

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

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Los Alamos Computational Condensed Matter Summer School 2026
16 June 2026

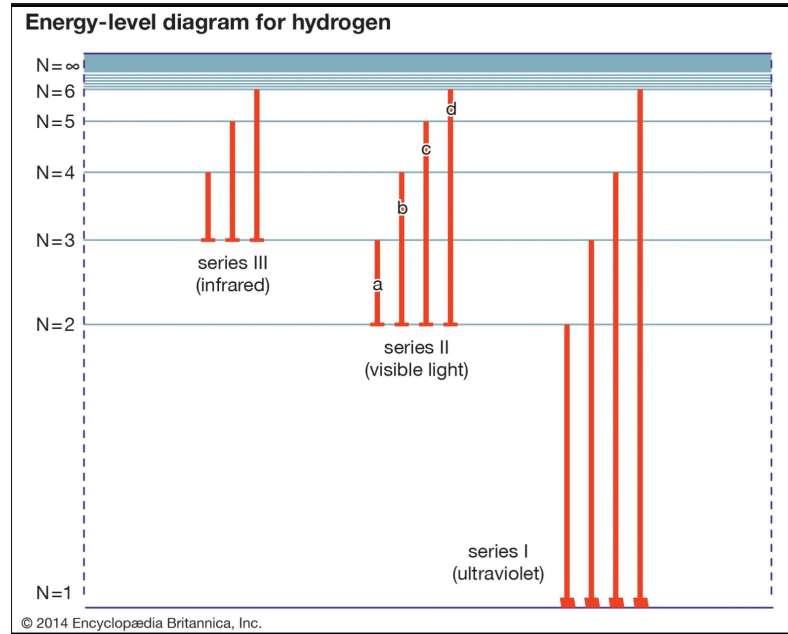
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Electronic Structure in Crystals

Adapted from:

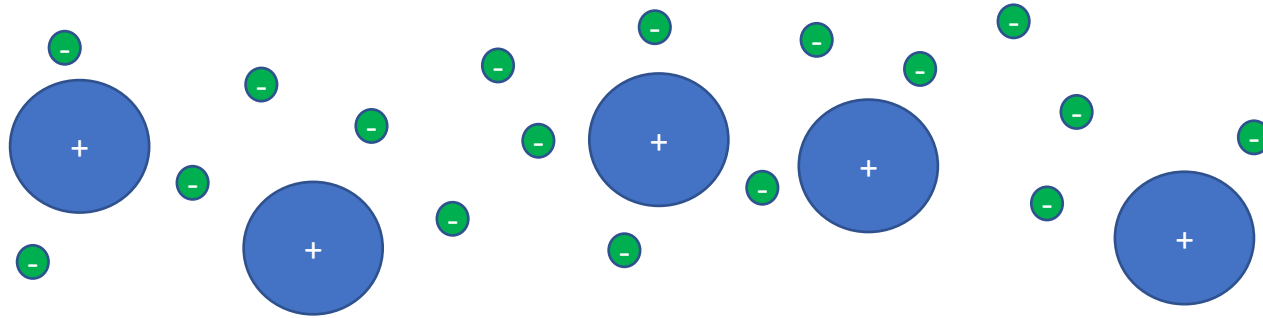
Steven H. Simon, The Oxford Solid State Basics, Oxford University Press, 1st Edition (2013)
(reprinted with corrections 2016)

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
$\hat{H} = \underbrace{\sum_i \frac{\hat{p}_i^2}{2m}}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i,j} \frac{e^2}{ r_i - r_j }}_{\text{Coulomb}} + \underbrace{\sum_A \frac{\hat{P}_A^2}{2M_A}}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{A,B} \frac{Z_A Z_B e^2}{ R_A - R_B }}_{\text{Coulomb}} - \underbrace{\sum_{i,A} \frac{Z_A e^2}{ r_i - R_A }}_{\text{Coulomb}}$				

