Multi-Center Electronic Structure Calculations for Plasma Equation of State

Computational Challenges in Warm Dense Matter

Institute for Pure& Applied Mathematics (UCLA)

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Brian Wilson (LLNL)
Duane Johnson (DOE AMES)
Dan Finkenstadt (USNA)

Lawrence Livermore National Laboratory

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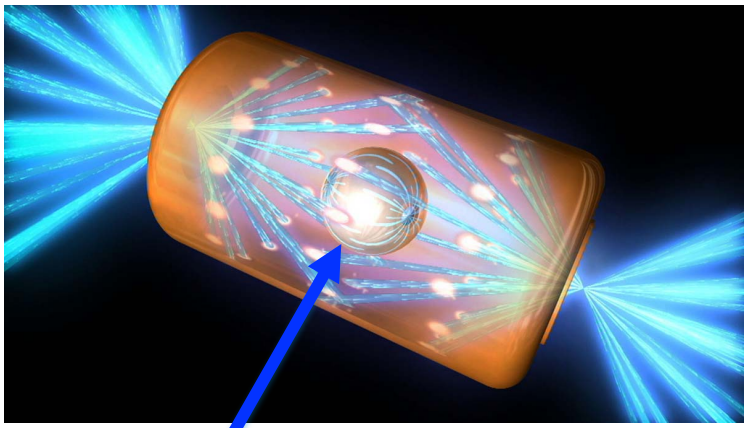
Outline

- INFERNO-like models: What are they and what's wrong with it.
- Be a KKR expert in 7 vufoils!
- Implementation and challenges for plasmas, basic multi-center effects, and approximations

Why do you care about dense plasmas?

- Dense plasma regimes are of interest in many of our applications: ICF, LCLS, pulsed power,…

- Hydrodynamic modeling requires an equation of state (EOS) as well as transport coefficients



Dense fuel
rho-R ~ 2 g/cm^2
rho~ 1000 g/cc
T~ 100's eV

The standard approach in SESAME

- Assume the total EOS is composed of three parts which can be computed separately

$$P(\rho,T) = P_e(\rho,T) + P_i(\rho,T) + P_c(\rho)$$

$$E(\rho,T) = E_e(\rho,T) + E_i(\rho,T) + E_c(\rho)$$

→ In general, the pressure and energy do not separate into additive contributions

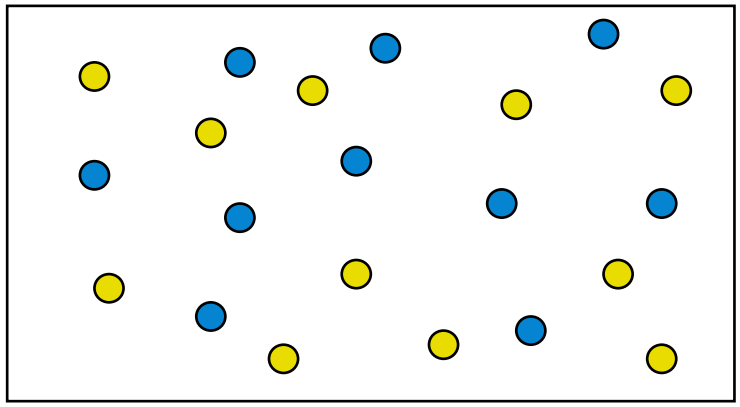
- Electron thermal contribution → Average Atom
- Ion thermal contribution
  1. Solid Region - Debye Theory
  2. Above melting - Interpolate smoothly to Ideal Gas
- Cold curve → Fit to shock data

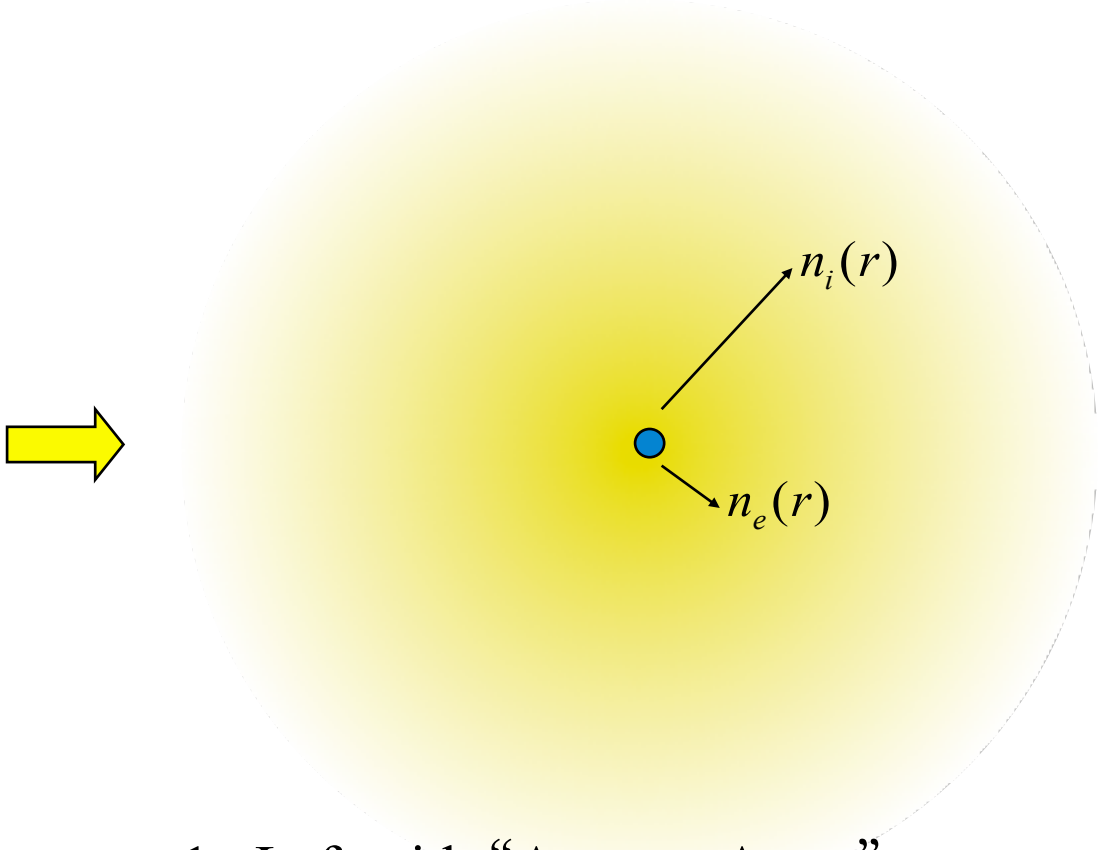
Weakness

1. High-Z material can be strongly coupled even at T > 10 keV
2. Shock data is typically less than 1 eV
3. Large intermediate range to rely on interpolation
4. Relatively small differences in the EOS are sometimes interesting for High Energy Density applications.

