A Scattering Theory Approach to the Bound States

A Preparation for the Understanding of KKR Method #2

Yang Wang

Pittsburgh Supercomputing Center

Carnegie Mellon University

Acknowledgement: This work is supported in part by NSF OAC and DMR under award number 1931525, and by NSF XSEDE Program.

Motivations

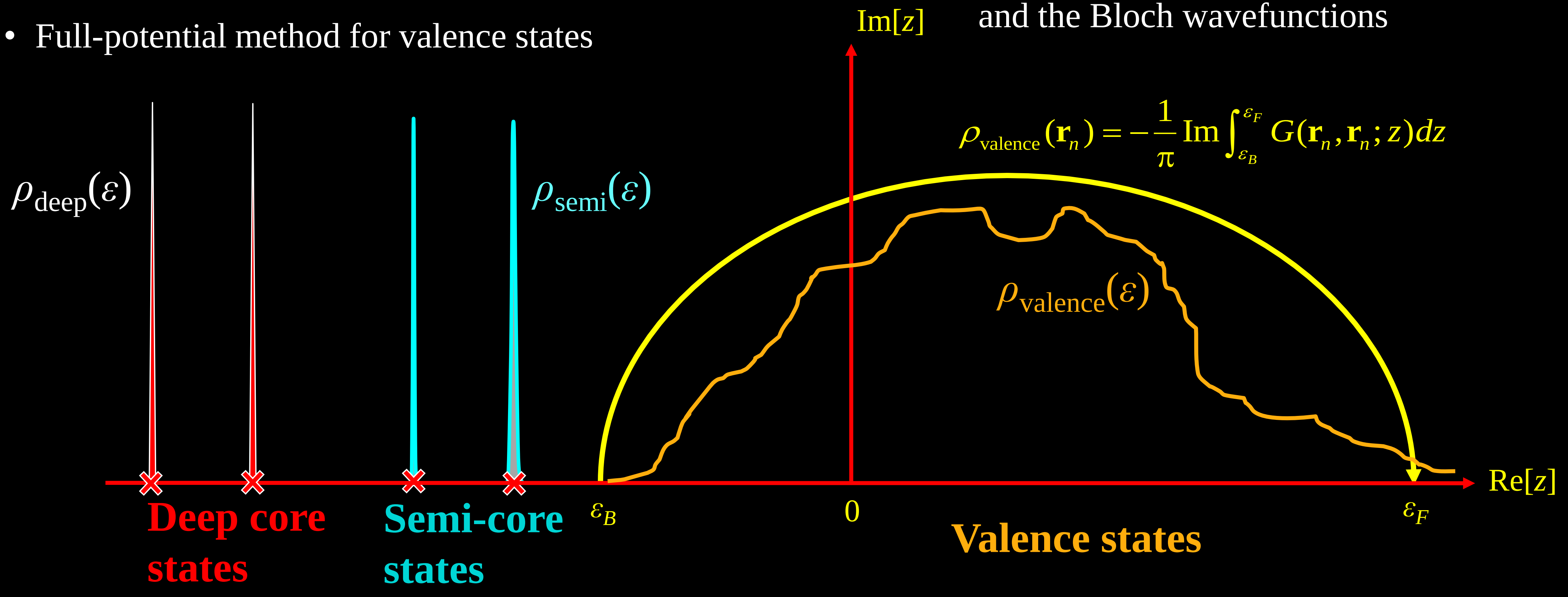
- Allow a full-potential treatment of the cores states
  - The crystal field is indeed non-spherical
  - We usually consider $-Ze^2/r$ as the dominating term of the LDA (or GGA) potential for the core states
  - However, for those “shallow” semi-core states, this consideration is questionable, and may not be valid in some situations
- Establish a unified approach to both valence and semi-core states
- Be able to identify a bound state from scattering theory
- Be able to compute the charge density of the bound state

The KKR approach to the core and valence states

Ab initio electronic structure calculation based on multiple scattering theory, also known as KKR method, within DFT

- All-electron method
- Full-potential method for valence states

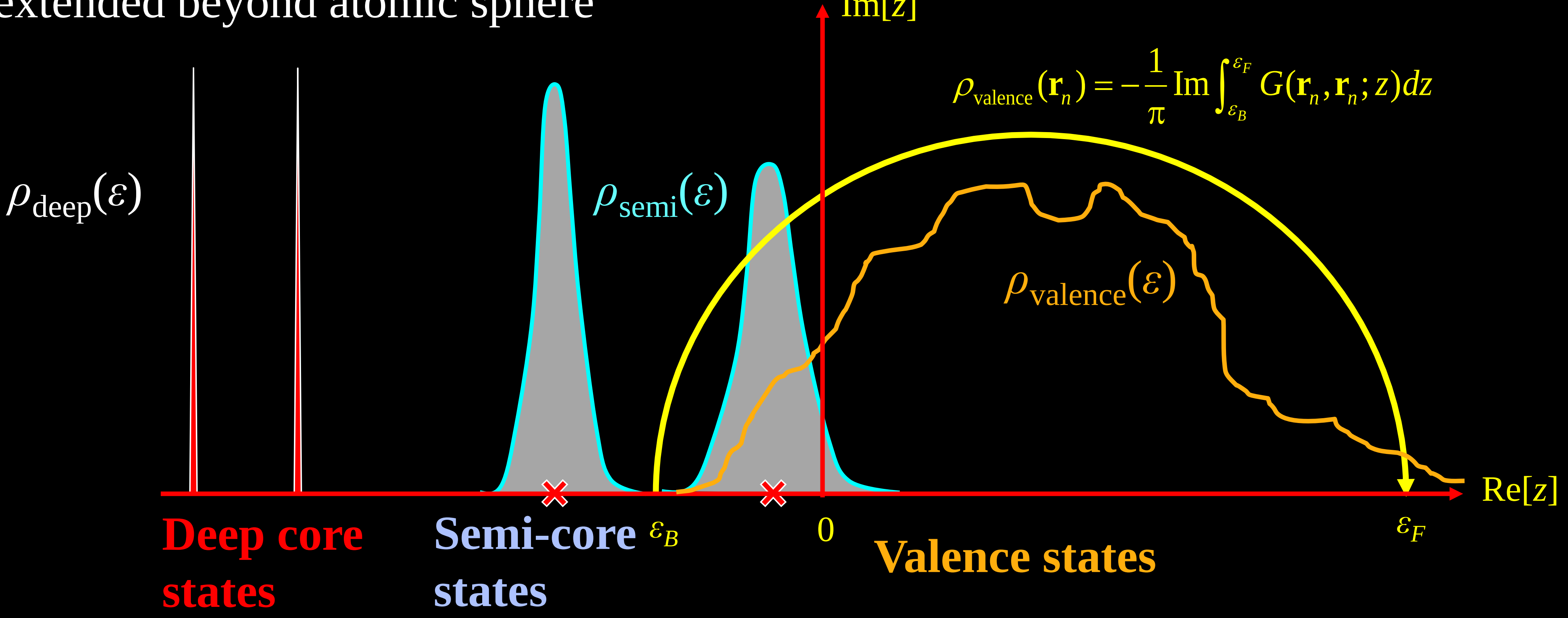
Green function ***G*** can be calculated in from multiple scattering theory (KKR method), without the need to know the band structure and the Bloch wavefunctions



