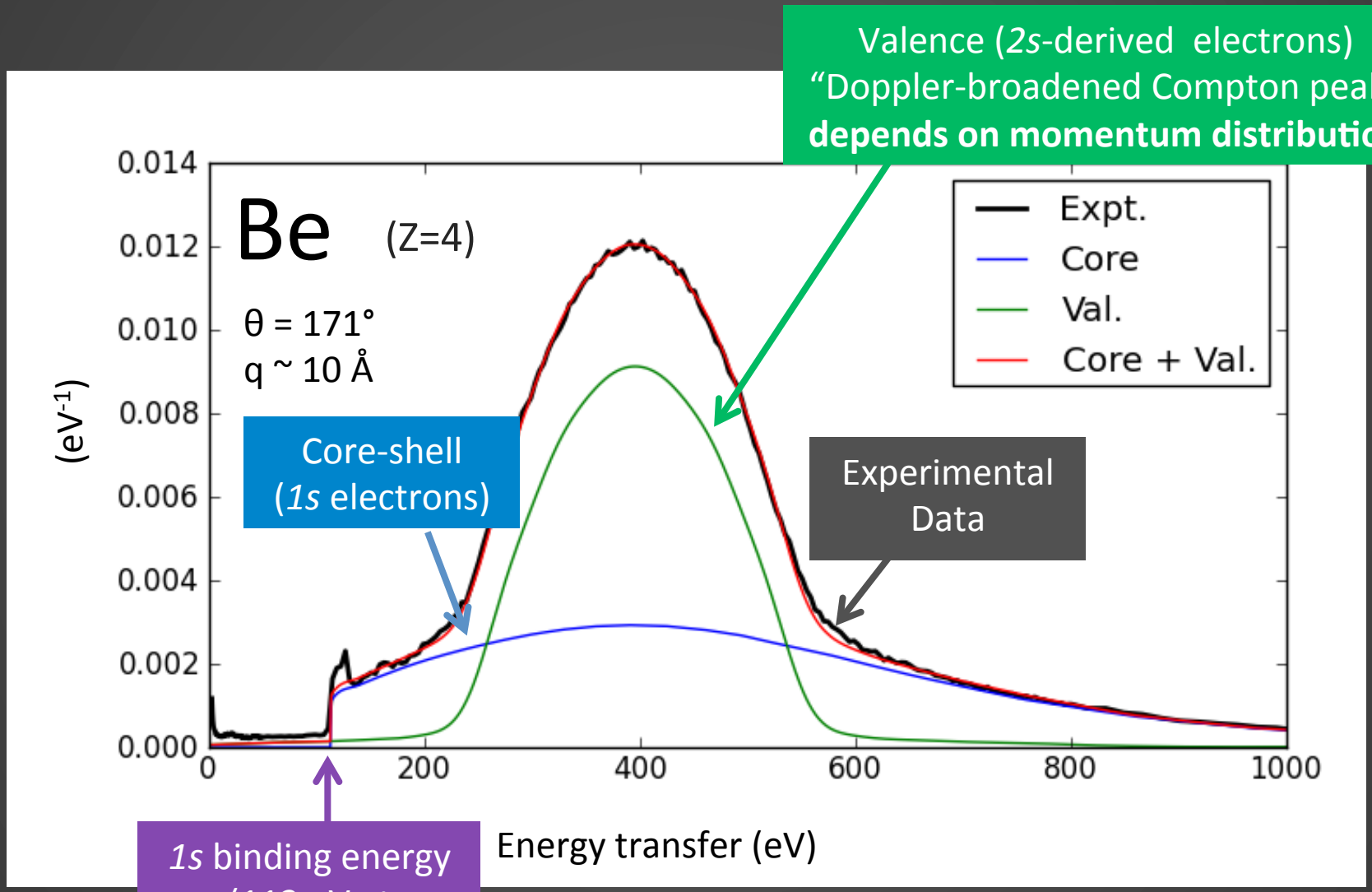
- Low-Z absorption edges
- Electron momentum distribution

"A quantum theory of the scattering of x-rays by light elements"
Compton, Phys. Rev **21** 483 (1923)

"Experimental Confirmation for Sommerfeld-Fermi-Dirac Degenerate Gas Theory of Conduction Electrons"
DuMond, Science **68** 452 (1928)

LERIX 1B Spectrometer
Advanced Photon Source, Beamline 20-ID-D
Fister, Seidler , et al. Rev. Sci. Inst. **77**, 063901 (2006)

Contributions to NIXS spectrum



Mattern, et al. PRB **85** 115135

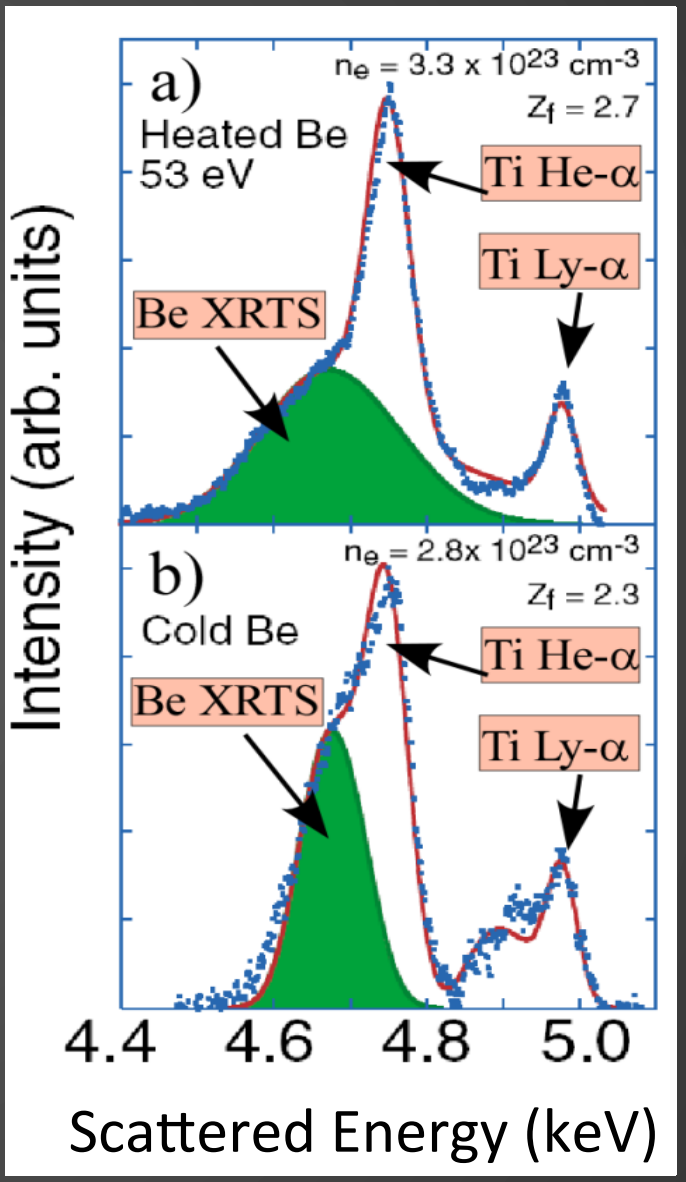
First demonstration of NIXS from WDM (2003)

- Be (ICF ablator candidate)
  heated using intense ns laser pulses

- X-ray source: "Backlighter"
  2p->1s emission from
  Ti metal ionized to:
  1 electron (Ly-α)
  2 electrons (He-α)

- Inelastic scattering spectrum ("XRTS")
  becomes much broader after heating

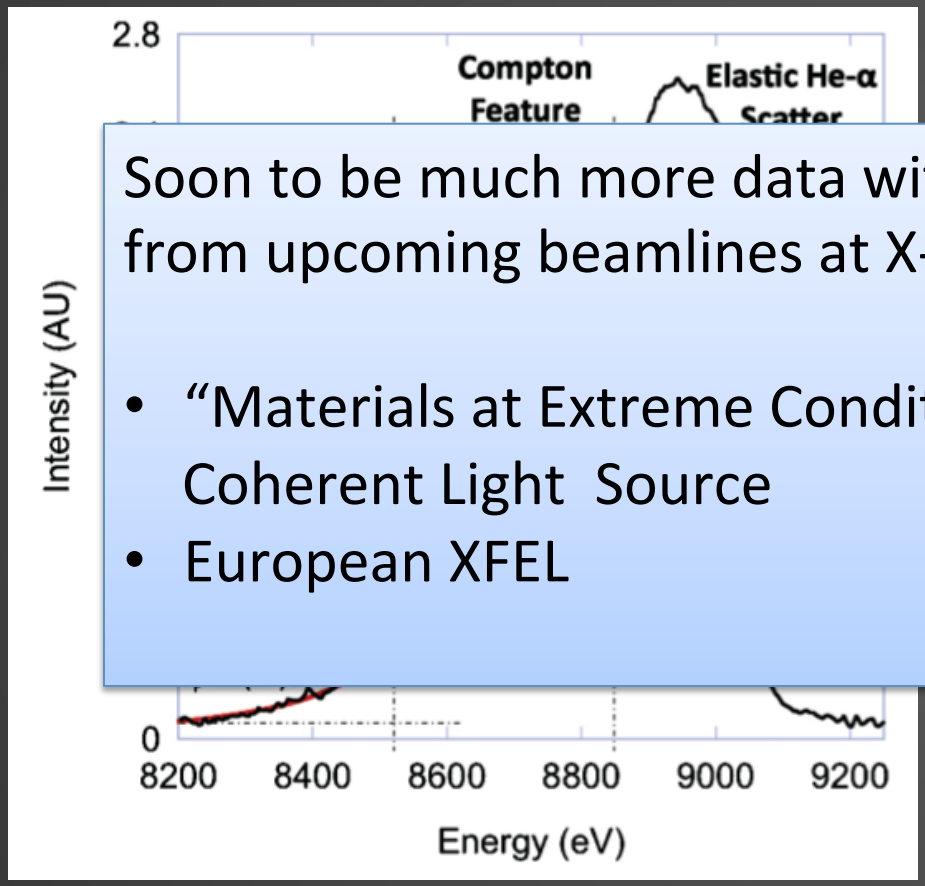
NIXS can be used as a thermometer for WDM



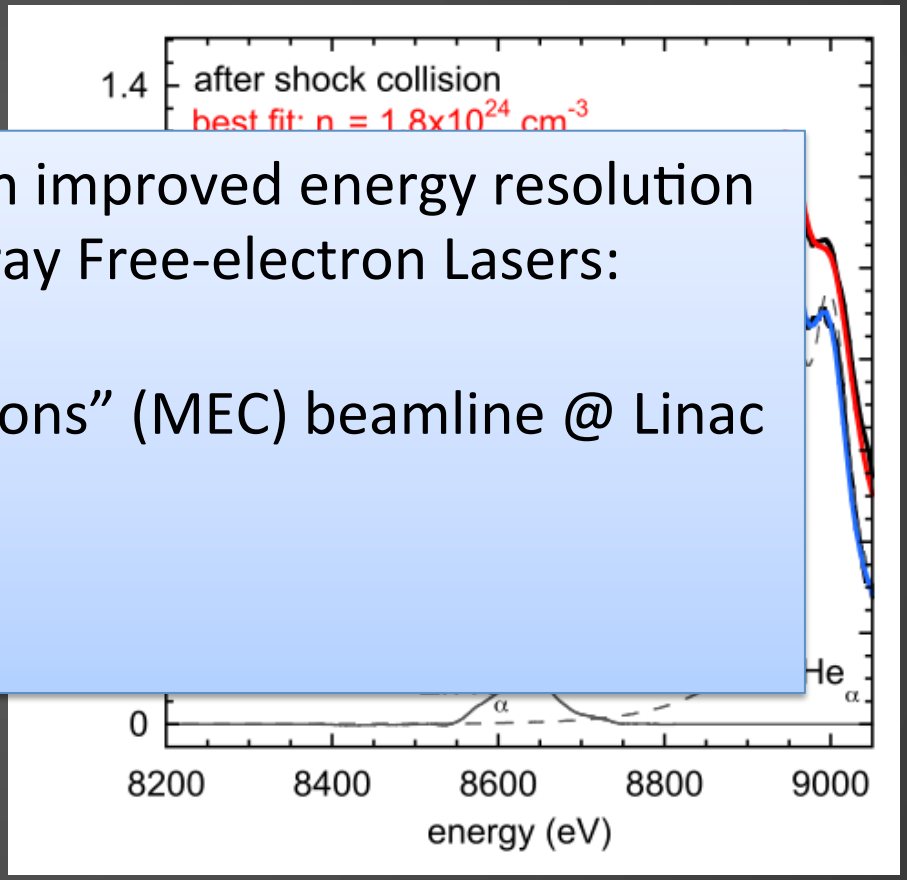
Glenzer, *et al.* PRL 90, 175002 (2003

Recent experimental studies of Be

Goal: Characterize adiabatic index of this ablator material to learn about EOS



Kritcher, et al. PRL **107**, 015002 (2011)



Fortmann, et al. PRL **108**, 175006 (2012)

Soon to be much more data with improved energy resolution from upcoming beamlines at X-ray Free-electron Lasers:

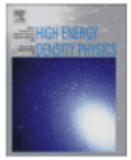
- "Materials at Extreme Conditions" (MEC) beamline @ Linac Coherent Light Source
- European XFEL

High Energy Density Physics 6 (2010) 1–8

Contents lists available at ScienceDirect

High Energy Density Physics

journal homepage: www.elsevier.com/locate/hedp



Review

Dense plasma X-ray scattering: Methods and applications

We have developed accurate x-ray scattering techniques to measure the physical properties of dense plasmas. Temperature and density are inferred from inelastic x-ray scattering data whose interpretation is model-independent for low to moderately coupled systems. Specifically, the spectral shape of the non-collective Compton scattering spectrum directly reflects the electron velocity distribution. In partially Fermi-degenerate systems that have been investigated experimentally in laser shock-compressed

In-Flight Measurements of Capsule Shell Adiabats in Laser-Driven Implosions

Fermi energy ($T_F^{1/2} \sim n_e^{1/3}$). The shape of the red wing is used to extract additional information on T_e. In these experiments the high SNR of our data enables highly resolved measurements of the Compton red wing shape, thus allowing us to obtain a model-independent measure of T_e from the electron velocity distribution.

Measurement of the Adiabatic Index in Be Compressed by Counterpropagating Shocks

[6,7] and the Compton feature [8]. In the Compton scattering regime, at a large scattering angle, the plasma response is essentially uncorrelated, and the Compton profile reflects the single-particle distribution function which is fully characterized by electron density n_e and temperature T. Inferring these parameters by fitting the Compton profile calculated from first principles is, hence, model-independent. Moreover, the electron temperature is constrained by the amount of elastic (Rayleigh) scattering.

