Predicting Properties from First-Principles I: Electronic and Magnetic Properties

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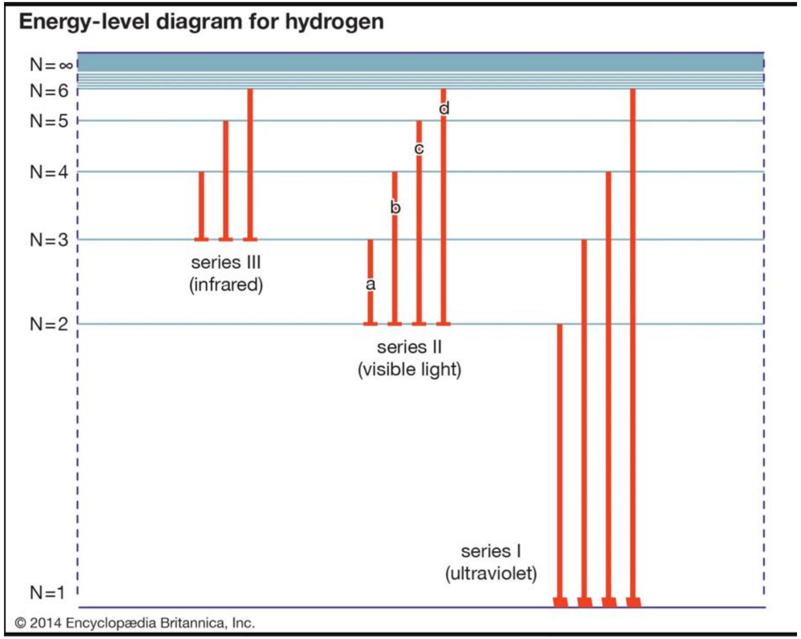
Electronic Structure in Crystals

Adapted from:

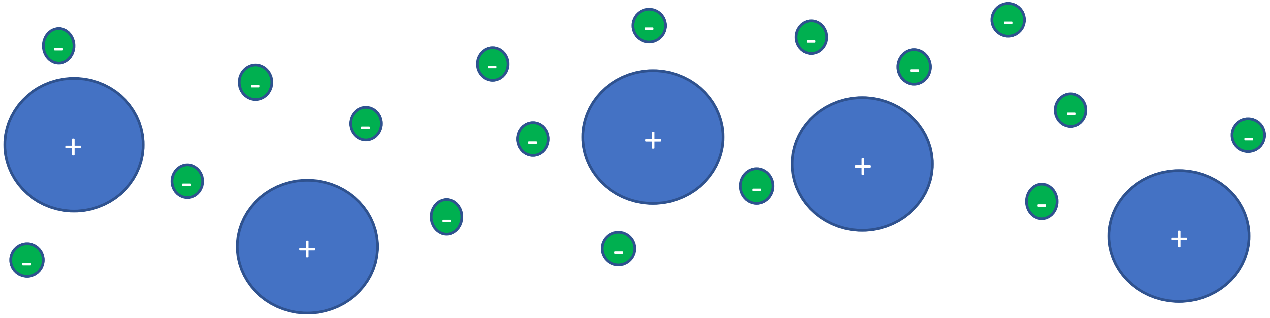
Steven H. Simon, The Oxford Solid State Basics, Oxford University Press, 1st Edition (2013) (reprinted with corrections 2016)

Energy spectrum for non-periodic systems



Allowed energy levels usually depicted by lines in non-periodic systems (atoms, molecules, etc.)

Many-body Hamiltonian



Electrons **Nuclei** **Electron-Nucleus**

$$\hat{H} = \sum_i \frac{\hat{\boldsymbol{p}}_i^{\,2}}{2m} + \frac{1}{2}\sum_{i,j} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_A \frac{\widehat{\boldsymbol{P}_A}^{\,2}}{2M_A} + \frac{1}{2}\sum_{A,B} \frac{Z_A Z_B e^2}{|\boldsymbol{R}_A - \boldsymbol{R}_B|} - \sum_{i,A} \frac{Z_A e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}$$

Kinetic Coulomb Kinetic Coulomb Coulomb

System of N electrons and M nuclei → **3N + 3M** degrees of freedom

Born-Oppenheimer Approximation

Electrons **Nuclei** **Electron-Nucleus**

$$\hat{H} = \sum_i \frac{\hat{\boldsymbol{p}}_i^{\,2}}{2m} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \cancel{\sum_A \frac{\hat{\boldsymbol{P}}_A^{\,2}}{2M_A}} + \boxed{\text{constant}} - \sum_{i,A}\frac{Z_A e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}$$

Kinetic Coulomb Kinetic Coulomb Coulomb fixed

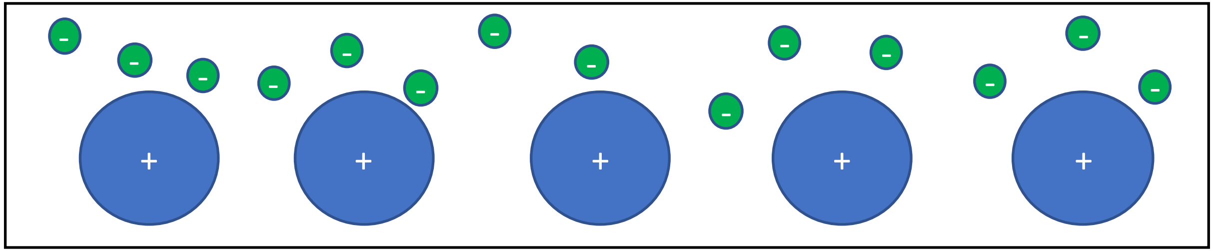
Born-Oppenheimer Approximation

- Nuclei are orders of magnitude bigger than the electrons so we assume the nuclei are moving much slower than the electrons
- The electron wavefunctions evolve adiabatically around changing nuclei positions

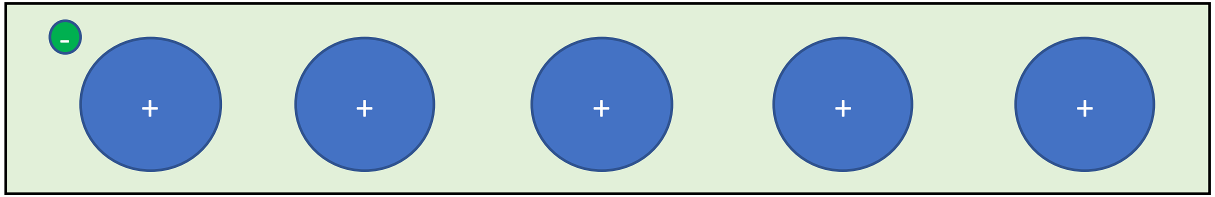
System of N electrons and M nuclei → **3N** degrees of freedom

Electrons in a periodic potential

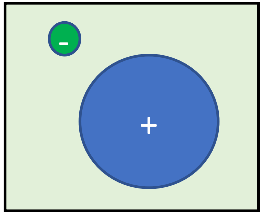
N electrons in infinite periodic array of nuclei



1 electron in infinite periodic array of nuclei and electron charge density ($\rho(r)$) background

