# Free Energy and Force Formulation in LDA+Gutzwiller

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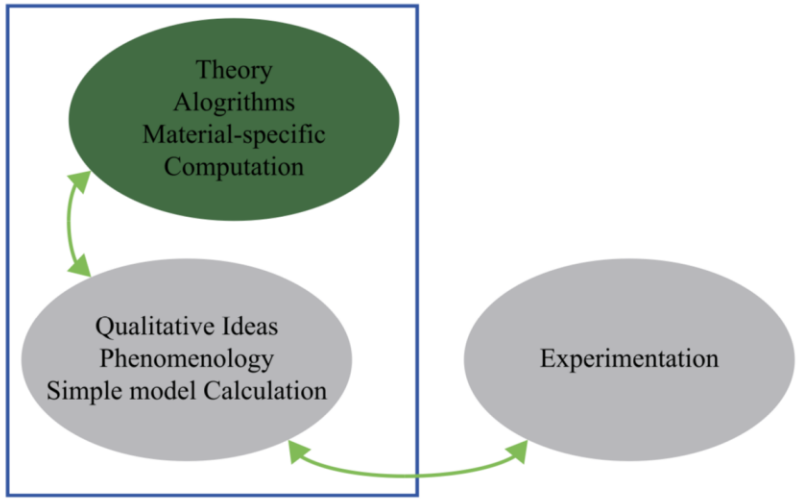
ENERGY

# Content

- Free Energy Expression
- Implementation of free energy
  - Iron BCC – FCC EOS
  - FeSe
- General approach to Pulay force (LDA)
- Force in LDA+GA
- Work in progress - Implementation

# Why do we need forces

Materials Design and Discovery



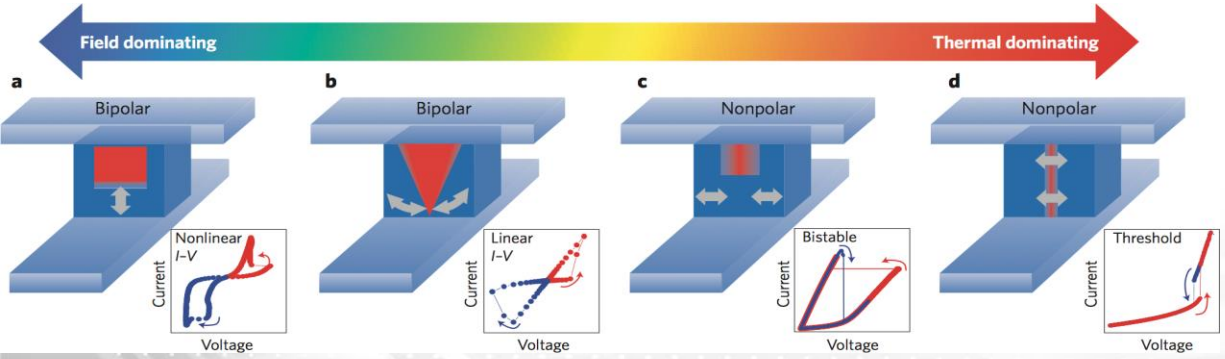

Adler, et al., Rep. Prog. Phys. **82**, 012504 (2019)


COLLECTION | 26 APRIL 2019

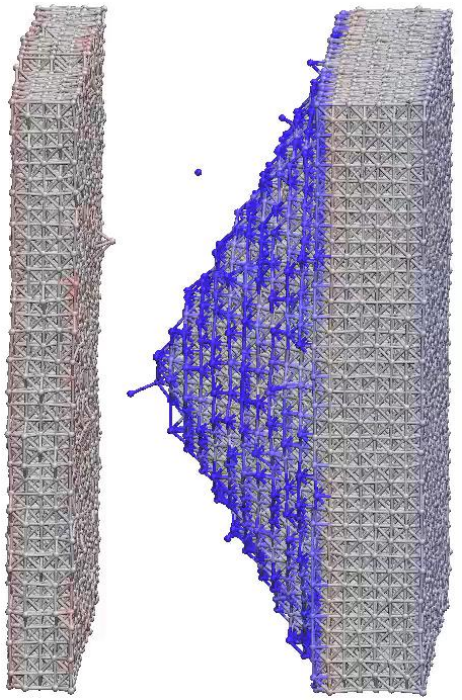
**Editor's choice: Machine learning for material discovery, design and characterisation**

Machine learning has been rapidly developing in the past decade and has become an important tool to the scientific community. Publicly available datasets can be exploited to automate the discovery of new materials, bringing unlikely solutions to material problems to... show more

Technology Development




Yang *et al*., Nature Nanotech. 2012



Onofrio, Guzman & Strachan, Nature Mat. 2015

# Free Energy Functional:

## LDA

$$\Gamma[\rho, V_{KS}] = -TrLn[-i\omega + T + V_{KS} - \mu] - Tr((V_H + V_{xc})\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} + \mu N$$

## LDA + U

$$\Gamma[\rho, V_{KS}, \lambda, n] = -TrLn[-i\omega + \tilde{\varepsilon}_{\mathbf{k}} - \mu] - Tr((V_H + V_{xc})\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} - \lambda^{\sigma}_{ab} n^{\sigma}_{ab} + E^U[n^\sigma] - E^U_{DC}[n^\sigma] + \mu N$$

## LDA + DMFT

$$\Gamma[\rho, V_{KS}, \Sigma, G_{loc}] = -Tr\ Ln\left(-i\omega_n + T + V_{KS} + \sum_{mm'\mathbf{R}_\mu} |\phi^\mu_m\rangle\langle\phi^\mu_m|\Sigma_{i\omega_n} - V_{DC}|\phi^\mu_{m'}\rangle\langle\phi^\mu_{m'}|\right) - Tr((V_H + V_{xc})\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} - Tr((\Sigma - V_{DC})\langle\phi|G|\phi\rangle) + \sum_{\mathbf{R}_\mu} \Phi^{DMFT}[G^\mu_{loc}] - \Phi^{DC}[\rho^\mu_{loc}]$$

Haule, et al., PRB **94**, 195146 (2016)

# LDA + Gutzwiller Free Energy: Functional

$$\Gamma^{GA}\Big[\rho, V_{KS};|\Phi\rangle, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \mu; \mathcal{D}, \mathcal{D}^\dagger, \lambda^c; \Delta_p\Big]$$

$$= TrLn\left[\frac{1}{i\omega - \mathcal{R}[T^{hop} + V_{KS}^{hop}]\mathcal{R}^\dagger - \lambda + \mu}\right]$$
$$+ \sum_i \Big[\langle\Phi_i|H_i^{\rm emb}|\Phi_i\rangle + E_i^c(1 - \langle\Phi_i|\Phi_i\rangle)\Big]$$
$$- \sum_i \Big[\sum_{ab}\big([\lambda_i]_{ab} + [\lambda_i^c]_{ab}\big)[\Delta_{pi}]_{ab} + \sum_{ca\alpha}\big([\mathcal{D}_i]_{a\alpha}[\mathcal{R}_i]_{c\alpha}[\Delta_{pi}(1-\Delta_{pi})]^{\frac{1}{2}}_{ca} + \text{c.c}\big)\Big]$$
$$- Tr(V_{KS}\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} + \mu N$$

Where the embedded Hamiltonian is given by

$$H_i^{\rm emb} = -\nabla^2_{i,\rm loc}\Big[\{c^\dagger_{i\alpha}\},\{c_{i\alpha}\}\Big] + J_{i,\rm loc}\Big[\{c^\dagger_{i\alpha}\},\{c_{i\alpha}\}\Big] + H_i^{\rm int}\Big[\{c^\dagger_{i\alpha}\},\{c_{i\alpha}\}\Big]$$
$$- V_i^{\rm dc}\sum_\alpha c^\dagger_{i\alpha}c_{i\alpha} + \sum_{a\alpha}\big([\mathcal{D}_i]_{a\alpha}c^\dagger_{i\alpha}f_{ia} + \text{H.c.}\big) + \sum_{ab}[\lambda_i^c]_{ab}f_{ib}f^\dagger_{ia}.$$

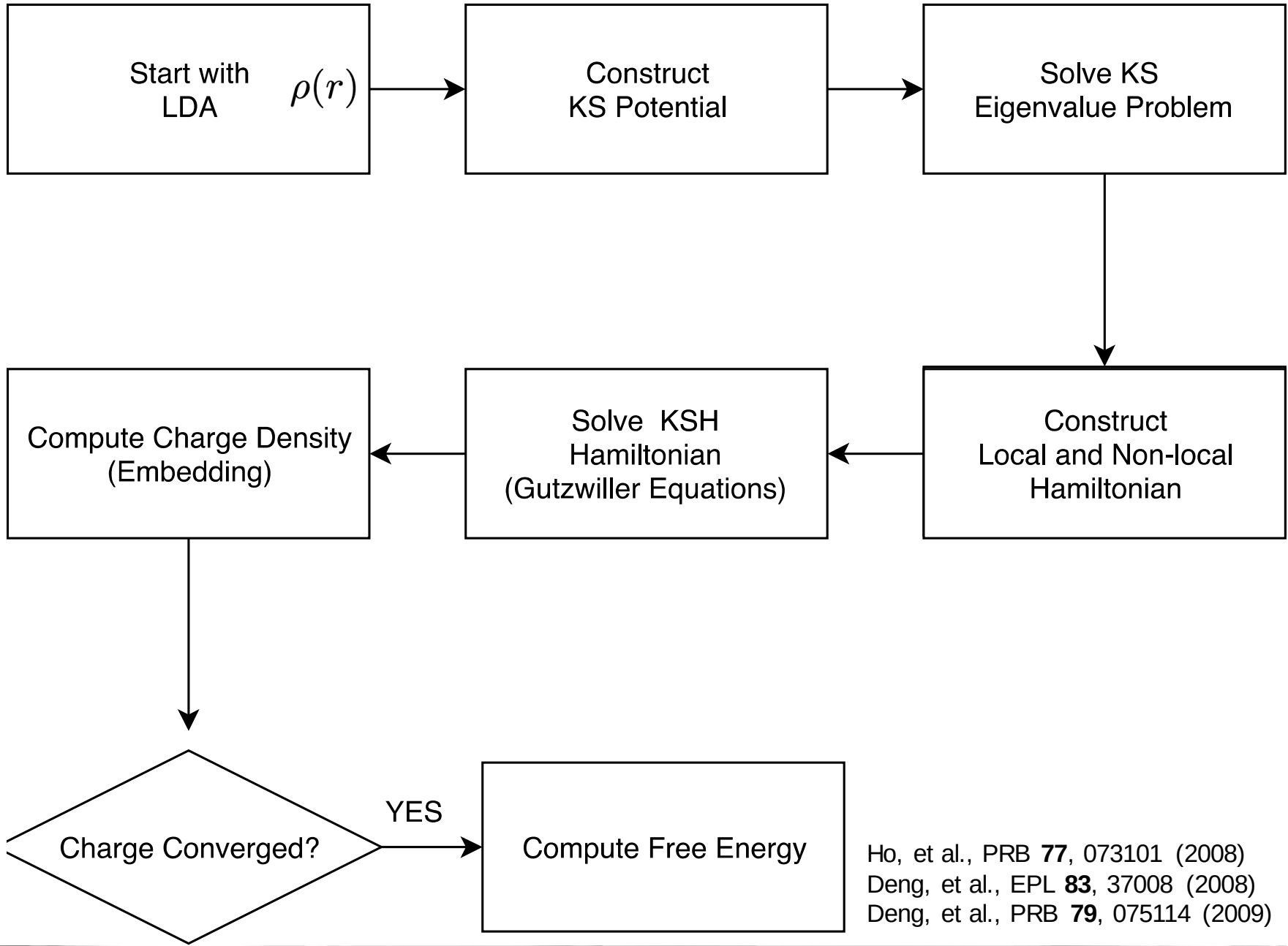
Lanatà, et al., PRX **5**, 011008 (2015)