$$\rho_{\text{valence}}(\mathbf{r}_n) = -\frac{1}{\pi}\,\mathrm{Im}\int_{\varepsilon_B}^{\varepsilon_F} G(\mathbf{r}_n,\mathbf{r}_n;z)\,dz$$

What happens when atoms are brought closer to one another

- Valence band, core states, Fermi energy, and total energy will rise
- Semi-core states are broadened and eventually become part of the valence band
- Spherical potential is no longer a good approximation for solving the semi-core states
- The region for normalizing the charge density of the semi-core states needs to be extended beyond atomic sphere



$$\rho_{\text{valence}}(\mathbf{r}_n) = -\frac{1}{\pi}\,\mathrm{Im}\int_{\varepsilon_B}^{\varepsilon_F} G(\mathbf{r}_n,\mathbf{r}_n;z)\,dz$$

Conventional Approach to the Core States

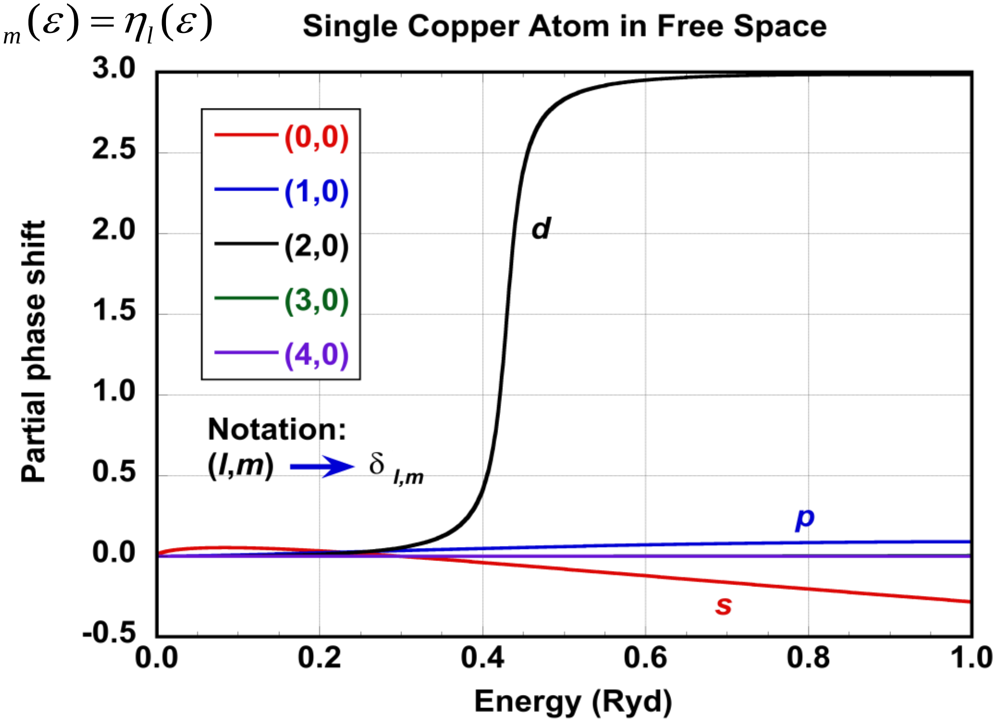
- The LDA potential is assumed to be spherical around each atom
  - so that the wave function can be written as a product of a radial function and a spherical harmonic, $\varphi_{nl}(r)Y_{lm}(\theta,\phi)$
  - $\varphi_{nl}(r)$ is a solution of the radial Schrödinger (or Dirac) equation (with single variable r)
- Choose a bounding sphere of radius $R \sim R_{\mathrm{mt}}$
  - Solve the radial Schrödinger (or Dirac) equation inward with a proper boundary condition at the bounding sphere radius, e.g., $\varphi_{nl}(R) \sim h_l(\sqrt{\varepsilon}R)$
  - Solve the radial Schrödinger (or Dirac) equation outward with a proper boundary condition at the origin: $r\varphi_{nl}(r) \sim 0$
  - An energy eigenvalue is found by applying the matching condition that both inward and outward solutions meet smoothly
  - The wave function solution is normalized within the bounding sphere
- Can we solve the core states in full-potential so the valence and cores states are truly treated on the same footing ?