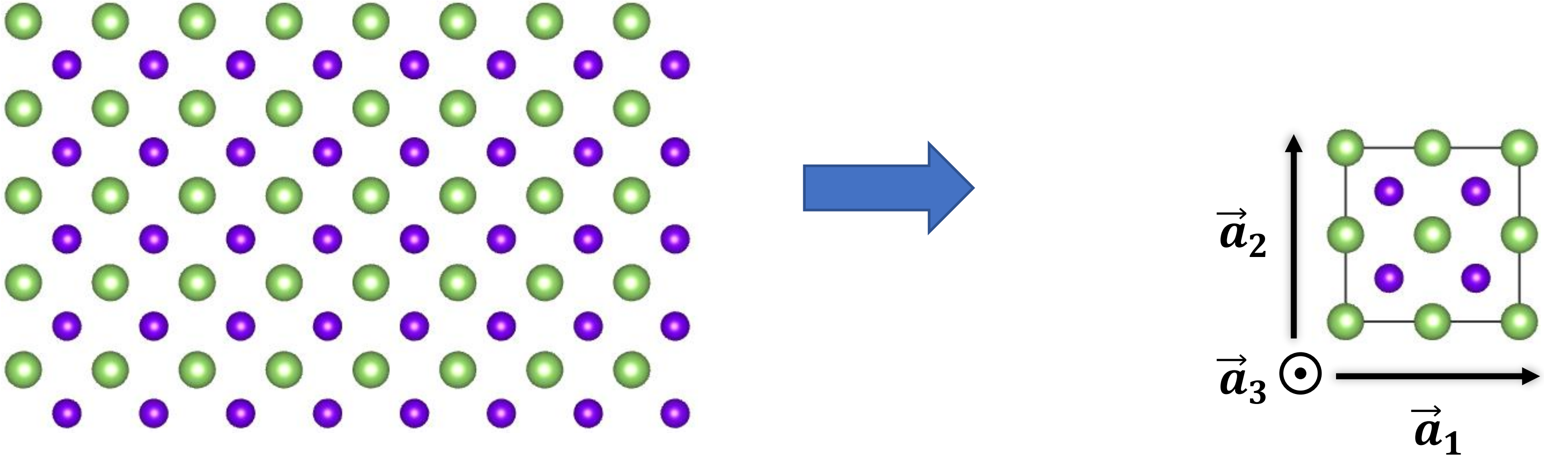


1 electron in unit cell of nuclei and electron charge density ($\rho(r)$) background



$\rightarrow$ **3** degrees of freedom

Translation Symmetry: Unit Cells

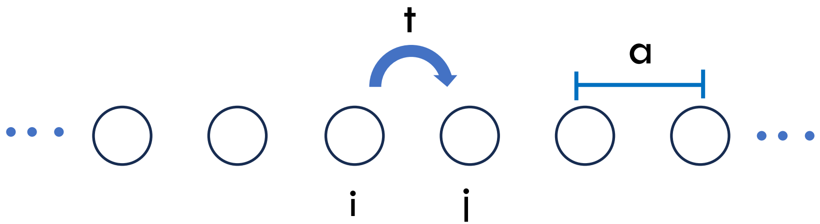


Translation symmetry allows us to study unit cells

- Smallest chunk of crystal that represents the bulk crystal structure when translated in all 3 directions
- Represented by three lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$

Intro to band structures: 1D tight binding model

1D chain with nearest-neighbor hopping



Orbitals $\{\phi_i(\boldsymbol{r})\}$ located at $\boldsymbol{R}_i = ia\hat{\boldsymbol{x}}$

Ref:
The Oxford Solid State Basics
Steven H. Simon

Band Structure

Simple Tight Binding Model - 1D Chain

a: lattice site spacing

t: hopping energy

localized orbitals $\{ \phi_i (\vec{r}) \}$ centered at $\vec{R}_i = ia\hat{x}$

↳ orthonormal

$$\langle i|j \rangle = \int \phi_i^*(\vec{r})\, \phi_j(\vec{r})\, d\vec{r} = \delta_{ij}$$

$$H = \begin{array}{c} \\ \\ \end{array}\begin{array}{cc} \begin{array}{ccc} i-1 & i & i+1 \end{array} & \\ \begin{bmatrix} \ddots & & & \\ & 0 & -t & \\ & -t & 0 & -t \\ & & -t & 0 & -t \\ & & & -t & 0 \\ & & & & & \ddots \end{bmatrix} & \begin{array}{c} i-1 \\ i \\ i+1 \end{array} \end{array}$$

$\langle i|H|j \rangle$

$$H_{ij} = -t\left[\delta_{i+1,j} + \delta_{i-1,j}\right]$$

Fourier Transform $\Psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_i e^{-i\vec{k}\cdot\vec{R}_i}\, \phi_i(\vec{r})$

Energy $E(\vec{k}) = \int d\vec{r}\, \Psi_k^*(\vec{r})\, H\, \Psi_k(\vec{r})$

$$= \int d\vec{r} \left[\frac{1}{\sqrt{N}} \sum_i e^{+i\vec{k}\cdot\vec{R}_i}\, \phi_i^*(\vec{r})\right] H \left[\frac{1}{\sqrt{N}} \sum_j e^{-i\vec{k}\cdot\vec{R}_j}\, \phi_j(\vec{r})\right]$$

$$= \frac{1}{N} \sum_{ij} e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} \int d\vec{r}\, \phi_i^*(\vec{r})\, H\, \phi_j(\vec{r})$$

$$= \frac{1}{N} \sum_{ij} e^{i\vec{k}\cdot(R_i - R_j)} \langle i|H|j \rangle$$

$$= \frac{1}{N} \sum_{ij} e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} \left[-t \left(\delta_{i+1,j} + \delta_{i-1,j} \right) \right]$$

$$= -t \; \frac{1}{N} \sum_{ij} e^{i\vec{k}\cdot(ia\hat{x} - ja\hat{x})} \left(\delta_{i+1,j} + \delta_{i-1,j} \right)$$

$$= -t \; \frac{1}{N} \sum_{i} \left[e^{i\vec{k}\cdot(ia\hat{x} - (i+1)a\hat{x})} + e^{i\vec{k}\cdot(ia\hat{x} - (i-1)a\hat{x})} \right]$$

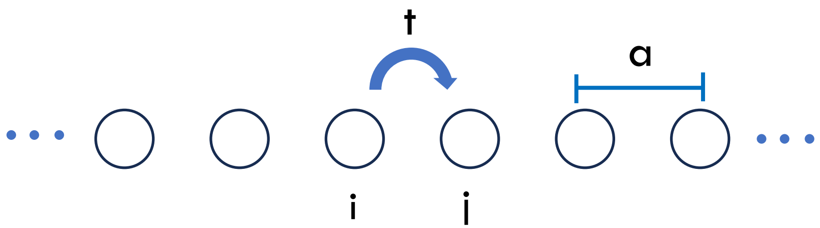
$$= -t \; \frac{1}{N} \sum_{i} \left[e^{-ik_x a} + e^{+ik_x a} \right] \qquad \left\{ \frac{1}{N} \sum_i = 1 \right\}$$

$$= -t \left(e^{-ik_x a} + e^{ik_x a} \right)$$

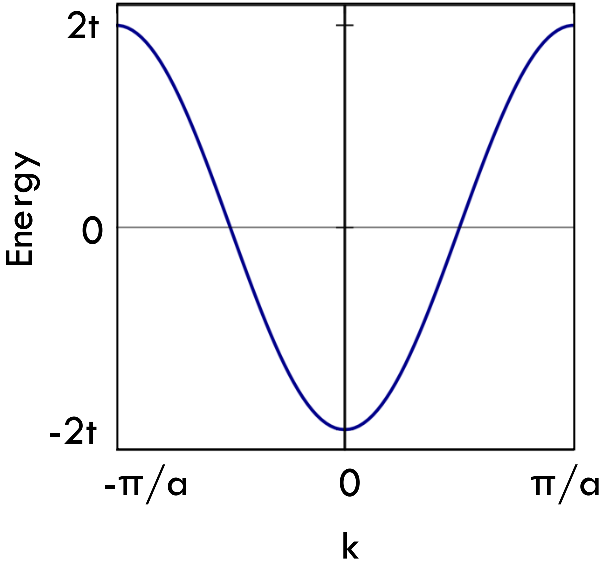
$$= -t \left(2\cos(k_x a) \right)$$

$$E(\vec{k}) = -2t\cos(ka) \qquad \left(\text{dropping } k_x \to k \text{ for brevity} \right)$$