# LDA + Gutzwiller Free Energy: Equation at saddle point

We compute the Free Energy at the saddle point as follows

$$\Gamma^{GA}\Big[\rho, V_{KS}; |\Phi\rangle; \mathcal{R}, \mathcal{R}^{\dagger}, \lambda, \mu; \Delta_p\Big]$$
$$= \frac{T}{\mathcal{N}} \sum_{\omega_n} \sum_{\mathbf{k}} TrLn \left[ 1 + Exp \left[ -\beta \sum_{mm'} \mathcal{R}_{nm} [T^{hop} + V_{KS}^{hop}]_{\mathbf{k},mm'} \mathcal{R}^{\dagger}_{m'n'} - \lambda_{nn'} + \mu \right] \right]$$
$$+ \sum_i \Big[ \langle \Phi_i | H_i^{\mathrm{emb}} | \Phi_i \rangle \Big] - \sum_i \sum_{ab} [\lambda_i]_{ab} [\Delta_{pi}]_{ab}$$
$$- Tr(V_{KS}\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} + \mu N$$

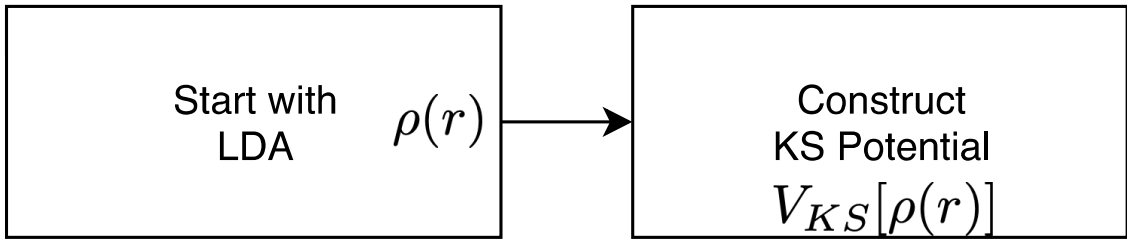
# LDA + Gutzwiller Flow Chart





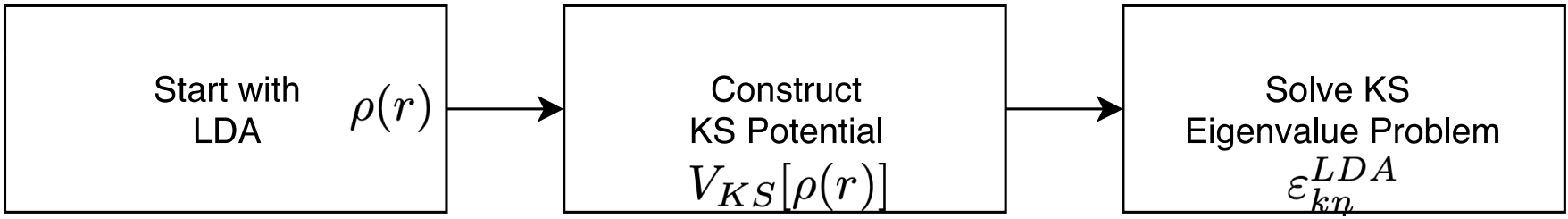
Ho, et al., PRB **77**, 073101 (2008)
Deng, et al., EPL **83**, 37008 (2008)
Deng, et al., PRB **79**, 075114 (2009)

# LDA + Gutzwiller Flow Chart



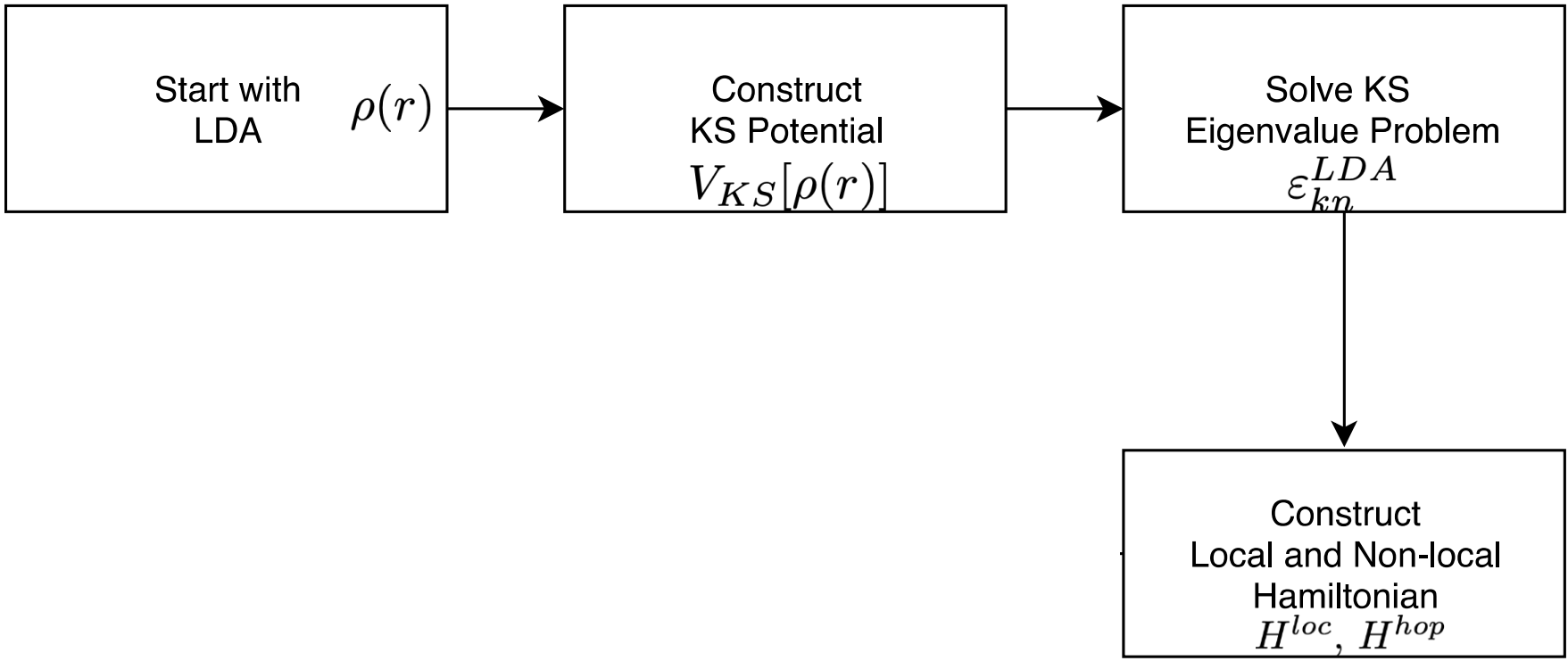

$$V_{KS}[\rho(r)] = V_H[\rho(r)] + V_{xc}[\rho(r)] + V_{nuc}$$

# LDA + Gutzwiller Flow Chart




$$[T + V_{KS}(\mathbf{r})]\psi_{kn}(\mathbf{r}) = \psi_{kn}(\mathbf{r})\varepsilon_{kn}^{LDA}$$

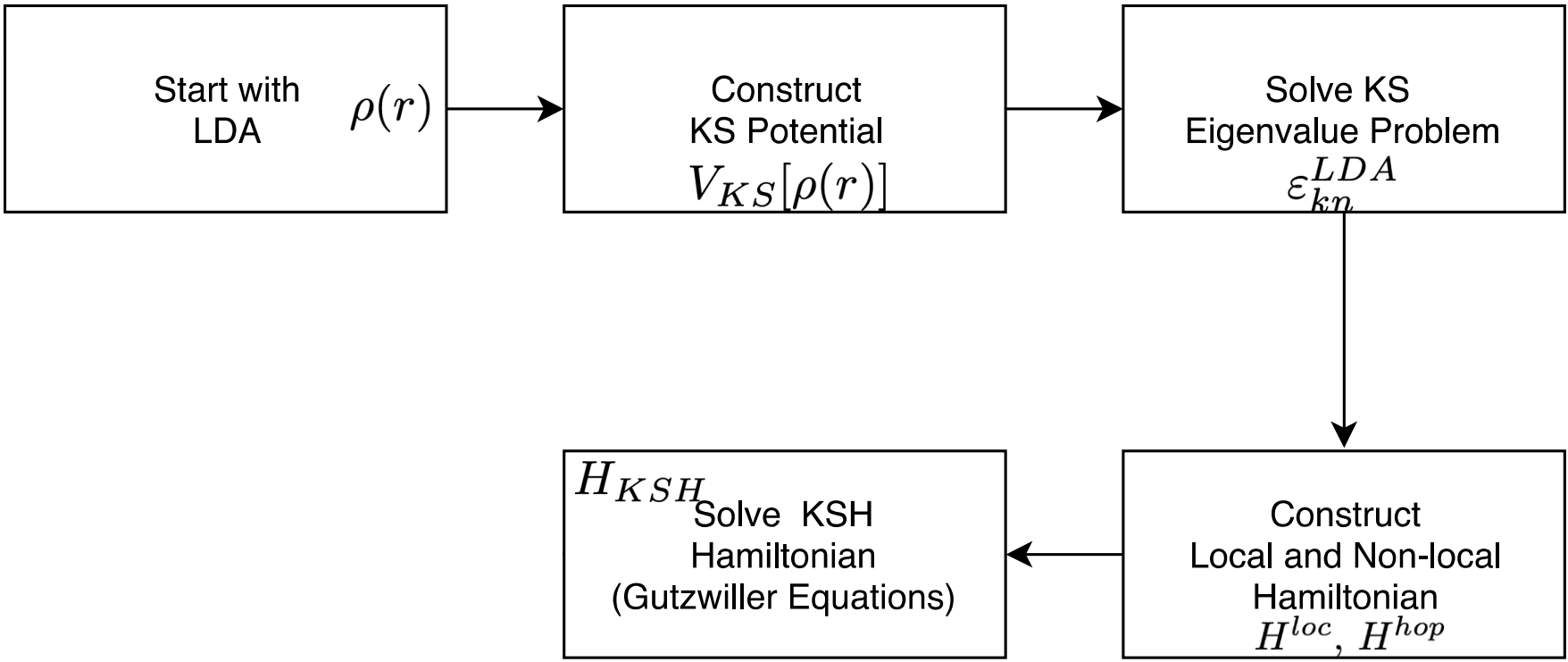
# LDA + Gutzwiller Flow Chart




$$H^{\mathrm{hop}}_{\mathbf{k}nn'} = H_{\mathbf{k}nn'} - \sum_i H^{\mathrm{loc}}_{\mathbf{k}nn'}$$

$$H^{\mathrm{loc}}_{i\alpha\alpha'} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} P^{\dagger}_{i\mathbf{k}n\alpha} H_{\mathbf{k}nn'} P_{i\mathbf{k}n'\alpha'}$$