Average Atom Model

1. Reference frame on ion
2. Ensemble average

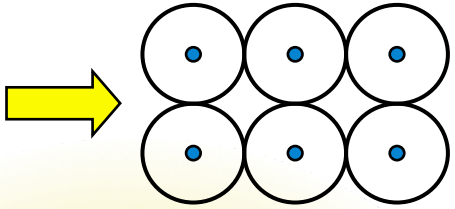




1. Left with "Average Atom"
2. Spherically symmetric
3. Fractional bound charge
4. Charge cloud $n_i(r)$ and $n_e(r)$

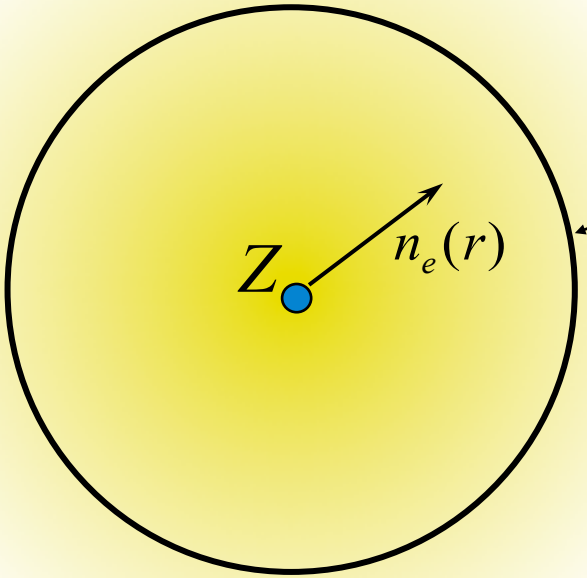
Standard Approach - Ion cell model

Confine each ion to a cell



$$2a = 2\left(\frac{3}{4\pi n_i}\right)^{1/3}$$

Each cell contains Z electrons and is charge neutral



$$E = -\frac{\partial V}{\partial r} = 0$$

Function of V(r)
1. Thomas-Fermi
   SESAME
2. Kohn-Sham
   INFERNO

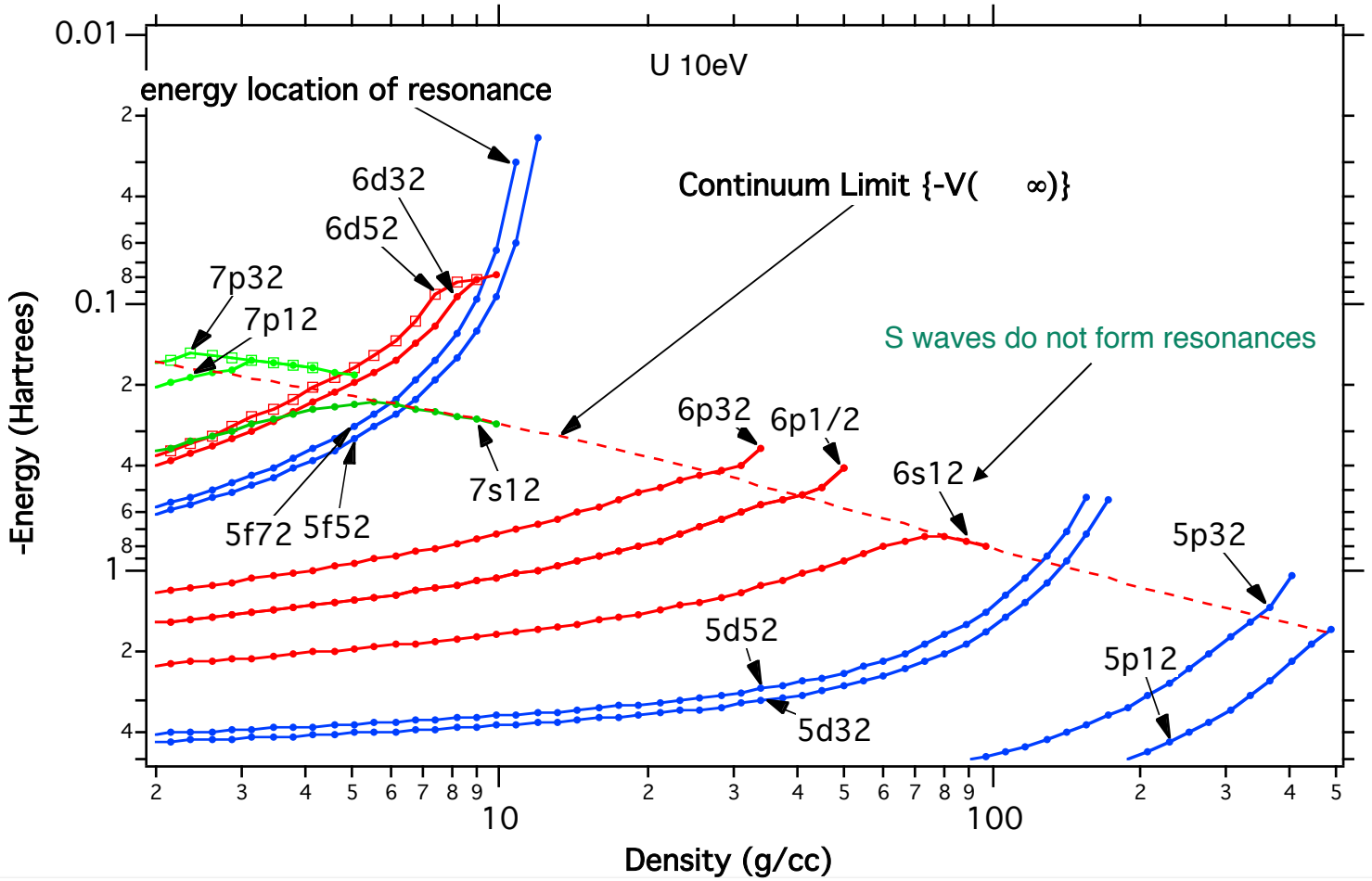
Solve for self-consistent potential

$$-\nabla^2 V(r) = 4\pi Ze\delta(r) - 4\pi e n_e(r)$$

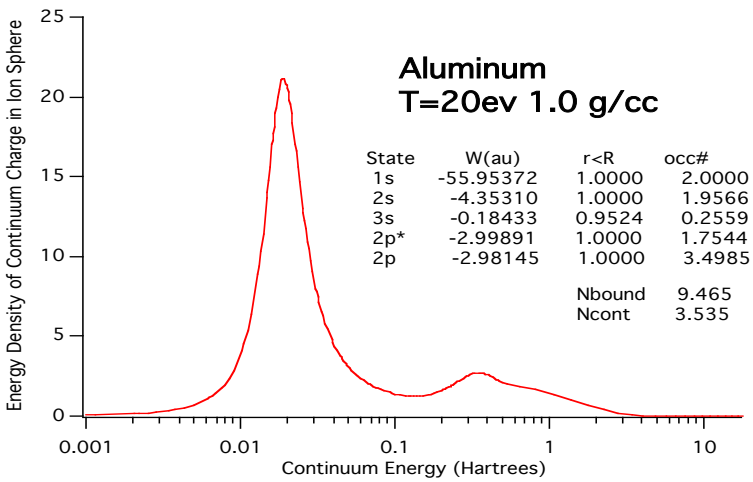
Approach only gives electron contribution to EOS !

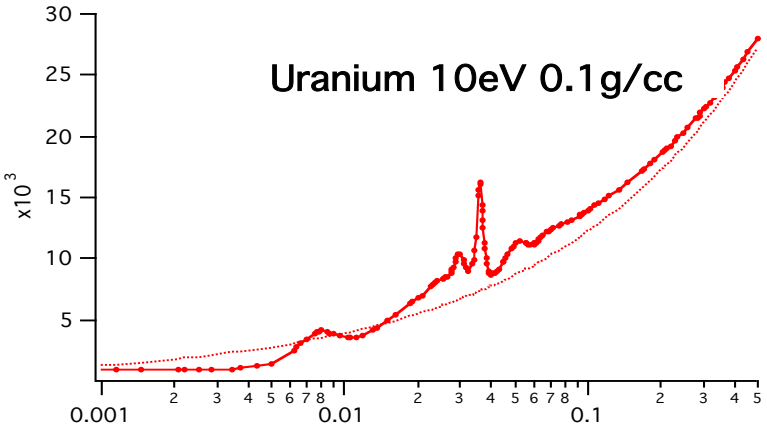
A Quantum treatment of continuum electrons is key to accurate EOS

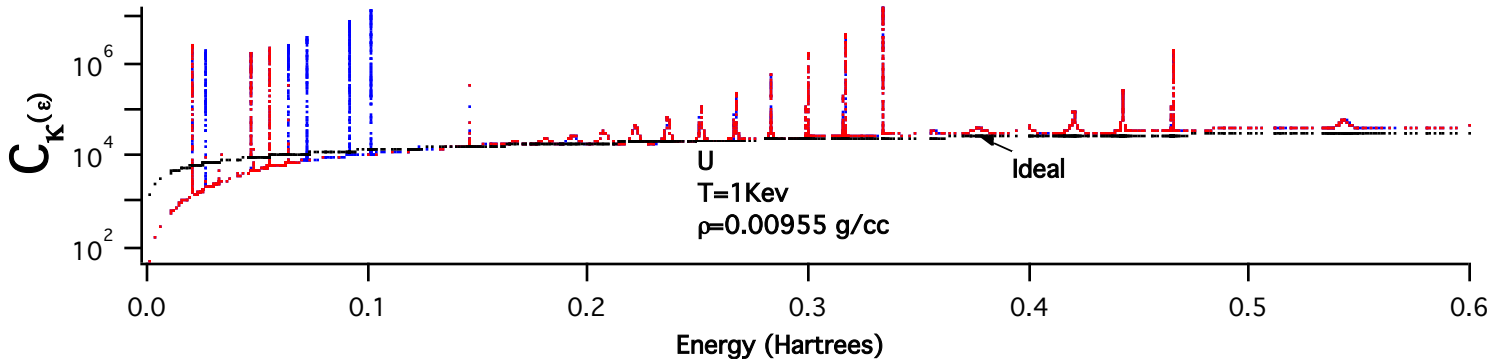
One must be able to follow bound states as they are pressure ionized and reappear as resonances in the continuum.