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

Born-Oppenheimer Approximation

$$\begin{array}{ccccccc}
 \text{Electrons} & & \text{Nuclei} & & \text{Electron-Nucleus} \\
 \hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \cancel{\sum_A \frac{\hat{p}_A^2}{2M_A}} + \boxed{\text{constant}} - \sum_{i,A} \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} \\
 \text{Kinetic} \quad \text{Coulomb} \quad \text{Kinetic} \quad \text{Coulomb} \quad \text{Coulomb}
 \end{array}$$

fixed

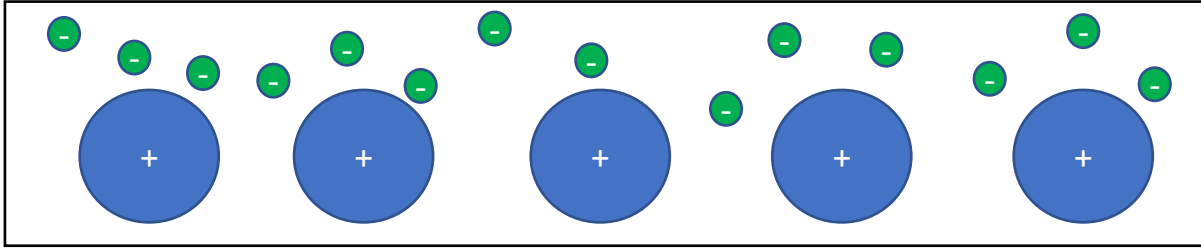
Born-Oppenheimer Approximation

- Nuclei masses 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

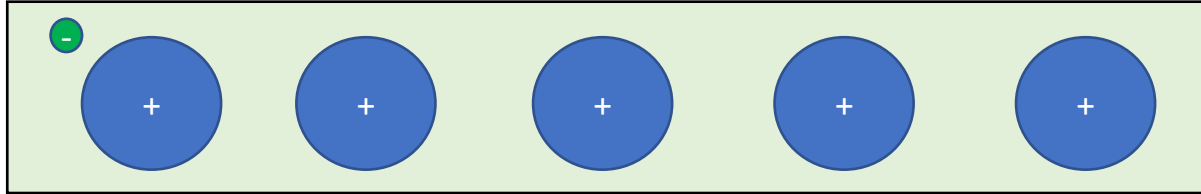
System of N electrons and M nuclei → **3N** degrees of freedom

Electrons in a periodic potential

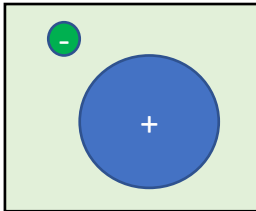
N electrons in infinite periodic array of nuclei



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

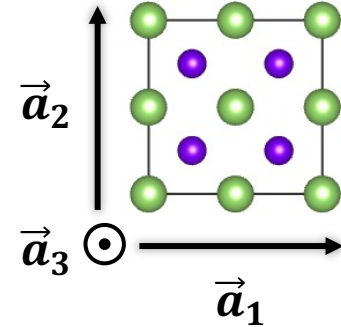
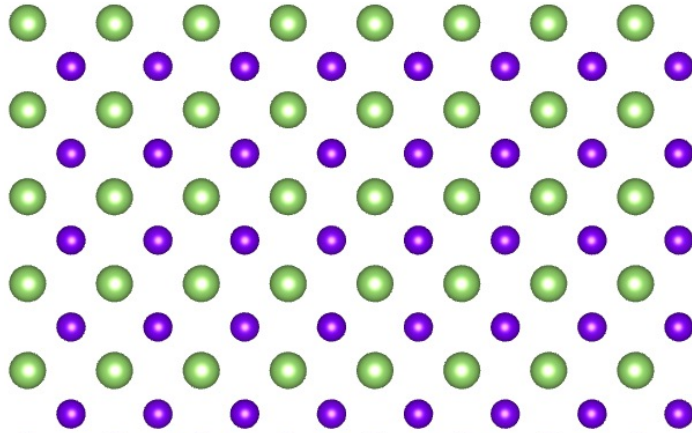


1 electron in unit cell of nuclei and electron charge density ($\rho(r)$) background