Model independent?

- *Very* hard to believe
- Thermometry depends on material properties and material properties of WDM are *not* simple. If they were, we could reliably calculate the EOS and wouldn't have a need for these experiments.

- Three pieces are important for interpreting NIXS spectra:
  - Density dependence of binding energy (Continuum lowering)
  - Core-shell contribution
  - Valence contribution
- Each piece must be correctly modeled to *accurately* extract T, n_e
  (low resolution data can still be fit using by incorrect models)
- I have found that:
  - Model for core is theoretically unjustified (violates energy conservation) and disagrees with high-resolution ambient pressure data.
  - Model for valence is too simple (neglects the ion-electron interaction)

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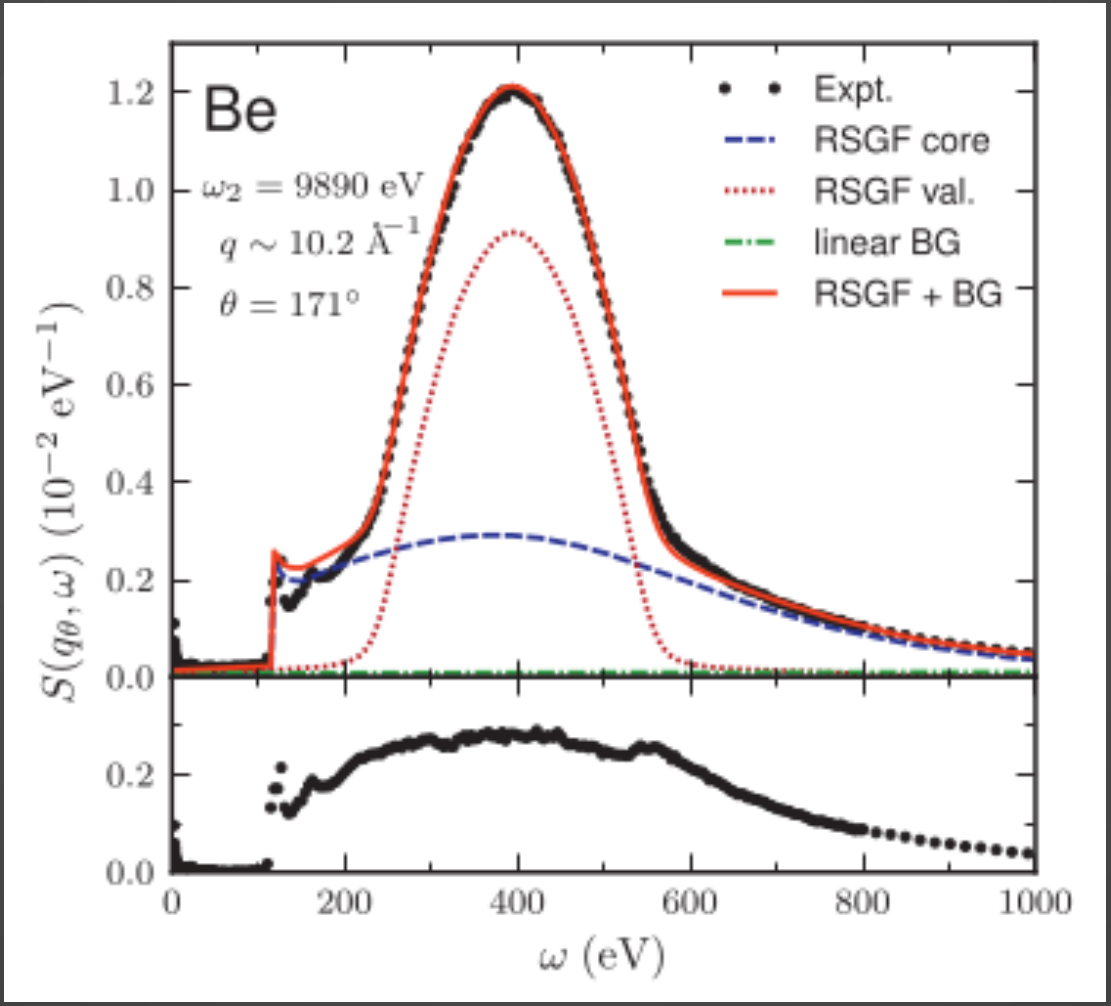
PHYSICS OF PLASMAS **20**, 022706 (2013)

Theoretical treatments of the bound-free contribution and experimental best practice in X-ray Thomson scattering from warm dense matter

Brian A. Mattern and Gerald T. Seidler[a)]
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA



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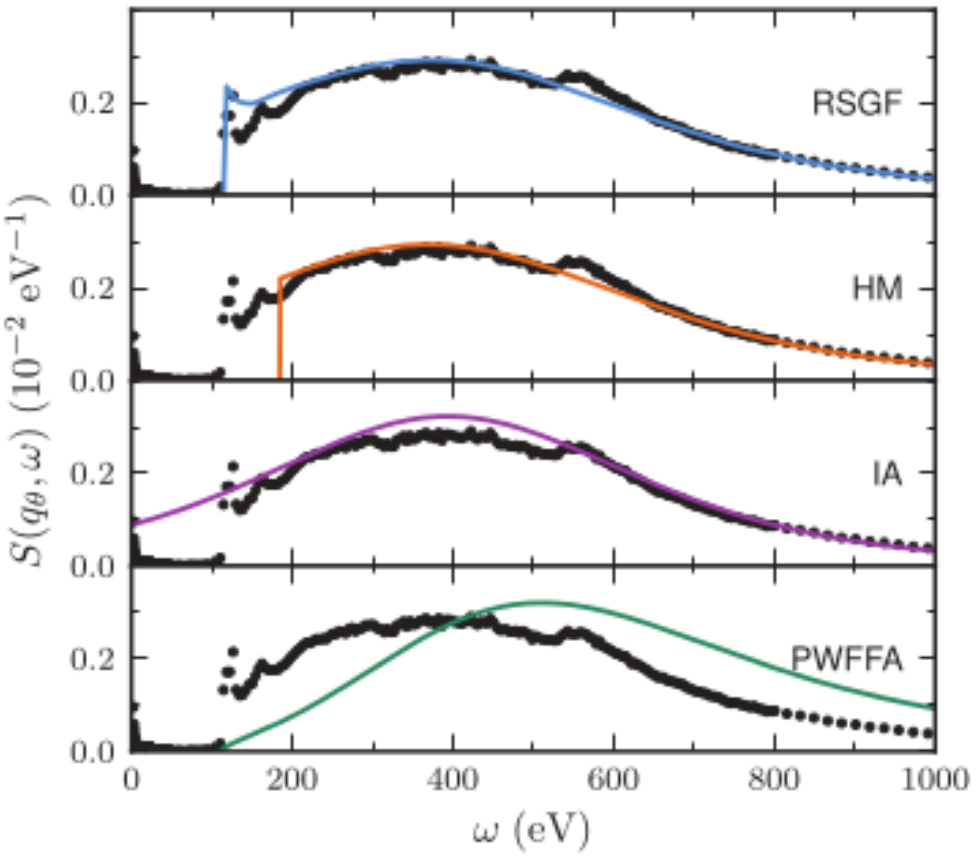

Core-shell (1s) contribution to NIXS from polycrystalline Be under ambient conditions

Real-space Green's function (FEFF)
Extensive use in condensed matter studies
Soininen, et al. PRB **72**, 045136 (2005)

Hydrogenic model (Z_{eff} = 3.685)
Eisenberger, Platzman PRA **2**, 415 (1970)

Impulse approximation (Hartree-Fock)
Momentum distribution of initial state
Eisenberger, Platzman PRA **2**, 415 (1970)

Plane-wave form-factor approximation
Assume final states are plane waves
Schumacher, et al. J. Phys. B **8** 1428 (1975)
Used ubiquitously in WDM studies!

Consequences of using PWFFA:

- Miscalculating core contribution modifies shape of estimated valence contribution and thus extracted T, n_e
- Unfortunately, difficult to precisely determine ***how*** this happens due to competing errors in analysis .
- Details forthcoming in: Mattern, Seidler, in prep.

Literature using the PWFFA for analysis of WDM NXIS data:

J. Quant. Spect. Rad. Transf. **99**, 225 (2006)
Laser and Part. Beams **25**, 465 (2007)
Phys. Plasmas **14**, 122703 (2007)
PRE **77**, 046402 (2008)
PRL **102**, 115001 (2009)
PRL **103**, 245004 (2009)
Rev. Mod. Phys. **81**, 1625 (2009)
HEDP **6**, 1 (2010)
PRL **107**, 015002 (2011)
PRL **108**, 175006 (2012)
PRL **110**, 065001 (2013)
PRL **20**, 056316 (2013)
New J. Phys. **15**, 085011 (2013)

At heart of **PW**FFA is the use of ***Plane Waves*** for final state.
This *ignores the strong ionic potentials* in dense matter.

As I will now show:
The same conceptual error affects the valence contribution

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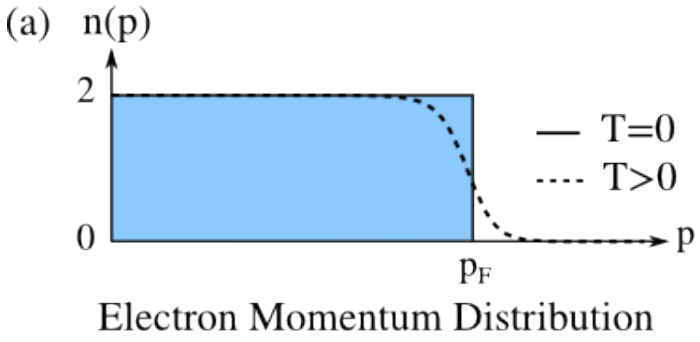
Toy model: Free Fermi gas

$\omega = (p+q)^2/2m - p^2/2m = q^2/2m + p\cdot q/m$

Compton Shift (set by *kinematics*)

Doppler Shift (set by *momentum distrib.*)

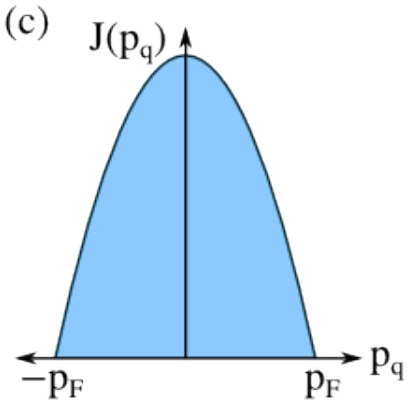


Electron Momentum Distribution

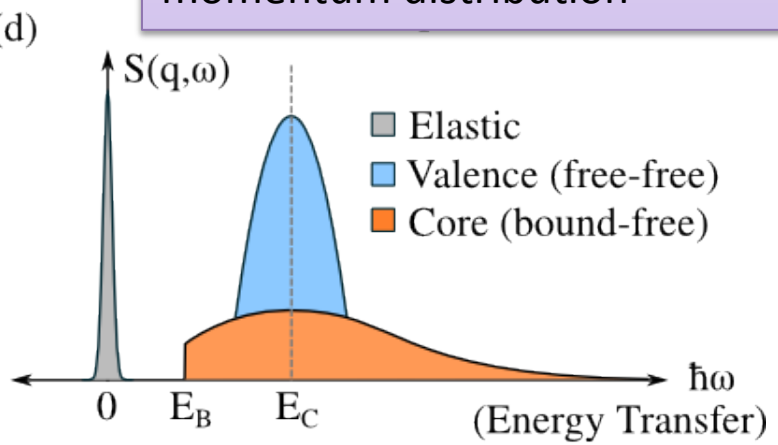
Impulse approximation: (large q NIXS)

Same story. But, replace *n(p)* with that for actual system (depends on *material properties*)

NIXS directly measures electron momentum distribution



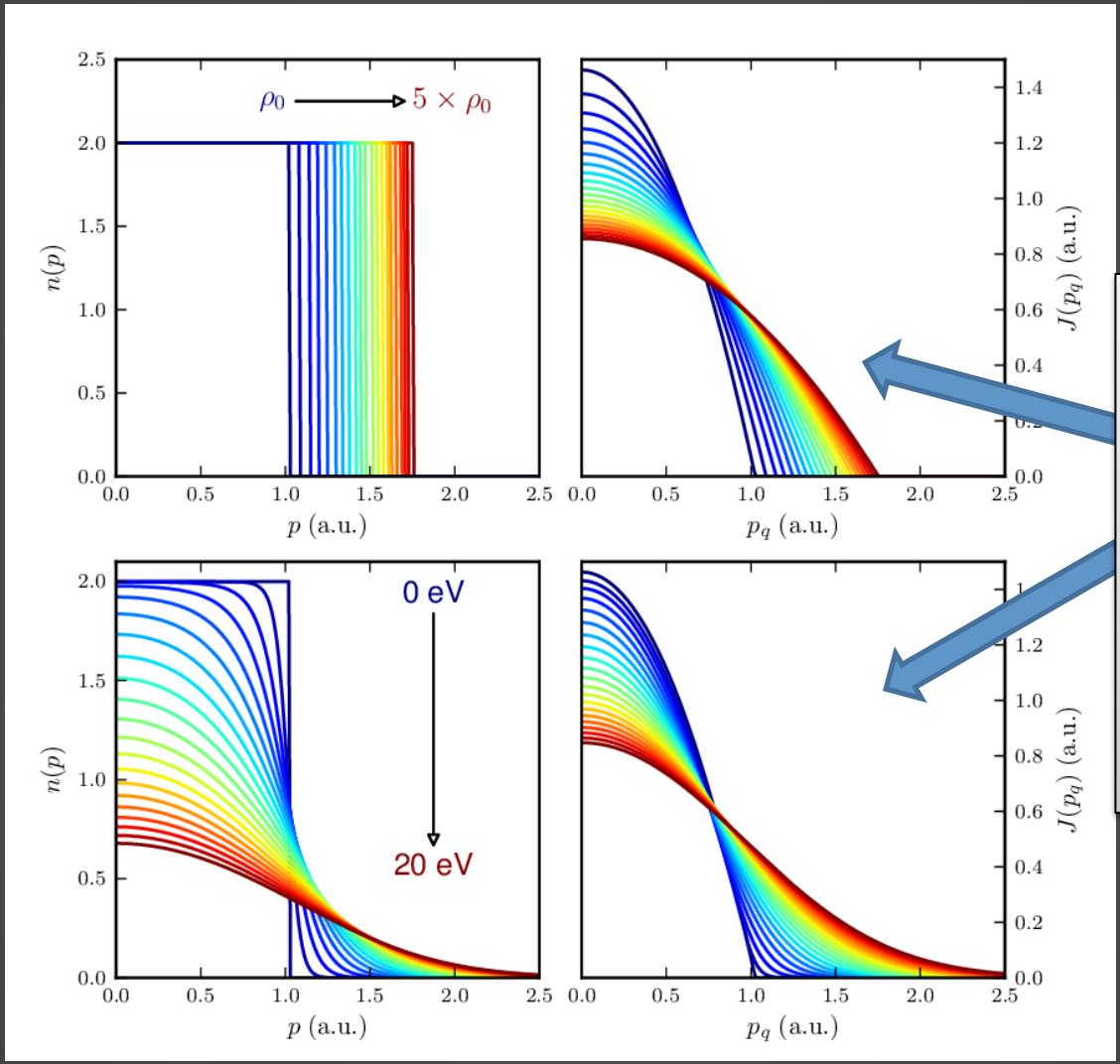
Compton Profile (CP)