1D chain band structure in k-space

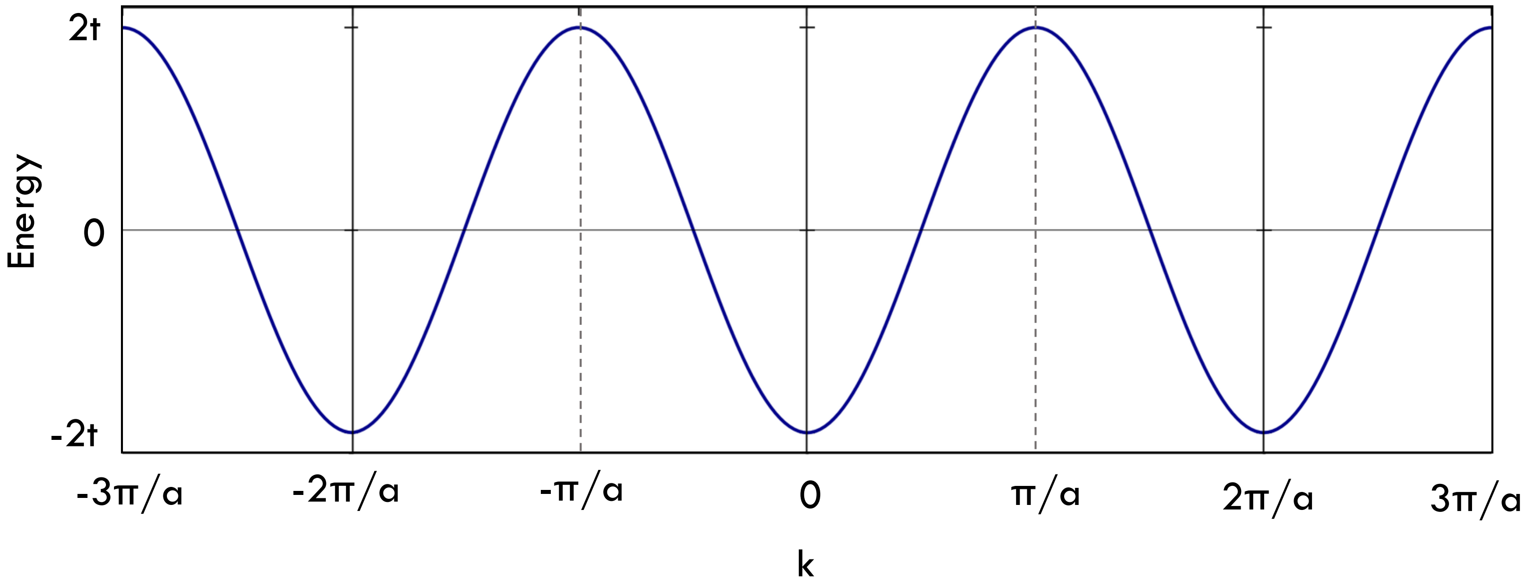


$E(k) = -2t\ cos(ka)$

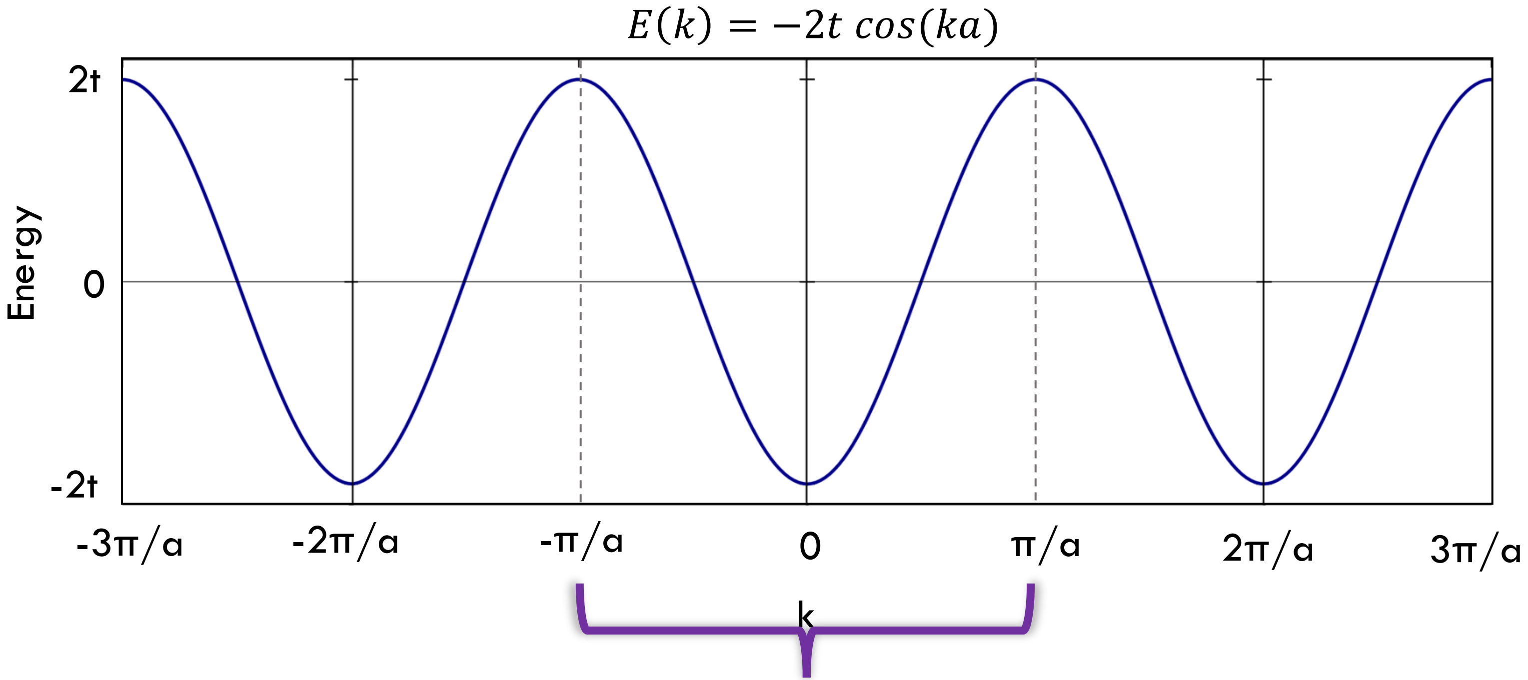


Note that band structure is periodic in k-space

$$E(k) = -2t\ cos(ka)$$



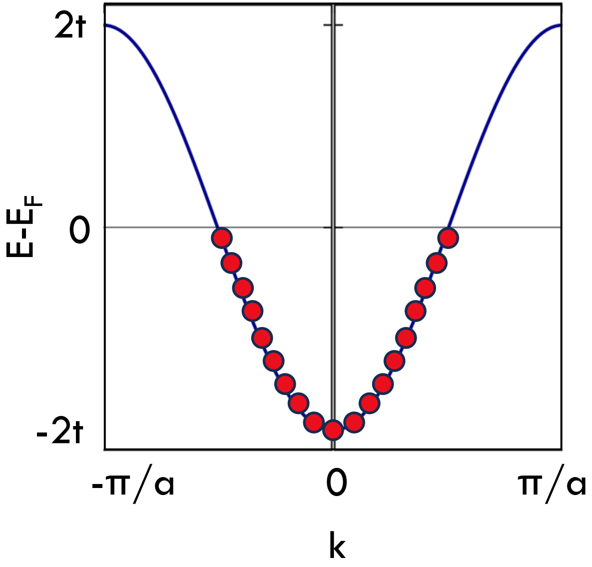
Note that band structure is periodic in k-space



