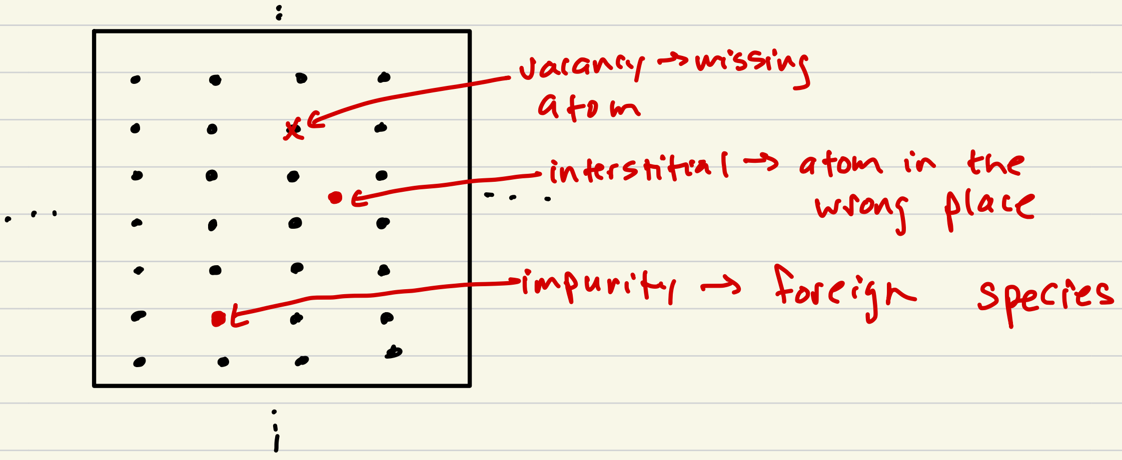
Quantum embedding for point defects

- What is a point defect? Consider a crystal lattice

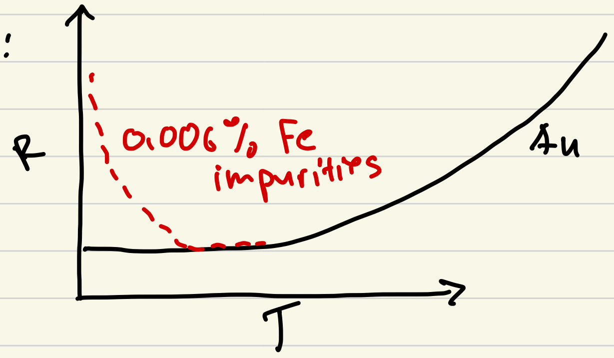


- Why are we interested in point defects?
  - Exist in all materials: $C \propto e^{-E_{form}/k_BT}$ due to configurational entropy
  - Profoundly change material properties at low densities

Examples: * 1 dopant per 10,000 unit cells makes $SrTiO_3$ superconductor

* 1 defect per 100,000 unit cells will kill solar cell or LED

* Kondo effect:

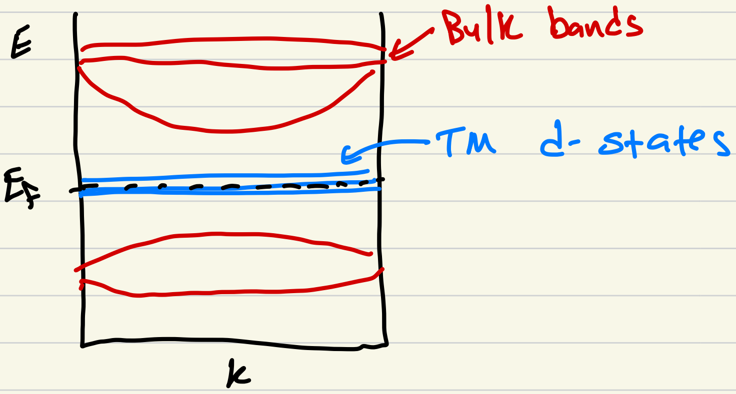


* Defects can be used as qubits

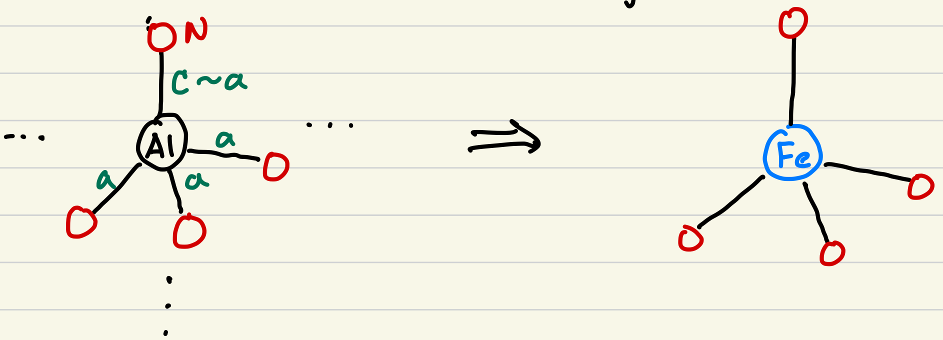
Challenge: Point defects with strong correlations

- Example: Transition-metal impurity in semiconductor

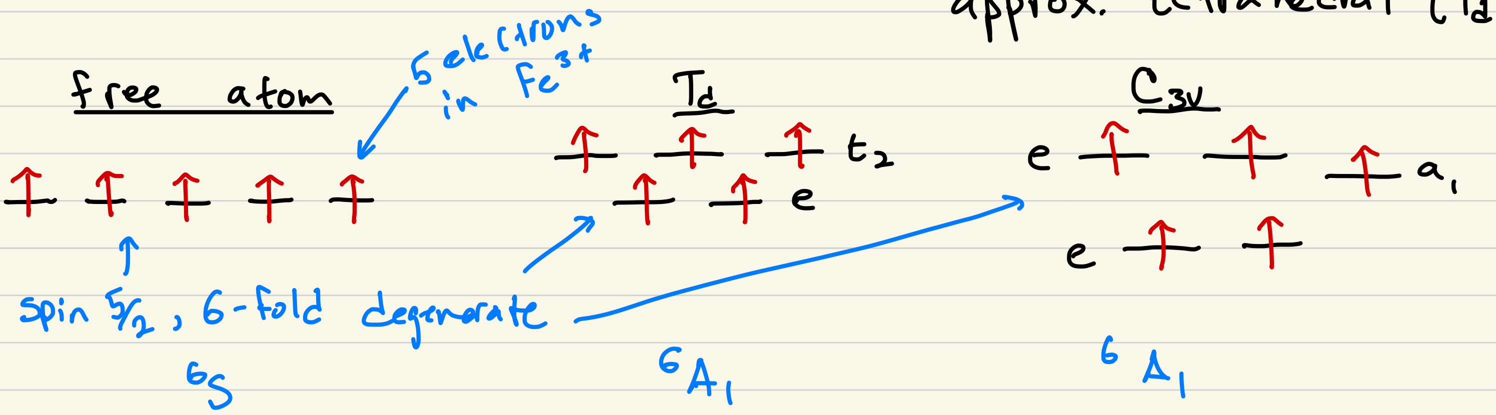
Band structure from mean field theory: (DFT, HF, QPGW)



- Consider Fe replacing Al in AlN



"crystal field" felt by Fe: hexagonal (C_{3v}) but approx. tetrahedral (T_d)



How can we describe this wave function?

$$\psi(r_1,r_2,r_3,r_4,r_5) = \xcancel{\phi_1(r_1)\phi_2(r_2)\phi_3(r_3)\phi_4(r_4)\phi_5(r_5)}$$

Needs to be antisymmetric under swapping electrons

- Write as slater determinant:

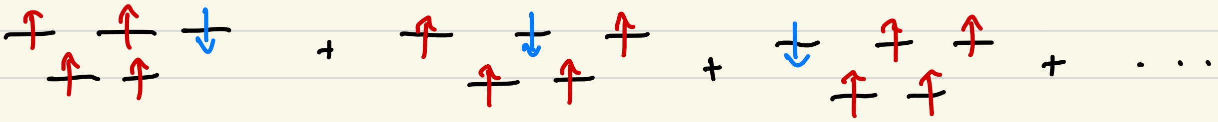
$$\psi(r_1, \cdots, r_5) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots \\ \phi_1(r_2) & \cdot & \cdot \\ \vdots & & \cdots \end{vmatrix} = |\phi_1 \phi_2, \cdots, \phi_5\rangle$$

- In second quantization, utilize creation / annihilation operators: (now w/ spin)

$$\psi(r_1, \cdots, r_5) = \underbrace{c^\dagger_{1\uparrow} c^\dagger_{2\uparrow} c^\dagger_{3\uparrow} c^\dagger_{4\uparrow} c^\dagger_{5\uparrow}}_{\text{automatically enforce antisymmetry since}} |0\rangle = |\overset{\downarrow}{00000};\overset{\uparrow}{11111}\rangle$$

$$\{c_i^\dagger, c_j^\dagger\} = c_i^\dagger c_j^\dagger + c_j^\dagger c_i^\dagger = 0 \Rightarrow c_i^\dagger c_j^\dagger = -c_j^\dagger c_i^\dagger$$

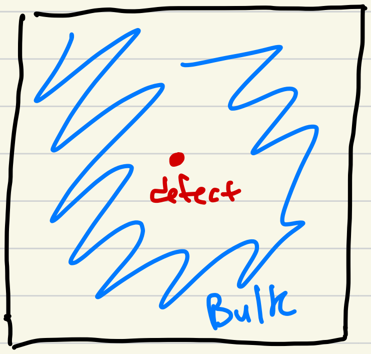
- Now consider first excited state:



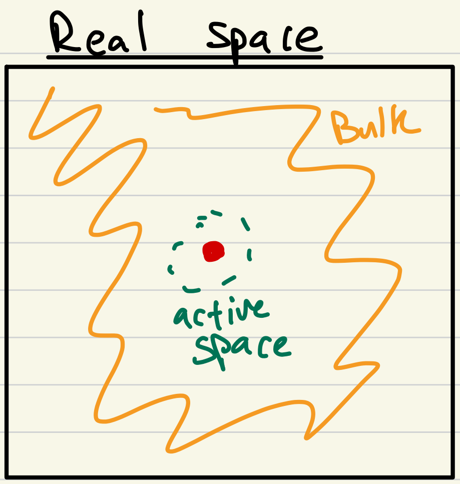
$$\alpha|10000;01111\rangle + \beta|01000;10111\rangle + \gamma|00100;11011\rangle + \cdots$$

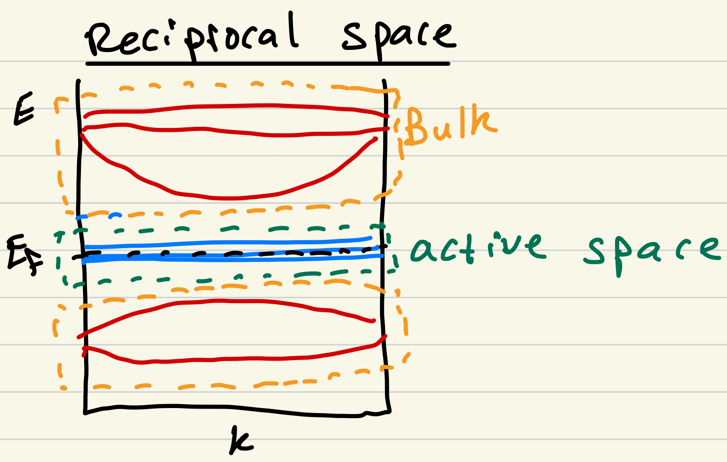
$\Rightarrow$ multiple slater determinants!! Have to go beyond mean field!