Toy model: Free Fermi gas

Density Dependence

Temperature Dependence



If experimental resolution is low, these become more difficult to distinguish:

Strong *covariance* in extracted T ,ne

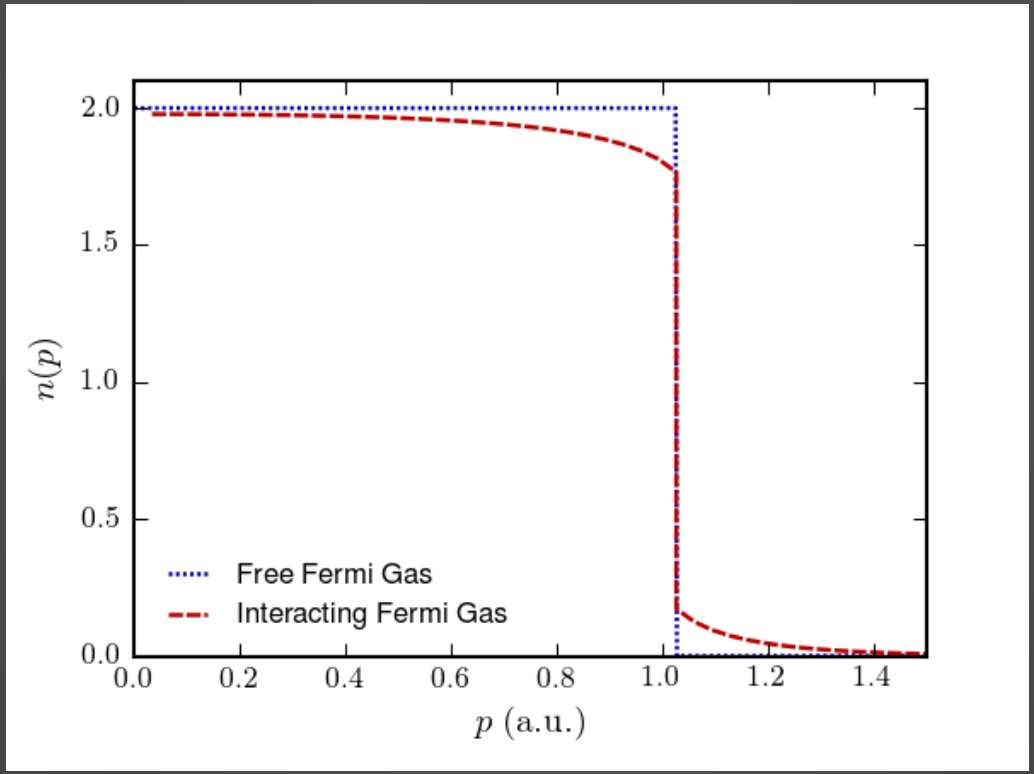
Momentum distribution
$n(p)$

Compton Profile
$J(p\downarrow q)$

What happens if we turn on interactions?

Pauli exclusion => only one thing *can* happen:
Occupation shifts from states below p_F to states above

Turn on Coulomb interactions between electrons:



Calculation by J. J. Kas (2013)

Model used for valence electrons in WDM studies:

Interacting Fermi gas
Calculate dielectric function $\epsilon(q,\omega)$ in *random phase approximation*
This is related to $S(q,\omega)$ by *fluctuation-dissipation* theorem

This gives identical NIXS spectra at high-q as the non-interacting Fermi gas.

The *Born-Mermin Approximation* (BMA).

- Very recent studies also include a *perturbative* correction to account for collisions between electrons and ions (calculated in the Born approximation)
- However, at high q, this has only a slight effect on the calculated spectra.

What happens if we include the interactions between ions and electrons **non-perturbatively**?

PHYSICAL REVIEW B **85**, 115135 (2012)

Real-space Green's function calculations of Compton profiles

Brian A. Mattern, Gerald T. Seidler,* Joshua J. Kas, Joseph I. Pacold, and John J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
(Received 2 February 2012; revised manuscript received 16 March 2012; published 29 March 2012)

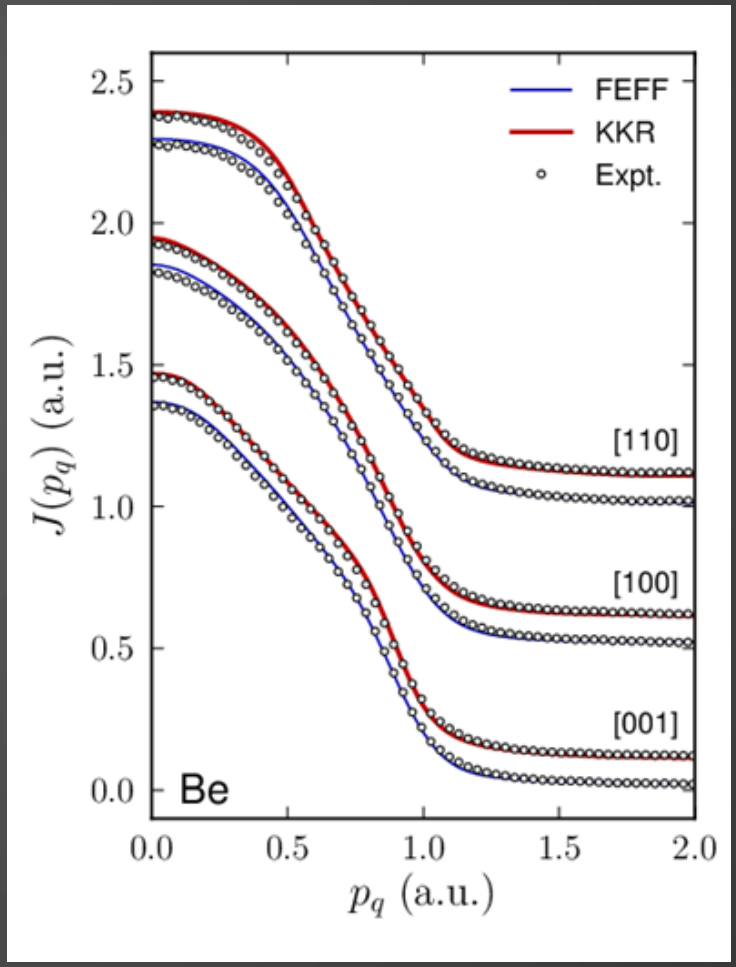
Developed method for calculating Compton-scattering profiles from the real-space Green's function using the Rehr group's FEFF code.

Solves quantum mechanics of electrons in ionic potentials.

Found good agreement with high-resolution experimental data under ambient conditions.

Have since extended to higher electron temperature.

Use this tool to study effect of ion-electron interactions.



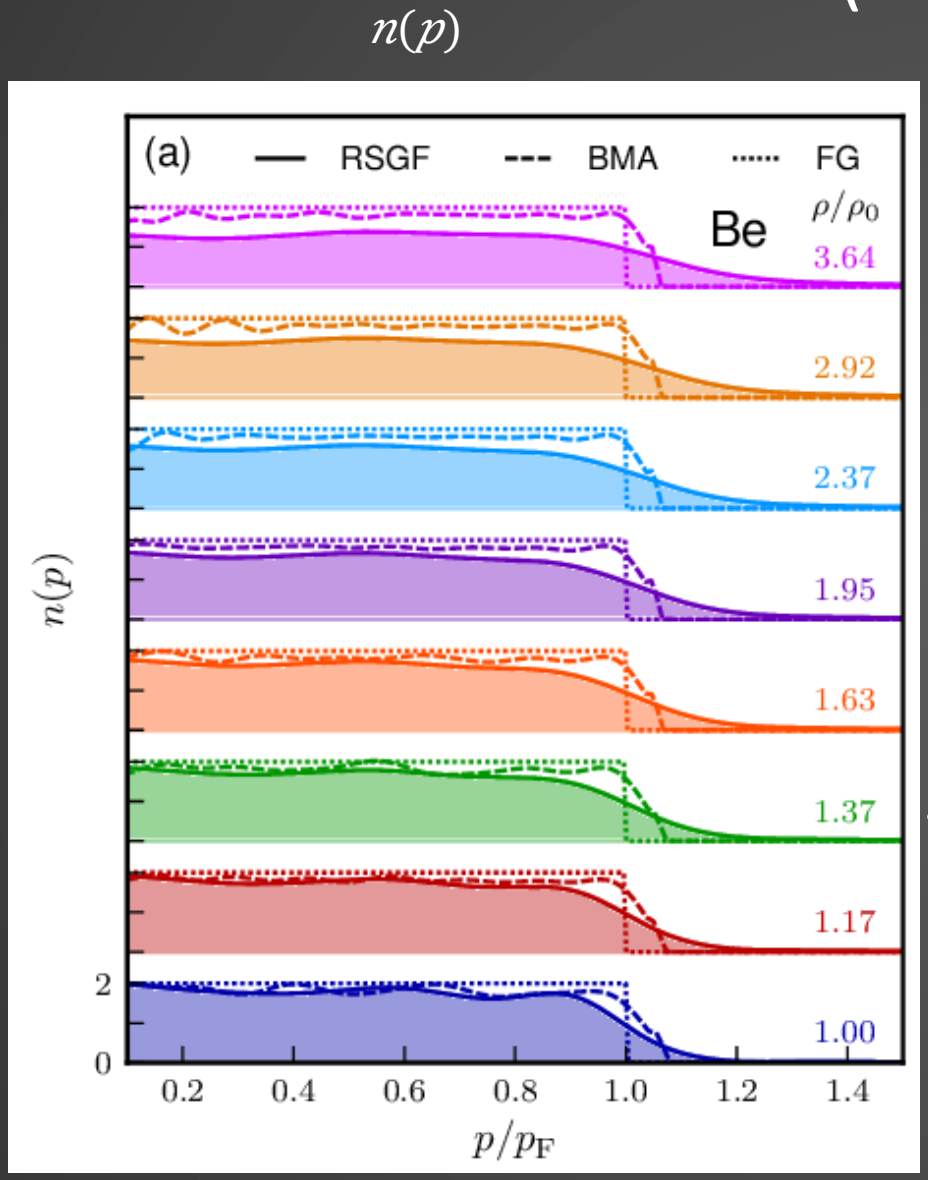
Condensed phase effects on the electronic momentum distribution in the warm dense matter regime

Brian A. Mattern, Gerald T. Seidler,* and Joshua J. Kas
Department of Physics, University of Washington, Seattle, WA 98195-1560
(Dated: August 15, 2013)

We report *ab initio* calculations of the valence electron momentum distribution function $n(p)$ and dynamic structure factor for warm dense Be at Mbar pressures. We observe an unexpected, strong reshaping of the Compton profile upon increasing density, even well before any significant core-wavefunction overlap or electride behavior occurs. We propose that this nonperturbative effect, which is due to a growing influence on $n(p)$ of the orthogonalization of valence and core electron wavefunctions with increasing density, is observable by inelastic x-ray scattering at x-ray free-electron lasers and large-scale laser-shock heating facilities, and may also be more generally important for thermodynamic properties of dense, partially-ionized plasmas.

(Submitted Phys. Rev. Lett. Aug. 2013)

Effect of non-perturbative ion-electron interaction (T = 0)



Scaled by p_F to account for uninteresting density dependence

Occupation shifts:
from states below $p \downarrow F$
to states above $p \downarrow F$

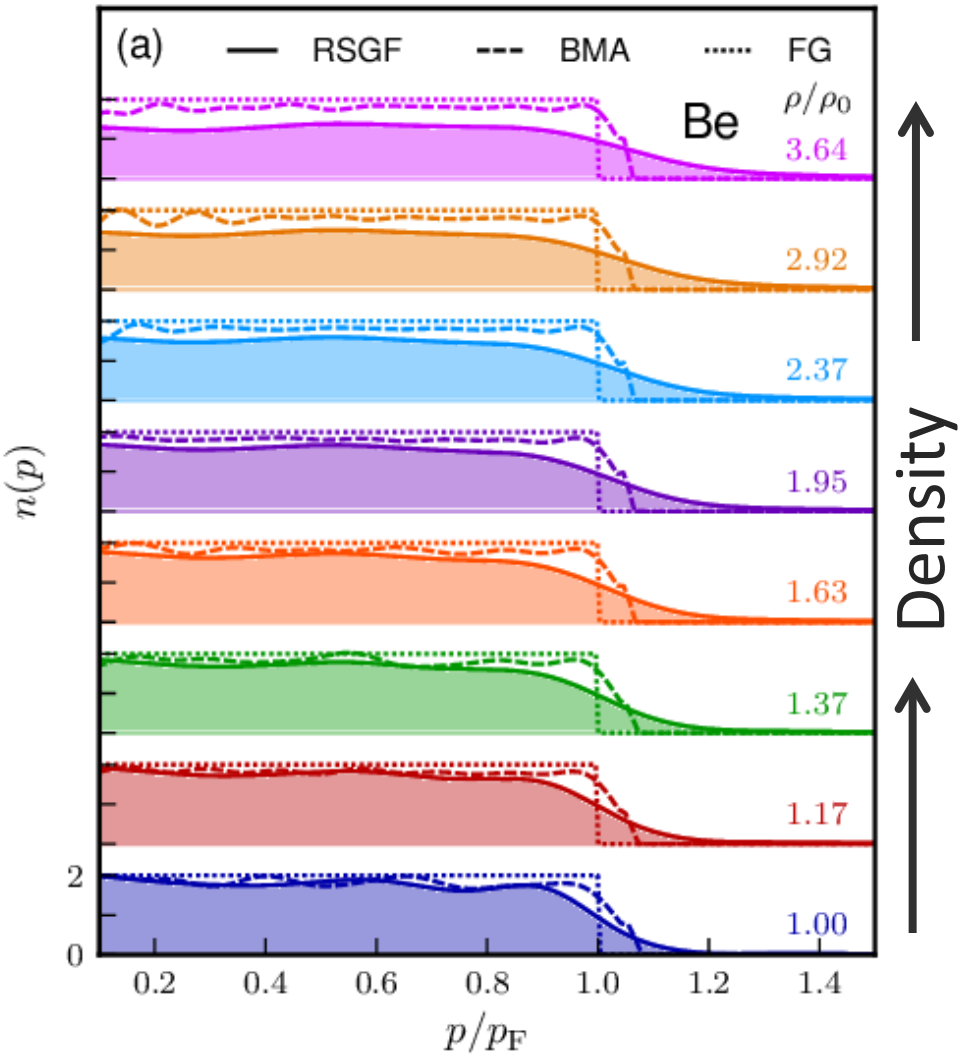
Nearly uniform decrease of occupation for $p < p_F$