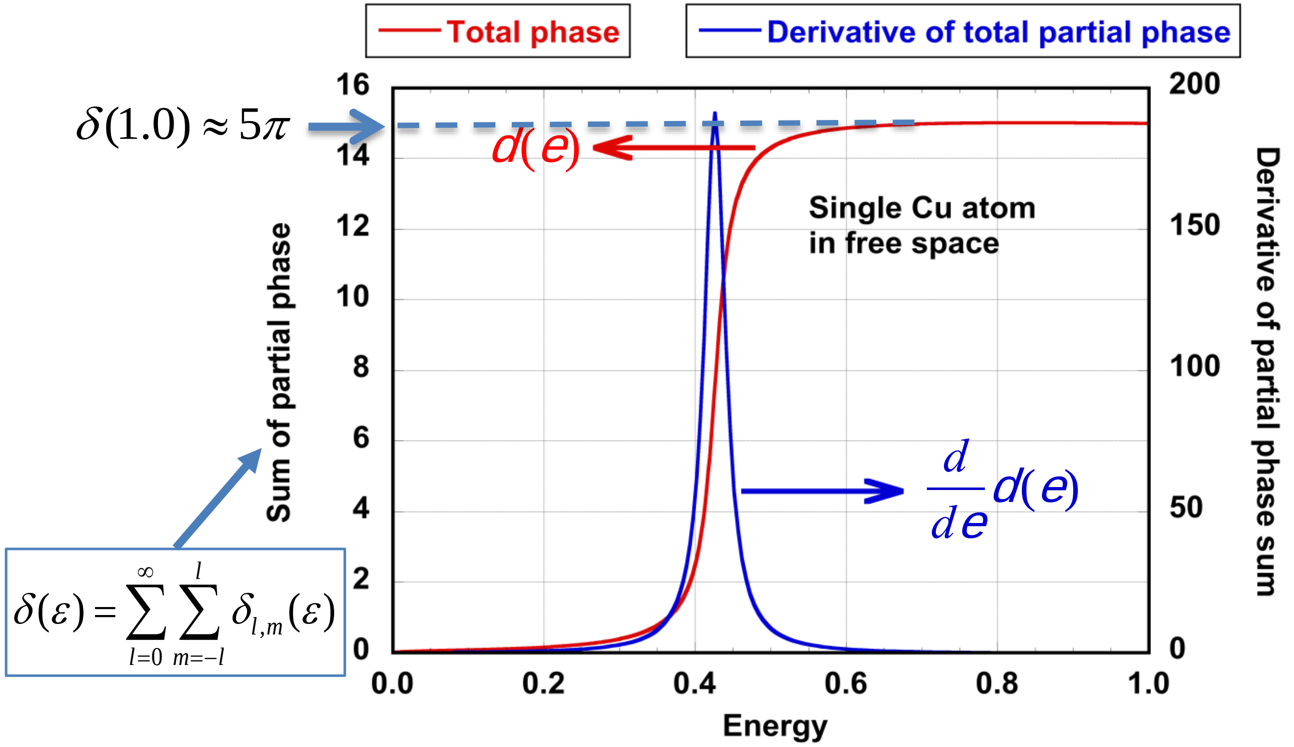
Problems in the Conventional Approach

- Spherical potential is required for the core states, while non-spherical potential, commonly known as **full-potential**, is applied to the valence states
- Normalization for each core state is applied within a bounding sphere, rather than the entire space
- Hybridization of the semi-core states between the neighboring atoms needs to be properly taken into account
- A more general question is: Is there an effective way to solve bound states from scattering theory,
  - which does not require to solving the Kohn-Sham equation with spherical potential assumption
  - which does not require normalization step when Green function is used

Recall the physical meaning of partial phase shifts

$\delta_{l,m}(\varepsilon) = \eta_l(\varepsilon)$





$$\delta(\varepsilon) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \delta_{l,m}(\varepsilon)$$

I have used both η_l and $\delta_{l,m}$ to denote partial phase shift . Sorry for the confusion!

$\eta_l(\varepsilon)/\pi$ is the integrated density of states (IDOS), relative to the free electron IDOS

$$\boxed{\text{For spherical potential: } S_l(\varepsilon) = e^{2i\eta_l(\varepsilon)} \rightarrow \eta_l(\varepsilon) = \frac{1}{2i} \ln S_l(\varepsilon)}$$

$1/\pi \cdot d\eta_l(\varepsilon)/d\varepsilon$ is the density of states (DOS), relative to the free electron DOS

$$\boxed{S_l(\varepsilon) = 1 - 2i\sqrt{\varepsilon}\, t_l(\varepsilon)} \xrightarrow[\text{with } (l,m) \text{ as the index}]{\text{In matrix form}} \boxed{\underline{S}(\varepsilon) = 1 - 2i\sqrt{\varepsilon}\, \underline{t}(\varepsilon)}$$

At a bound state, $d\eta_l(\varepsilon)/d\varepsilon$ is a delta function, and $\eta_l(\varepsilon)$ is a step function, jumping from $n\pi$ to $(n+1)\pi$

Scattering Theory Approach to the Bound and Resonance States

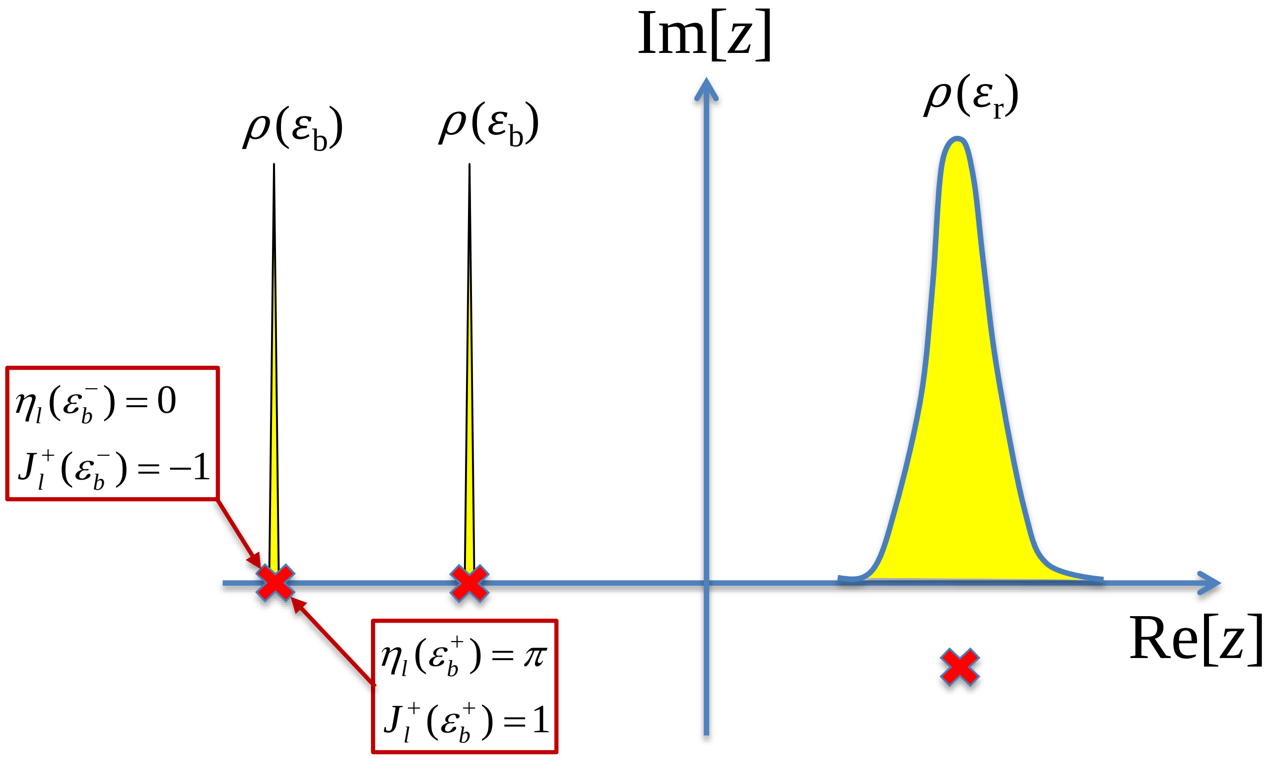
- The *S*-matrix for a spherical potential