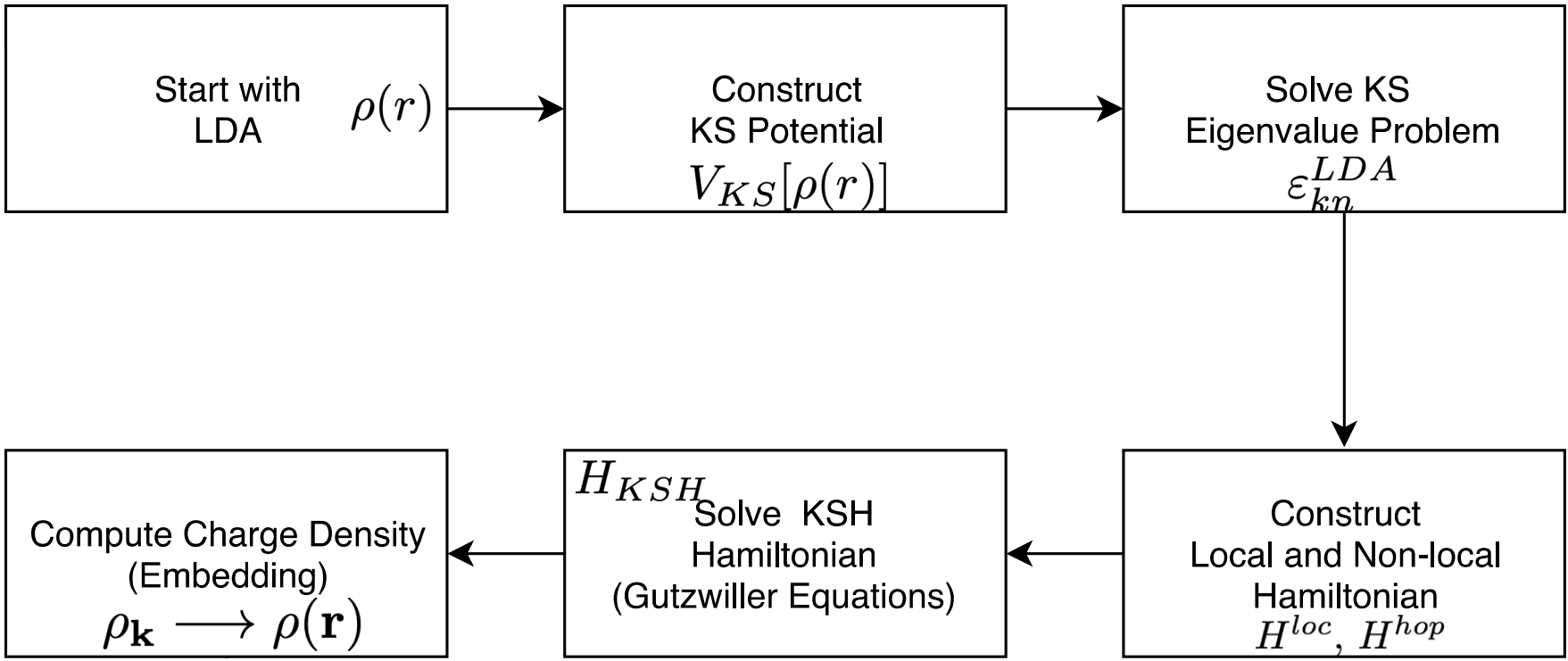
# LDA + Gutzwiller Flow Chart




$$H_{KSH} = \sum_{\mathbf{k}} \sum_{i\alpha\beta} H^{\mathrm{hop}}_{i\mathbf{k},\alpha\beta} c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}\beta} + \sum_{Ri} \mathcal{H}^{\mathrm{loc}}_{Ri}[\{c^{\dagger}_{Ri\alpha}\},\{c_{Ri\alpha}\}].$$

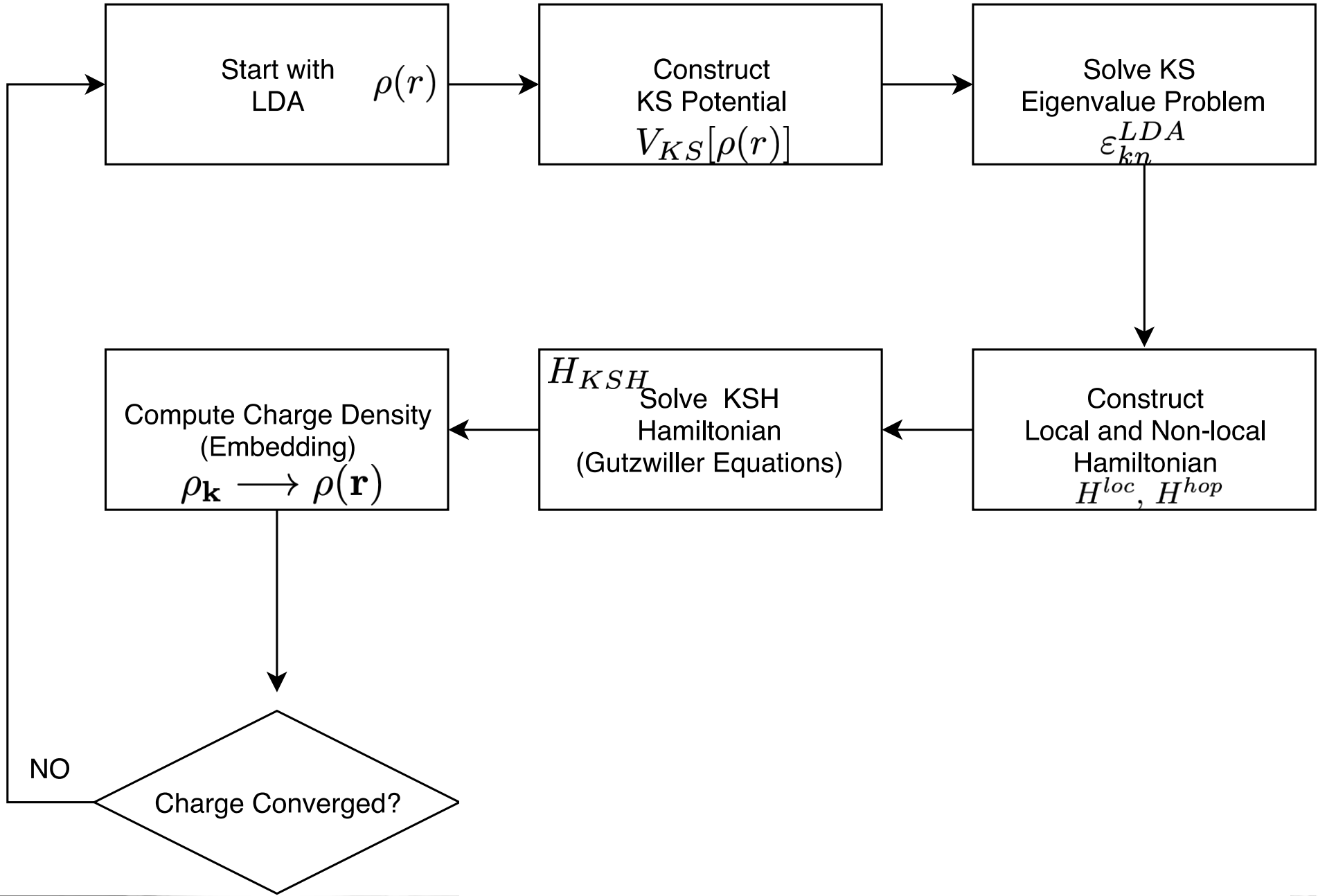
**Gutzwiller Solver**
**(Saddle point equations)**