Effect becomes stronger as density increases

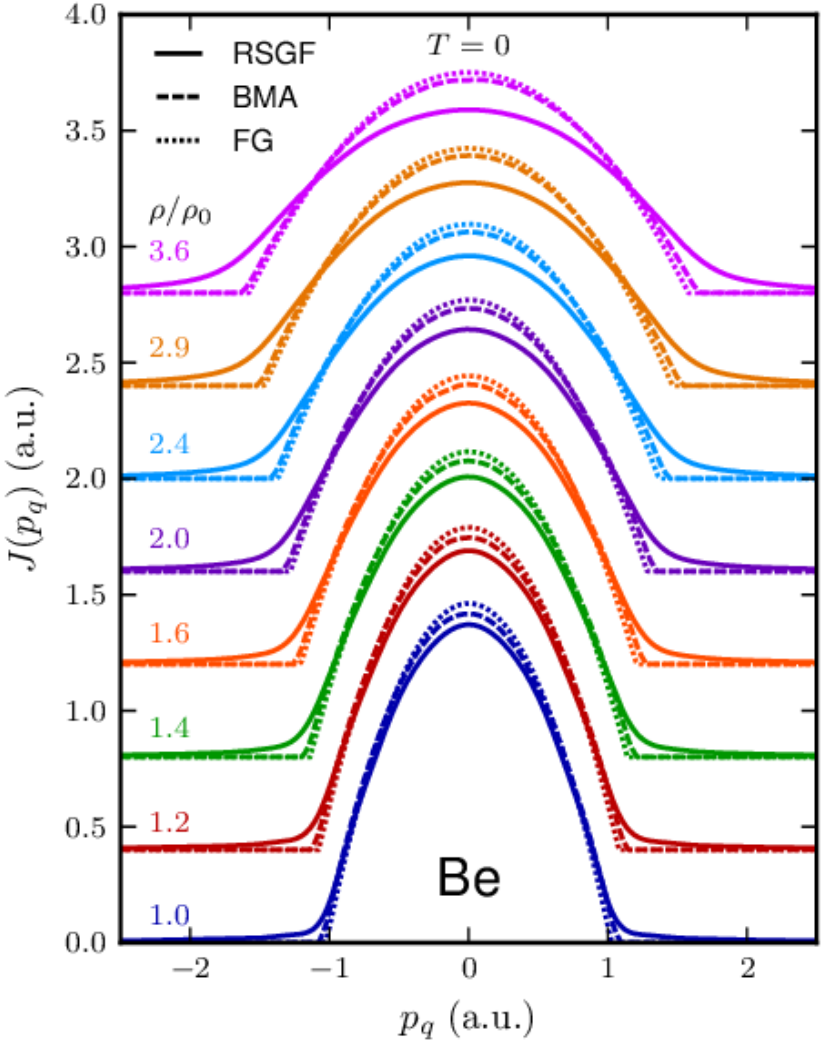
Born-Mermin (BMA) shows little density dependence beyond change in p_F

Effect of non-perturbative ion-electron interaction (T = 0)

$n(p)$ $J(p\downarrow q)$



Density



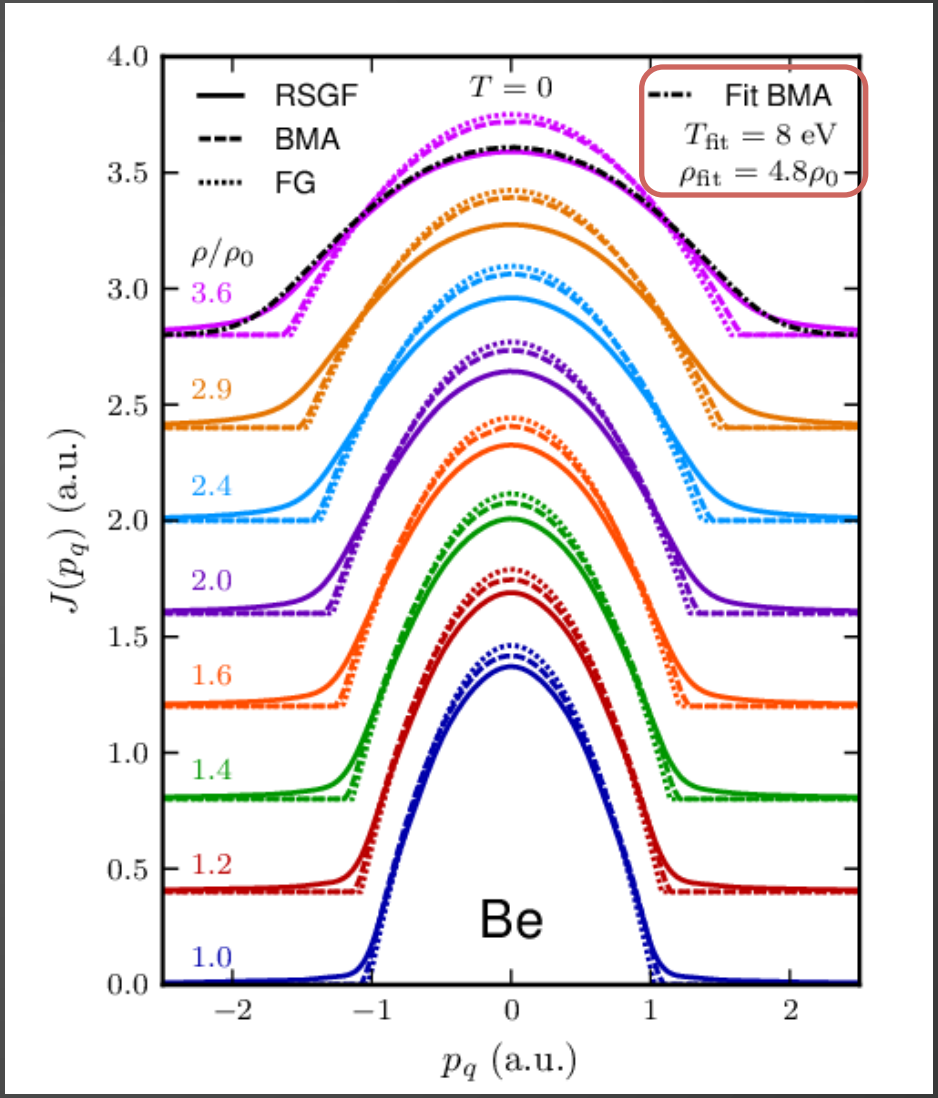
Effect of non-perturbative ion-electron interaction (T = 0)

$J(p\downarrow q)$

Electron-ion Interactions cause:

Increased width of CP
Broad tails for $|p\downarrow q| > p\downarrow F$

Using BMA, cold, compressed metal *appears* to have T ~ 100,000 K!



Effect of non-perturbative ion-electron interaction (T= 10 eV)

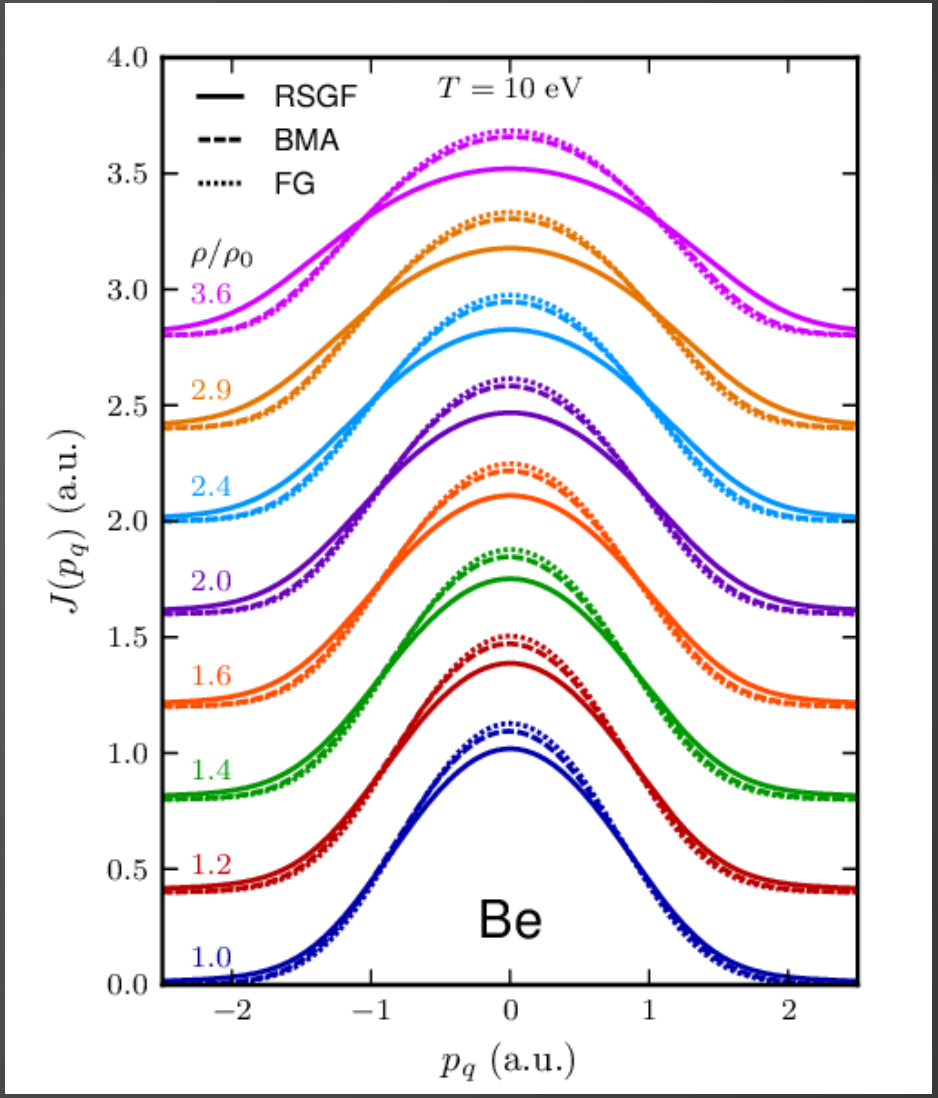
$J(p\downarrow q)$

Electron-ion Interactions cause:

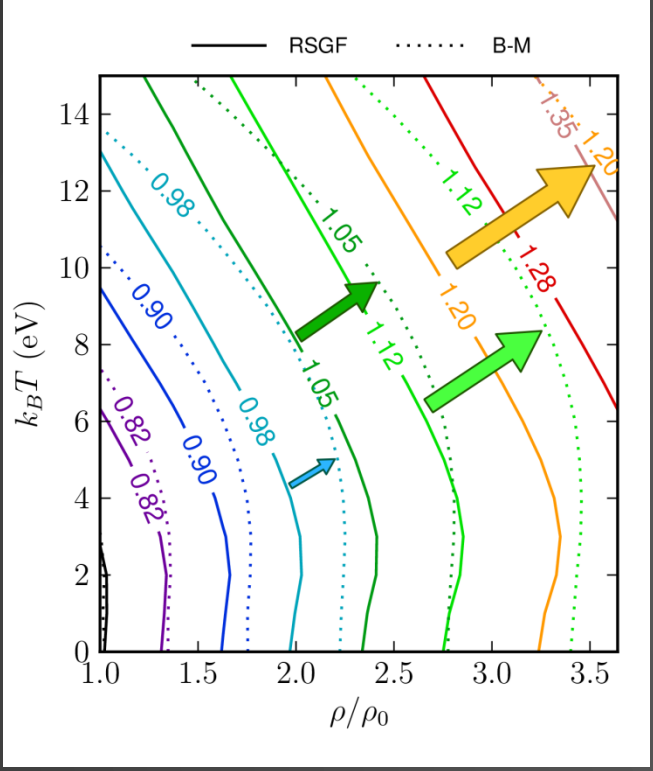
Increased width of CP
Broad tails for $|p\downarrow q| > p\downarrow F$

Using BMA, cold, compressed metal *appears* to have T ~ 100,000 K!

Effect remains as temperature is increased.



Implications for experiment



Contours are constant HWHM of Compton profile

Neglecting ion-electron interactions results in *over-estimation* of density, temperature or both.

In summary

- NIXS studies of WDM either entirely neglecting the ion-electron interaction, or treat it perturbatively (with only minor effect).
- Non-perturbative ion-electron interactions result in significant broadening of momentum distribution and Compton profile
- Neglecting this effect **results in significant systematic overestimation of T, n_e**

Aren't valence electrons in simple metals free-electron like?