→ **3** degrees of freedom

Translation Symmetry: Unit Cells

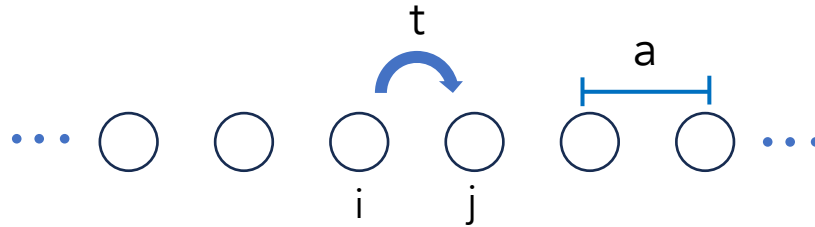


Translation symmetry allows us to study **unit cells**

- 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

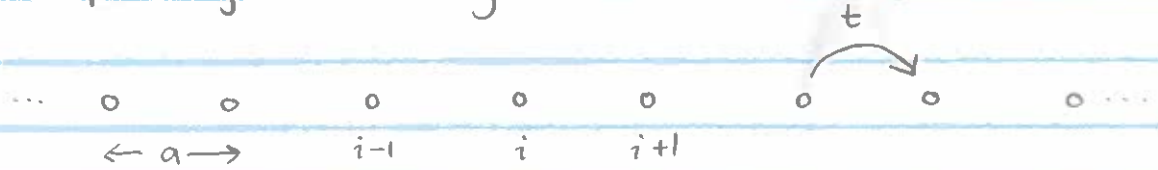


Orbitals $\{\phi_i(\mathbf{r})\}$ located at $\mathbf{R}_i = ia\hat{x}$

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

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

$$H = \begin{bmatrix} & i-1 & i & i+1 \\ & & 0 & -t \\ & -t & 0 & -t \\ & & -t & 0 & -t \\ & & & -t & 0 \\ & & & & \ddots \end{bmatrix} \begin{matrix} i-1 \\ i \\ i+1 \end{matrix}$$

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

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

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

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

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

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

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

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

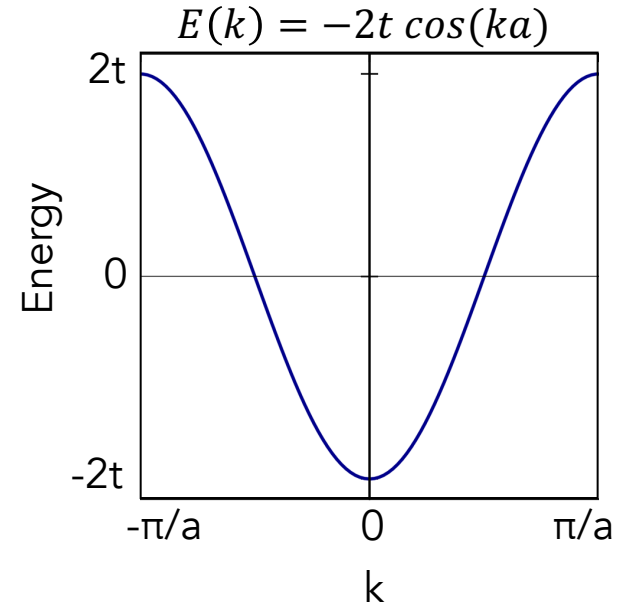
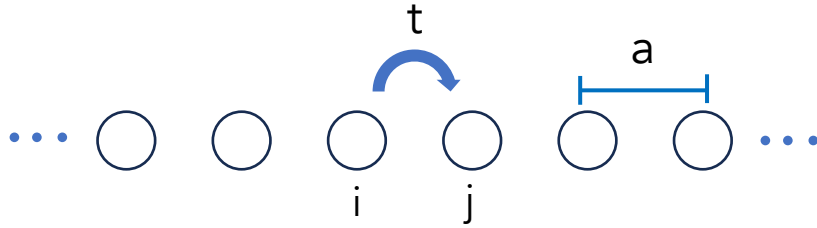
$$= -t \frac{1}{N} \sum_i \left[e^{-ik_x a} + e^{+ik_x a} \right] \quad \left\{ \frac{1}{N} \sum_i = 1 \right\}$$