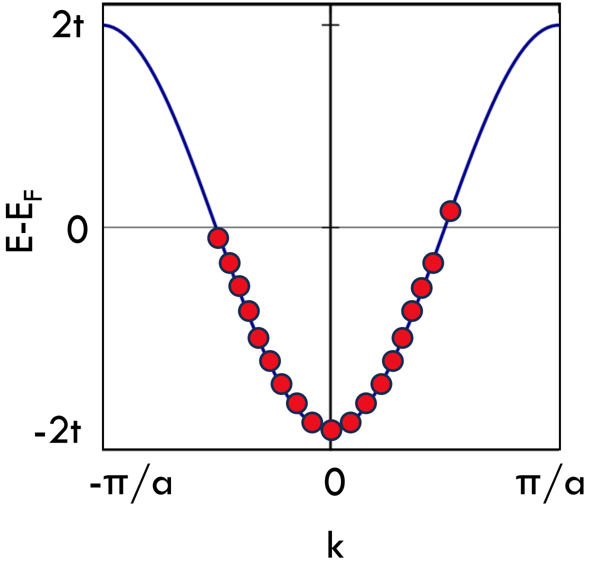
(1st) Brillouin zone

unit cell in k-space

Electron Filling - Metal



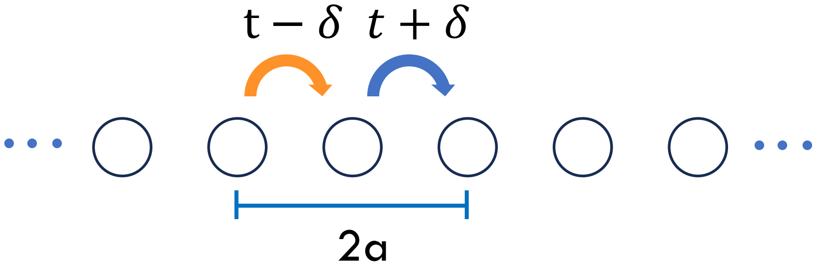
Electrons fill up to Fermi Energy (E_F)
Filled bands do not conduct



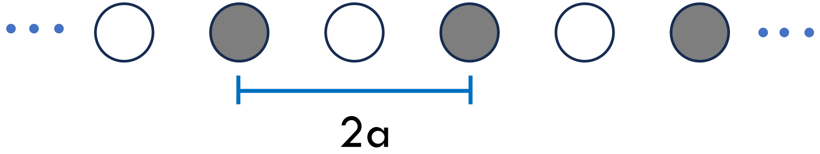
Metal: Very small amount of energy required to excite electron to conduction state

What if the unit cell has more atoms?

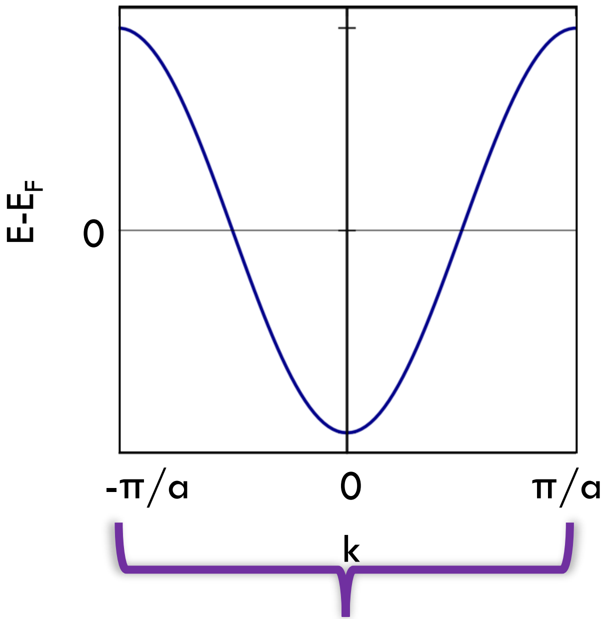
1D chain with alternating nearest-neighbor *hopping*

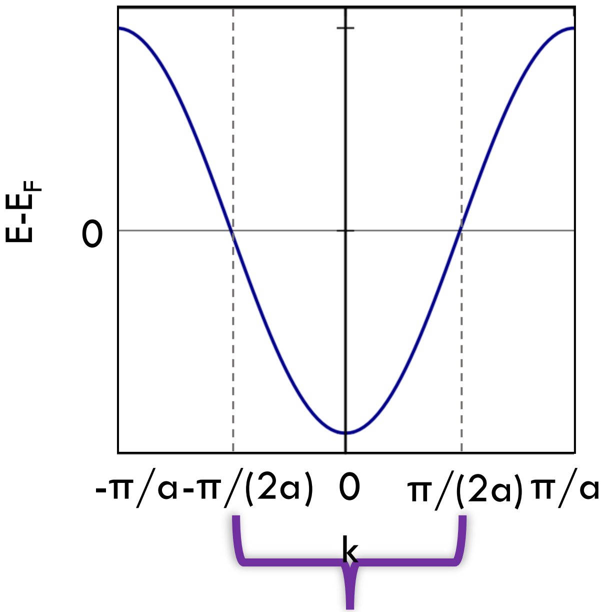


1D chain with bipartite on-site energy (e.g. different elements)