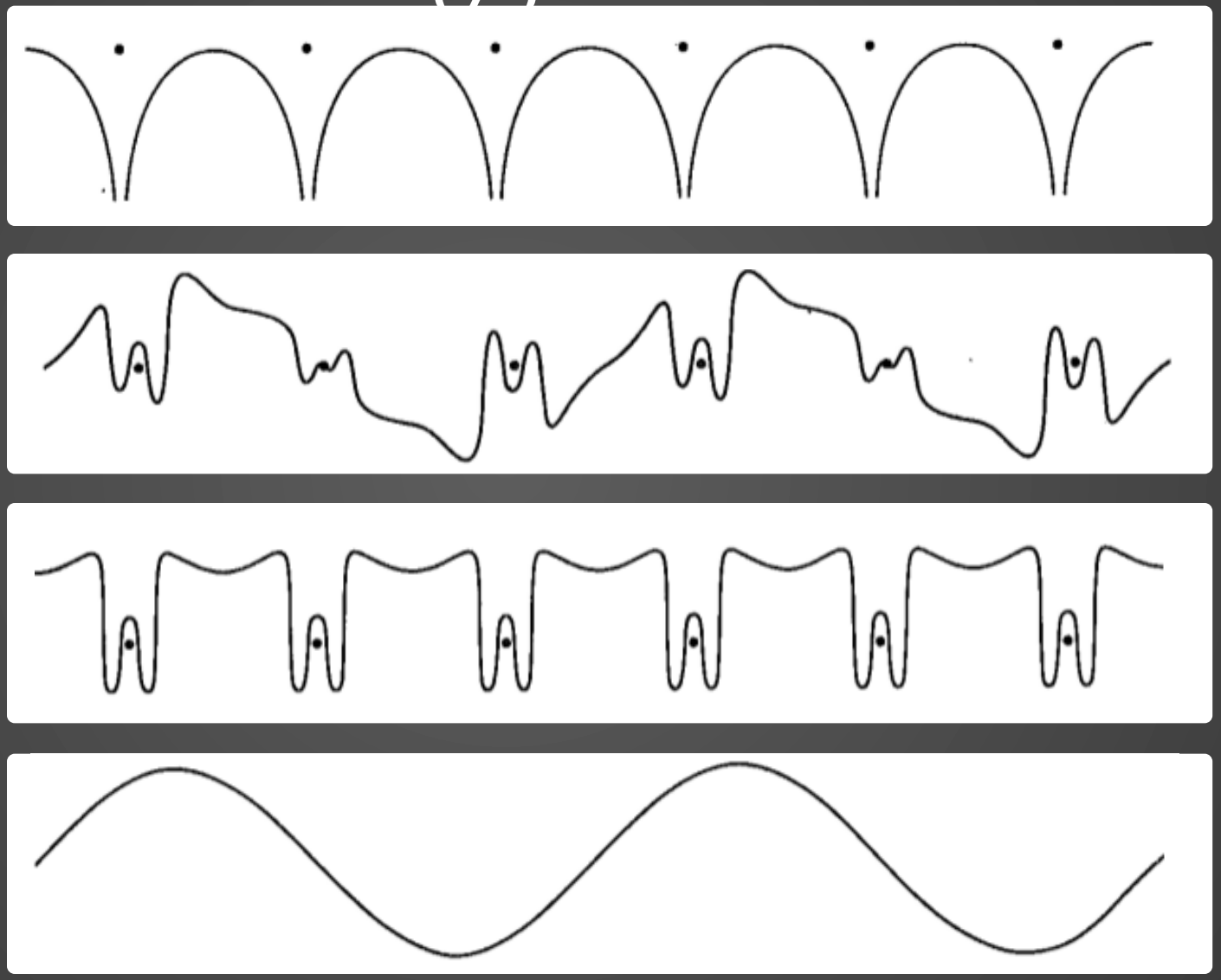
What physical phenomenon underlies this broadening?

Answer lies at the heart of the history of electronic structure calculations in condensed matter.

Outline

- Warm Dense Matter
- Thermometry
- X-ray based diagnostics
  - Heavier elements: X-ray Absorption and Emission
  - Light elements: Non-resonant Inelastic X-ray Scattering (NIXS)
- Core-shell contribution to NIXS
- Valence contribution to NIXS
- The importance of valence-core orthogonalization
  - Psuedopotentials and the nearly-free-electron approximation
  - Effect of orthogonalization on the momentum distribution
- Conclusions

Bloch's Theorem: $\psi_k(r) = e^{ikr} u_k(r)$



Harrison, "Solid State Physics"

Orthogonalized Plane Wave (OPW) basis

$\psi_k(r)$

- Rapid oscillations near core require many states in plane-wave expansion
- Near core, ψ_k is very similar to free atomic wavefunction
- This is due to constraint of *orthogonality* with occupied core states.
- Why not use a better basis set that builds in this orthogonality?

C. Herring Phys. Rev. **57** 1169 (1940)

Orthogonalized Plane Wave (OPW) basis

- Core Projection operator: $P=\sum_{c\uparrow\downarrow} |c\rangle\langle c|$

  Sum over occupied core states of all atoms

- OPWs: $|k\rangle$

$$\psi_{k\uparrow}^{OPW} = (1-P)|$$

(Only need a few!)

- Expand in OPW Basis: $|k\uparrow\rangle$

$$\psi_{k} = \sum_{k\uparrow\downarrow} a_{k\uparrow\downarrow} \psi_{k\uparrow\downarrow}^{OPW}$$

ϕ_k

- Define pseudo-wavefunction:

$$\psi_{k\uparrow} = (1-P)\sum_{k\uparrow\downarrow} a_{\downarrow}$$

C. Herring Phys. Rev. **57** 1169 (1940)

$|k\uparrow\rangle$

Pseudo-potential

$$\psi_k = (1-P)\phi_k$$

Insert into Schroedinger eq. and rearrange to find:

$$(-p^2/2m + W)\phi_k = E\phi_k$$

Same Energy!

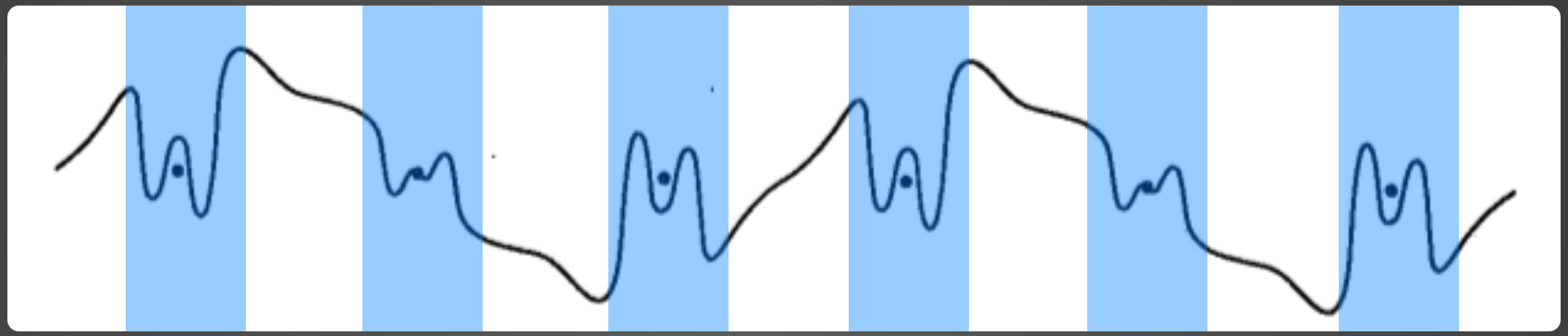
$$W = V + \sum c^{\blacksquare} (E - E_C)\ |c\rangle\langle c|$$

Attractive

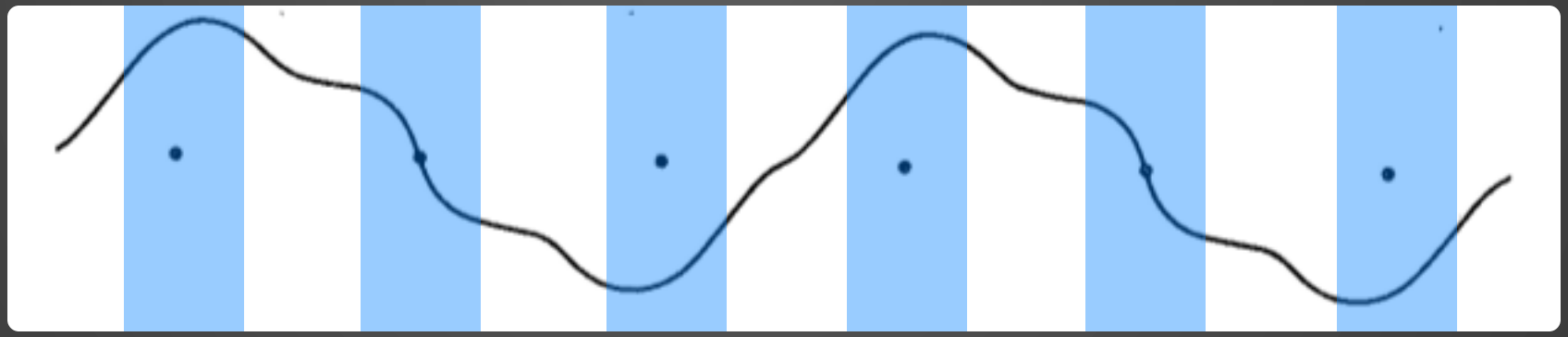
Repulsive

Actual wavefunction

$\psi_{\downarrow k}$



$\phi_{\downarrow k}$

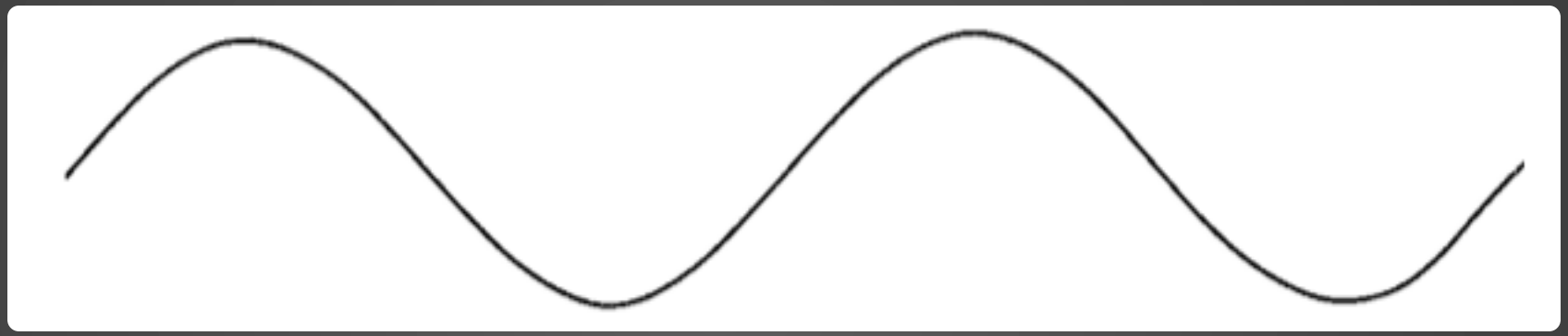


Pseudo-wavefunction

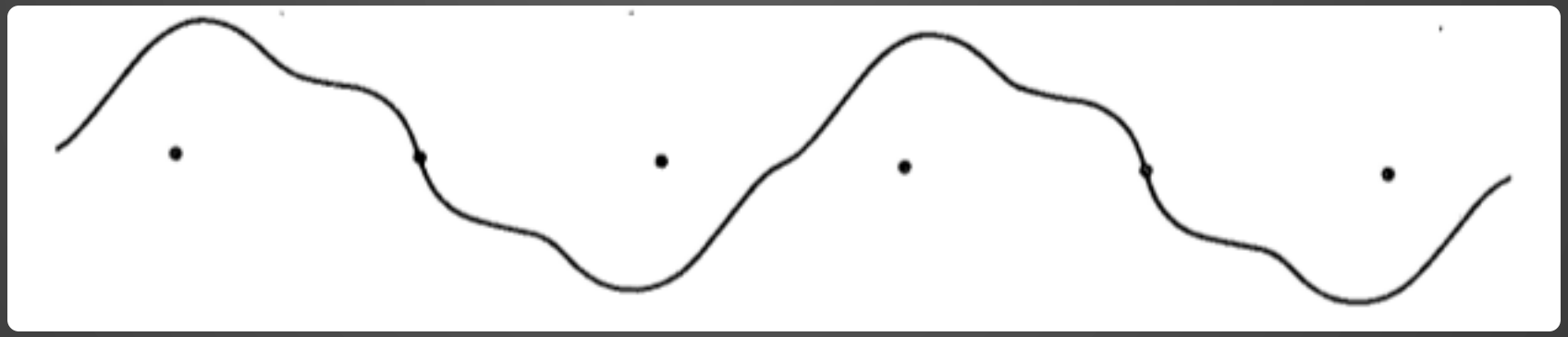
Harrison, “Solid State Theory” (Dover) 1979