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

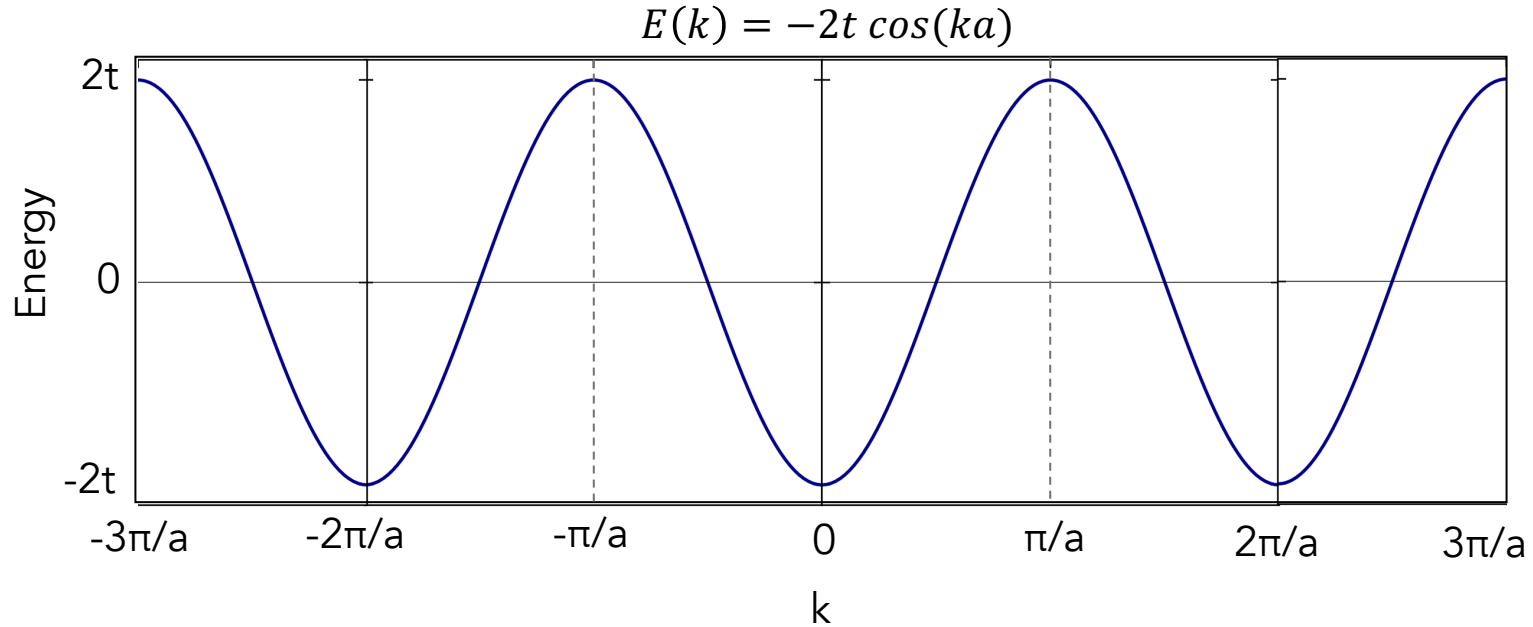
$$= -t (2 \cos(k_x a))$$

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

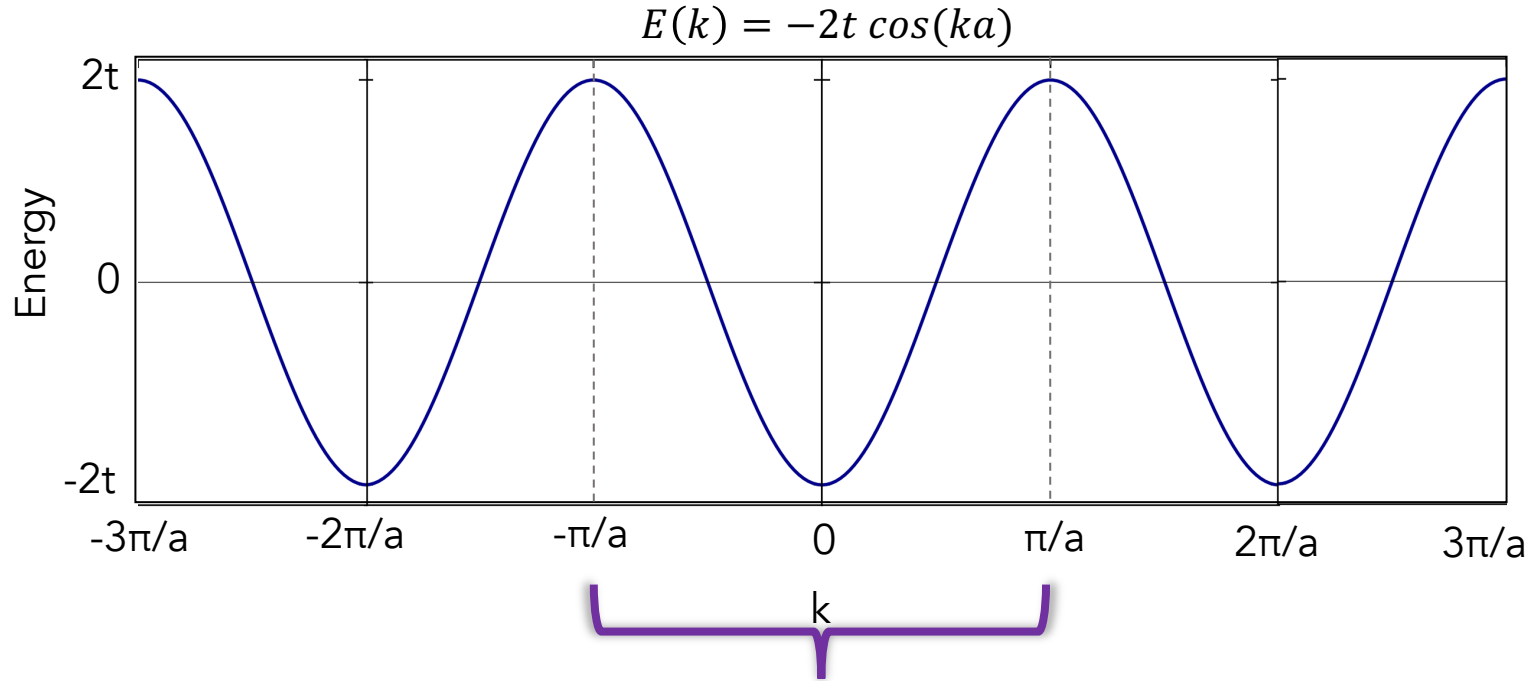
1D chain band structure in k-space



Note that band structure is periodic in k-space