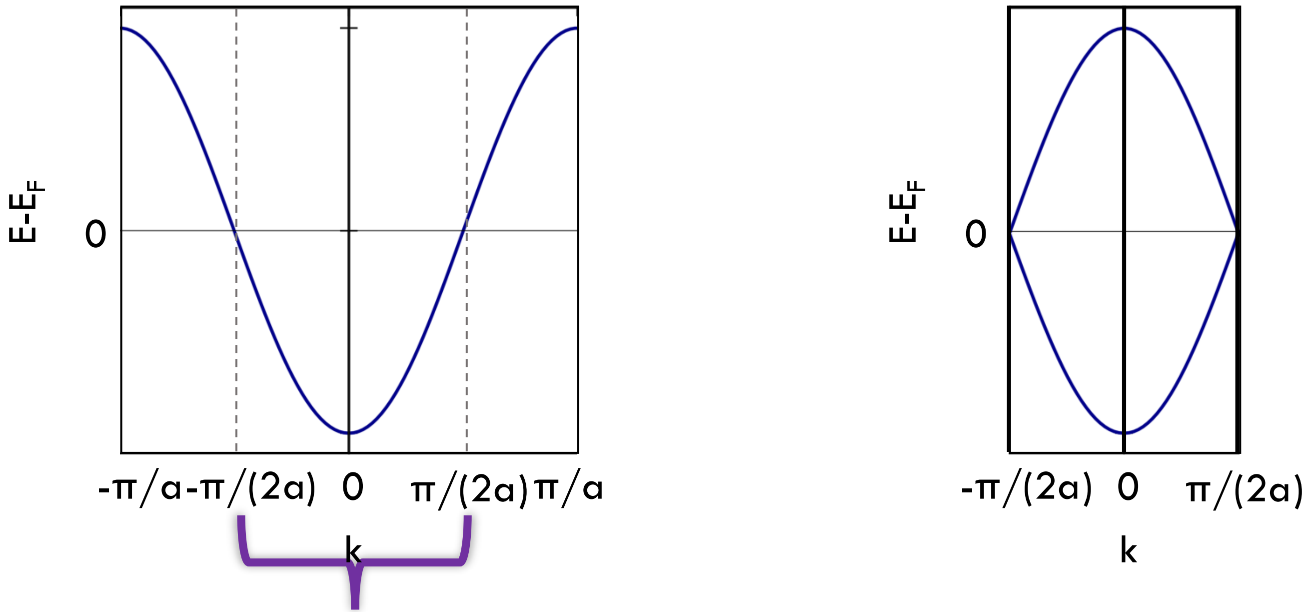


Increase lattice parameter → Decrease BZ length



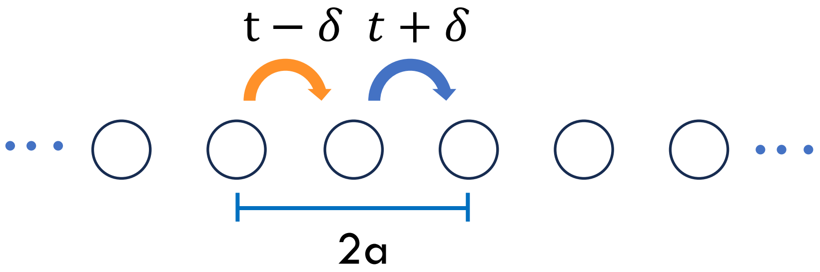


Reduced BZ → Band folding

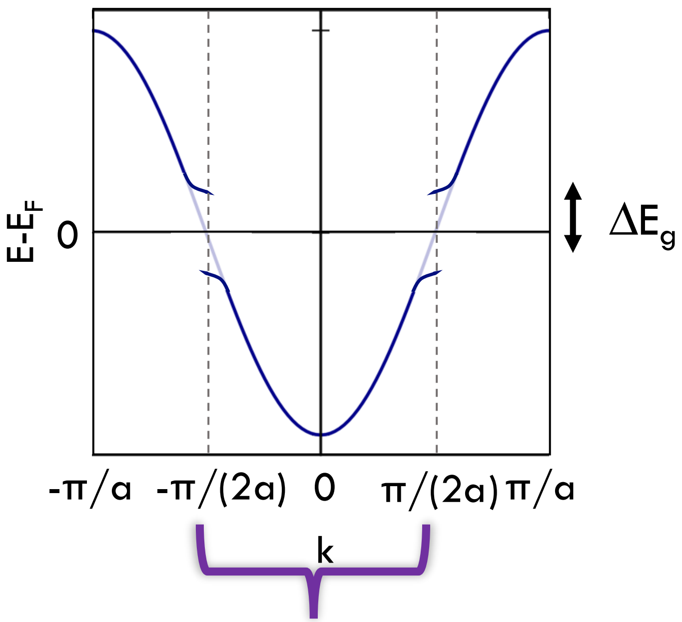


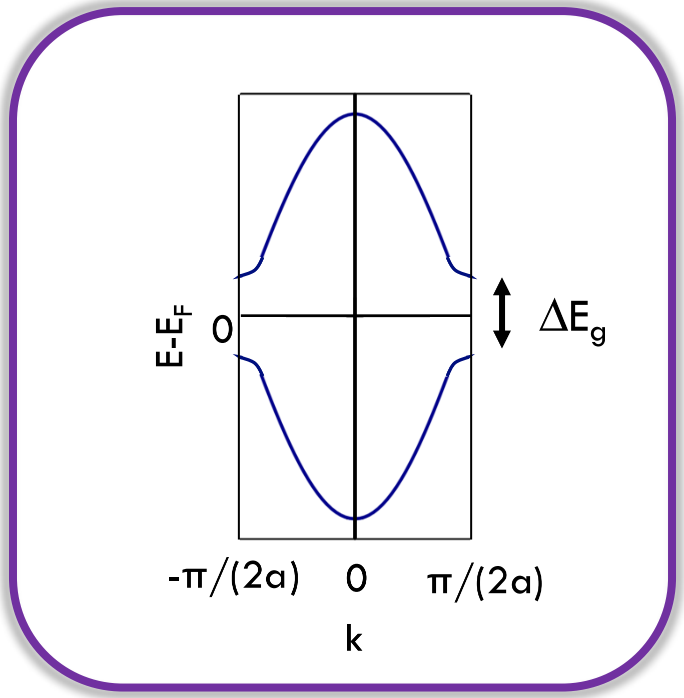
1D Su-Schrieffer-Heeger (SSH) model

1D chain with *alternating* nearest-neighbor hopping

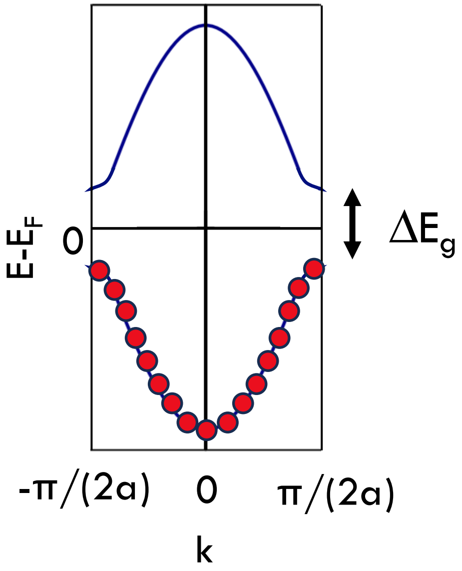


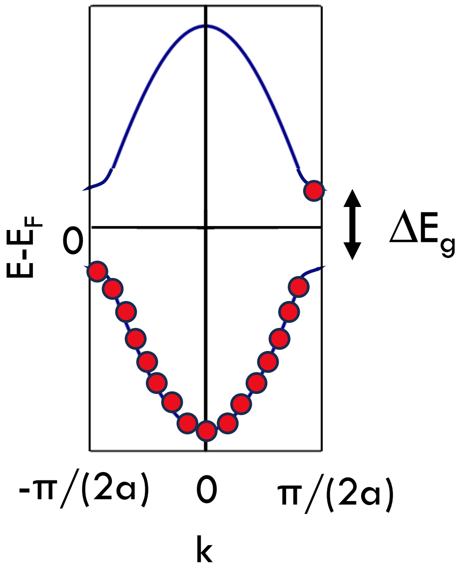
Band folding to 1st Brillouin zone → multiple bands





Electron Filling – Insulator



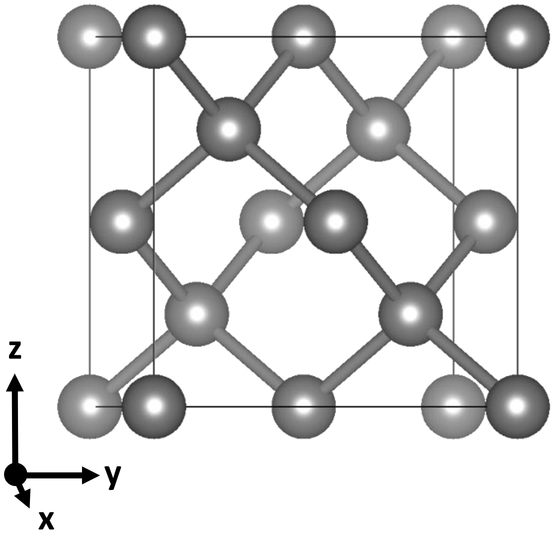


Electrons fill up to Fermi Energy (E_F)
Filled bands do not conduct

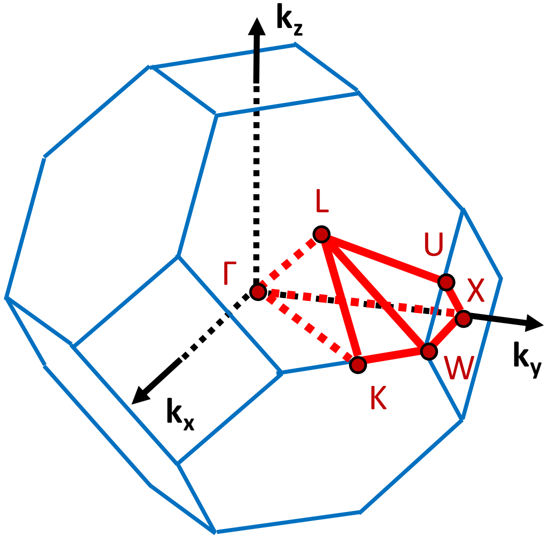
Insulator: Finite amount of energy (ΔE_g) required to excite electron to conduction state

Electronic Structure of 3D Crystals

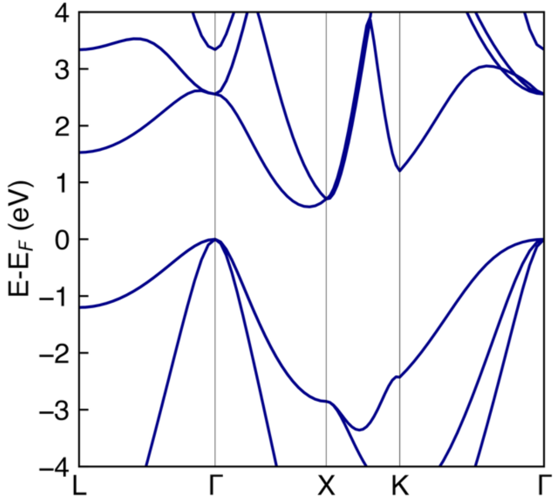
Crystal Structure
Real Space



Brillouin Zone
Reciprocal Space



Band Structure
Electronic Eigenenergies in Reciprocal Space



Hohenberg-Kohn Theorem

$$\hat{H}\,\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = \left[\sum_i \frac{\hat{\boldsymbol{p}_i}^2}{2m} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,A}\frac{Z_A e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right]\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = E\,\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$$

not analytically solvable

Hohenberg-Kohn Theorem

Hohenberg-Kohn Theorem

The ground state total energy can be written exactly as a functional of the ground state charge density

$$\rho(\boldsymbol{r}) = N \int d^3 r_2 \ldots \int d^3 r_N \, \Psi^*(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\Psi(\mathbf{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$$