- Problem: Many-body methods are computationally expensive
  - Need a large system to model a defect:



- Solution: Embedding → treat defect w/ MB method, Bulk w/ mean field



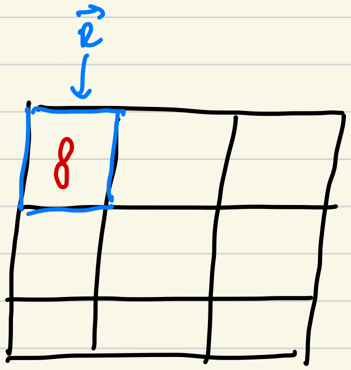


- We can connect the two w/ Wannier orbitals
  - At every state k we have a Bloch function

$$\psi_k(r) = e^{ik\cdot r}\, u_k(r)$$

cell periodic

plane wave



  - Discrete Fourier transform:

$$\phi_R(r) = \frac{1}{\sqrt{N}} \sum_k e^{-ik\cdot R}\, \psi_k(r)$$

Now real space

  - Can include multiple bands:

$$\phi_{nR}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_k \sum_m U^{(k)}_{mn}\, \psi_{mk}(r)\, e^{-ik\cdot R}$$

unitary matrix, chosen to make $\phi(r)$ more localized

- Wannier functions give us a "tight-binding" description:

$$H_0 = -\sum_{ij\sigma} t_{ij}\, c^\dagger_{i\sigma} c_{j\sigma} + h.c. \qquad t_{ij} = -\langle \phi_i | H_{mf} | \phi_j \rangle$$

spin

KS for DFT or HF

active space orbitals

⇒ "Bulk" enters via shape of WFs, i.e., CFS

- Next step, include Coulomb interactions

- In second quantization notation, bare Coulomb:

$$H_{int} = \frac{1}{2} \sum'_{ijkl\sigma\sigma'} V_{ijkl}\, c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{l\sigma} c_{k\sigma'}$$

$$V_{ijkl} = \langle \phi_i \phi_j \mid V_c \mid \phi_k \phi_l \rangle = \int dr_1 \int dr_2\, \phi_i(r_1) \phi^*(r_2) \frac{e^2}{|r_1 - r_2|} \phi_j(r_1) \phi_k(r_2)$$

$\Rightarrow$ Bulk enters via screening of the Coulomb interaction in the active space

$$u = \frac{V}{\varepsilon} = \frac{V}{1 + V\underset{\substack{\uparrow \\ \text{RPA: ind. particle polarizability}}}{\chi_{ir}}} = (1 - V\chi_r)V$$

Recall:

$$V_{tot} = \frac{V_{ext}}{\varepsilon}$$

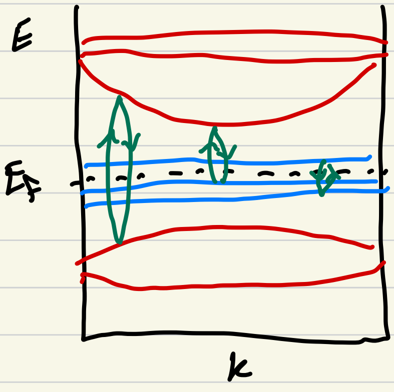
$$\rho_{ind} = \chi_r V_{ext} = \chi_{ir} V_{tot}$$

$$\chi^0_{ir}(r, r', \omega) = \sum_i^{occ} \sum_j^{unocc} \psi_i(r) \psi_i^*(r') \psi_j(r) \psi_j(r')$$

$$\times \left(\frac{1}{\omega - \varepsilon_j + \varepsilon_i + i\eta} - \frac{1}{\omega - \varepsilon_j - \varepsilon_i - i\eta} \right)$$

What do bubbles correspond to physically?