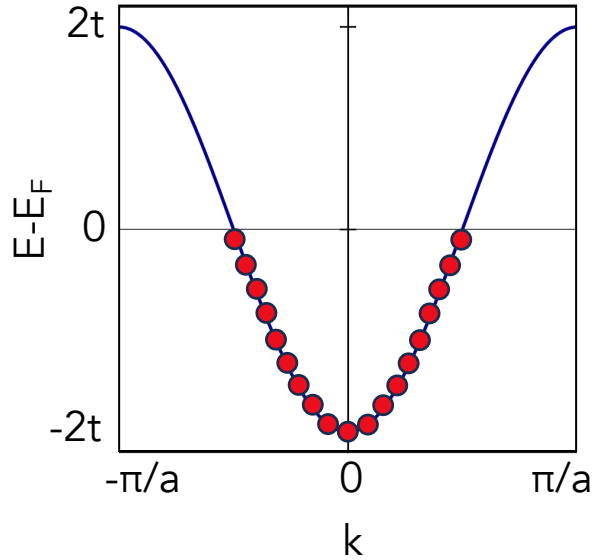


Note that band structure is periodic in k-space

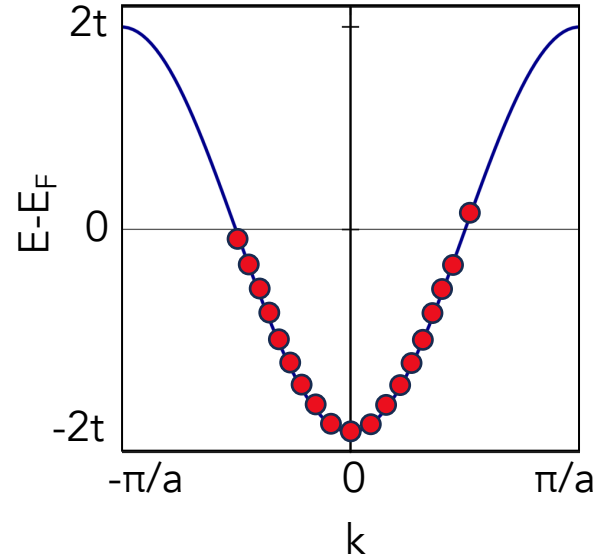


(1st) Brillouin zone
unit cell in k-space

Electron Filling - Metal



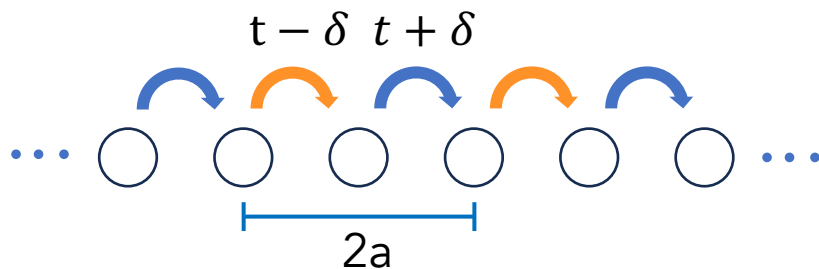
Electrons fill up to Fermi Energy (E_F)
Filled bands do not conduct