$$\boxed{S_l(\varepsilon)=e^{2i\eta_l(\varepsilon)}=\frac{J_l^-(\varepsilon)}{J_l^+(\varepsilon)},}$$

where $\eta_l(\varepsilon)$ is the partial phase shift, and $J_l^+(\varepsilon)$ and $J_l^-(\varepsilon)$ are called Jost functions, given by $J_l^+(\varepsilon)=i\sin\eta_l(\varepsilon)-\cos\eta_l(\varepsilon),\quad J_l^-(\varepsilon)=-i\sin\eta_l(\varepsilon)-\cos\eta_l(\varepsilon)$.

- The analytical properties of the *S*-matrix on the complex energy plane *z*:
  - Bound states (at energy ε_b) correspond to the poles on the negative real energy axis
  - Resonance states (at energy ε_r) correspond to the poles in the fourth quadrant
- Therefore, the cores states can be found by searching the zeros of the Jost function $J_l^+(\varepsilon)$ for $\varepsilon < 0$ on real energy axis
- From Krein theorem (Wang, Stocks, and Faulkner, 2014 *J. Phys.: Condens. Matter* **26** 274208), we have:

The number of core states below energy $\varepsilon = \frac{1}{2\pi i}\ln\left(\det \underline{S}(\varepsilon)\right)$



✖ : pole of *S*-matrix in complex energy plane *z*

From Jost Function to Jost Matrix

- In full-potential case, the angular moment *l* is no longer a good quantum number, and the concept of partial phase shift $\eta_l(\varepsilon)$ is no longer valid
  - The sine, cosine, and Jost functions of the partial phase shift become matrix, so that

$$\boxed{\underline{S}(\varepsilon) = \frac{\underline{J}^-(\varepsilon)}{\underline{J}^+(\varepsilon)}}$$

$$\boxed{\begin{aligned} \underline{J}^-(\varepsilon) &= -i\cdot\underline{s}(\varepsilon) - \underline{c}(\varepsilon) \\ \underline{J}^+(\varepsilon) &= i\cdot\underline{s}(\varepsilon) - \underline{c}(\varepsilon) \end{aligned}}$$

The matrix index is $L = (l,m)$, with $l = 0, 1, 2, \ldots$, and $m = -l, -l+1, \ldots, l-1, l$

$$\boxed{\begin{aligned} s_{L'L}(\varepsilon) &= \sqrt{\varepsilon}\iiint_{\Omega_n} j_{l'}(\sqrt{\varepsilon}r)Y^*_{L'}(\hat{r})V(\mathbf{r})\phi_L(\mathbf{r};\varepsilon)d^3\mathbf{r}, \quad \text{and} \\ c_{L'L}(\varepsilon) &= \sqrt{\varepsilon}\iiint_{\Omega_n} n_{l'}(\sqrt{\varepsilon}r)Y^*_{L'}(\hat{r})V(\mathbf{r})\phi_L(\mathbf{r};\varepsilon)d^3\mathbf{r} - \delta_{LL'}. \end{aligned}}$$

$$\boxed{\begin{aligned} &\left[-\nabla^2 + V(\mathbf{r})\right]\phi_L(\mathbf{r};\varepsilon) = \varepsilon\phi_L(\mathbf{r};\varepsilon), \\ &\phi_L(\mathbf{r};\varepsilon) \xrightarrow[r\to 0]{} j_l(\sqrt{\varepsilon}r)Y_L(\hat{r}), \text{ with } L = (l,m). \end{aligned}}$$

- The core states can be found by searching the zeros of the Jost matrix

$$\boxed{\det\underline{J}^+(\varepsilon_c) = \det\left[i\cdot\underline{s}(\varepsilon_c) - \underline{c}(\varepsilon_c)\right] = 0.}$$

Searching for Zeros of the Jost Matrix

Liu, Wang, Eisenbach, Stocks, *Comput. Phys. Comm.* **224**, 265 (2018)

The zeros of the Jost matrix can be found by the following steps:

- Picking an energy “window” (ε_1, ε_2), and taking a quadratic expansion of the Jost matrix around a chosen energy ε_0, which is at the center of the window, i.e., $\varepsilon_1 < \varepsilon_0 < \varepsilon_2$, so that

$$\boxed{\underline{J}^{+}(\varepsilon) = \underline{J}^{+}(\varepsilon_0 + \lambda) = \underline{J}^{(0)}(\varepsilon_0) + \underline{J}^{(1)}(\varepsilon_0)\lambda + \underline{J}^{(2)}(\varepsilon_0)\lambda^2}$$

- det[$\underline{J}^{+}(\varepsilon)$] = 0 is equivalent to the following secular matrix equation

$$\boxed{\det\begin{bmatrix} \lambda - \underline{D} & -\underline{I} \\ \underline{D}^2 & \lambda - \underline{B} + \underline{D} \end{bmatrix} = 0,} \qquad \text{where } \underline{B} = -\left[\underline{J}^{(2)}(\varepsilon_0)\right]^{-1}\underline{J}^{(1)}(\varepsilon_0), \text{ and } \underline{D} = -\left[\underline{J}^{(1)}(\varepsilon_0)\right]^{-1}\underline{J}^{(0)}(\varepsilon_0)$$

- Solving the eigenvalue problem for λ
- The poles of $\underline{J}^{+}(\varepsilon)$ are $\varepsilon_0 + \lambda$, with $\varepsilon_1 < \varepsilon_0 + \lambda < \varepsilon_2$.
- Those $\varepsilon_0 + \lambda$ with negative and real value correspond to the core states (bound states)
- Implemented in the MuST package (`https://github.com/mstsuite/MuST`), which includes several multiple scattering theory based *ab initio* methods.