Plane wave

e^{ikr}



ϕ_k



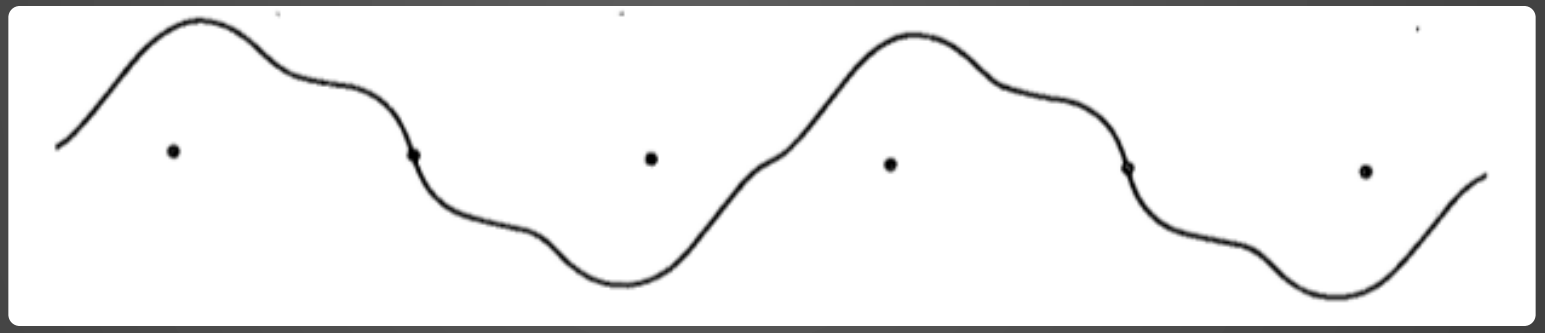
Pseudo-wavefunction

Harrison, “Solid State Theory” (Dover) 1979

Psuedo-potentials

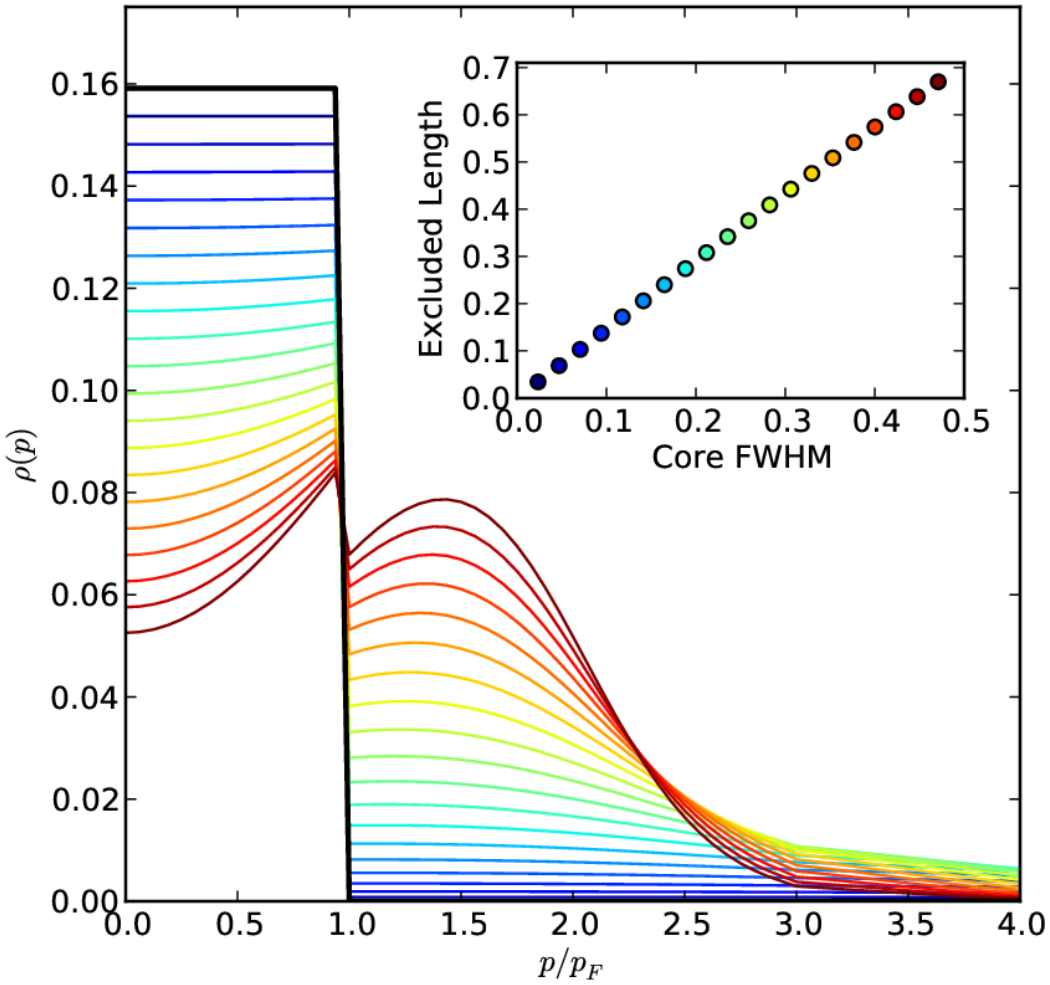
- Pseudo-wavefunction is solution of psuedo-potential with *same eigenvalue* as actual wavefunction in actual potential.
- Weak pseudopotential => Nearly-free electron **band structure**
- But, clearly ***not*** the **momentum distribution**

$\phi_{\downarrow k}$



$\psi_{\downarrow k}$

n(p) for 1-d model OPW model



Numerically orthogonalize plane waves against model (Gaussian) core states.

Look at momentum distribution
$\rho(p)=L/2\pi\, n(p)$
as a function of width of core states.

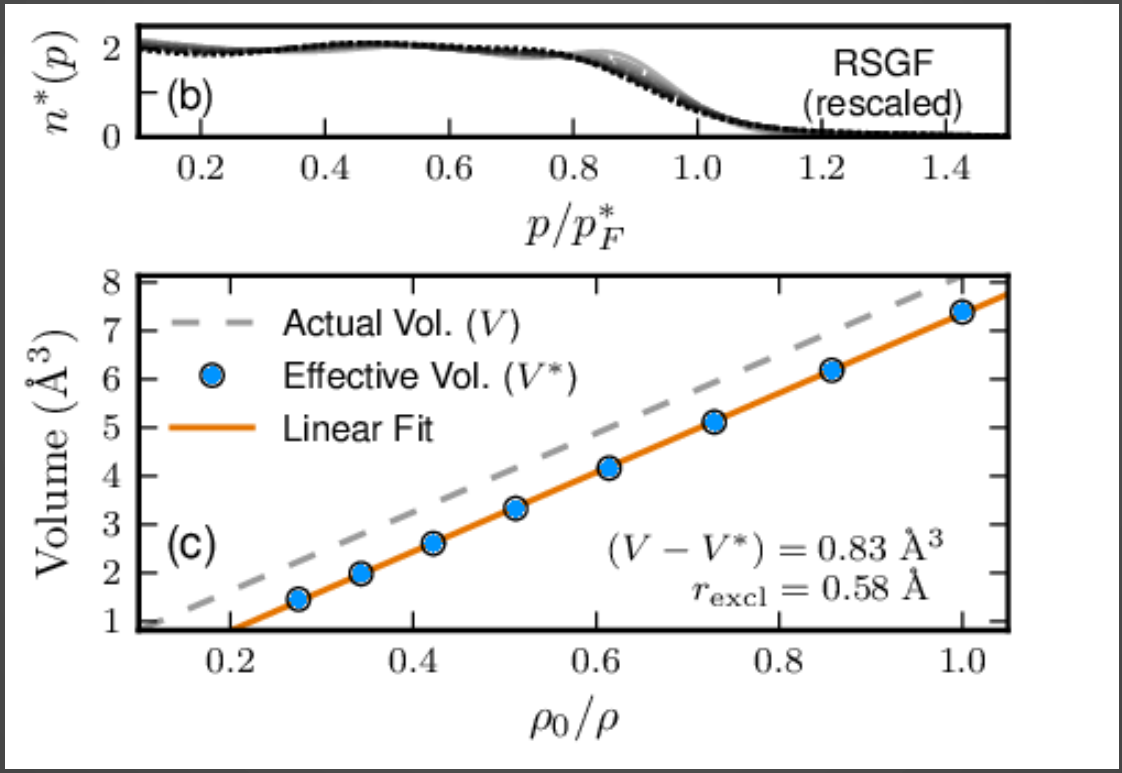
Same qualitative behavior as in RSGF calculations.

$\rho(0)$ is same as that for a gas completely excluded from a region the size of the core state

Orthogonalization drives change in momentum distribution

Interpret decrease in n(p) as due to an *effective volume* in which the electrons live

As density increases, *excluded volume* **remains constant and equal to the size of the core state**



Impactful final slide

- NIXS can be used as a WDM thermometry, but…
- Thermometry requires ***material properties***
- WDM experiments exclusively use models for material properties which make a recurring conceptual error:
  plane wave valence states
- ***This results in significant systematic errors in thermometry***
- -> Improved models for core
- -> Need to improve model for valence
  (include ***valence-core orthogonality***)
- Significant theoretical work still to be done…
- …but, currently, energy resolution is too low to discriminate between models
- Really, need ***better data***
  (coming soon from MEC beamline @ LCLS, Eu. XFEL)

Thanks

Research Advisor: Gerald Seidler

Committee: George Bertsch, Dave Castner, Subhadeep Gupta, Marjorie Olmstead, John Rehr

Seidler Group: Joe Pacold, Devon Mortensen, Oliver Hoidn, Nichole Barry, Marshall Styczinksi, Joseph Bradley, Ken Nagle

Rehr Group: Josh Kas, Fer Villa, Kevin Jorissen, Egor Clevac, John Vinson, Towfiq Ahmed

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DOE Fusion Energy Sciences

Family: Suzanne and Andreas

The plane-wave form-factor approximation

$$S(q,\omega)=\sum_f \left|\langle f|e^{iq\cdot r}|i\rangle\right|^2 \delta(E_f-E_i-\omega)$$

$|i\rangle$ = Hydrogenic initial state

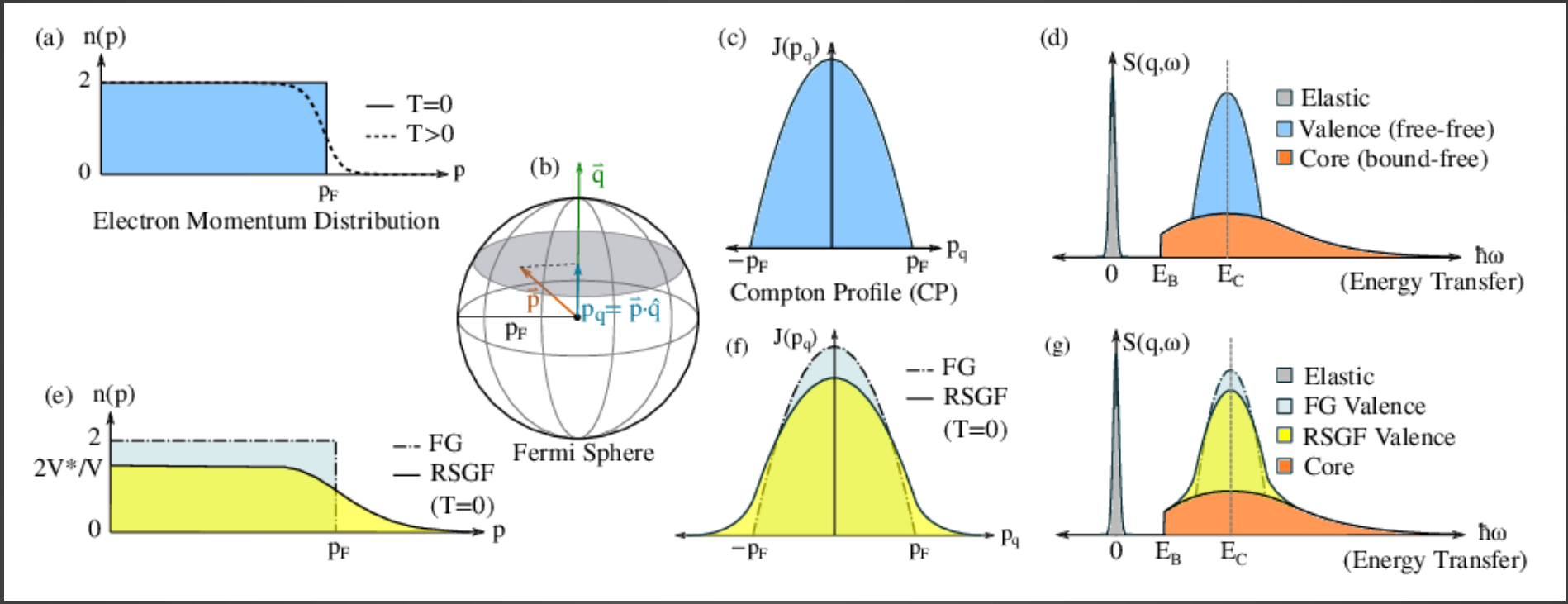
$|f\rangle$ = Plane wave

$$S(q,\omega)=\int d^3p\,\rho(p)\,\delta(E_p+q-E_B-\omega)$$

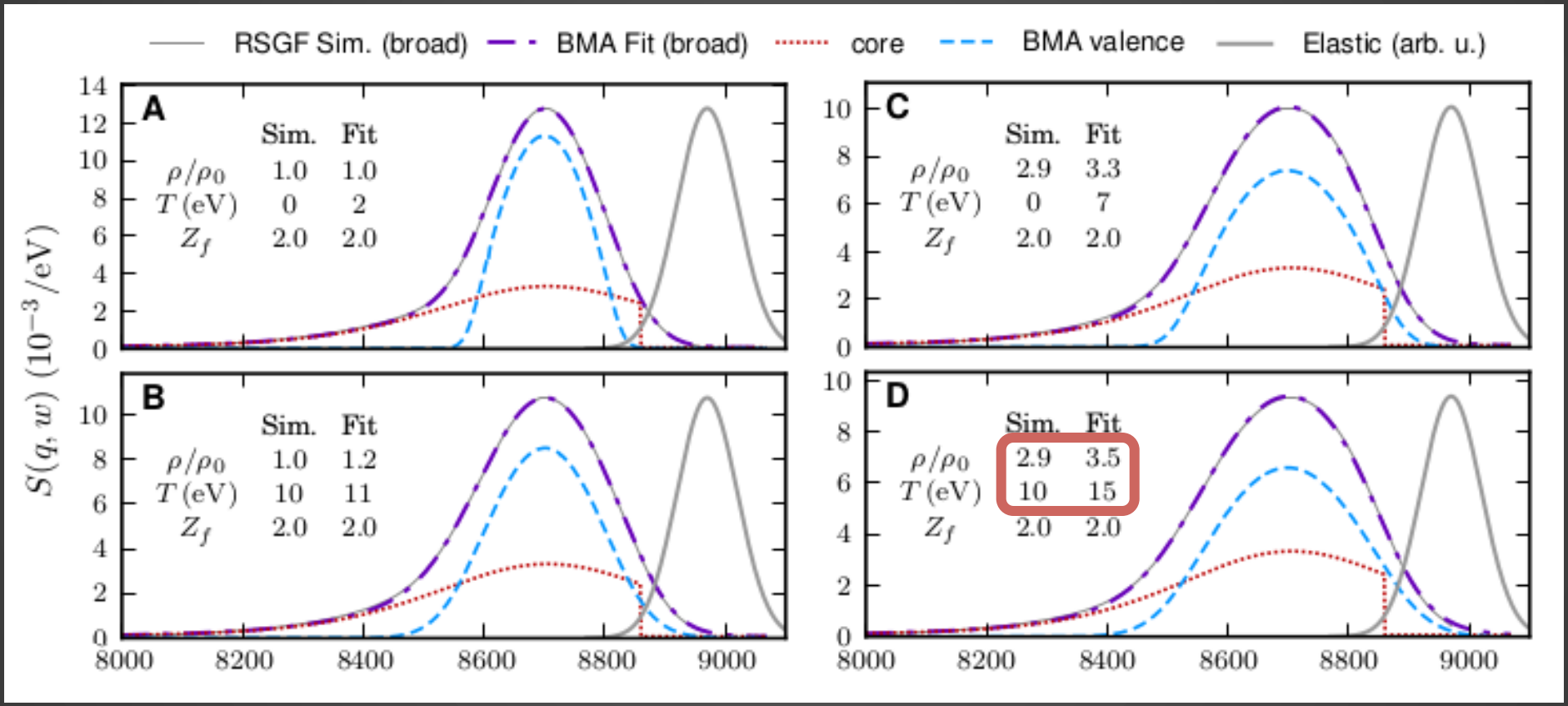
Compare with Impulse Approximation:

$$S(q,\omega)=\int d^3p\,\rho(p)\,\delta(E_p+q-E_p-\omega)$$

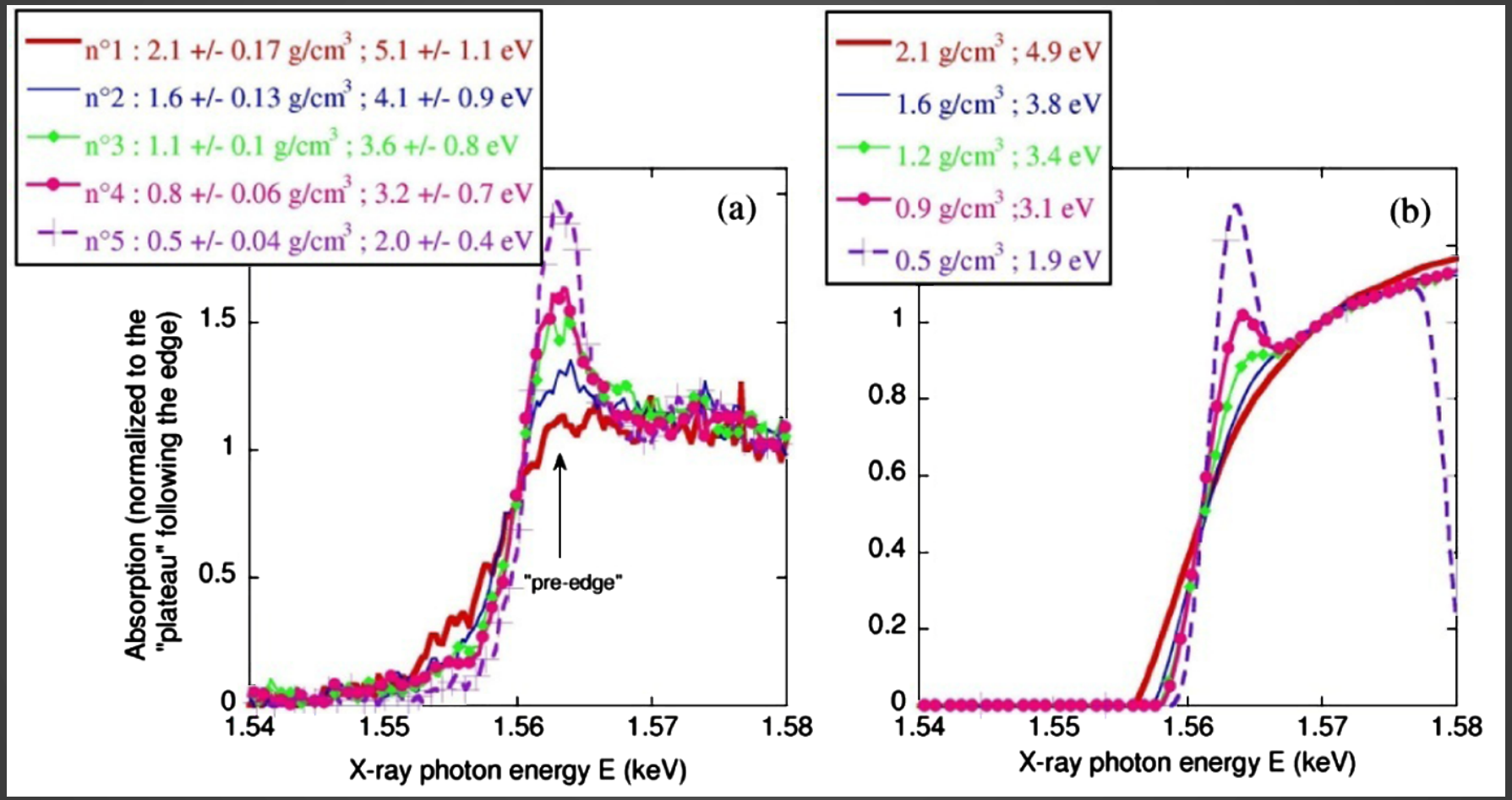
In summary:


(a) n(p)
2
0
p
p_F
— T=0
---- T>0
Electron Momentum Distribution
(b)
$\vec{q}$
$\vec{p}$
$p_q = \vec{p}\cdot\hat{q}$
p_F
Fermi Sphere
(c) $J(p_q)$
$-p_F$
p_F
p_q
Compton Profile (CP)
(d) $S(q,\omega)$
Elastic
Valence (free-free)
Core (bound-free)
0
E_B
E_C
$\hbar\omega$
(Energy Transfer)
(e) n(p)
2
2V*/V
0
p
p_F
-·- FG
— RSGF
(T=0)
(f) $J(p_q)$
-·- FG
— RSGF
(T=0)
$-p_F$
p_F
p_q
(g) $S(q,\omega)$
Elastic
FG Valence
RSGF Valence
Core
0
E_B
E_C
$\hbar\omega$
(Energy Transfer)

Insufficient information to distinguish theories due to low energy resolution



“X-Ray Diagnosis of the Pressure Induced Mott Nonmetal-Metal Transition” (2012)



Levy, et al. PRL **108**, 055002 (2012)

“Electronic Structure of Warm Dense Copper Studied by Ultrafast X-Ray Absorption Spectroscopy” (2011)

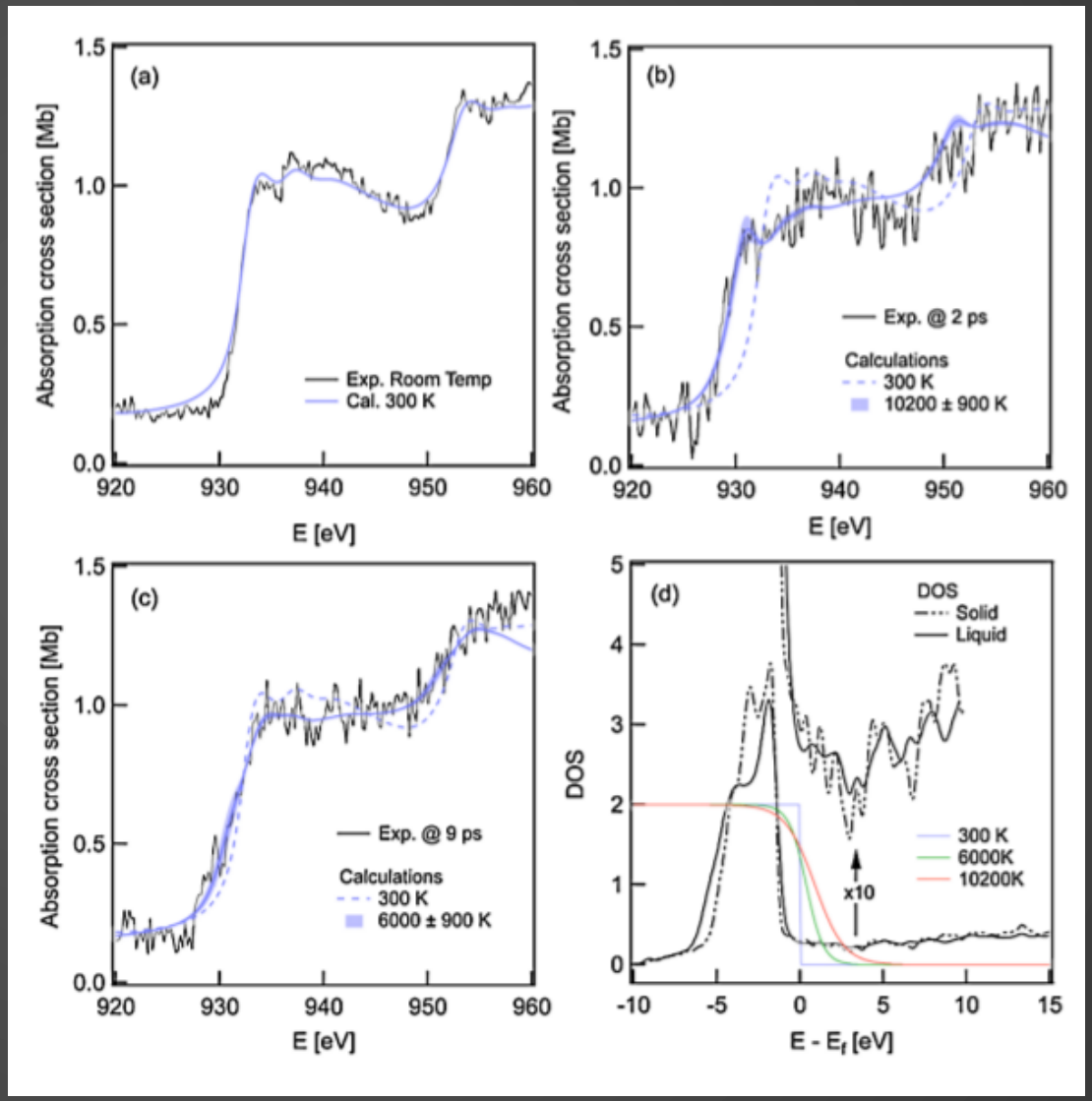
Cu $L_{2,3}$ edge ($2p$) XAS
Time-resolved (ps resolution)

Sample Heated at ambient density to ~ 1 eV using intense 150-fs optical laser pulse

Probed using 70-ps x-ray pulse from ALS synchrotron

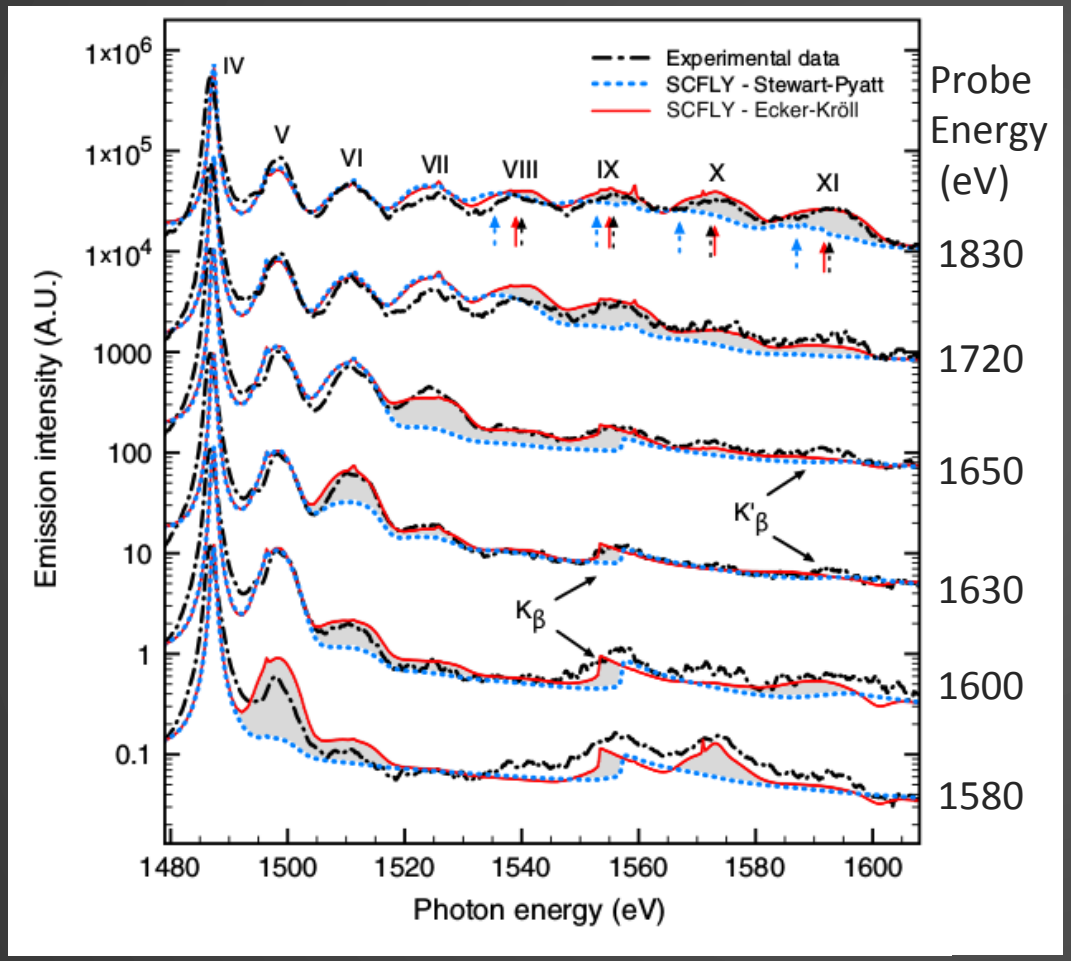
Broadening of edge due to Fermi distribution gives measure of temperature.

DFT calculations using Quantum Espresso with 32 atom super-cell



Cho, et al. PRL **106**, 167601 (2011)

“Direct Measurements of the Ionization Potential Depression in a Dense Plasma” (2013)



Al plasma heated to ~100 eV using 80-fs XFEL pulse

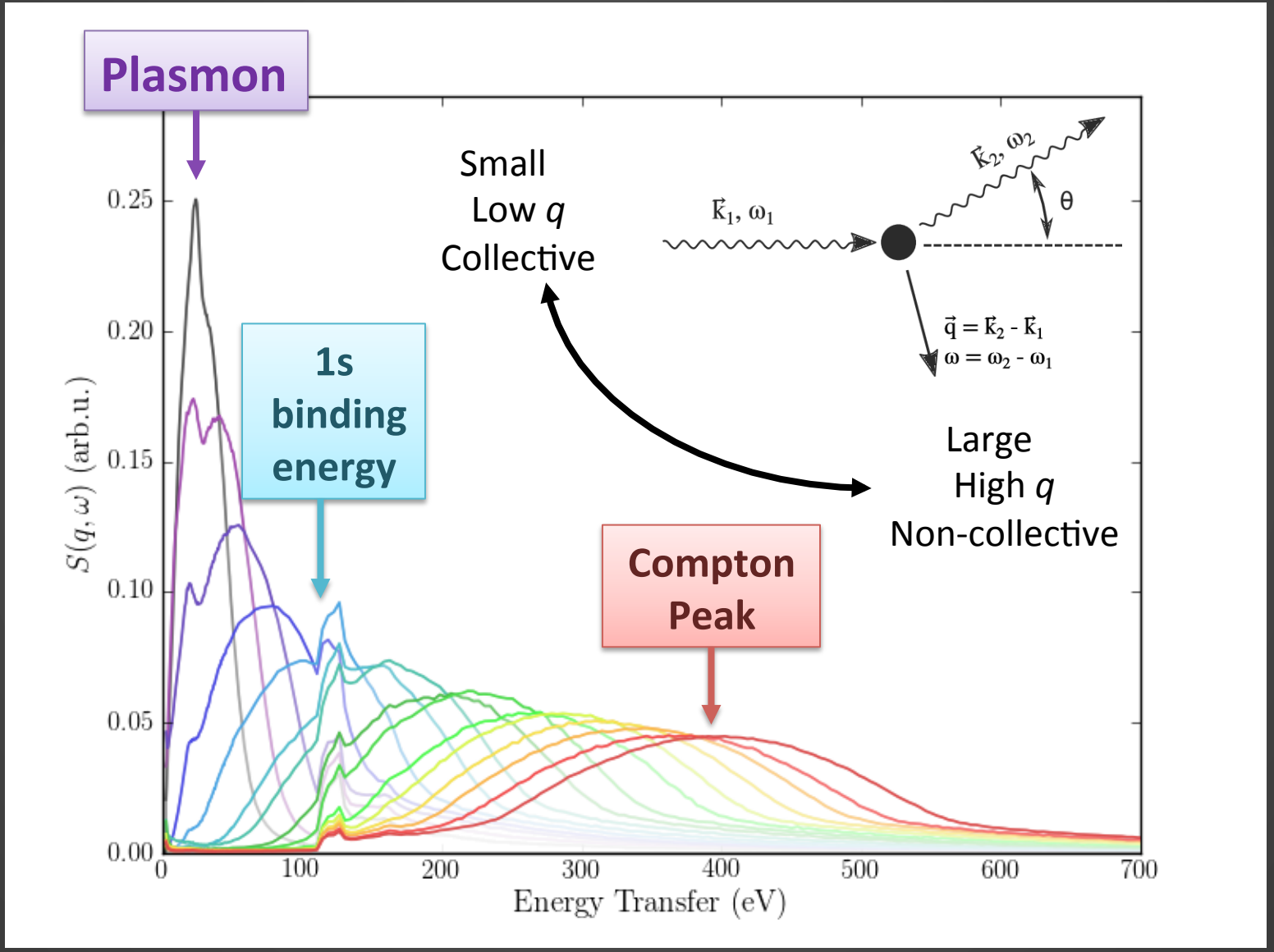
Probe energy varied above Al *1s* binding energy: 1560 eV