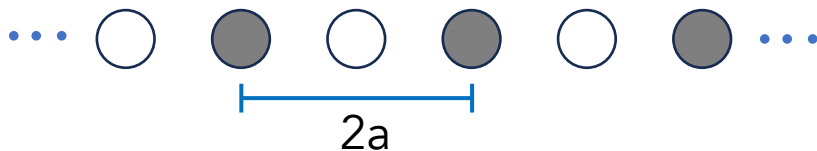
Metal: Very small amount of energy required to excite electron to conduction state

What if the unit cell has more atoms?

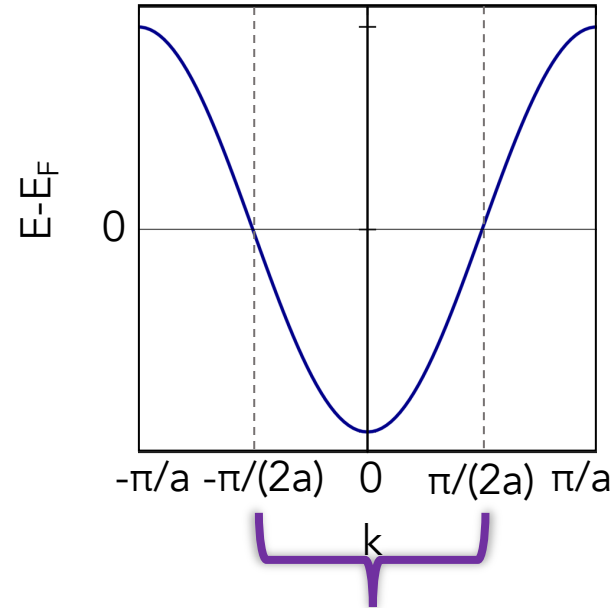
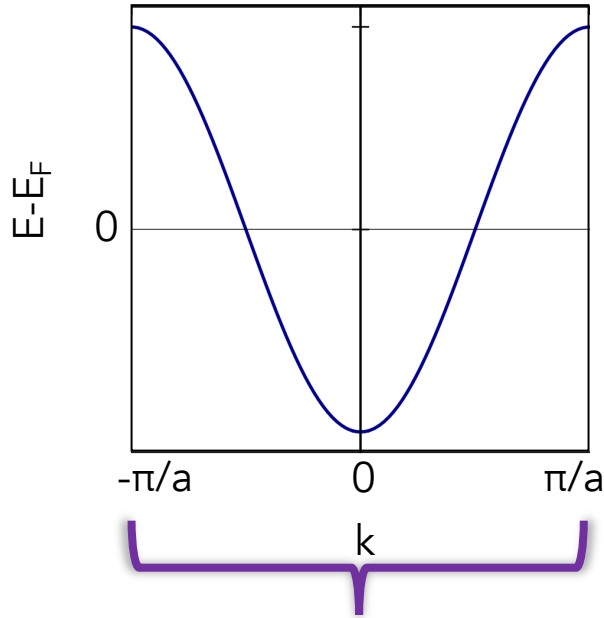
1D chain with alternating nearest-neighbor *hopping*