Resonances hold charge that can change Z* by several electrons

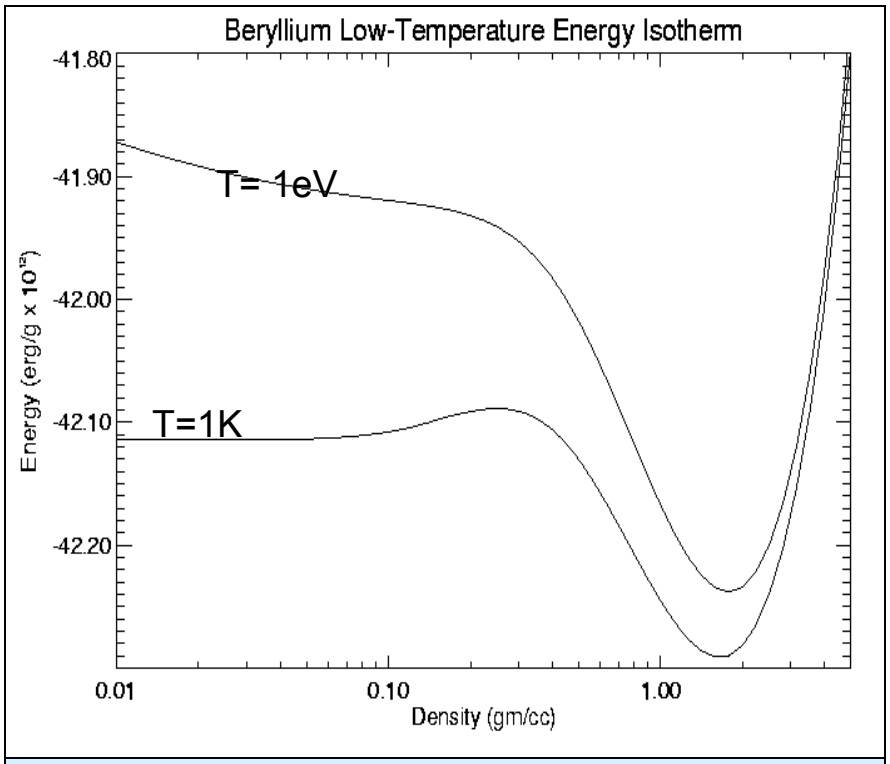




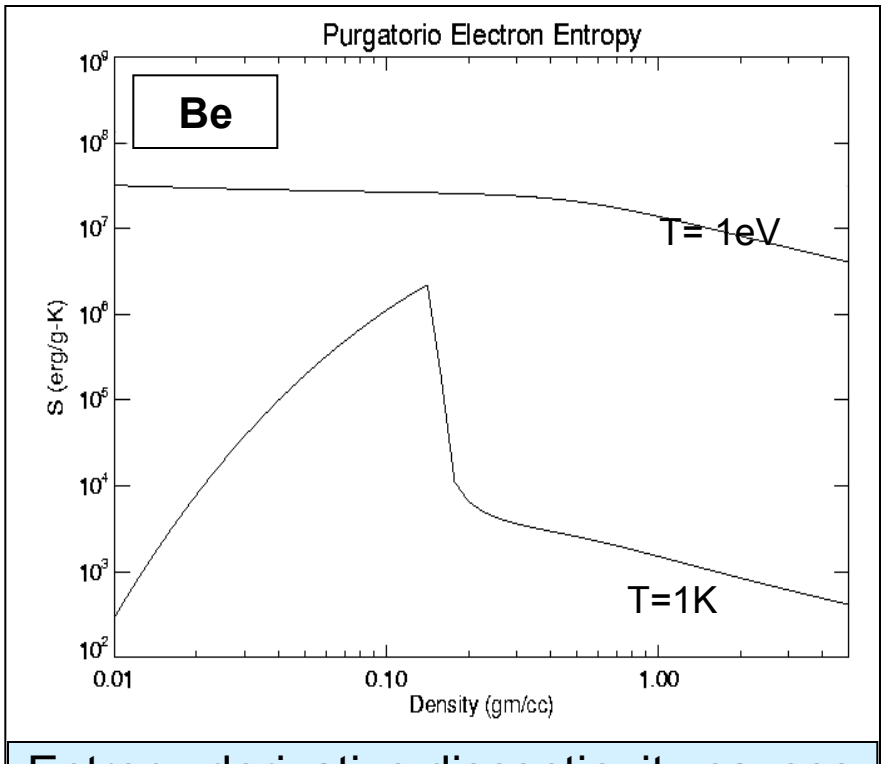


But do complex resonance structures exist in a more realistic plasma model?

Ion sphere energies and entropies show anomalous behavior at low T



Unphysical peak in energy between atomic limit and energy minimum



Entropy derivative discontinuity causes problems when differentiating free energy to calculate pressure

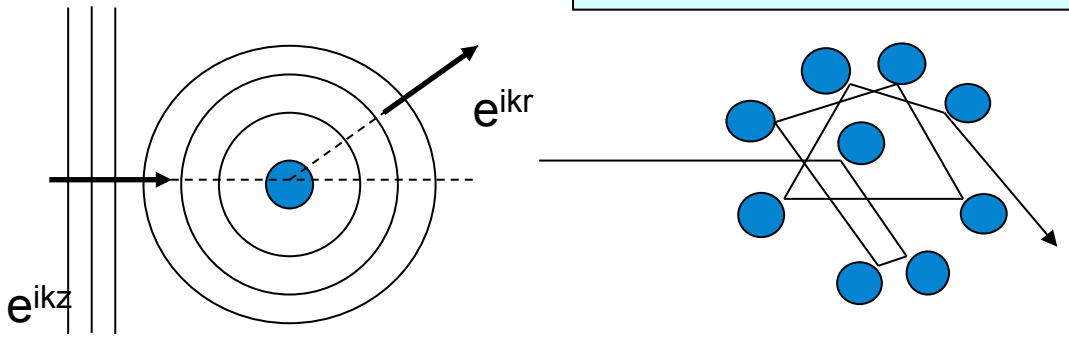
When bound states extend outside the sphere, compensating charge must come from the continuum

Wave tails leaking out of (and into) sites is the physics of valence band formation

- The same physics has an analogue in the continuum – *which must be treated on the same footing* - multiple scattering of the continuum electrons

In the Hot dilute plasma regime a single "ion-in-jellium" along with ideal gas mixing of components is adequate

In the Warm Dense Matter regime the wave-function behavior strongly reflects the influence of multiple ion-centers



Single site *Multiple sites*

- single scatterer
  - ➔ single scattering event
  - ➔ analytic solution

- two or more scatterers
  - ➔ *infinite* number of possible scattering events
  - ➔ recursive solutions required for wave functions

We want a formalism to bridge from the cold solid state to hot plasmas

- All electron (no pseudo-potentials)
  - Continuous in T & ρ
  - Can reach very high T limit
- No ad hoc continuum lowering models
- Ab-initio plasma mixtures
- Can obtain accurate spectral properties and energetics
- Can be straightforwardly parallelized

A Typical DFT Toolbox

Gaussian DFT "The Chemist Code"

Linear Combination of Gaussian Orbitals:

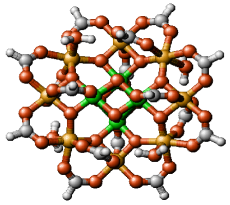
MR Pederson, DV Porezag, J Kortus and D.C. Patton, Phys. Stat. Solidi B 217, 197 (2000).

Gaussian basis: $\Psi(\mathbf{r}) = \Sigma_i C_i \exp[-\alpha_i(\mathbf{r}-\mathbf{R_i})^2]$.

Massively parallelized over molecule symmetry.

Relaxes molecular structures, not crystals.

(i.e. no periodic boundary conditions).



NRL-Tight Binding "The Quick & Dirty"

NRL tight-binding method: http://cst-www.nrl.navy.mil/bind/dodtb/

Slater-Koster parametrization, fit to Linearized Augmented Plane Wave (LAPW) calculated structural database.

TBMD (Molecular Dynamics)

Scales favorably w/ >1000 atoms.

MD ran for a duration of 10,000+ configs.

VASP "The Right Answer?"

Vienna Ab-initio Simulation Package:

Phys. Rev. B **59**, 1758 (1999).

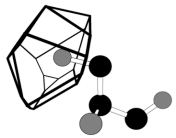
Pseudopotential plane-waves, e^{ikr} basis.

Ultrasoft Pseudopotentials. *Phys. Rev. B* **41**, 7892 (1990).

GGA/LDA: E_{xc} Ceperley & Alder *Phys. Rev. Lett.* **45**, 566 (1980).

Cluster Expansion

KKR "The Elegant Method"



Korringa-Kohn-Rostoker method:

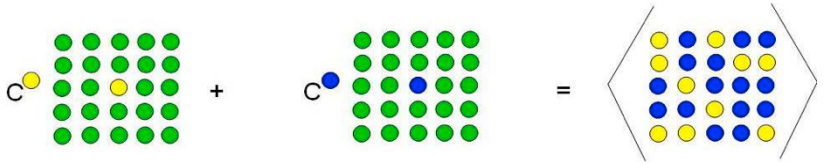
Physica **13**, 392 (1947) ; *Phys. Rev.* **94**, 1111 (1954)

Max. L=3 (s-, p-, d-, f-symmetry), $Y_{lm}(\theta,\phi)$ basis.

Parallelized over complex energies (E-pts).

GGA/LDA: . *J. Phys. Condens. Matter* **5**, 1629 (1972).

CPA (Coherent-Potential Approximation) treats site disorder, in a mean-field approx.



What is KKR

Walter Kohn

•**Korringa – Kohn – Rostoker** [1][2]

•It is a ***Green's function*** method, not a wavefunction method, for the solid-state electronic properties: DOS, ρ(r), band structure

$$\left(E - H\right)G(\vec{r},\vec{r}';Z) = \delta(\vec{r} - \vec{r}')$$

•Green's function is expressed in terms of multiple locally spherically symmetric coordinate systems

•The choice to calculate the Green's function, rather than the wavefunction, allows a certain degree of flexibility in calculations, e.g., having disorder & finite temperature !