# LDA + Gutzwiller Flow Chart

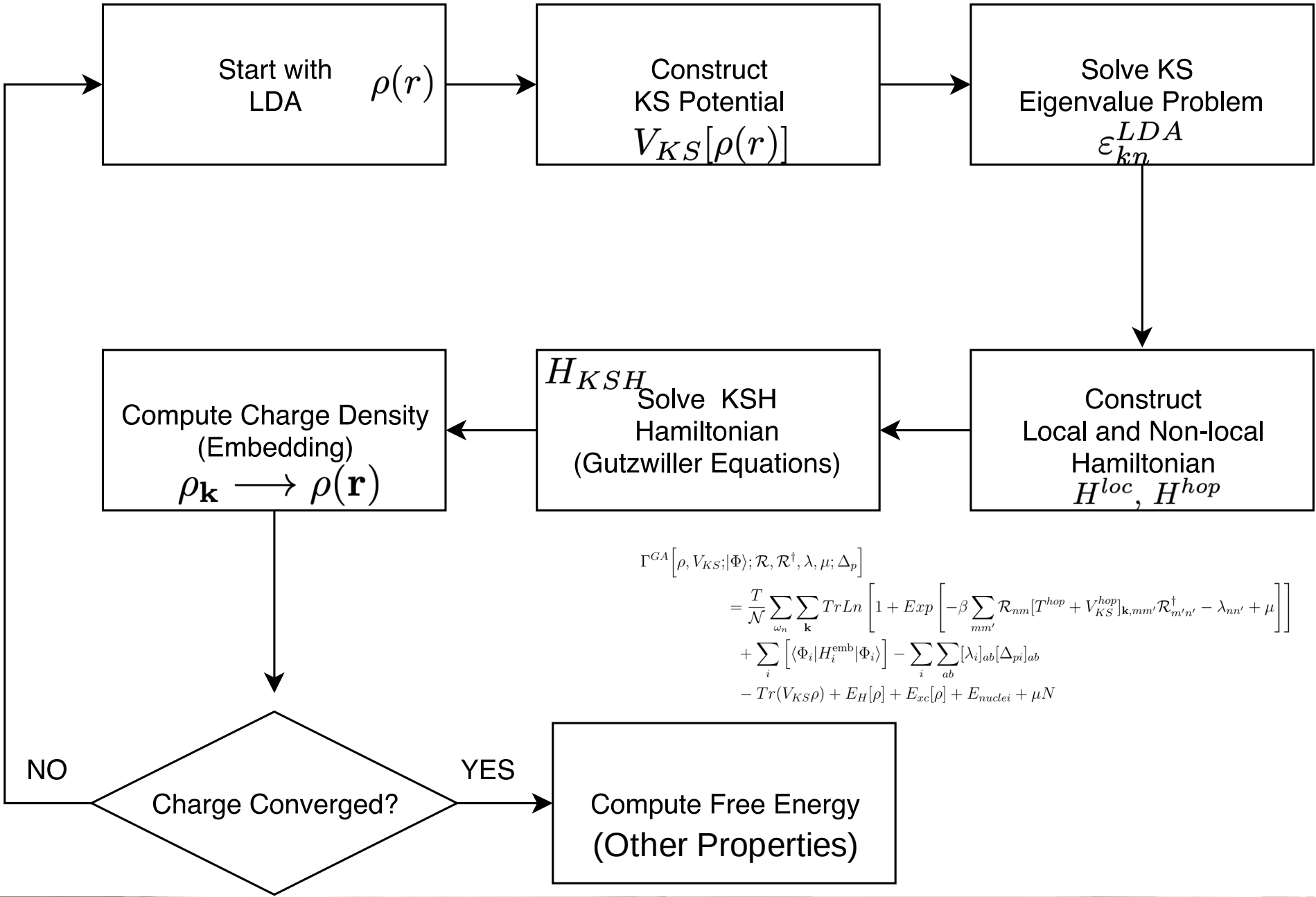



$$\rho_{\mathbf{k}} = \sum_n \sum_i P_{i\mathbf{k}n\beta}\Big(\langle\Phi_i|c_{i\alpha}^{\dagger}c_{i\beta}|\Phi_i\rangle\Big)P_{i\alpha\mathbf{k}n}^{\dagger} + \sum_n \Big[(1-\sum_i \hat{E}_i\hat{P}_i)\mathcal{R}_{mn}^{\dagger}n_F\big(\mathcal{R}_{nm}[H_{\mathbf{k},mm'}^{\mathrm{hop}}]\mathcal{R}_{m'n'}^{\dagger}+\lambda-\mu\big)\mathcal{R}_{n'm'}\Big]$$

# LDA + Gutzwiller Flow Chart

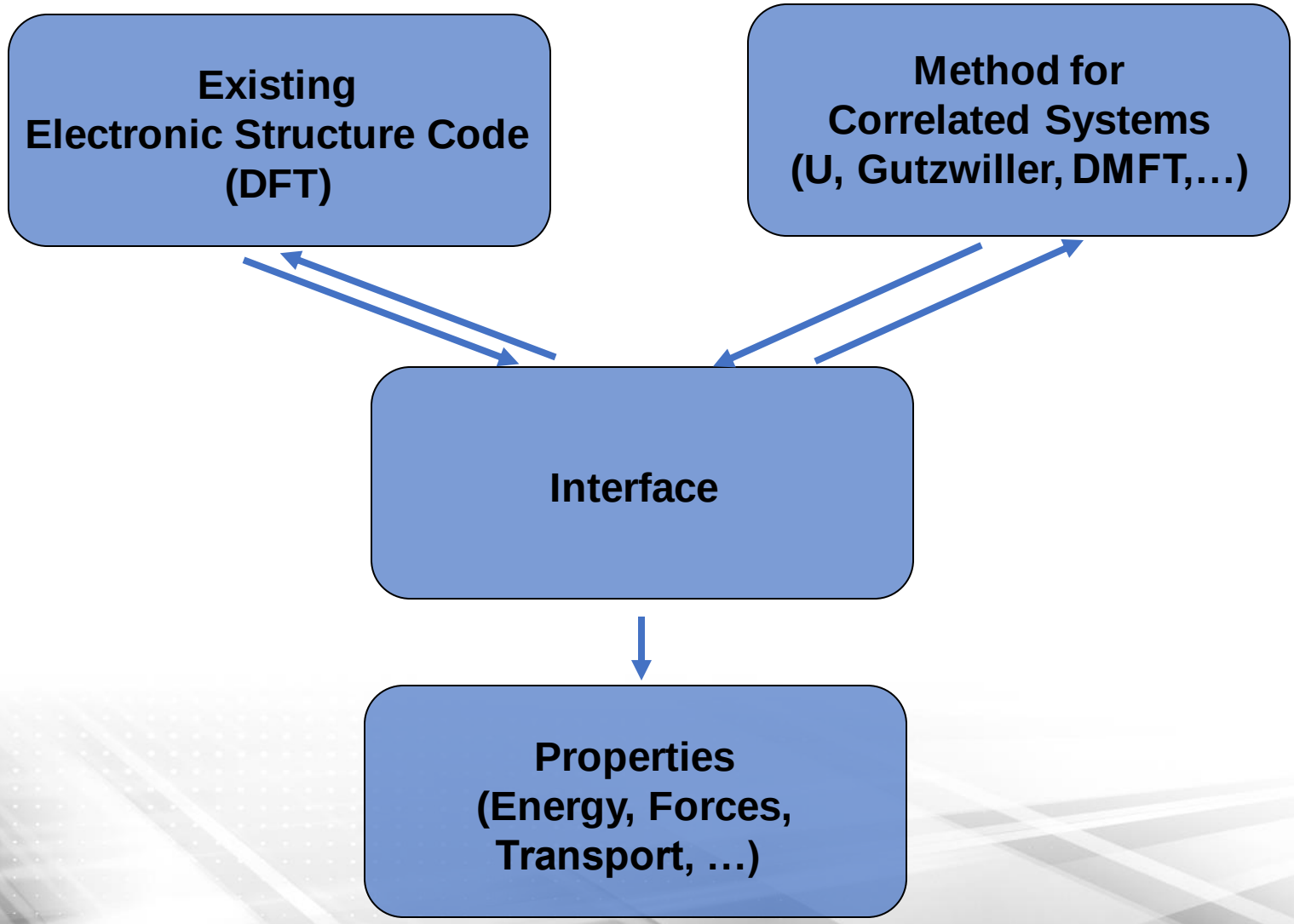


# LDA + Gutzwiller Flow Chart



# The Portobello Framework

## A Modern Software Ecosystem



# The Portobello Framework

## A Modern Software Ecosystem

**Existing Electronic Structure Code (DFT)**

**Method for Correlated Systems (U, Gutzwiller, DMFT,…)**

**Properties (Energy, Forces, Transport, …)**

**PORTOBELLO**

# The Portobello Framework

How to compute Free Energy within LDA+GA

**FlapwMBPT**

Same term in LDA+GA, except that it contains $H_{qp}$ instead of $H_{KS}$

$$\Omega_{DFT} = -\frac{1}{\beta N_{\mathbf{k}}} \sum_{\alpha \mathbf{k} \lambda} Ln\left[1 + e^{-(\varepsilon_{\lambda}^{\alpha \mathbf{k}} - \mu)\beta}\right] - Tr(V_H \rho) - Tr(V_{xc} \rho) + E_{coul}[\rho] + E_{xc}[\rho]$$

$$F_{DFT} = \Omega_{DFT} + \mu N$$

# The Portobello Framework

How to compute Free Energy within LDA+GA

**FlapwMBPT**

**Gutzwiller Implementation**

$$H_{qp} = \mathcal{R}\varepsilon_k\mathcal{R}^{\dagger} + \lambda$$

$$\Omega_{DFT} = -\frac{1}{\beta N_{\mathbf{k}}}\sum_{\alpha\mathbf{k}\lambda} Ln\left[1 + e^{-(\varepsilon_{\lambda}^{\alpha\mathbf{k}}-\mu)\beta}\right]$$

$$- Tr(V_H\rho) - Tr(V_{xc}\rho)$$

$$+ E_{coul}[\rho] + E_{xc}[\rho]$$

# The Portobello Framework

## How to compute Free Energy within LDA+GA

### Python Code

```
for k, si in gutz.irr_k_si_pairs():

    HkB = Matrix(gutz.HkBands[k, :,:, si])

    R = Matrix(np.eye(gutz.num_bands, gutz.num_bands, dtype=np.complex128))
    R += gutz.EmbeddedIntoKBandWindow((gutz.R - gutz.ID)[:,:,si], k, si)
    L = Matrix(gutz.EmbeddedIntoKBandWindow(gutz.Lambda[:,:,si], k, si))

    # Quasi particle hamiltonian
    Hqp = R * HkB * R.H + L

    Eqp, _u = np.linalg.eigh(Hqp)
```

Construction of $H_{qp}$

```
    assert(FG.Hqp.shape[0] == Eqp.shape[0])
    FG.Hqp[:,k, si] = Eqp[:]
```