- Virtual transitions from occupied to unoccupied



- "Constrained" RPA: Remove virtual transitions inside of active space
- Give "bare" Coulomb interaction for the effective model in the active space, screened by Bulk

$$\boxed{U^{cRPA} = \left[1 - V\left(\chi_{ir}^{full} - \chi_{ir}^{def} \right) \right] V}$$

Hamiltonian so far:

$$H = -\sum_{ij\sigma}\left(t_{ij}\, c_i^{\dagger} c_j + h.c.\right) + \frac{1}{2}\sum_{ijkl\sigma\sigma'} U^{cRPA}_{ijkl}\, c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{k\sigma} c_{l\sigma'}$$

- **Problem:** t_{ij} comes from mean-field calculation, already has approx Coulomb interaction!
- **Solution:** "Double Counting" correction, remove interactions **within** active space
- For mean-field methods:
  - Hartree-Fock:

$$H^{HF}_{int} = \sum_{ij\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \sum_{kl} \overset{\substack{\text{density matrix element}\\ \downarrow}}{P_{kl}} \left(\underset{\substack{\uparrow\\ \text{(screened): direct}}}{U^{cRPA}_{iljk}} - \frac{1}{2} \underset{\substack{\uparrow\\ \text{exchange}}}{U^{cRPA}_{ilkj}} \right)$$

  - DFT:

$$H^{DFT}_{int} = \overbrace{\sum_{ij\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \sum_{kl} P_{kl} \left(U^{cRPA}_{iljk} - \overset{\substack{\text{mixing parameter if}\\ \text{hybrids}\\ \downarrow}}{\alpha}\, U^{cRPA}_{ilkj} \right)}^{H^{HF}_{den}} + \underset{\substack{\uparrow\\ ??}}{V^{\text{active space}}_{xc}}$$

Problem: V_{xc} is functional of density, cannot decompose inside / outside active space

  - DFT + G_0W_0: Replace $V_{xc} \to iG_0W_0$

$$H^{GW}_{int} = H^{HF}_{den} + i\, G^{A}_{0} W_0$$

$$\hookrightarrow G^{A}_{0} = \sum_{i \in \text{active space}} \frac{\psi_i(r)\,\psi_i^{*}(r)}{\omega - \varepsilon_i + i\eta}$$

- Final Hamiltonian:

$$H = -\sum_{ij\sigma}\left(t_{ij}\, c^{\dagger}_{i\sigma} c_{j\sigma} + h.c.\right) + \frac{1}{2}\sum_{\substack{ijkl\\ \sigma\sigma'}} U_{ijkl}\, c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{k\sigma} c_{l\sigma'}$$

$$- H_{DC} + \sum_{i\sigma} \mu\, c^{\dagger}_{i\sigma} c_i \leftarrow \text{enforces particle number}$$

- How do we solve it? Exact diagonalization a.k.a. full configuration interaction

  - Let's limit ourselves to states w/ 5 electrons
  - Basis states: Any slater determinant state w/ 5 electrons occupied
    ↳ label w/ binary

State	Binary label
$\lvert 00000;11111\rangle$	31
$\lvert 00001;01111\rangle$	47
$\lvert 00001;10111\rangle$	55
$\lvert 00001;11011\rangle$	59
$\vdots$	$\vdots$
$\lvert 11111,00000\rangle$	992

- Construct Hamiltonian matrix:

$$\begin{array}{c|ccccc} & 31 & 47 & 55 & 59 & 992 \\ \hline 31 & \langle 31|H|31\rangle & \langle 31|H|47\rangle & \langle 31|H|55\rangle & \cdots & \cdots \\ 47 & \langle 47|H|31\rangle & & & & \\ 55 & \langle 55|H|31\rangle & \ddots & & & \\ 59 & \vdots & & \ddots & & \\ \vdots & \vdots & & & \ddots & \\ 992 & \vdots & & & & \ddots \end{array}$$

- Size of matrix: $\binom{10}{5} = \frac{10!}{5!\,5!} = 252$

- Total Hilbert space: $2^{10} = 1024$

  e.g.: $\binom{10}{0} + \binom{10}{1} + \binom{10}{2} + \cdots + \binom{10}{10} = 1024$