Hohenberg, Kohn, *Phys. Rev.* **136,** B864 (1964)

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$$E[\rho(\boldsymbol{r})] = \int \rho(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) d\boldsymbol{r} + F[\rho(\boldsymbol{r})]$$

$$V_{ext}(\boldsymbol{r}) = \sum_A \frac{Z_A e^2}{|\boldsymbol{r} - \boldsymbol{R}_A|}$$

Positions/types of ions

Universal

Hohenberg, Kohn, *Phys. Rev.* **136,** B864 (1964)

Kohn-Sham Density Functional Theory

Kohn-Sham Density Functional Theory (DFT)

Map the N-electron problem to N 1-electron problems

$$E[\rho(\boldsymbol{r})] = \int \rho(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) d\boldsymbol{r} + T_s[\rho(\boldsymbol{r})] + E_H[\rho(\boldsymbol{r})] + E_{XC}[\rho(\boldsymbol{r})]$$

Kohn, Sham, *Phys. Rev.* **140,** A1133 (1965)

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Single-particle kinetic energy

$$T_s[\rho] = \sum_{i=1}^{N} \int d\boldsymbol{r} \psi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\boldsymbol{r})$$

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Hartree energy

$$E_H[\rho] = \int d\boldsymbol{r} d\boldsymbol{r}' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

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Single-particle kinetic energy

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Hartree energy

$$E_H[\rho] = \int d\boldsymbol{r} d\boldsymbol{r}' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

Exchange-correlation energy

(all of the many-body effects we don't know)

$$E_{XC}[\rho(\boldsymbol{r})] = ???$$

Kohn, Sham, *Phys. Rev.* **140**, A1133 (1965)

Reciprocal Space for Periodic Systems

Bloch functions

$$\psi_i(\boldsymbol{r}) \rightarrow \psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$

$\boldsymbol{k} \in$ 1st Brillouin zone (reciprocal space unit cell)

$\mathrm{n} \in \mathbb{Z}^{+}$: band index

$$u_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$\boldsymbol{R} = n_1\vec{\boldsymbol{a}}_{\boldsymbol{1}} + n_2\vec{\boldsymbol{a}}_{\boldsymbol{2}} + n_3\vec{\boldsymbol{a}}_{\boldsymbol{3}}$$

$$n_i \in \mathbb{Z}$$

$$u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum\nolimits_{\boldsymbol{G}} c_{\boldsymbol{G}n\boldsymbol{k}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

$$\boldsymbol{G} = m\vec{\boldsymbol{b}}_{\boldsymbol{1}} + m_2\vec{\boldsymbol{b}}_{\boldsymbol{2}} + m_3\vec{\boldsymbol{b}}_{\boldsymbol{3}}$$

$$m_i \in \mathbb{Z}$$

Plane wave basis convenient for periodic systems

Bloch functions

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$

Plane-wave basis functions

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} c_{\boldsymbol{G}n\boldsymbol{k}} e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

$\boldsymbol{k} \in 1^{st}$ Brillouin zone (reciprocal space unit cell)

n: band index

$\boldsymbol{G}$ linear combination of reciprocal space lattice vectors

Kohn-Sham Density Functional Theory

The N-electron Schrödinger equation (Born-Oppenheimer approximation)

$$\left[\sum_i \frac{\widehat{p_i}^2}{2m} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,A}\frac{Z_A e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_A|}\right]\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = E\,\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$$

Turns into N 1-electron Schrödinger equations

$$\left[-\frac{1}{2}\nabla^2 + \sum_A \frac{Z_A e^2}{|\boldsymbol{r} - \boldsymbol{R}_A|} + \int d\boldsymbol{r}'\,\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{XC}[\rho]}{\delta\rho}\right]\psi_{n\boldsymbol{k}}^{KS} = \left[-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{XC}[\rho]\right]\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}}^{KS}\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r})$$

$\{\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r})\}$:plane wave basis

Kohn, Sham, *Phys. Rev.* **140**, A1133 (1965)

DFT Eigenvalues

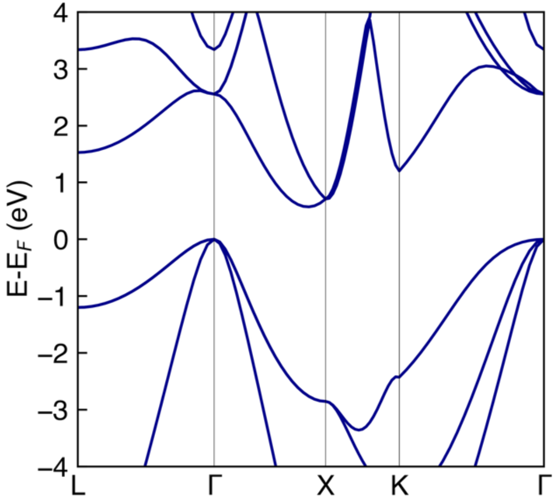
$$\left[-\frac{1}{2}\nabla^2 + \sum_A \frac{Z_A e^2}{|\boldsymbol{r}-\boldsymbol{R}_A|} + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{XC}[\rho]}{\delta\rho}\right]\psi_{n\boldsymbol{k}}^{KS} = \left[-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{XC}[\rho]\right]\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}}^{KS}\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r})$$

DFT band structure usually plots of $\varepsilon_{n\boldsymbol{k}}^{KS}$

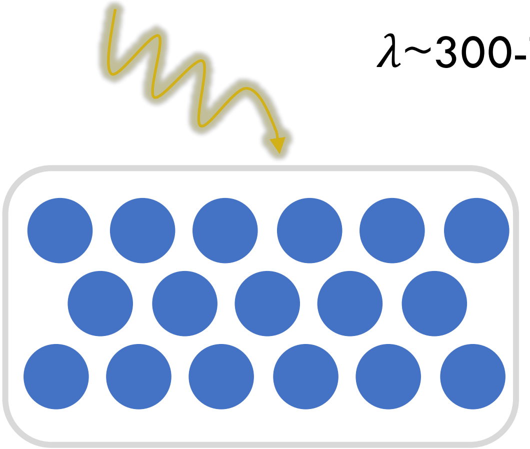
$\varepsilon_{n\boldsymbol{k}}^{KS}$ obtained from DFT are:

- Lagrange multipliers
- *Not* energy eigenvalues of the full many body Hamiltonian

Still produce qualitatively good band structures!