→ To Fortran code

# The Portobello Framework

## How to compute Free Energy within LDA+GA

Fortran Code

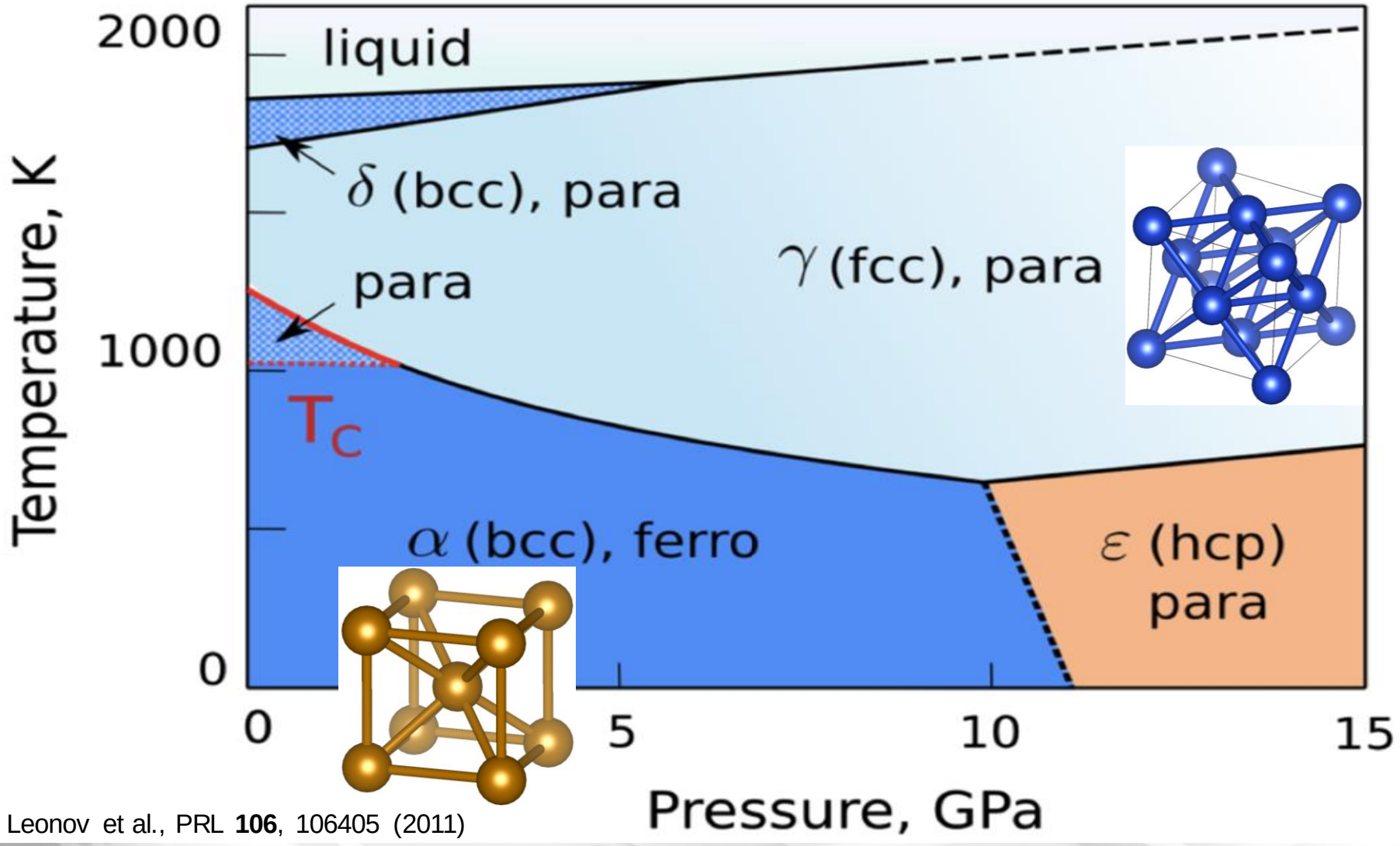
```
e_bnd(FE%min_band:Fe%max_band,:,:) = FE%Hqp_(:,:,:)/rydberg +chem_pot
```

```
call set_g
call etot_gw_2
```

Subroutine in FlapwMBPT that computes the Free Energy

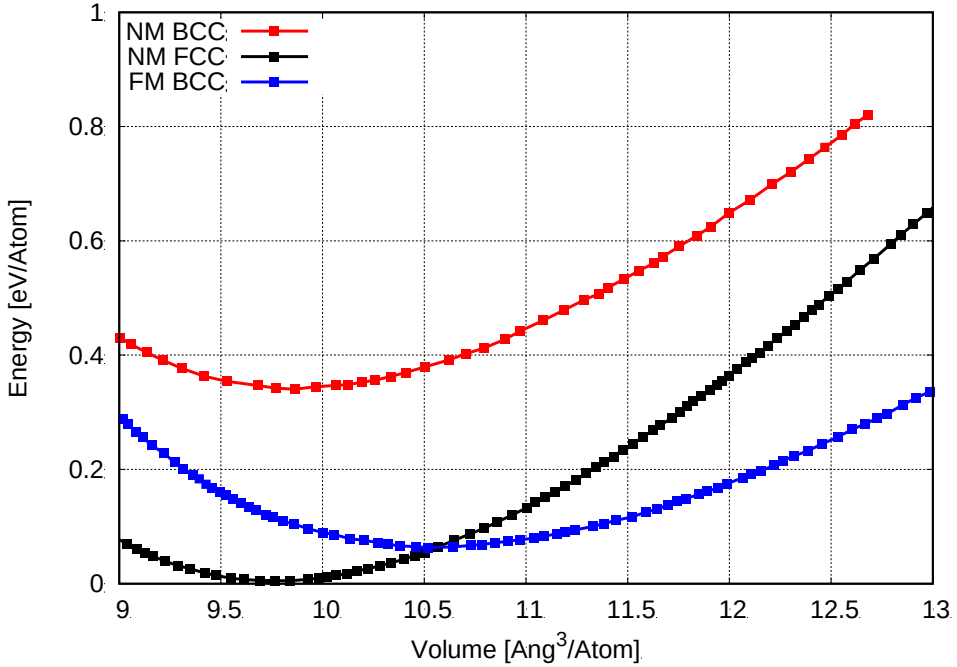
```
print *, "LDA+GUTZWILLER ENERGIES"
print *, "  LDA+GA Free Energy:", AddUpFreeEnergy() + Fe%corr_energy_term/rydberg
print *, "  Correlation Term:", Fe%corr_energy_term/rydberg
```

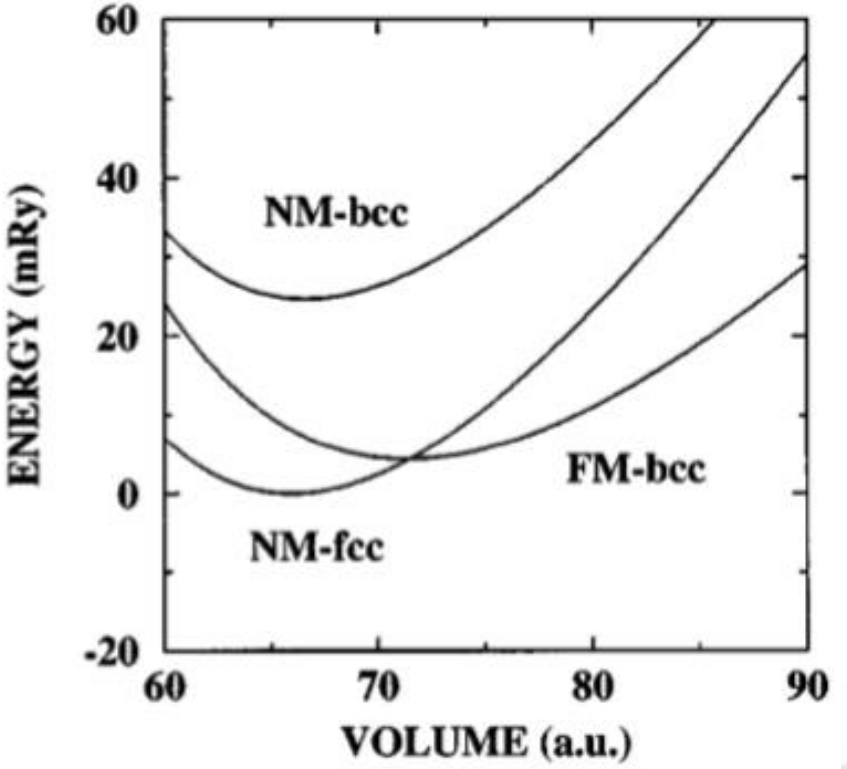
# Example #1: Ground State of Iron




Leonov et al., PRL **106**, 106405 (2011)

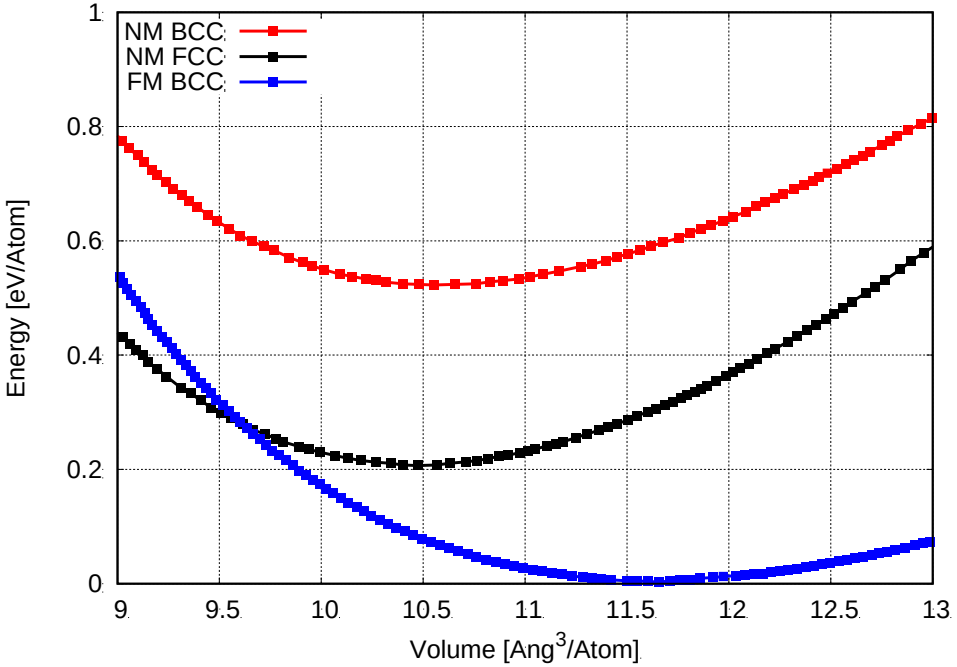
# Ground State of Iron: LDA

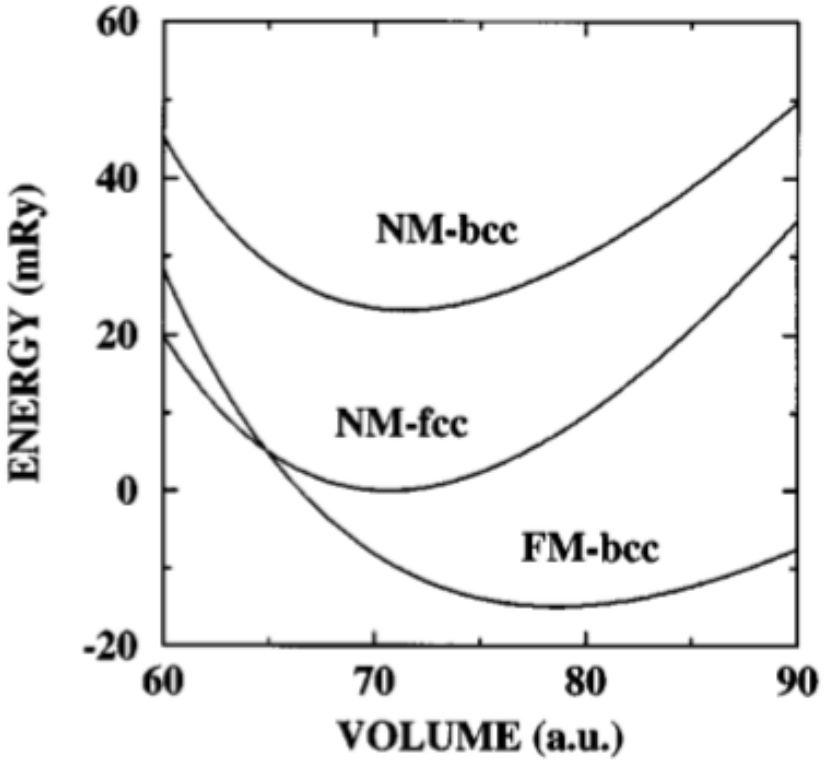



Cho et al., PRB **53**, 10685 (1996)