[1] *Physica* **13**, 392 (1947) ; [2] *Phys. Rev.* **94**, 1111 (1954).

Densities and (most other) expectation values evaluate from G(r,r';E)

Density of States

$$n(E) = -\frac{\mathrm{Im}}{\pi}\int d\vec{r}\; G(\vec{r},\vec{r},E)$$

Particle Density

$$\rho(\vec{r}) = -\frac{\mathrm{Im}}{\pi}\int_{E_b}^{E_f} dE\; G(\vec{r},\vec{r},E)$$

Expectation Values (onsite)

$$< A >= -\frac{\mathrm{Im}}{\pi}\int_{E_b}^{E_f} dE \int_V d\vec{r}\; A(\vec{r};E)G(\vec{r},\vec{r},E)$$

The elegance of KKR arises from analyticity of the Green's Function

Extend real energies E into complex energies Z!

$$(Z - H)G(\vec{r},\vec{r}';Z) = \delta(\vec{r} - \vec{r}') \qquad G(\vec{r},\vec{r}',Z) = \lim_{\varepsilon \to 0} \sum_i \frac{\psi_i(\vec{r})\psi_i^{\dagger}(\vec{r}')}{Z - E_i + i\varepsilon}$$

G is analytic with no poles in the upper-half plane for Im Z ≠ 0.

Muller-Hartman (1967)
Herglotz properties of G

$$G^{\dagger}(\vec{r}',\vec{r};Z^*) = G(\vec{r},\vec{r}';Z)$$

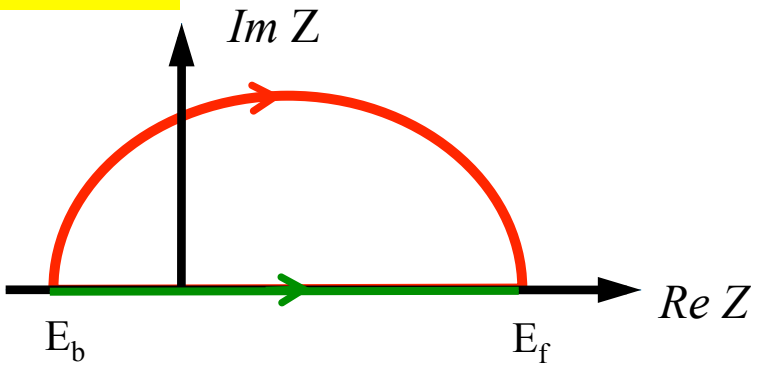
Thus, we may distort the linear integral on real E to some convenient contour to perform the integrals and obtain charge density for self-consistency of G.

FEWER POINTS ARE NEEDED OFF THE REAL AXIS!

$$\rho(\mathbf{r}) = -\frac{\mathrm{Im}}{\pi}\int dE\, G(\mathbf{r},\mathbf{r};E) \equiv -\frac{\mathrm{Im}}{\pi}\oint dZ\, G(\mathbf{r},\mathbf{r};Z)$$

Linear Real E

Contour with Complex E



Evaluating the Green's Function

Given in terms of regular and irregular waves about each center:

$$G\ (\vec{r}_n,\vec{r}'_m;E)=\sum_{LL'}\ \{Z_L(\vec{r}_n;E)\tau^{nm}_{LL'}(E)Z^{\dagger}_{L'}(\vec{r}'_m;z)-\delta_{nm}Z^{\dagger}_L(\vec{r}_n;z)J^{\dagger}_L(\vec{r}'_n;z)\}$$

And the scattering path operator is given by a Dyson eqn:

$$\tau^{nm}(E)=t^n(E)\delta_{nm}+t^n(E)\sum_{k\neq n}G^{nk}_0(E)\tau^{km}(E)$$

Single site scattering

Structure constants
"stitch the centers together"

with $\left[t^n\right]_{LL'}=t^n_L\delta_{LL'}$ $\left[\tau^{nm}\right]_{LL'}=\tau^{nm}_{LL'}$ $\left[G^{nm}_o\right]_{LL'}=G^{nm}_{o,LL'}(1-\delta_{nm})$

NOTE: even when single site scattering 't'-matrix is diagonal, τ is NOT!

Solving for the Scattering path matrix

- For finite collection of scatterers, matrices are finite

$$\tau(\vec{k};E) = t(E) + t(E)G_o(\vec{k};E)\tau(\vec{k};E)$$

$$\tau(E) = \left[1 - t(E)G_o(E)\right]^{-1} t(E) = \left[t^{-1}(E) - G_o(E)\right]^{-1}$$

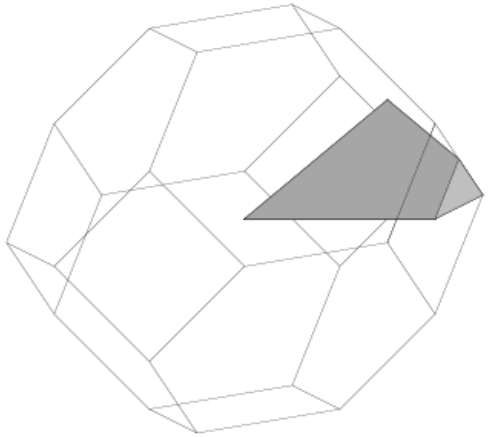
Matrix dimensions for τ, t, and G_0 are $N_{scatterers}(l_{\max}+1)^2$

- For infinite periodic array of scatterers, matrices use Fourier transforms

$$\tau^{nm}(E) = \frac{1}{\Omega_{BZ}}\int_{\Omega_{BZ}} d\vec{k}\ \tau(\vec{k};E) = \frac{1}{\Omega_{BZ}}\int_{\Omega_{BZ}} d\vec{k}\ \left[t^{-1}(E) - G_o(\vec{k};E)\right]^{-1} e^{-i\vec{k}\bullet(\vec{R}_n - \vec{R}_m)}$$

If $G_0(k;E) \sim G_0(k;E_{ref}) + D(k;E_{ref})(E-E_{ref})$ one obtains LMTO tail-cancellation theorem.

Brillouin-Zone Integrations



$$\tau^{nm}(E) = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\vec{k} \left[t^{-1}(E) - G_o(\vec{k};E) \right]^{-1} e^{-i\vec{k}\bullet(\vec{R}_n - \vec{R}_m)}$$

Symmetry in periodic solid permits use of irreducible wedge

K-space integrand can be independently evaluated on parallel processors

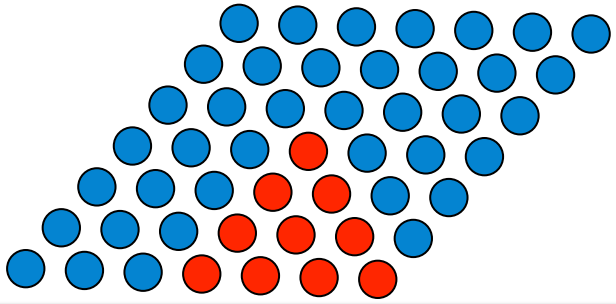
Special-Point Sampling Methods

Monkhorst-Pack method can be used but less reliable near Real E axis because you are sampling a function with a pole with finite points. Ray Method better.

$$\tau^{nn}(E) = \sum_{s=1}^{h} U^s \tau^{nn}_{1stBZ}(E)(U^s)^{\dagger}$$

$$\tau^{nn}_{1stBZ}(E) = \sum_{\vec{k}} w_{\vec{k}} \tau\ (\vec{k};E)$$

Special point meshes in IBZ



Where has all the KKR gone or come from?

A good book:

Electron Scattering in Solid Matter (Springer 2005)

By Zabloudil, Hammerling, Szunyogh, Weinberger

KKR researchers:

D.D. Johnson (Ames), J. Rehr (Seattle), G.M. Stocks and W.A. Shelton (ORNL), B.L. Györffy (Bristol), J.B. Staunton (Warwick), P. Weinberger (Wien), P. Dederichs and R. Zeller (Jülich), B. Ginatempo (Messina), …