A computational result

Example: Copper (in a FCC structure) with full-potential

By solving the differential (Kohn-Sham-Dirac) equation with spherical component of the potential

n	***l***	***j***	**core energy**
3	0	1/2	-7.28138551844
3	1	1/2	-4.38141002034
3	1	3/2	-4.38141001903

By searching the zeros of Jost function matrix

degeneracy	**core energy**
1	-7.281387131361
3	-4.381419809318

How to compute the charge density of the core states?

- In conventional approach, with spherical potential approximation, we solve the differential (Kohn-Sham) equation and
  - ✓ calculate the eigenvalues ε_{nl}
  - ✓ calculate the corresponding eigenfunctions $\varphi_{nl}(r)$
  - ✓ normalize the eigenfunctions $\varphi_{nl}(r)$ so that

$$4\pi\int_0^R \left|\varphi_{nl}(r)\right|^2 r^2 dr = 1$$

  - ✓ calculate the charge density of the core states $\rho(r) = \sum_{n,l}(2l+1)\left|\varphi_{nl}(r)\right|^2$
- How to calculate the charge density without knowing the eigenfunctions?
  - ✓ Determine the single site Green function in terms of the Jost matrix
  - ✓ Integrate the Green function around the poles of the Jost matrix

Green function approach to the charge density of the core states

For real energy ε, the imaginary part of the single site Green function is given by

$$\operatorname{Im} g(\mathbf{r},\mathbf{r}';\varepsilon) = \operatorname{Im}\sqrt{\varepsilon}\sum_{L,L'}\phi_L(\mathbf{r};\varepsilon)\left[\left[\underline{J}^{+}(\varepsilon)\right]^{-1}\cdot\underline{s}^{-T*}(\varepsilon)\right]_{LL'}\phi^{*}_{L'}(\mathbf{r}';\varepsilon)$$

Near a core state energy ε_c, the Jost matrix inverse can be written as

$$\left[\underline{J}^{+}(\varepsilon)\right]^{-1} = \frac{\underline{X}_c}{\varepsilon-\varepsilon_c}.$$

$$\left[-\nabla^2 + V(\mathbf{r})\right]\phi_L(\mathbf{r};\varepsilon) = \varepsilon\phi_L(\mathbf{r};\varepsilon),$$

$$\phi_L(\mathbf{r};\varepsilon)\xrightarrow[r\to 0]{} j_l(\sqrt{\varepsilon}r)Y_L(\hat{r}),\ \text{with } L=(l,m).$$

$$s_{L'L}(\varepsilon) = \sqrt{\varepsilon}\iiint_{\Omega_n} j_{l'}(\sqrt{\varepsilon}r)Y^{*}_{L'}(\hat{r})V(\mathbf{r})\phi_L(\mathbf{r};\varepsilon)d^3\mathbf{r},\quad \text{and}$$

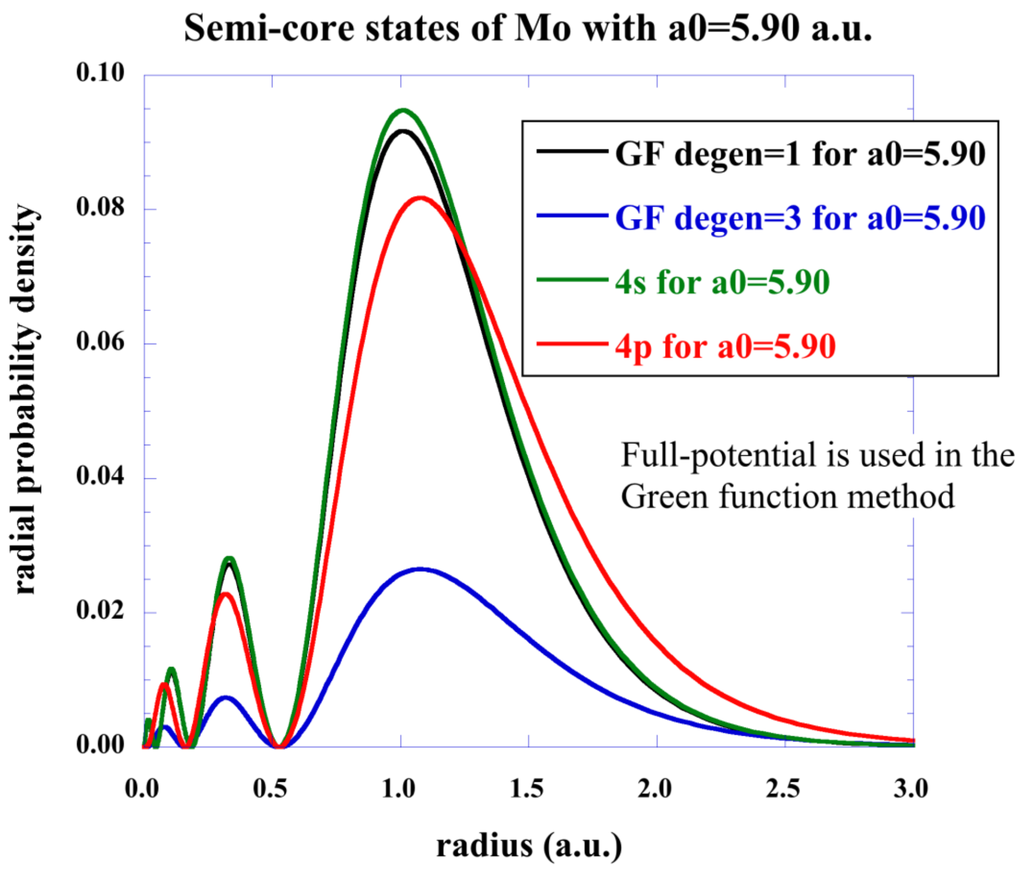
$$c_{L'L}(\varepsilon) = \sqrt{\varepsilon}\iiint_{\Omega_n} n_{l'}(\sqrt{\varepsilon}r)Y^{*}_{L'}(\hat{r})V(\mathbf{r})\phi_L(\mathbf{r};\varepsilon)d^3\mathbf{r} - \delta_{LL'}.$$