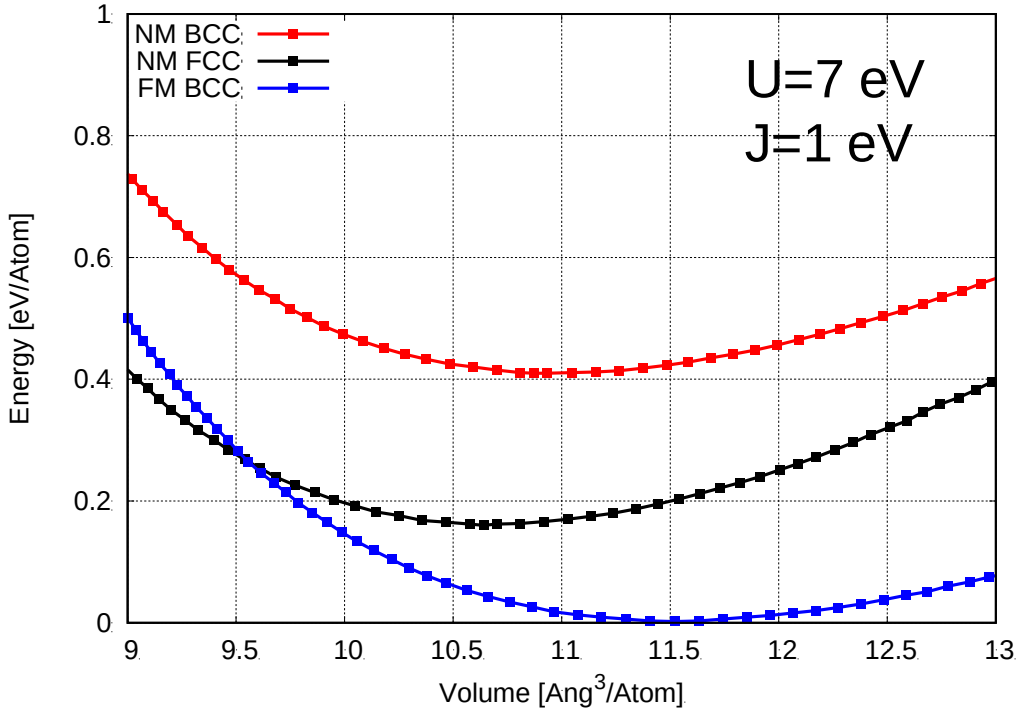
# Ground State of Iron: GGA

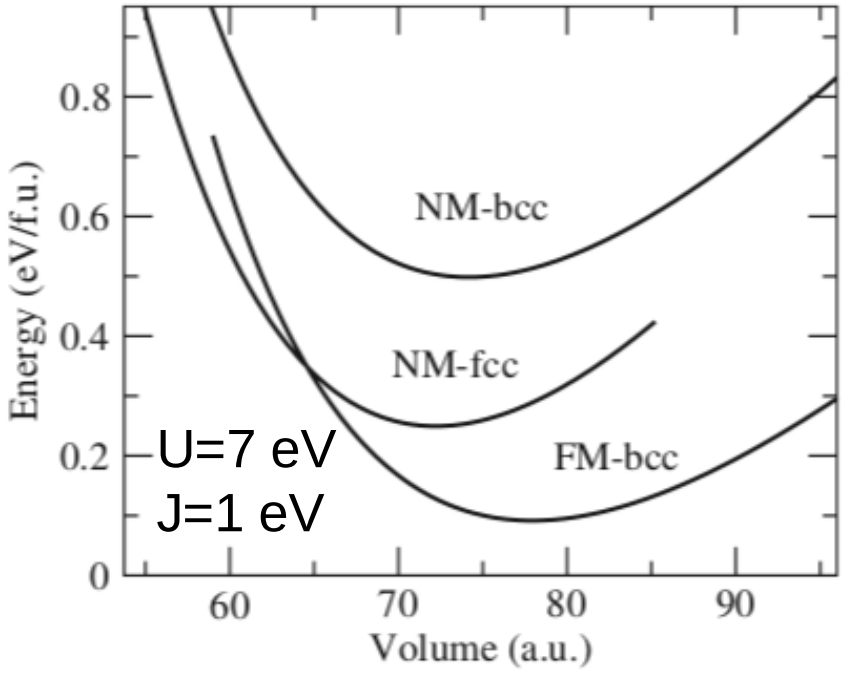



Cho et al., PRB **53**, 10685 (1996)

# Ground State of Iron: LDA+Gutzwiller



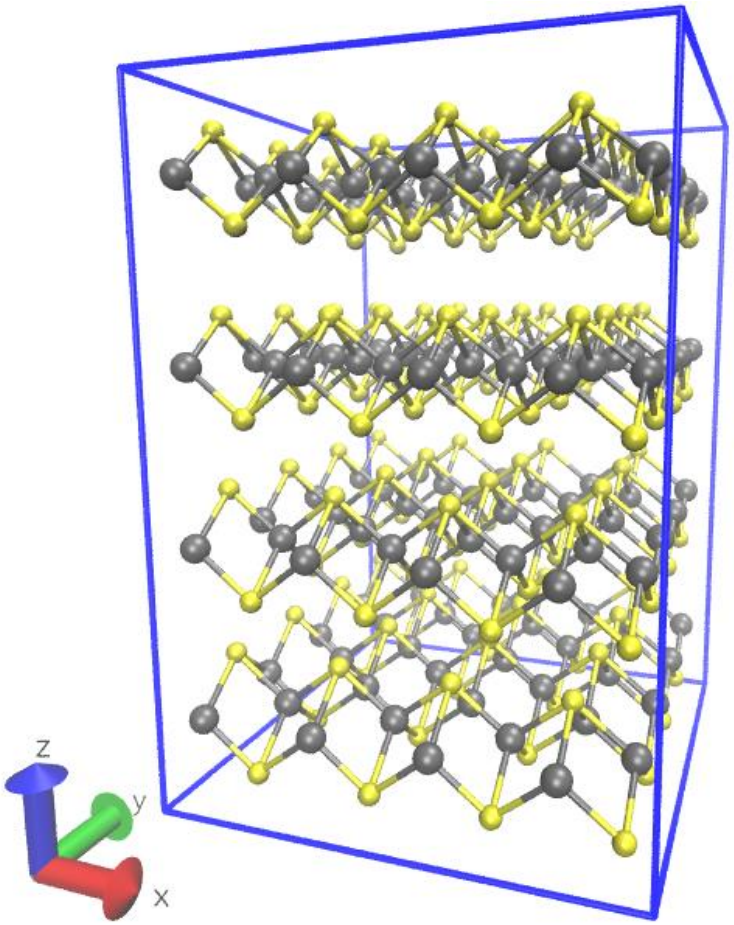

Deng, et al., EPL **83**, 37008 (2008)

# Ground State of Iron: Mechanical Properties

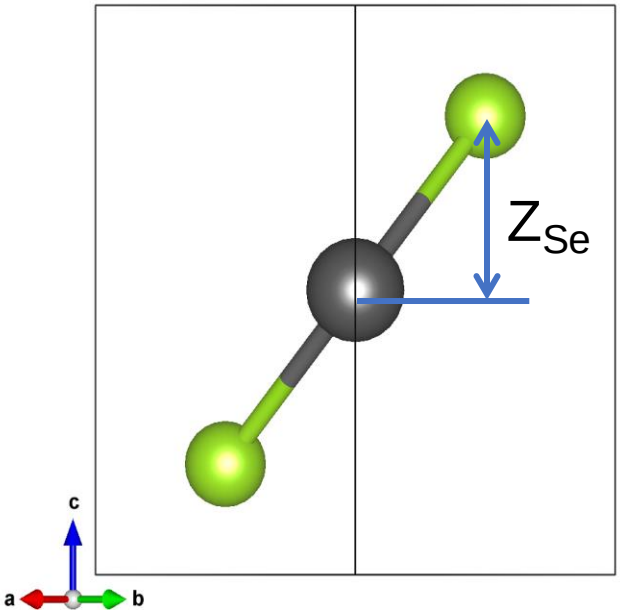
| | LDA | GGA | LDA + GA | EXP* |
|---|---|---|---|---|
| Lattice Parameter [Å] | 2.75 | 2.83 | 2.85 | 2.87 |
| Bulk Modulus [GPa] | 230 | 182 | 162 | 168 |
| Magnetic Moment [$\mu_B$] | 2.08 | 2.16 | 2.30 | 2.22 |

*Villars, Inorganic Solid Phases Springer Materials (2016)