Note About Optical Energy Transitions



Visible light

λ~300-700nm (3000-7000 Å)

Crystal Structure

a~1-10Å

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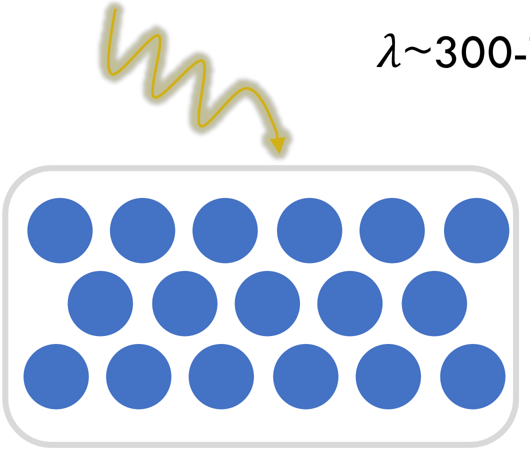


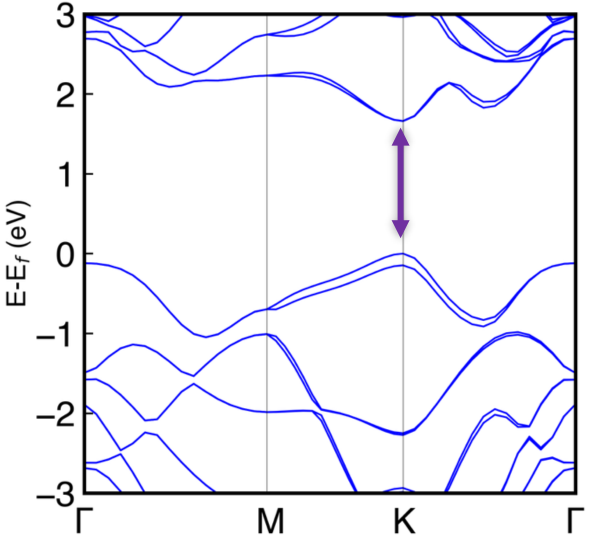
Crystal Structure

a~1-10Å

Electron excitation via visible light has (effectively) ZERO momentum transfer

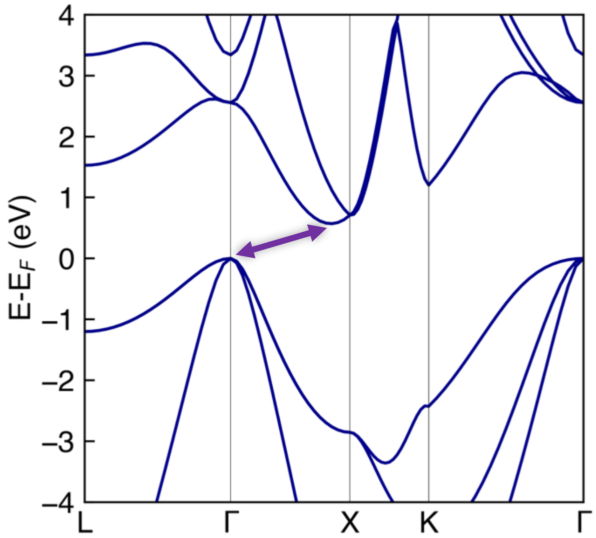
Lowest energy excitation (fundamental band gap) …

Direct Gap
(monolayer MoS_2)



…can be optically excited

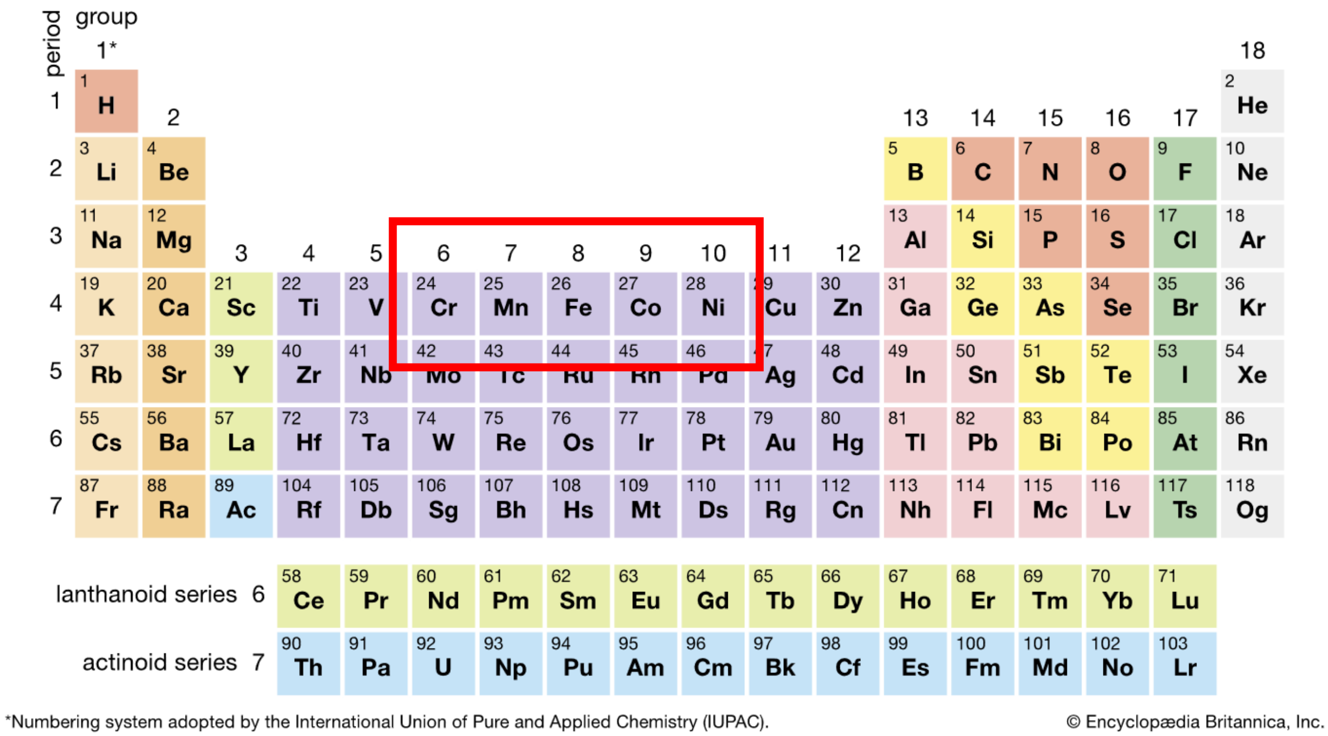
Indirect Gap
(silicon)



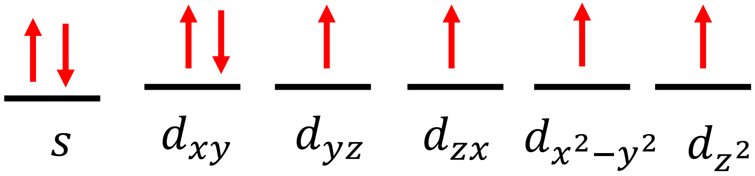
…requires additional momentum transfer (e.g. ionic vibrations)

Magnetism

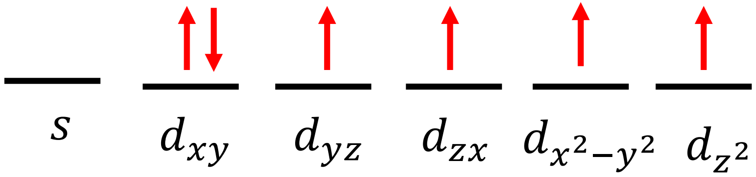
Magnetic elements



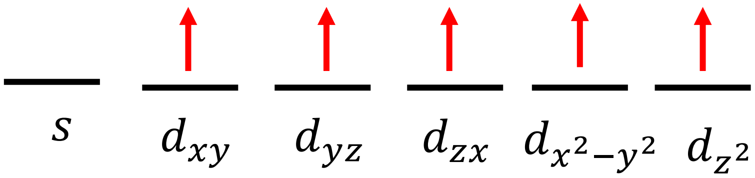
Different numbers of up-spin and down-spin electrons