Extension to Free-Energy at Finite-Temperatures is straightforward

- Generalize the band energy

$$E_{band} = -\frac{\mathrm{Im}}{\pi}\oint dZ\,\left(Z - E_f\right)G(Z)f(Z)$$

Fermi Factor

$$f(Z) = \left(1 + e^{-\beta(Z-E_f)}\right)^{-1}$$

- Determine F(T) = E(T) – TS(T) via Electronic Entropy

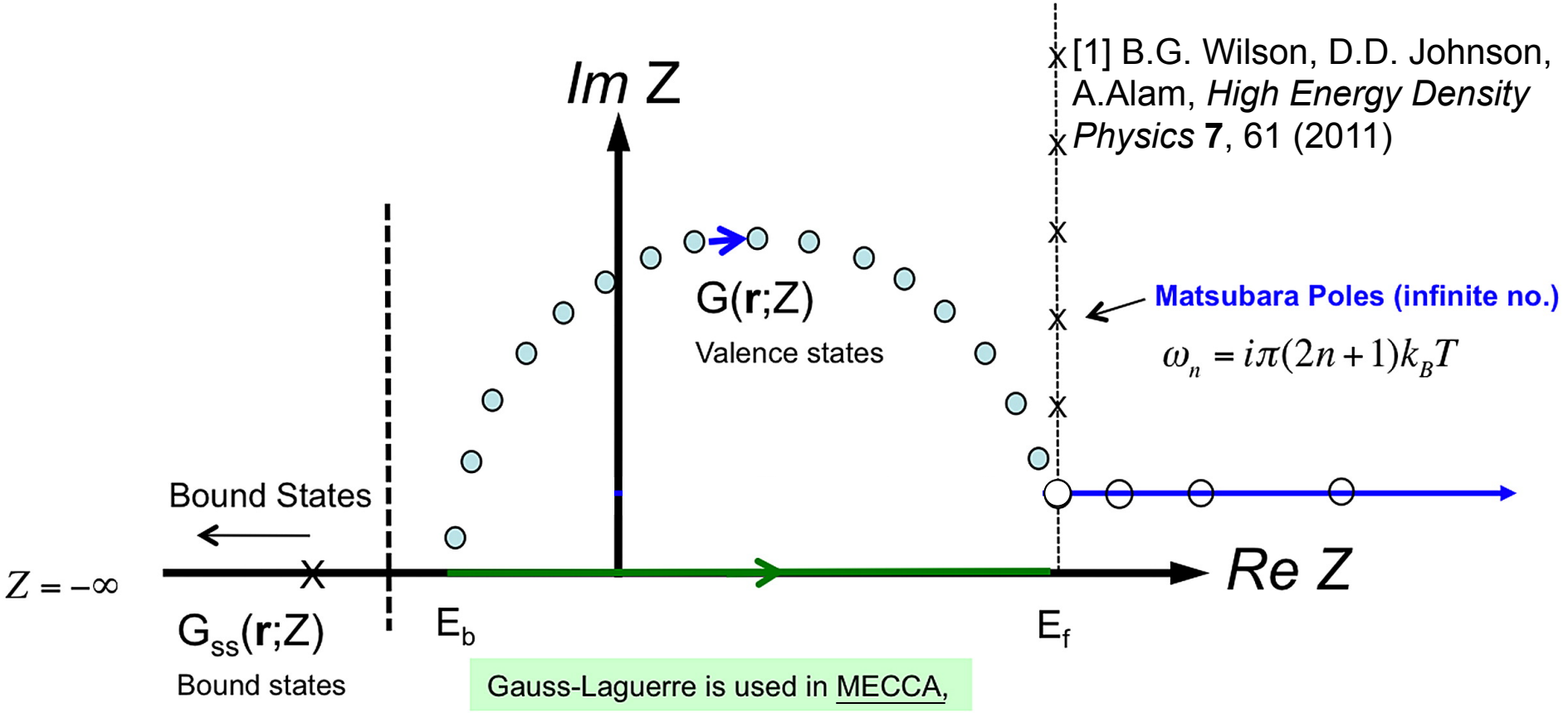
$$S(T) = f(Z)\ln f(Z) - (1 - f(Z))\ln(1 - f(Z))$$

- Use contour that encloses energy infinity and beware Matsubara (fermi) poles

- Complex Energy Integration: Zeller et al., Solid State Comm. 44, 993 (1982)
- Simple contour: Johnson et al., Phys. Rev. B 30, 5508 (1984)
- simple Finite-T contour: Pinski and Stocks, Phys. Rev. B 32, 4204 (1985)
- Free Energy and Stationarity: Nicholson et al. PRB 50, 146186 (1994)
- Approximating Occupation Functions: Nicholson and Zhang, PRB 56, 12805 (1995)

Finite-T Contours in MECCA KKR code

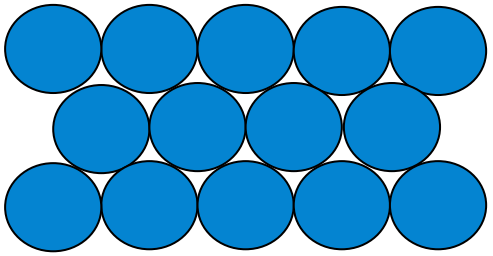
$$\oint dZ\ f(Z)G(r;Z) = \sum_{bs} n_{bs} - \frac{\mathrm{Im}}{\pi}\oint dZ\ f(Z)G\ (r;Z)$$



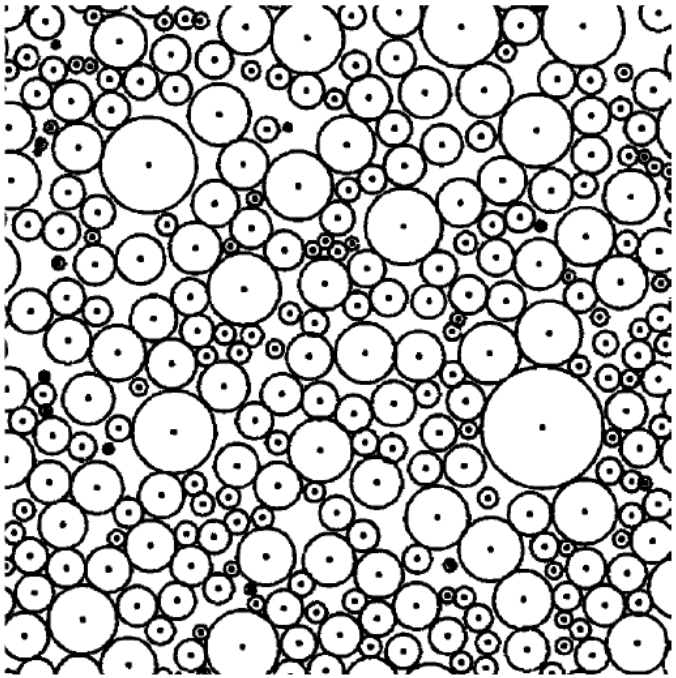
- Independent evaluations of energy points can be farmed to parallel processors
- Automate distinction between 'deep' core and valence

But plasmas are not crystals of hot electrons

Many crystals are close-packed systems (fcc, bcc, & hcp)
Most of the space is filled by atomic spheres



KKR works best when the system is close packed, otherwise *we have to pack the system with empty spheres to fill space*



In a plasma we don't have periodicity and the luxury of Bloch's theorem

One must generate positions and radii.

Approximating plasmas with spatially amorphous systems

There are three approaches:

1. Generate ensembles of ion spatial configurations
   - Many and/or large clusters (super-cells)
   - Higher T plasmas access higher angular momentum channels
   - Computationally challenging

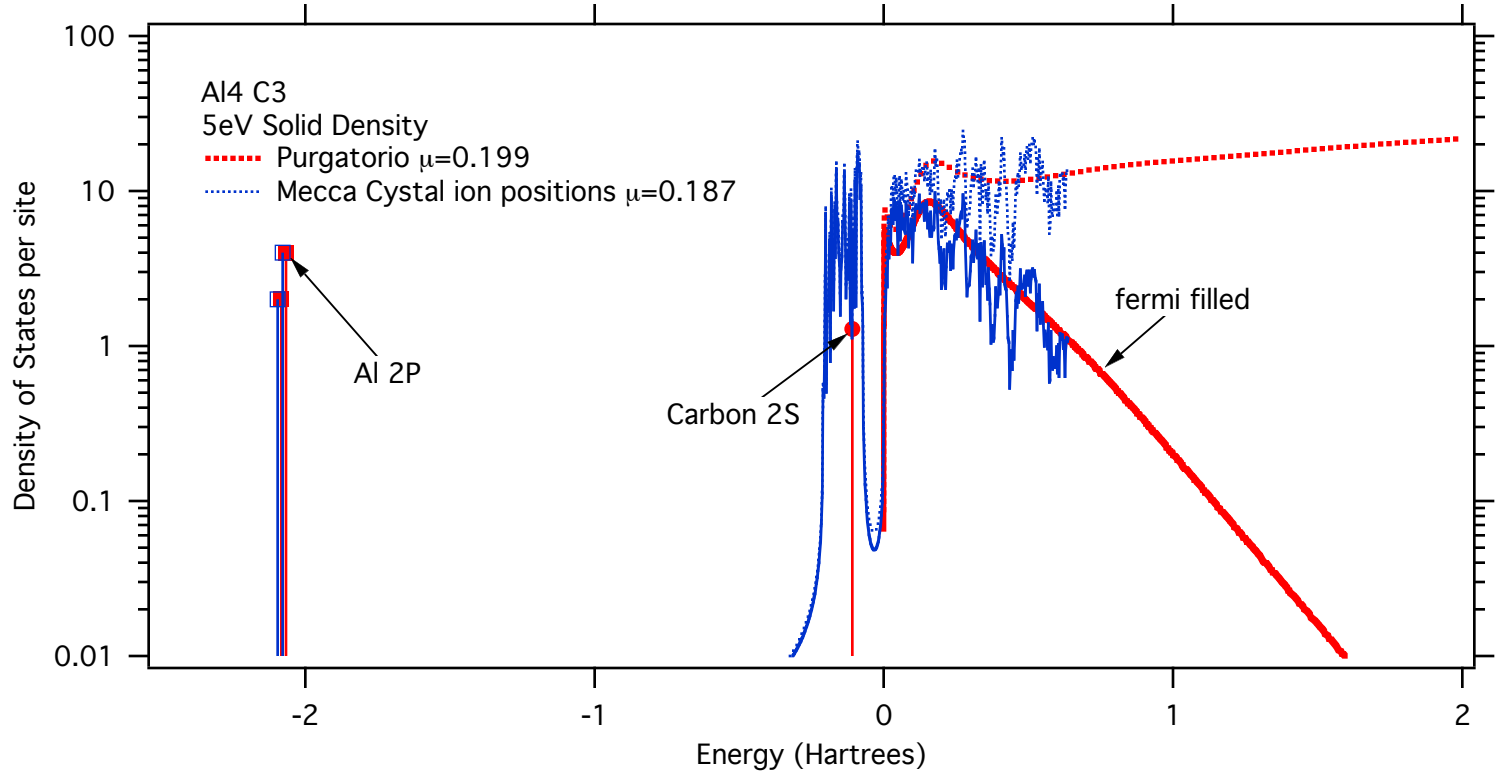
- **Pre-conditioning for Inversion of Complex non-Hermitian Matrices**
  - **Standard iterative methods (e.g., GMRES and TF-QMR)**
    For Im E small, G(E) requires extremely large N_{iter}, making them slower than direct inversion (if memory were available, which it is usually not for N > 400). GMRES is too memory intensive, while CG methods are much slower than Transpose-Free Quasi-minimal residual (QMR) methods.
  - **"Cluster inverse" approximation**
    A physical-based direct inversion of a diagonal block of the sparse (real-space) matrix to get an approximate G_{ii} . Fails near real E because G does not just depend on the band-diagonal elements.