# Example #2: Structure of FeSe



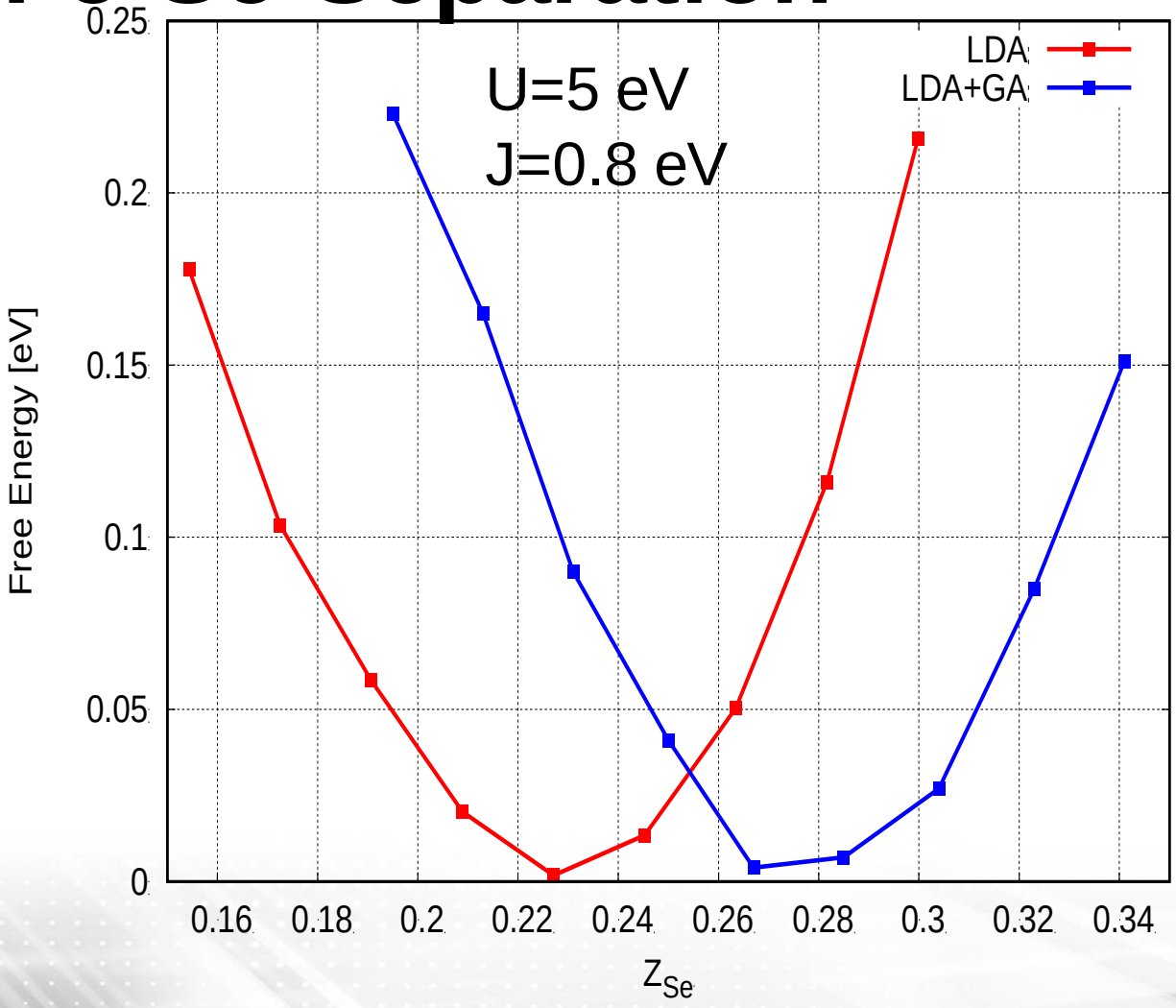

Layered material that crystalizes in a tetragonal phase with space group P4/nmm (#129)

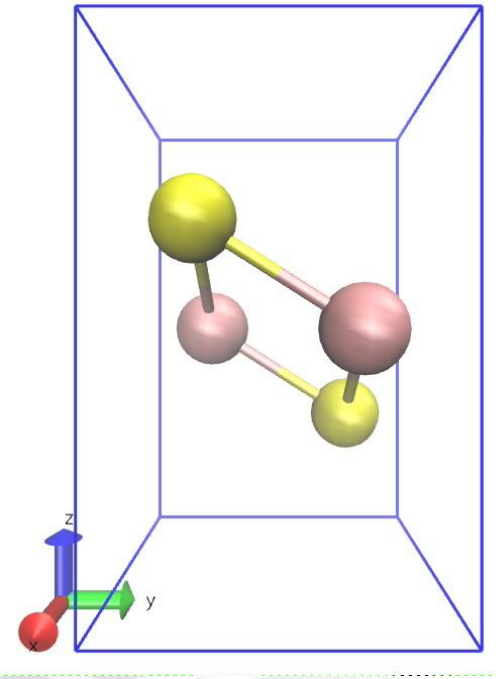




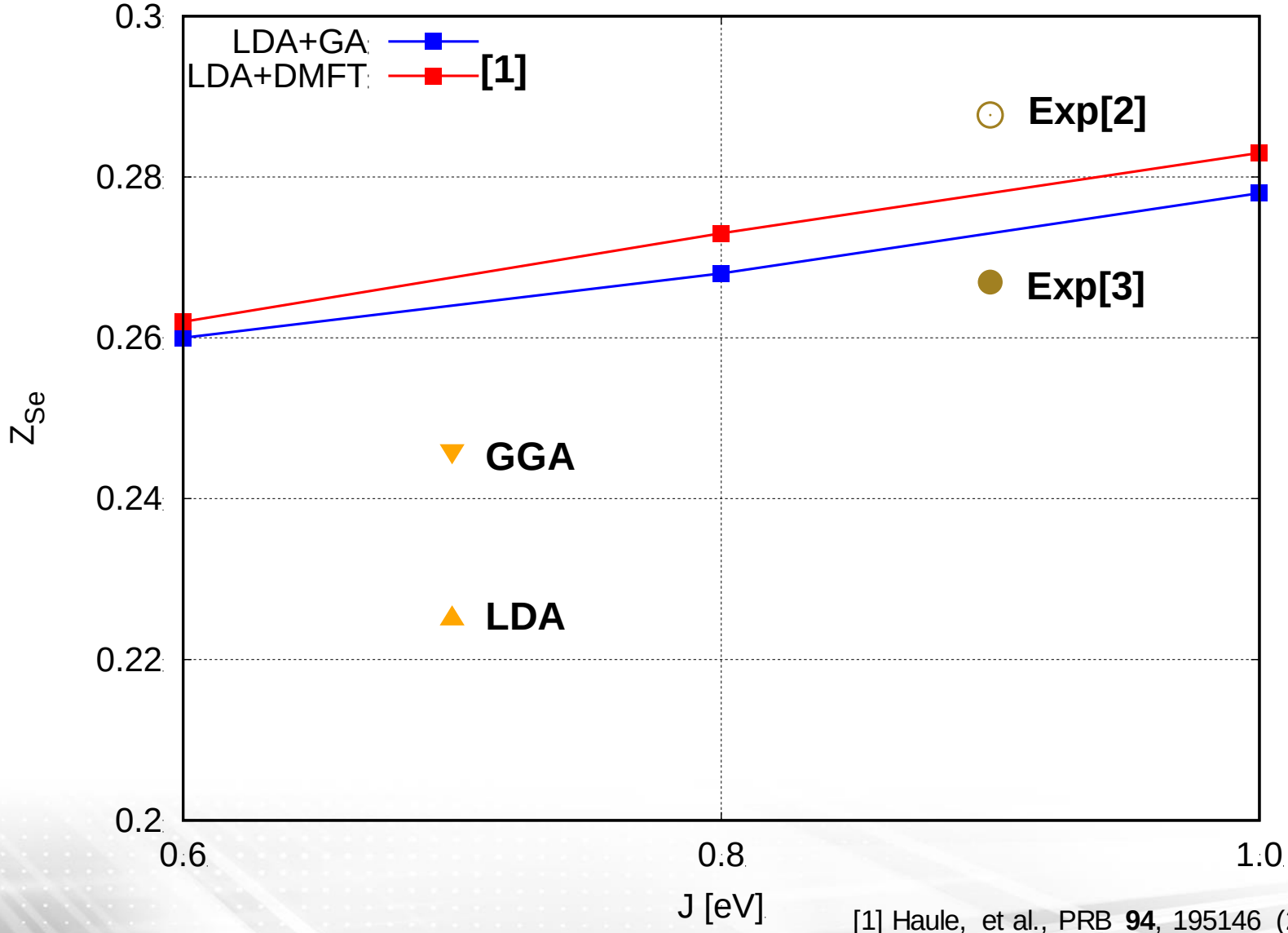
Subedi, et al., PRB **78**, 134514 (2008)
Hsu, et al., Proc. Natl. Acad. Sci. **105**, 14262 (2008)
Medvedev, et al., Nat. Mater. **8**, 630 (2009)
Liu, et al., Nat. Comm. **3**, 931 (2012)
Sunao, et al., Nat. Comm. **10**, 825 (2019)

# Structure of FeSe: Fe-Se Separation



# Fe-Se Separation





[1] Haule, et al., PRB **94**, 195146 (2016)
[2] Kumar, et al., J. Phys. Chem. B, 114 (2010)
[3] McQeen, et al., PRB **79**, 014522 (2009)

# Force Formulation: LDA

$$\Gamma[\rho, V_{KS}] = -TrLn[-i\omega + \varepsilon_{\mathbf{k}} - \mu] - Tr((V_H + V_{xc})\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} + \mu N$$

Variation of the energy functional with respect to small displacements of the atomic positions

$$d_{\mathbf{R}_\mu}\Gamma[\rho, V_{KS}] = Tr\left[\frac{\partial \varepsilon_{\mathbf{k}}}{i\omega - \varepsilon_{\mathbf{k}} + \mu}\right] - \sum_\mu \mathbf{F}^{HF} \partial \mathbf{R}_\mu$$

Hellman-Feynman Force

Pulay Force

$$\mathbf{F}^{Pulay} = -Tr\left[\frac{1}{i\omega - \varepsilon_{\mathbf{k}} + \mu}\frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{R}_\mu}\right]$$

$$\mathbf{F}^{HF} = -Tr\left(\rho \frac{\partial V_{nuclei}}{\partial \mathbf{R}_\mu}\right) - \frac{\partial E_{nuclei}}{\partial \mathbf{R}_\mu}$$

# Force Formulation: LDA

With an arbitrary basis set:

$$|\psi_{i\mathbf{k}}\rangle = \sum_{\mathbf{K}} A_{i\mathbf{K}} |\chi_{\mathbf{K}}\rangle \quad \longrightarrow \quad \sum_{\mathbf{K}} H^{KS}_{\mathbf{K}'\mathbf{K}} A_{i\mathbf{K}} = \sum_{\mathbf{K}} \mathcal{O}_{\mathbf{K}'\mathbf{K}} A_{i\mathbf{K}} \varepsilon_{i\mathbf{k}}$$

And the Pulay force can be written as:

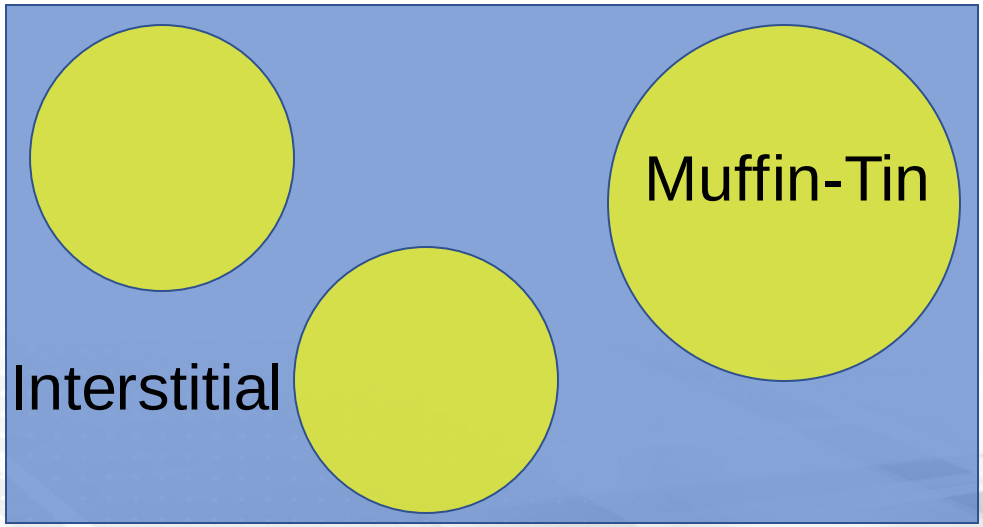
$$\begin{aligned}
\mathbf{F}^{Pulay} &= -Tr\left[\frac{1}{i\omega - \varepsilon_{\mathbf{k}} + \mu}\frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{R}_\mu}\right] \\
&= -Tr\left[\frac{1}{i\omega - \varepsilon_{\mathbf{k}} + \mu}\left(A^\dagger \frac{\partial H^{KS}}{\partial \mathbf{R}_\mu} A - \varepsilon A^\dagger \frac{\partial \mathcal{O}}{\partial \mathbf{R}_\mu} A\right)\right]
\end{aligned}$$

# Force Formulation: LDA (LAPW Basis)

Planewave

$$\chi_{\mathbf{K}}(\mathbf{r}) = \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} & \mathbf{r} \in Int \\ \sum_{lm,\mu} [a_{lm\mu\mathbf{K}} u_l(|\mathbf{r}-\mathbf{r}_\mu|) + b_{lm\mu\mathbf{K}} \dot{u}_l(|\mathbf{r}-\mathbf{r}_\mu|)] Y_{lm}(R_\mu(\mathbf{r}-\mathbf{r}_\mu)) & |\mathbf{r}-\mathbf{r}_\mu| \leq R_{MT_\mu} \end{cases}$$

Atomic-like



# Force Formulation: LDA (LAPW Basis)

$$\mathbf{F}^{Pulay} = -\sum_{\mathbf{K}\mathbf{K}',i} f_i \; A^{\dagger}_{i\mathbf{K}'} A_{i\mathbf{K}} \; i(\mathbf{K}-\mathbf{K}') \; \langle \chi_{\mathbf{K}'} | T + V_{KS} | \chi_{\mathbf{K}} \rangle_{MT}$$

$$+ \sum_{\mathbf{K}\mathbf{K}',i} f_i \varepsilon_i \; A^{\dagger}_{i\mathbf{K}'} A_{i\mathbf{K}} \; i(\mathbf{K}-\mathbf{K}') \; \langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle_{MT}$$

$$+ \sum_{\mathbf{K}\mathbf{K}',i} f_i \; A^{\dagger}_{i\mathbf{K}'} A_{i\mathbf{K}} [(\mathbf{k}+\mathbf{K}')\cdot(\mathbf{k}+\mathbf{K}) - \varepsilon_i] \oint d\mathbf{S}_{\mu} \; \chi^{*}_{\mathbf{K}'} \chi_{\mathbf{K}}$$

$$+ Tr(V_{KS} \nabla \rho)$$

LDA/GGA
Yu et al., PRB **43**, 6411 (1991)
Kluppelberg et al., PRB **91**, 035105 (2015)

LDA+DMFT
Haule, et al., PRB **94**, 195146 (2016)

# Force Formulation: LDA+GA

Similarly, starting from the LDA+GA functional:

$$\Gamma^{GA}\Big[\rho, V_{KS};|\Phi\rangle, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \mu; \mathcal{D}, \mathcal{D}^\dagger, \lambda^c; \Delta_p\Big]$$
$$= -TrLn[-i\omega + \tilde{\varepsilon}_{\mathbf{k}} - \mu]$$
$$+ \sum_i \Big[\langle\Phi_i|H_i^{\rm emb}|\Phi_i\rangle + E_i^c(1 - \langle\Phi_i|\Phi_i\rangle)\Big]$$
$$- \sum_i \Big[\sum_{ab}\big([\lambda_i]_{ab} + [\lambda_i^c]_{ab}\big)[\Delta_{pi}]_{ab} + \sum_{ca\alpha}\big([\mathcal{D}_i]_{a\alpha}[\mathcal{R}_i]_{c\alpha}[\Delta_{pi}(1-\Delta_{pi})]^{\frac{1}{2}}_{ca} + \text{c.c}\big)\Big]$$
$$- Tr((V_H + V_{xc})\rho) + E_H[\rho] + E_{xc}[\rho] + E_{nuclei} + \mu N$$

The Pulay force takes the familiar form:

$$\mathbf{F}^{Pulay} = -Tr\left[\frac{1}{i\omega - \tilde{\varepsilon}_{\mathbf{k}} + \mu}\frac{\partial\tilde{\varepsilon}_{\mathbf{k}}}{\partial\mathbf{R}_\mu}\right] + \sum_i\left\langle\Phi_i\left|\frac{\partial H_i^{emb}}{\partial\mathbf{R}_\mu}\right|\Phi_i\right\rangle$$

# Force Formulation: LDA+GA

With an arbitrary basis set:

$$|\psi_{i\mathbf{k}}\rangle = \sum_{\mathbf{K}} C_{i\mathbf{K}} |\chi_{\mathbf{K}}\rangle$$

The LDA+GA eigenvalue problem takes the form:

$$\sum_{\mathbf{K}} H^{GA}_{\mathbf{K}'\mathbf{K}} C_{i\mathbf{K}} = \sum_{\mathbf{K}} \mathcal{O}_{\mathbf{K}'\mathbf{K}} C_{i\mathbf{K}} \tilde{\varepsilon}_{i\mathbf{k}}$$

Where we can compute the variation of $\tilde{\varepsilon}$ as:

$$\partial\tilde{\varepsilon} = C^{\dagger}[\mathcal{R}[\partial T^{hop} + \partial V^{hop}_{KS}]\mathcal{R}^{\dagger} - \tilde{\varepsilon}\partial\mathcal{O}]C$$

# Force Formulation: LDA+GA

And the Pulay force can be written as:

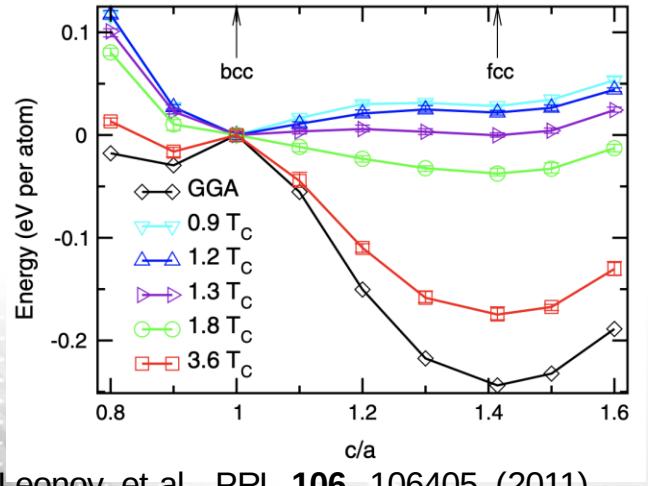
$$
\begin{aligned}
\mathbf{F}^{Pulay} &= -Tr\left[\frac{1}{i\omega-\tilde{\varepsilon}_{\mathbf{k}}+\mu}\frac{\partial\tilde{\varepsilon}_{\mathbf{k}}}{\partial\mathbf{R}_{\mu}}\right]+\sum_{i}\left\langle\Phi_{i}\left|\frac{\partial H_{i}^{emb}}{\partial\mathbf{R}_{\mu}}\right|\Phi_{i}\right\rangle \\
&= -Tr\left[\frac{1}{i\omega-\tilde{\varepsilon}_{\mathbf{k}}+\mu}\left(C^{\dagger}\frac{\partial H^{GA}}{\partial\mathbf{R}_{\mu}}C-\tilde{\varepsilon}C^{\dagger}\frac{\partial\mathcal{O}}{\partial\mathbf{R}_{\mu}}C\right)\right]+\sum_{i}\left\langle\Phi_{i}\left|\frac{\partial H_{i}^{emb}}{\partial\mathbf{R}_{\mu}}\right|\Phi_{i}\right\rangle \\
&= -Tr\left[\frac{1}{i\omega-\tilde{\varepsilon}_{\mathbf{k}}+\mu}\left(C^{\dagger}\left[\mathcal{R}\left(\frac{\partial T^{hop}}{\partial\mathbf{R}_{\mu}}+\frac{\partial V_{KS}^{hop}}{\partial\mathbf{R}_{\mu}}\right)\mathcal{R}^{\dagger}\right]C-\tilde{\varepsilon}C^{\dagger}\frac{\partial\mathcal{O}}{\partial\mathbf{R}_{\mu}}C\right)\right] \\
&\quad+\sum_{i}\left\langle\Phi_{i}\left|\frac{\partial T_{i}^{loc}}{\partial\mathbf{R}_{\mu}}+\frac{\partial V_{iKS}^{loc}}{\partial\mathbf{R}_{\mu}}\right|\Phi_{i}\right\rangle
\end{aligned}
$$

# Work in Progress

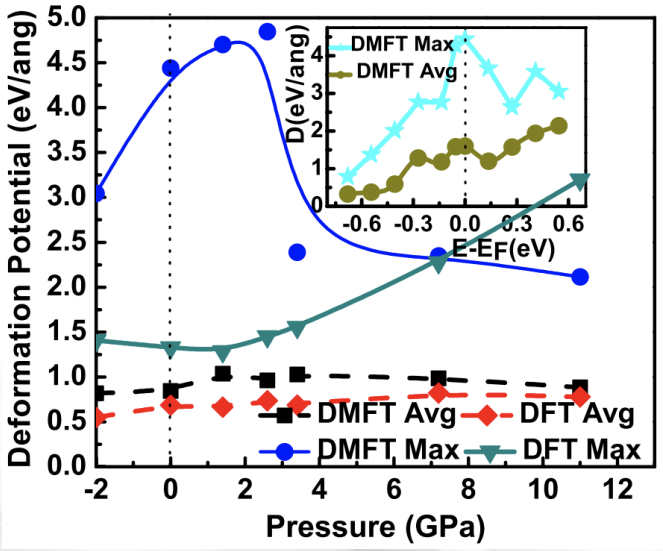
1. Implementation of LDA+GA forces within the Portobello framework

2. Calculation of Bain paths for BCC/FCC phase transformations (LDA+GA)

3. Deformation potential of FeSe (LDA+GA)




Leonov et al., PRL **106**, 106405 (2011)




Mandal et al., PRB **89**, 220502 (2014)