It can be shown that matrix $\underline{X}_c$ is a product of the left and right hand side eigenvectors of the quadratic expansion of the Jost matrix. Finally, we have

$$\begin{aligned}\rho_c(\mathbf{r}) &= -\frac{1}{\pi}\operatorname{Im}\left(\lim_{\eta\to 0}\int_{\varepsilon_c-\eta}^{\varepsilon_c+\eta} g(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon\right)\\ &= \operatorname{Re}\sqrt{\varepsilon_c}\sum_{L,L'}\phi_L(\mathbf{r};\varepsilon_c)\left[\underline{X}_c\cdot\underline{s}^{-T*}(\varepsilon_c)\right]_{LL'}\phi^{*}_{L'}(\mathbf{r};\varepsilon_c)\end{aligned}$$

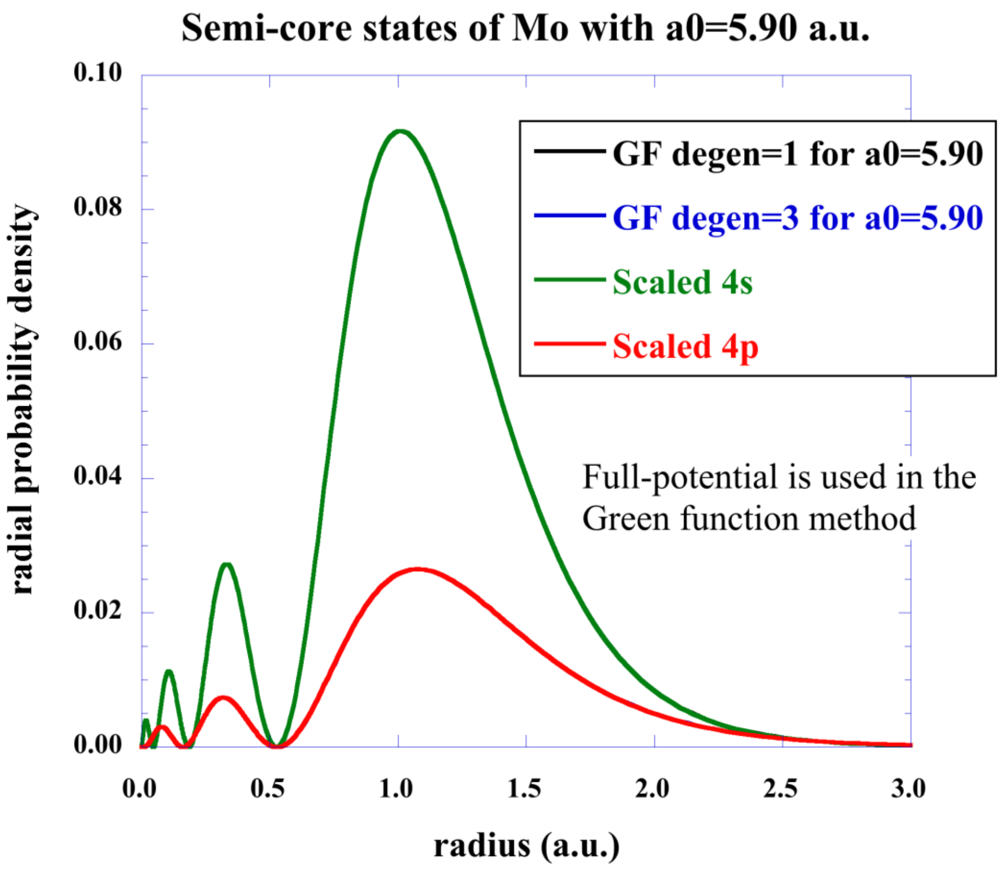
Semi-core Charge Density of Molybdenum

- In Green function method, the normalization is implicitly performed in the entire space
- After rescaling by multiplying a constant to the results of the conventional method, the results from both methods agree with one another