Neutral Atomic Fe

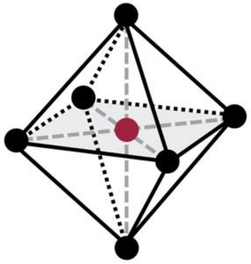


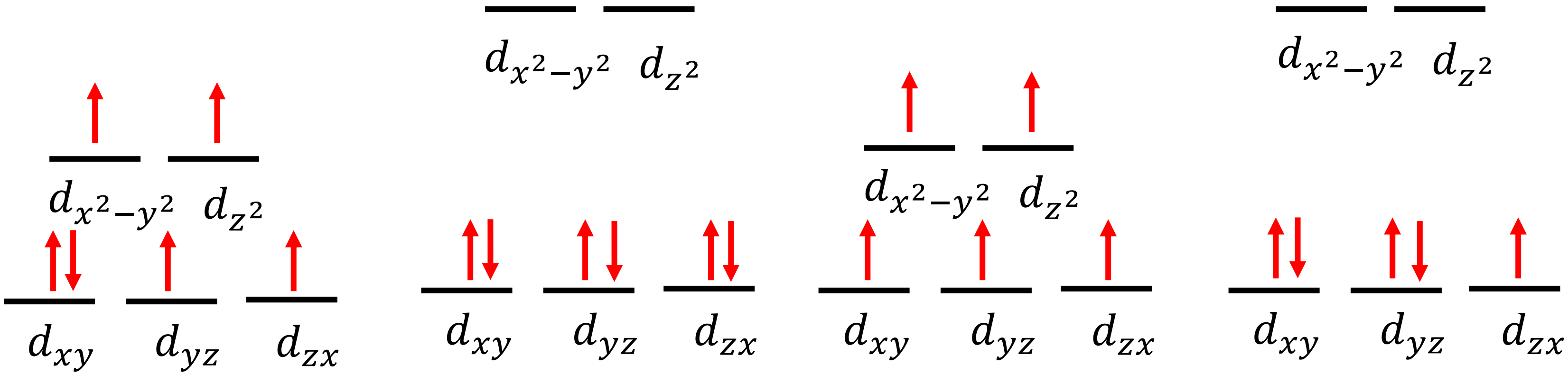
Atomic Fe^{2+}



Atomic Fe^{3+}

Octahedral Crystal Field Splitting





Octahedral Fe^{2+} (High spin)

Octahedral Fe^{2+} (Low spin)

Octahedral Fe^{3+} (High spin)

Octahedral Fe^{3+} (Low spin)

Spin-polarized charge densities

$$\left[-\frac{1}{2}\nabla^2 + \sum_A \frac{Z_A e^2}{|\boldsymbol{r}-\boldsymbol{R}_A|} + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{XC}[\rho]}{\delta\rho}\right]\psi_{n\boldsymbol{k}}^{KS} = \left[-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{XC}[\rho]\right]\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}}^{KS}\psi_{n\boldsymbol{k}}^{KS}(\boldsymbol{r})$$

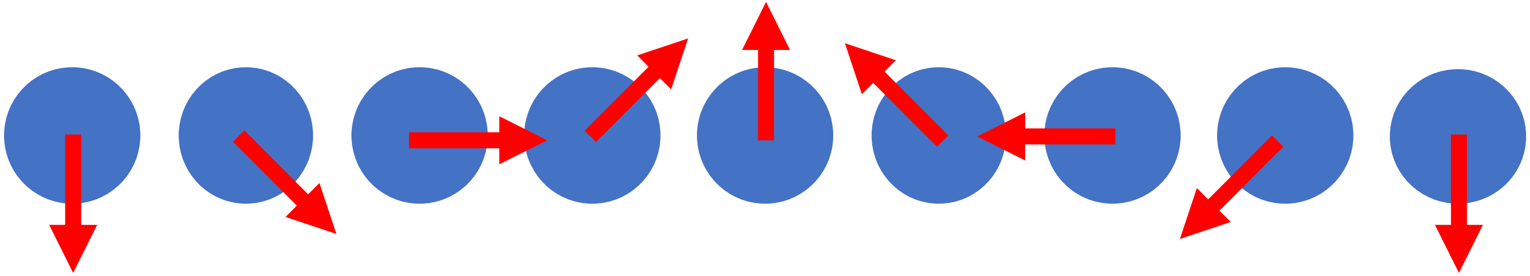
$\rho \rightarrow \rho_\uparrow + \rho_\downarrow$

LDA: $V_{XC}[\rho] \rightarrow V_{XC}[\rho_\uparrow, \rho_\downarrow]$

GGA: $V_{XC}[\rho, \nabla\rho] \rightarrow V_{XC}[\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow]$

Collinear magnetism: solve KS equation separately for two spin channels

Noncollinear magnetism



Examples

- Frustrated triangular lattices
- Spin spirals / magnons
- Skyrmions

D. Hobbs, G. Kresse, J. Hafner, *Phys. Rev. B*, **62**, 17 (2000)
J. Kübler, K. H. Höck, J. Sticht, A. R. Williams, *J. Appl. Phys.* **63**, 3482-3486 (1988)
J. Kübler, et al., *J. Phys. F: Met. Phys.*, **18**, 469 (1988)

- D. Hobbs, G. Kresse, J. Hafner, Phys Rev B, 62, 17 (2000)
- J. Kübler, K.-H. Höck, J. Sticht, A.R. Williams, J. Appl. Phys. 63, 3482 – 3486 (1988)
- J. Kübler, et al. J. Phys. F: Met. Phys. 18, 469 (1988)

LSDA non collinear magnetism

$\rightarrow$ 2×2 matrix $n^{\alpha\beta}(\vec{r})$

density matrix $\rho^{\alpha\beta}(\vec{r})$

electron density $Tr(\rho) = \Sigma_\alpha \rho^{\alpha\alpha}(\vec{r}) \equiv n(\vec{r})$

external potential

$$E[\rho^{\alpha\beta}] = T_0 + \Sigma_{\alpha\beta}\int \omega_{\alpha\beta}(\vec{r})\,\rho_{\beta\alpha}(\vec{r})\,d^3r + \iint \frac{n(\vec{r}\,')n(\vec{r})}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' + E_{xc}[\rho_{\alpha\beta}]$$

$\downarrow$

single particle KS equations

$$\Sigma_\beta\left[-\delta_{\alpha\beta}\nabla^2 + \omega^{eff}_{\alpha\beta}(\vec{r})\right]\varphi_{\beta i}(\vec{r}) = \varepsilon_i\,\varphi_{\alpha i}(\vec{r})$$

where $\rho_{\alpha\beta}(\vec{r}) = \Sigma_{i\in occ}\,\varphi_{\alpha i}(\vec{r})\,\varphi^*_{\beta i}(\vec{r})$

$$\omega^{eff}_{\beta\alpha}(\vec{r}) = \omega_{\beta\alpha}(\vec{r}) + 2\delta_{\alpha\beta}\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r' + \frac{\delta E_{xc}[\rho_{\alpha\beta}]}{\delta\rho_{\alpha\beta}}$$

charge density around an ion

$$q^{(v)}_{\alpha\beta} = \int_{S_v}\rho_{\alpha\beta}(\vec{r})\,d^3r$$

S_v : sphere of pre-defined radius around ion v

diagonalizing $q_{\alpha\beta}$ gives direction of magnetization locally

total energy

$$E = \Sigma_{i\in occ}\,\varepsilon_i - \iint\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' - \Sigma_\alpha\int d^3r\; n(r)\,\frac{\partial\epsilon_{xc}}{\partial\rho_\alpha}\,\rho_\alpha(\vec{r})$$

where $\rho_i = \Sigma_{\alpha\beta}\,U_{i\alpha}\,\rho_{\alpha\beta}\,U^+_{\beta i}$

and $q^{(v)}_i\,\delta_{ij} = \Sigma_{\alpha\beta}\,U^{(v)}_{i\alpha}\,q^{(v)}_{\alpha\beta}\,U^{(v)+}_{\beta j}$

[some unitary matrix that diagonalizes $\rho_{\alpha\beta}$]

$$\mathcal{U} = \begin{bmatrix} e^{\frac{1}{2} i \varphi_v} \cos \frac{1}{2} \theta_v & e^{-\frac{1}{2} i \varphi_v} \sin \frac{1}{2} \theta_v \\ -e^{\frac{1}{2} i \varphi_v} \sin \frac{1}{2} \theta_v & e^{-\frac{1}{2} i \varphi_v} \cos \frac{1}{2} \theta_v \end{bmatrix}$$

where φ_v, θ_v define principle axis of magnetic moment at ion v