Electronic Properties:Aluminum Carbide

An interesting case study because of the nominal presence of shallow Carbon 2S states

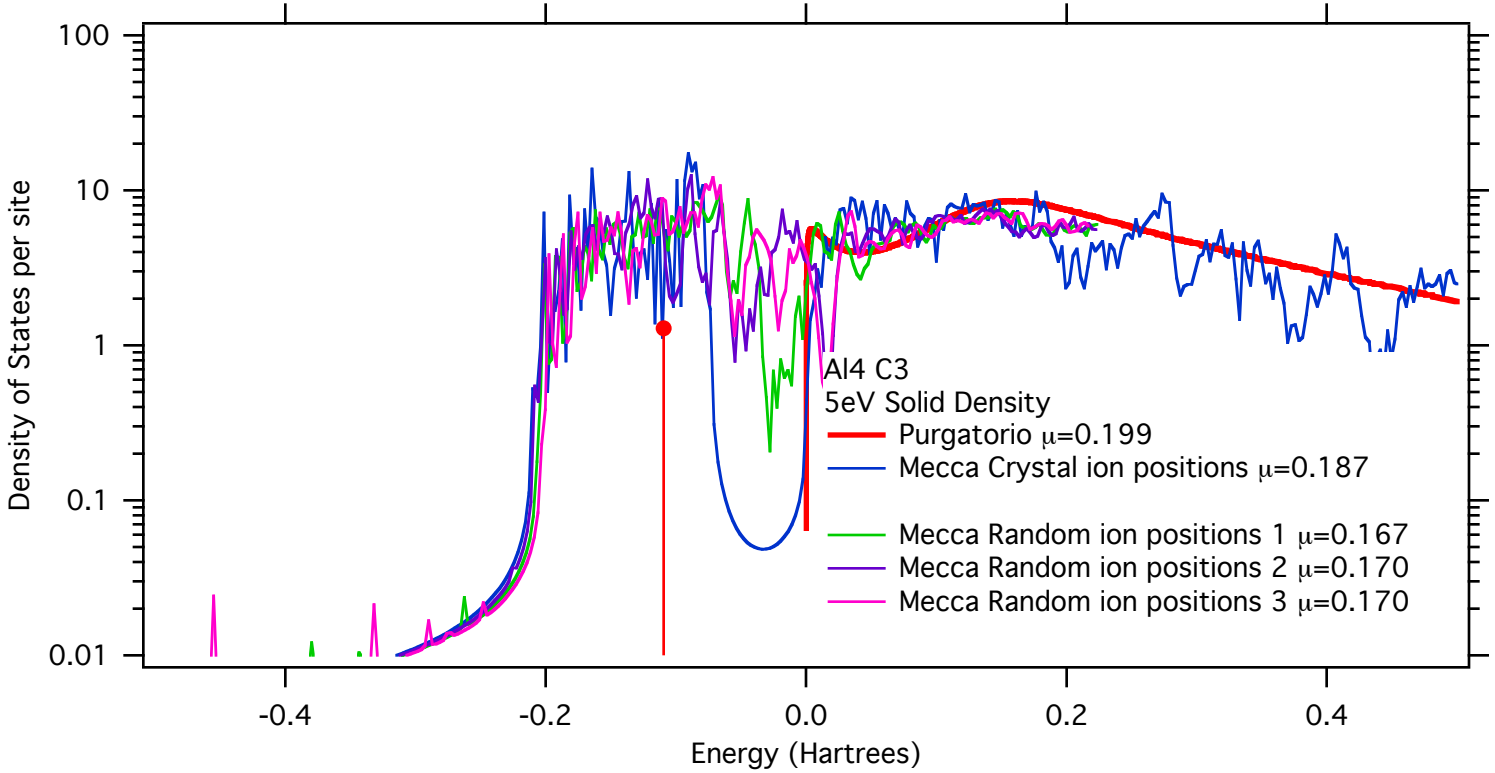
In the warm dense matter regime Purgatorio will predict shallow bound states and a smooth density of states near the bound-free threshold.

A more realistic multi-center scattering model predicts the shallow bound state is actually a band, and the simple bound free edge will show considerable structure



Electronic Properties:Aluminum Carbide

Along with electron heating the ion structure becomes amorphous – filling in the band gap



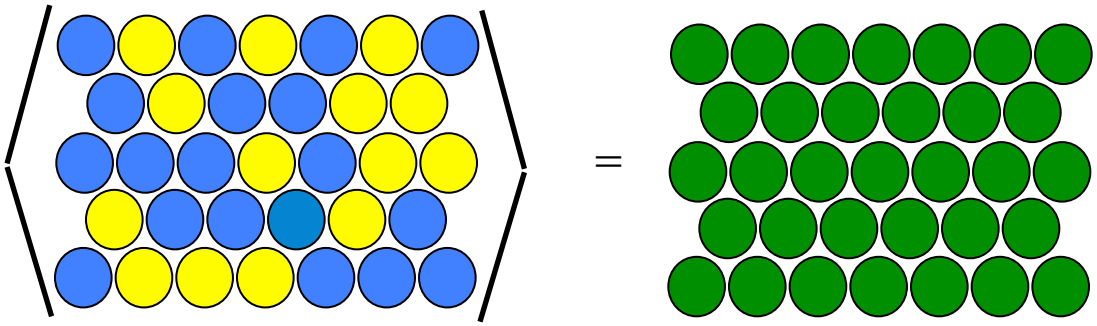
- **The chemical potential for the amorphous samples are in close agreement and indicate adequate micro-canonical sampling**
- **The amorphous ion positions contribute a 1ev linewidth onto the Al 2p bound states**

Approximating plasmas with spatially amorphous systems (cont.)

There are three approaches:

2. Approximate by a substitutionally disordered crystal structure

The Coherent Potential Approximation represents the electronic structure of a configurationally averaged random $A_{1-c}B_c$ alloy

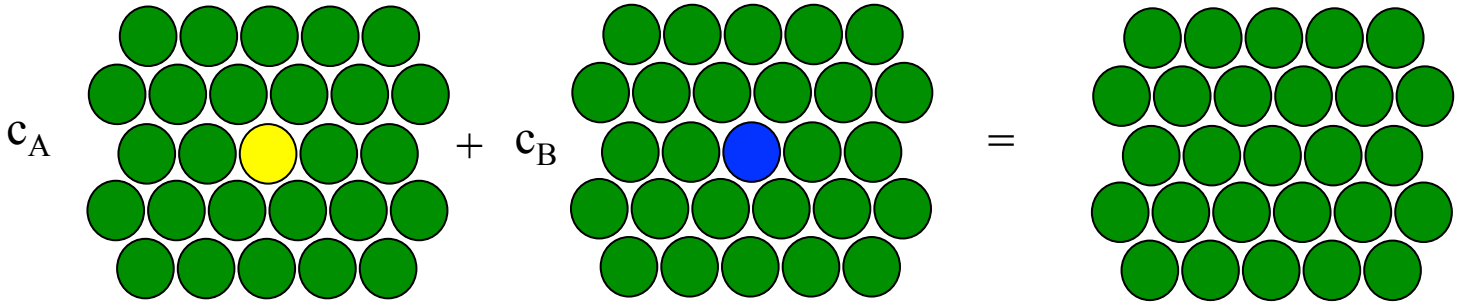


Use mean-field approach
Find optimal single-site medium

The Coherent Potential Approximation: KKR-CPA

Single-Site Effective Medium Theory:

Placing an atom A or B into the CPA medium should, on average, produce no additional scattering



CPA condition

$$c_A \tau_A^{00}[t_A, t_{CPA}] + c_B \tau_B^{00}[t_B, t_{CPA}] = \tau_{CPA}^{00}[t_{CPA}]$$

Find t_{CPA}

Where the Projected Scattering Path Operator is

$$\tau_\alpha^{00} = \tau_{CPA}^{00}\left[1 + \left(t_\alpha^{-1} - t_{CPA}^{-1}\right)\tau_{CPA}^{00}\right]^{-1} = \tau_{CPA}^{00} D_\alpha$$

CPA
P. Soven, Phys. Rev. 156, 809 (1967)

KKR-CPA variational energy and free energy
Johnson et al., Phys. Rev. Lett. 56, 2088-91 (1986); Phys. Rev. B 41, 9701-16 (1990).