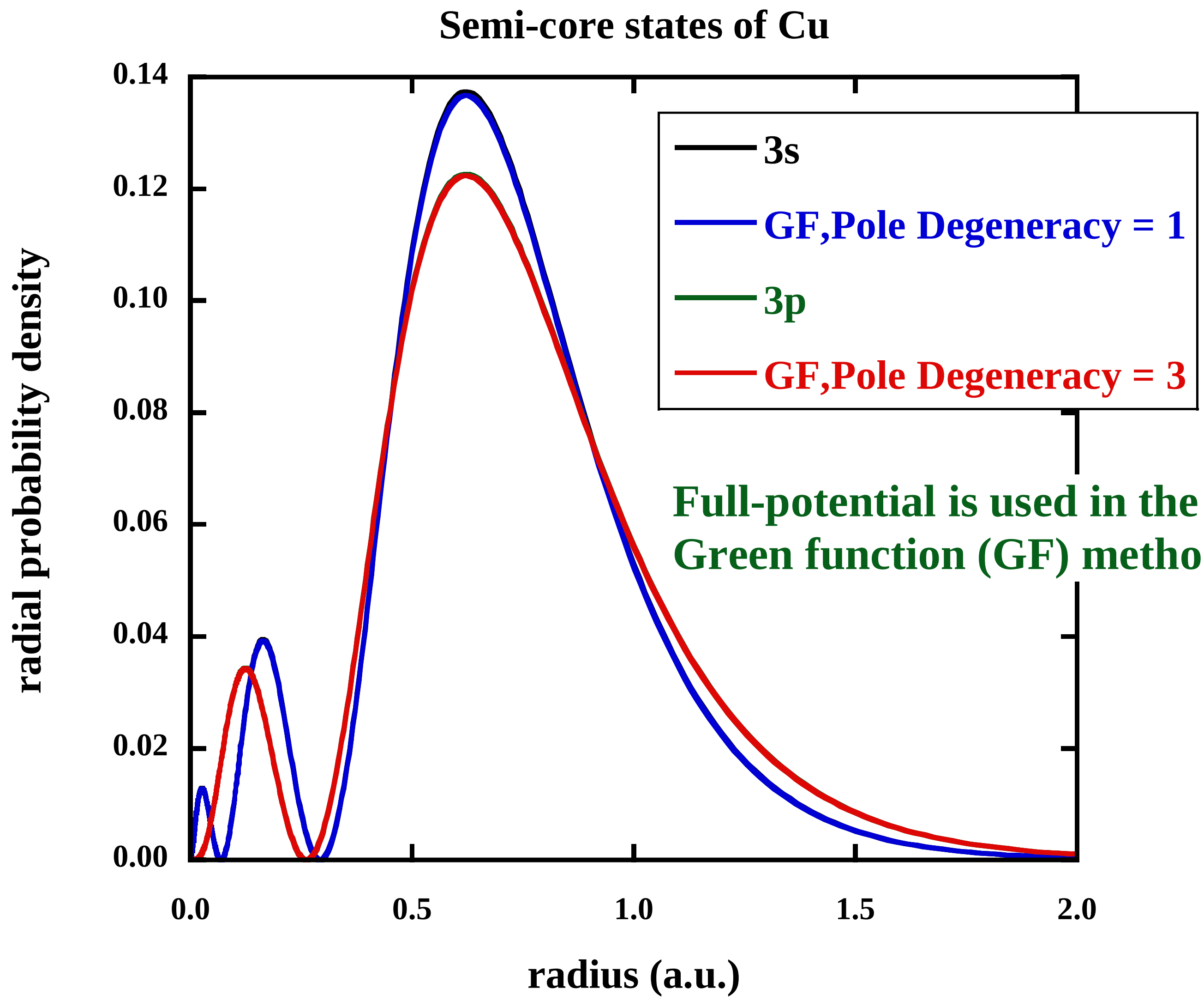

Semi-core states of Mo with a0=5.90 a.u.

Full-potential is used in the Green function method

Scale the *4s* and *4p* density


Semi-core states of Mo with a0=5.90 a.u.

Full-potential is used in the Green function method



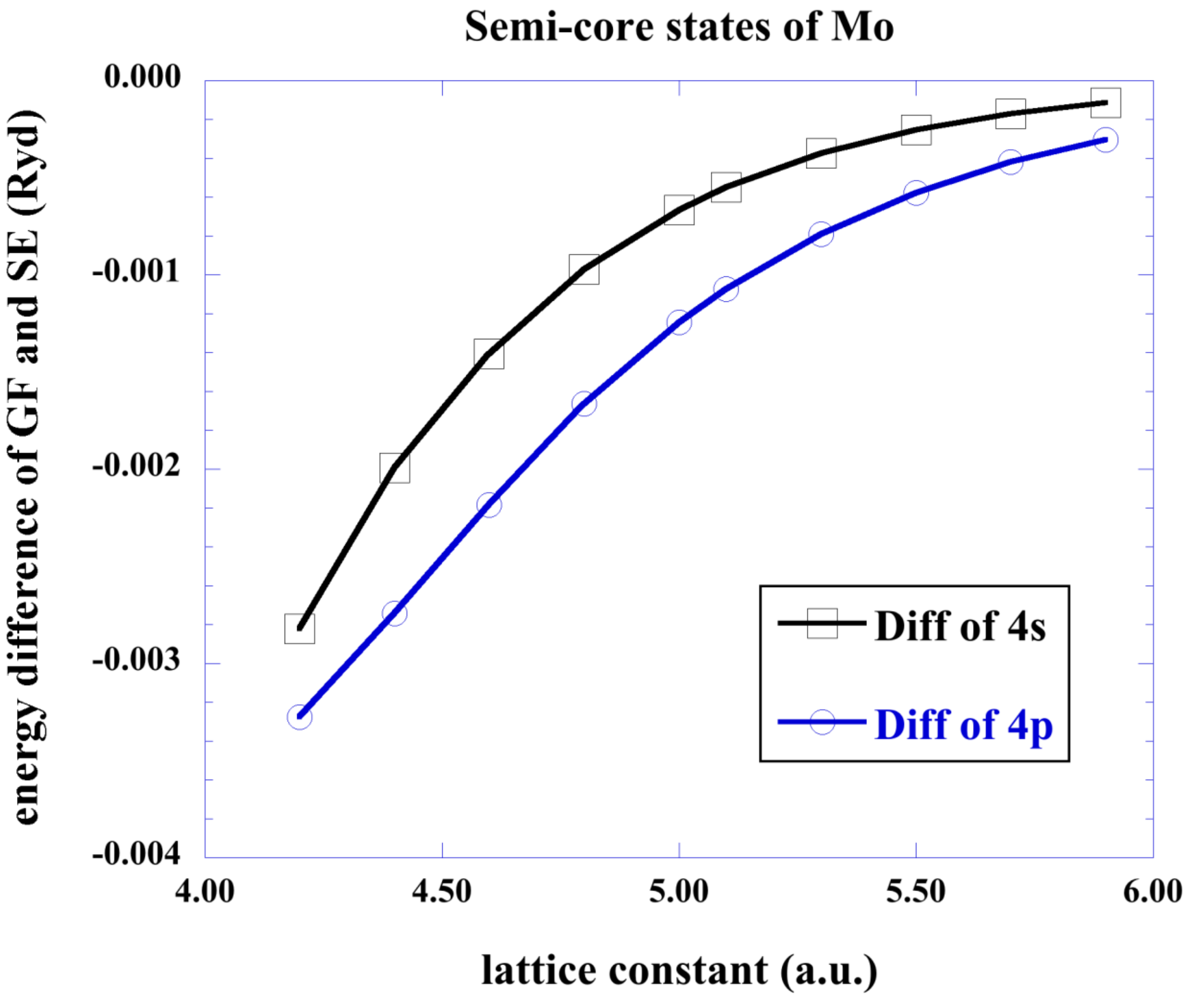
Semi-core states of Cu

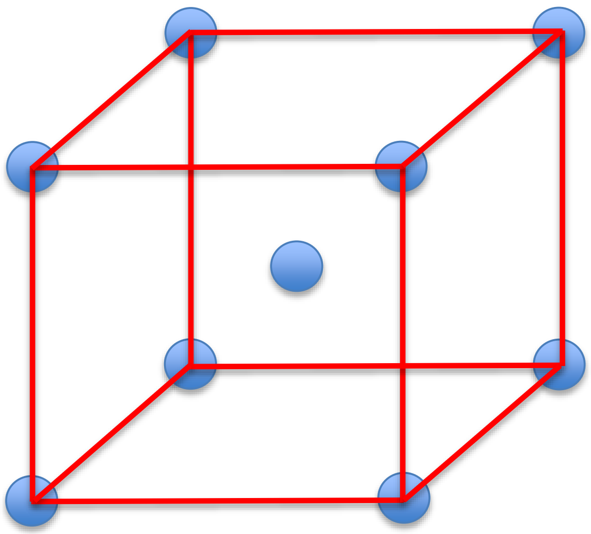
Full-potential is used in the Green function (GF) method