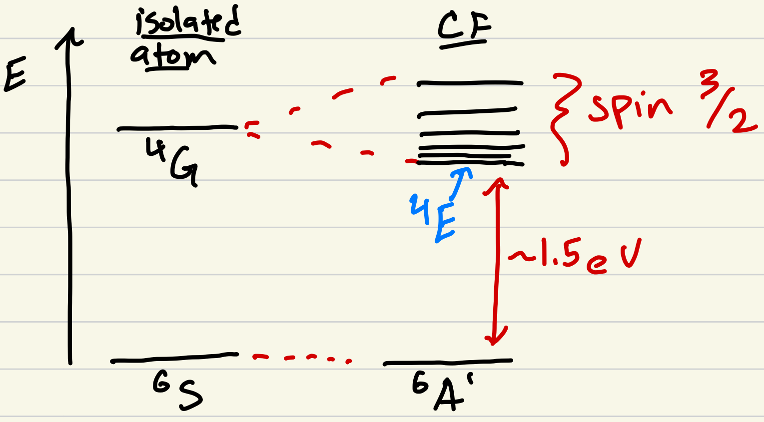
- Now diagonalize the matrix

- Eigenstates: $\Psi_a = \sum_{b}^{\text{basis}} w_{ab}\, c_m^\dagger c_n^\dagger c_o^\dagger c_p^\dagger c_q^\dagger |0\rangle$

  Each b corresponds to a combination of (m, n, o, p, q) in our basis

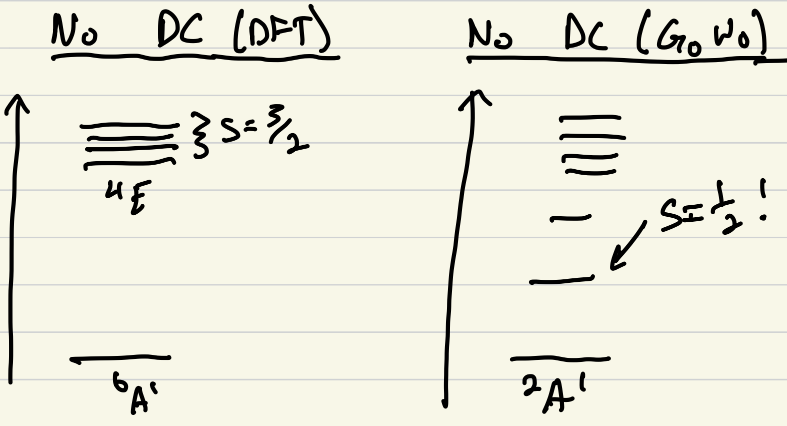
- Eigenvalues: Many body energies $\langle \Psi_a | H | \Psi_b \rangle$
- "charge density" from 1RDM: $\sum_i \langle \Psi_a | c_i^\dagger c_i | \Psi_a \rangle$
- dipole moments: $\langle \Psi_a | \sum_{ij} \langle \phi_i | \vec{r} | \phi_j \rangle c_i^\dagger c_j | \Psi_a \rangle$

Results for Fe in AlN

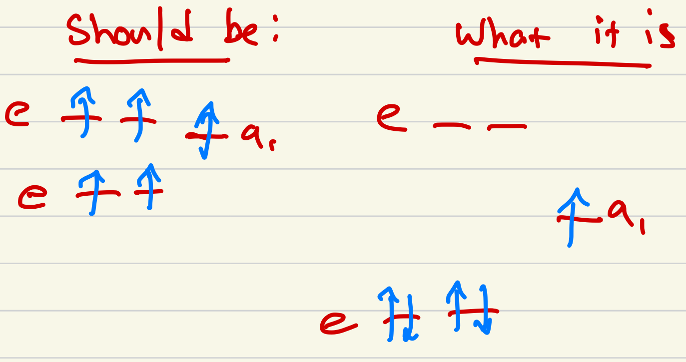


- Agrees well w/ experiment

- Role of the DC correction



Why? look at single particle part plus DC



Overestimates CFS!!

Summary

- Point defects are interesting corelated quantum systems
- Embedding for pt defects:
  - Bulk provides CFS
  - Bulk provides screening
  - Solve "exactly" in subspace
  - DC important !