Results for warm compressed Aluminum

- We will compare three *guesses* for the structure of WDM:

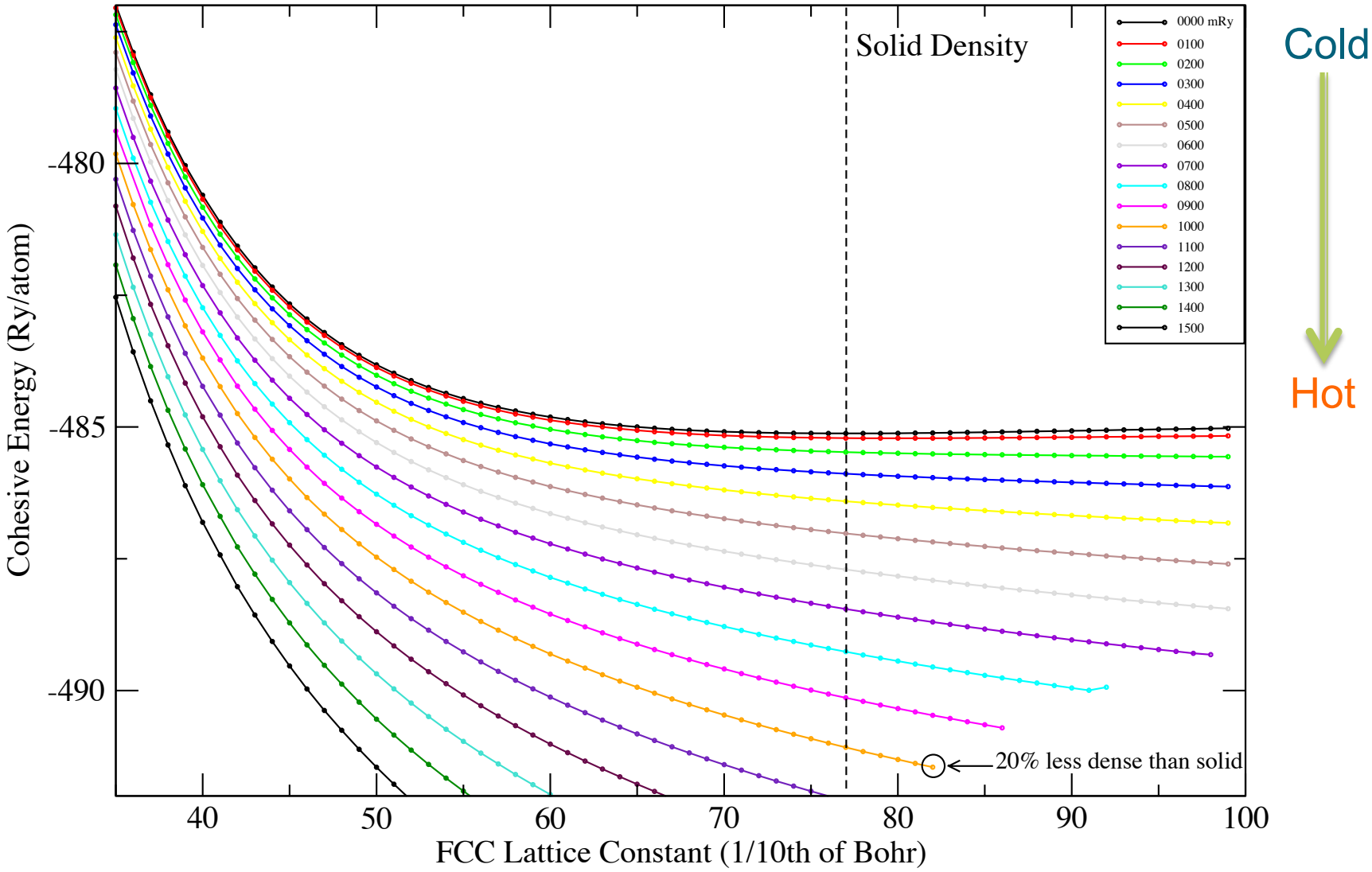
  1. plasma ≈ close-packed FCC. (at least locally & at high ρ)

  2. plasma ≈ avg. of random 12- and 36-atom unit cells.

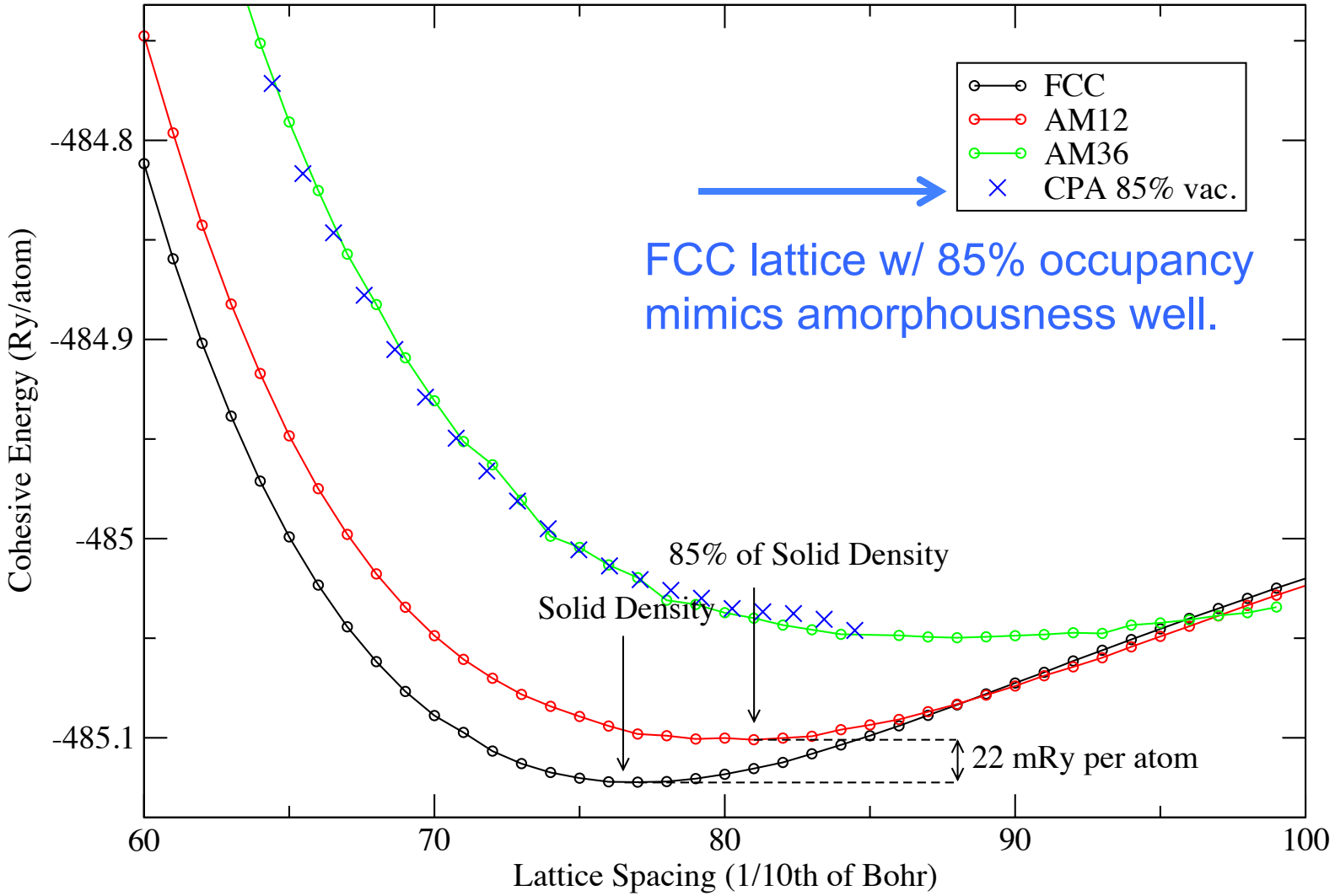
  3. Amorphous ≈ FCC w/ substitutional disorder:
     vacancies, impurities, etc. ← This is handled w/ CPA.

- Investigate suspicion that at super-high temp., it just doesn't matter.