Note: the radial probability density plotted here is the spherical component of the full-density

Molybdenum under Compression

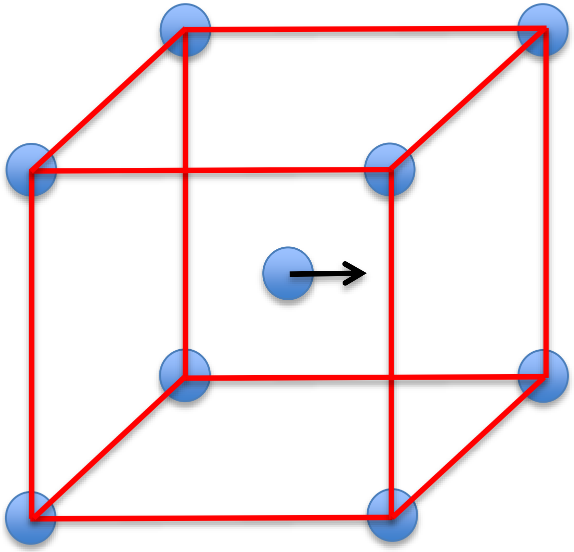
- The spherical component of the potential is used to calculate the core states by conventional method
- The full-potential is used to solve the core states with the Green function (GF)
- The energy difference between these two methods is plotted in the figure

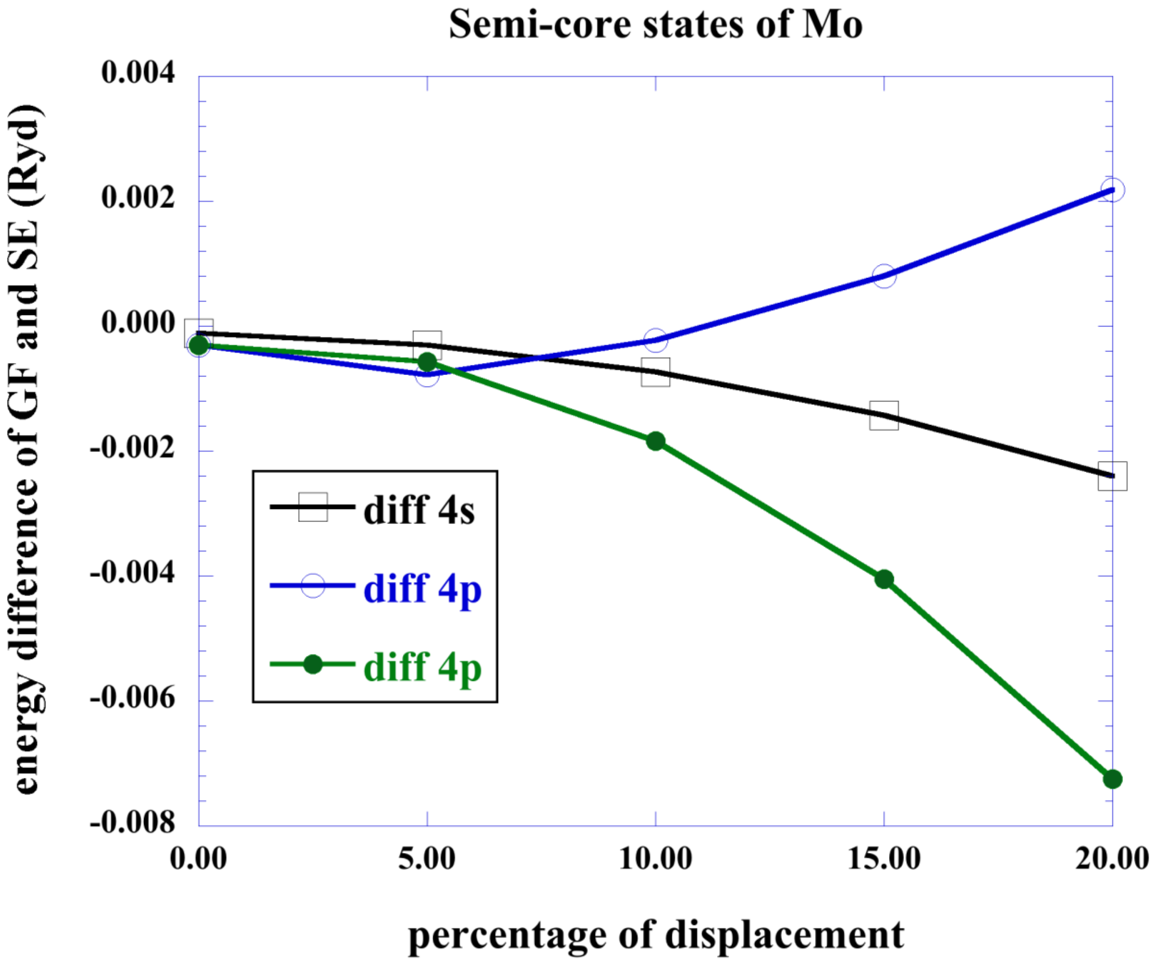




Molybdenum with Atomic Displacement

- The spherical component of the potential is used to calculate the core states by conventional method
- The full-potential is used to solve the core states with the Green function (GF)
- The energy difference between these two methods is plotted in the figure





Conclusions

A full-potential approach to the semi-core states is developed

- based on scattering theory
  - The zeros of the Jost matrix correspond to the energy eigenvalue of the core states
  - Green function technique is used to calculate the charge density, which can be non-spherical
- allowing to investigate the full-potential effects on semi-core states
  - Especially when atoms are brought close to each other, e.g., due to atomic displacement, under extreme conditions, etc.
  - Expected to improve the Hellmann-Feynman force calculation