Thermal cascade leads to ionization

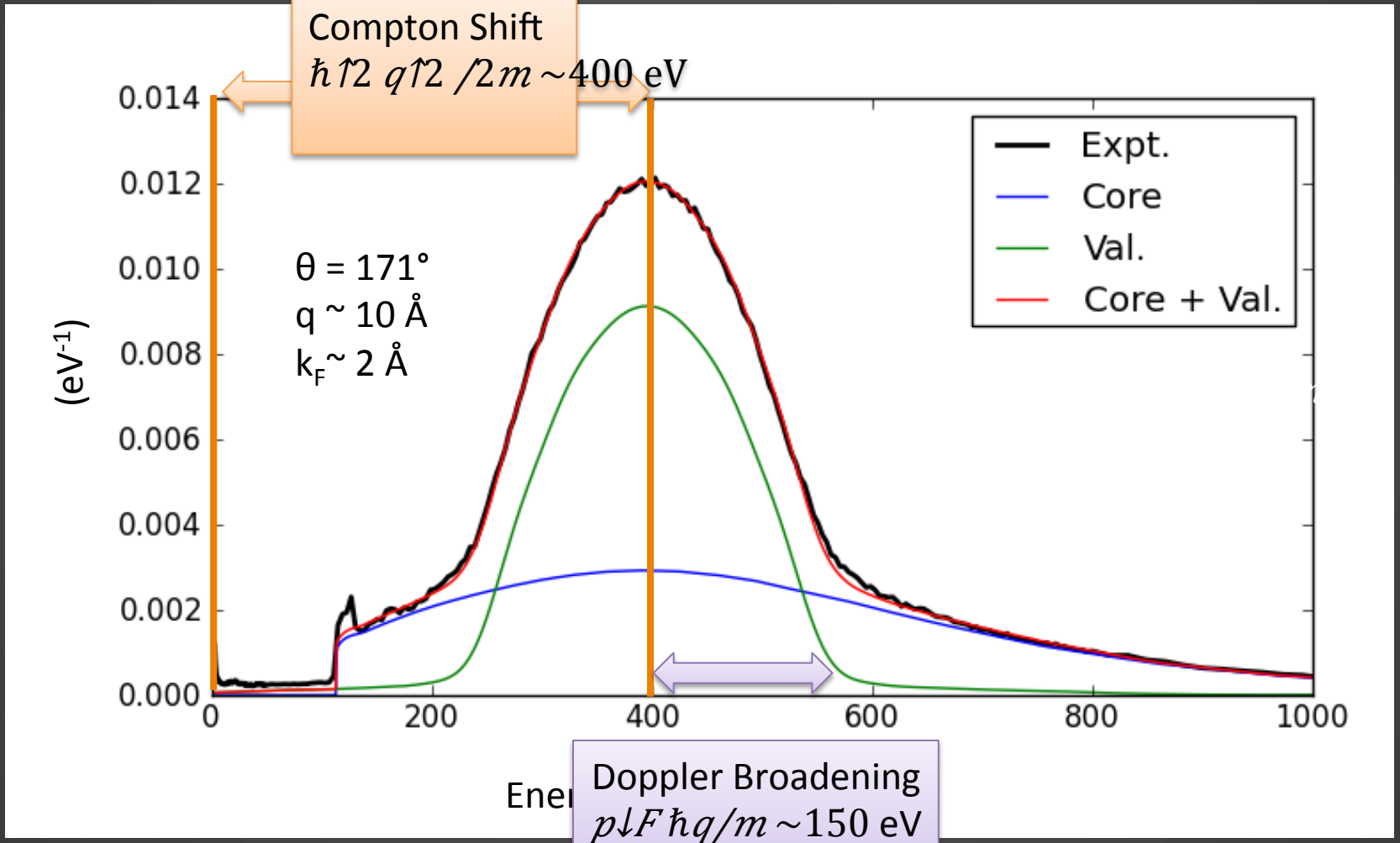
2p->1s fluorescence observed from different ionization states (labeled by Roman numerals)

Ciricosta, et al. PRL **109**, 065002 (2012)

High-resolution NIXS data



Impulse Approximation:
NIXS as Doppler-broadened Compton Scattering



Impulse Approximation (IA)

For large energy- and momentum transfer,
potential energy before and after scattering cancel.

$$\omega=(p+q)^2/2m+V-p^2/2m-V=q^2/2m+p\cdot q/m$$

Compton Shift
(set by *kinematics*)

Doppler Shift
(depends on *material state*)

Dynamic structure factor simplifies:

$$S(q,\omega)=m/q\ J(p_q)$$

Compton Profile (CP): $J(p_q)=\int d^3p\ \rho(p)\ \delta(p\cdot q-p_q)$

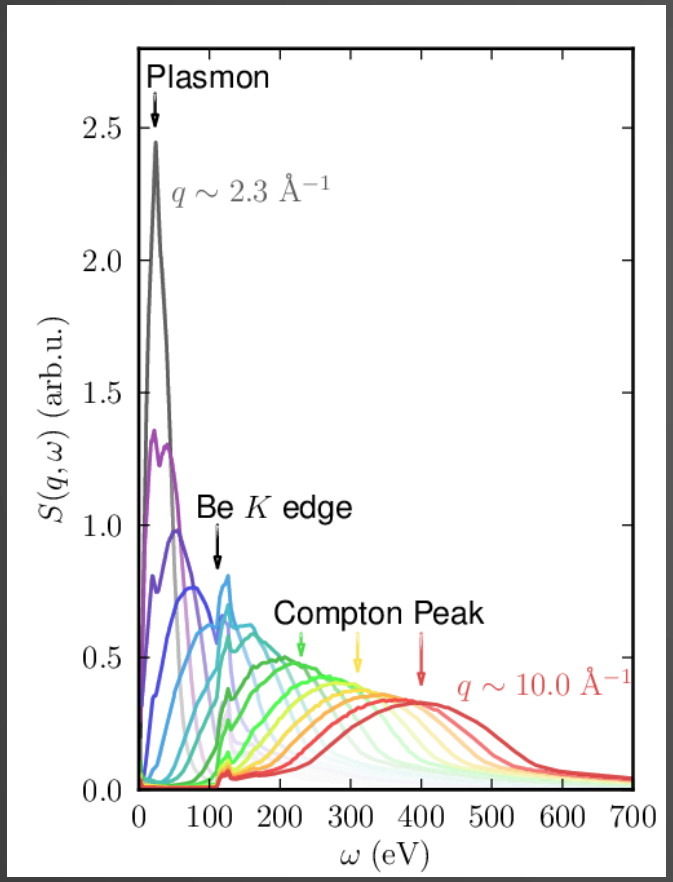
$$p_q\equiv p\cdot q=\omega m/q-\hbar q/2$$

Density of electrons with a given projection of momentum along q

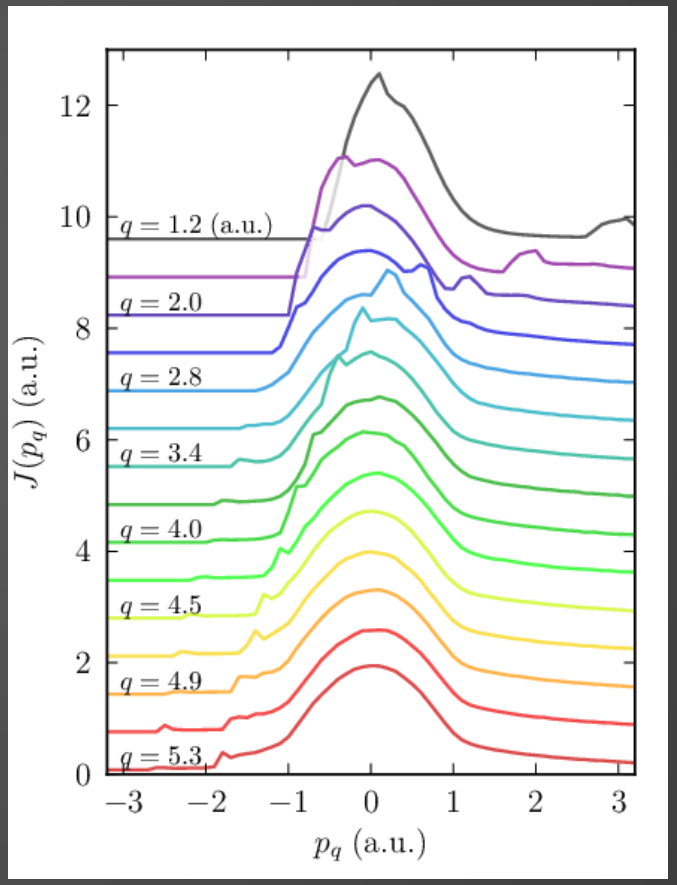
Scattering spectrum is entirely determined by electronic momentum distribution $\rho(p)$

Impulse Approximation (IA)

$S(q,\omega)$



$J(p_q)$



$S(q,\omega) = m/q\ J(p_q)$ $\quad p_q \equiv \omega m/q - \hbar q/2$

Mattern, *et al.* PRB 85, 115135 (2012)

Impulse Approximation (IA)

$J(p \downarrow q)$

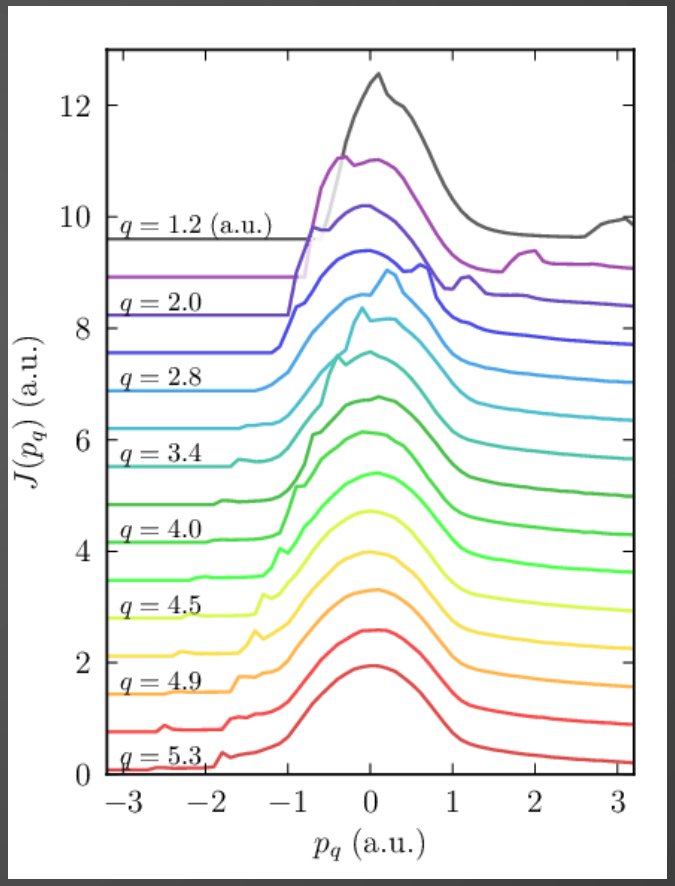
invalid

($q \sim 1/a$, collective/interband transitions important)

Impulse Approximation

valid

(for valence, and core at large p_q)



Mattern, *et al.* PRB 85, 115135 (2012)

The story so far

- NIXS at high *q* is directly determined by the electronic momentum distribution n(p)
- n(p) depends on both temperature and density
- So, one can in principle extract T and n_e from the NIXS spectrum…
- … provided one knows ***how*** n(p) depends on these parameters

Thus, need *accurate* calculations of WDM electronic structure

AND

Need alternative independent metrics for calibration / validation

The Born-Mermin Approximation (BMA): Fermi Gas + Perturbative corrections

- Start with free electron gas
- Calculate dielectric function $\epsilon(q,\omega)$ in *random-phase approximation (RPA)*
- Include electron-ion interactions in $\epsilon(q,\omega)$ by introducing a *dynamic collision frequency* calculated in the first-Born approximation
- Use *fluctuation-dissipation* theorem:

$$S(q,\omega) \sim q^2 / 1 - e^{-\hbar\omega / kT} \, \mathrm{Im} 1/\epsilon(q,\omega)$$

Non-perturbative electronic structure

FEFF

- Input: cluster of atoms at arbitrary locations

- Self-consistently solve for valence-electron Green's function starting with overlapped atomic potentials (including exchange-correlation in the *local density approximation*)

- Output:
  - Density of States
  - X-ray Absorption Spectra
  - X-ray Emission Spectra
  - Electron Energy-Loss Spectra (EELS)
  - …
  - Core-shell NIXS
  - Valence NIXS (Compton profile)

FEFF: Real-space Green's Function

- Input: cluster of atomic sites (arbitrary)
- Intermediate: Green's function $G(r,r';E)$
- Output:
  - Densities of States
  - X-ray Absorption Spectra
  - X-ray Emission Spectra
  - Electron Energy-Loss Spectra (EELS)
  - Core-shell NIXS
  - Valence NIXS (Compton profile)

Why is FEFF suited to WDM?

- All-electron (with accurate Dirac-Fock core states)
  - Valence states are orthogonal to cores
- Real-space: no requirement of translational symmetry
- Can handle large clusters (~500 atoms)