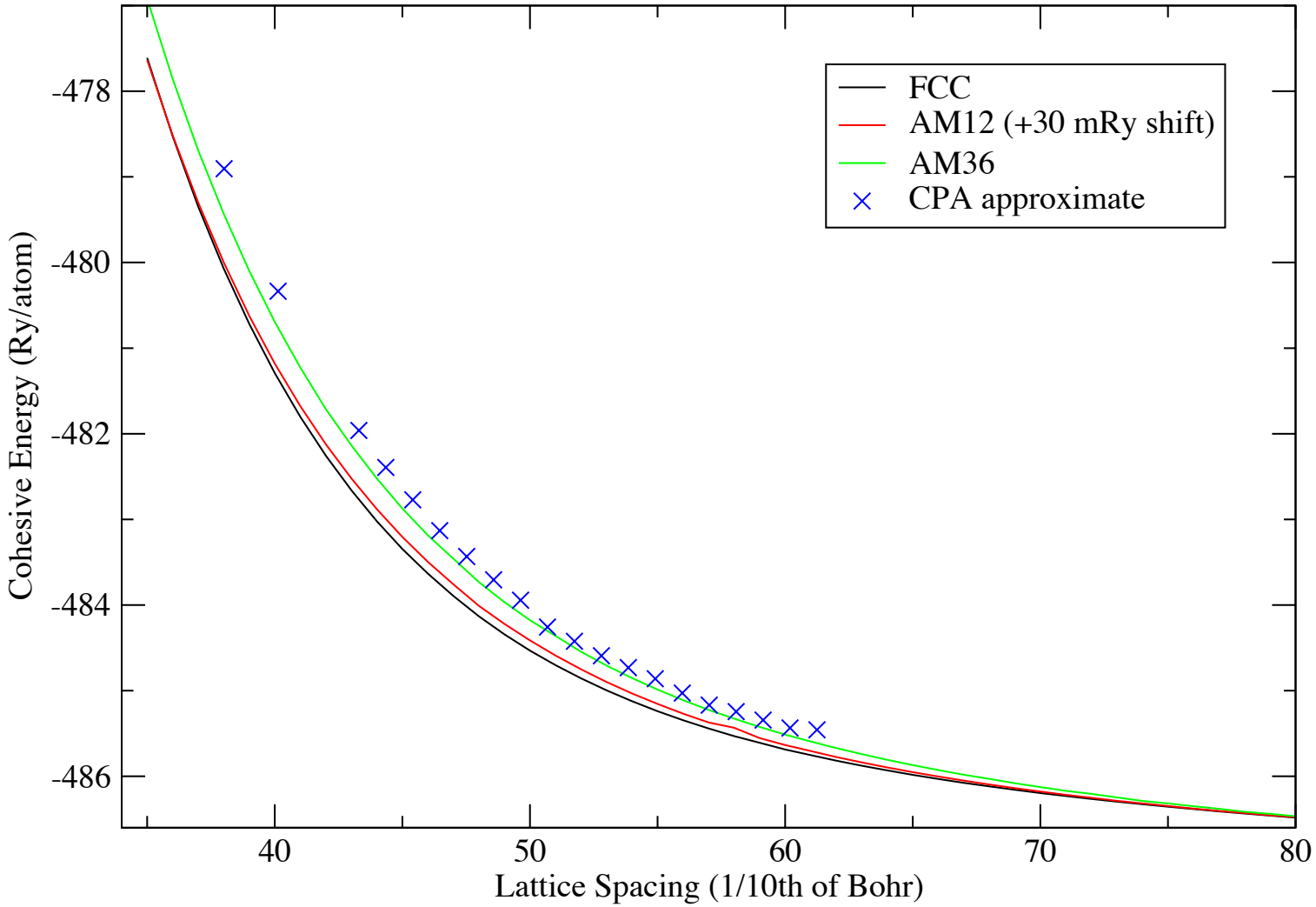
FCC Al: up to ¼ *M*K , 10× solid-density



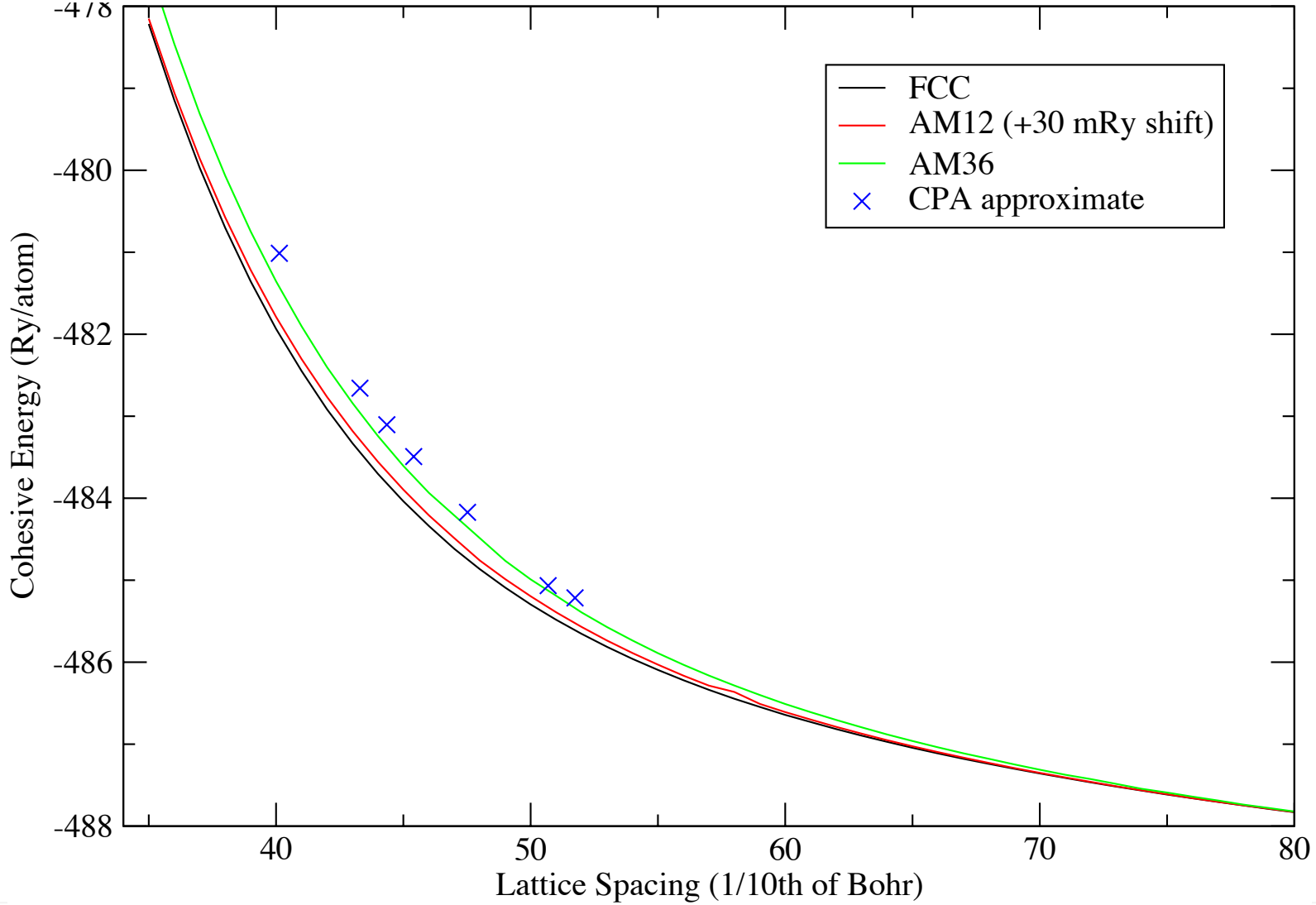
Al FCC vs. Amorph. Structures @20K



Al @ 63,000 K – Long range order matters



Al @ 95,000 K


FCC
AM12 (+30 mRy shift)
AM36
CPA approximate
Cohesive Energy (Ry/atom)
-478
-480
-482
-484
-486
-488
40
50
60
70
80
Lattice Spacing (1/10th of Bohr)

Approximating plasmas with spatially amorphous systems (cont.)

There are three approaches:

3. Analytically formulate an average Green's function for fluidly distributed scatterers
   - Respecting short range order is hard to do
   - Past attempts have disrupted Herglotz properties

Conclusions

- It would be worthwhile to further develop a KKR-based electronic-structure code that is reliably accurate from 0 K to 10 KeV.

  requirements –
  - •fully relativistic would be nice.
  - •forces can be obtained from Hellman-Feynman thm.
  - •screened exact-exchange (HSE) to handle gaps, excited-states, actinides…

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- Can a 1st approximation to warm dense plasma be excited FCC –CPA?
  - FCC has short range order analogous to dense amorphous.
  - Even at highest temperatures studied, CPA aprox. adequate.

Versions of the Source Code MECCA
Multiple-scattering Electronic-structure Code for Complex Applications
are downloadable
TO OBTAIN:
contact D.D. Johnson at AMES Lab ddj@ameslab.gov