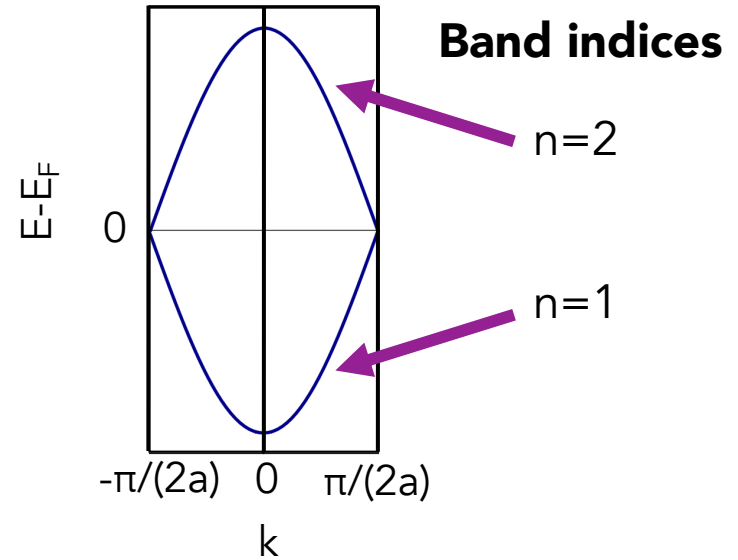
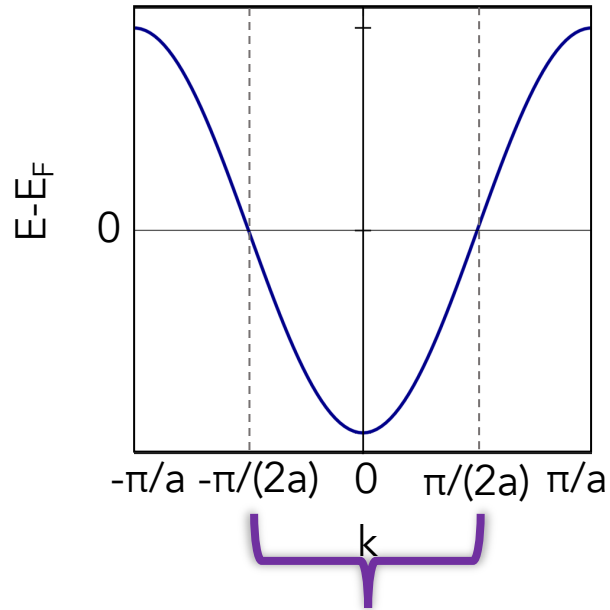
1D chain with bipartite on-site energy (e.g. different elements)



Increase lattice parameter $\rightarrow$ Decrease BZ length

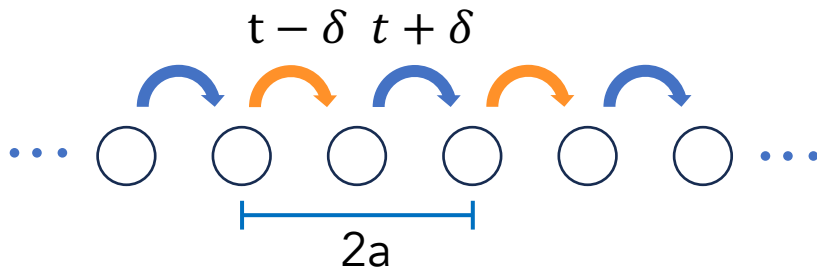


Reduced BZ $\rightarrow$ Band folding

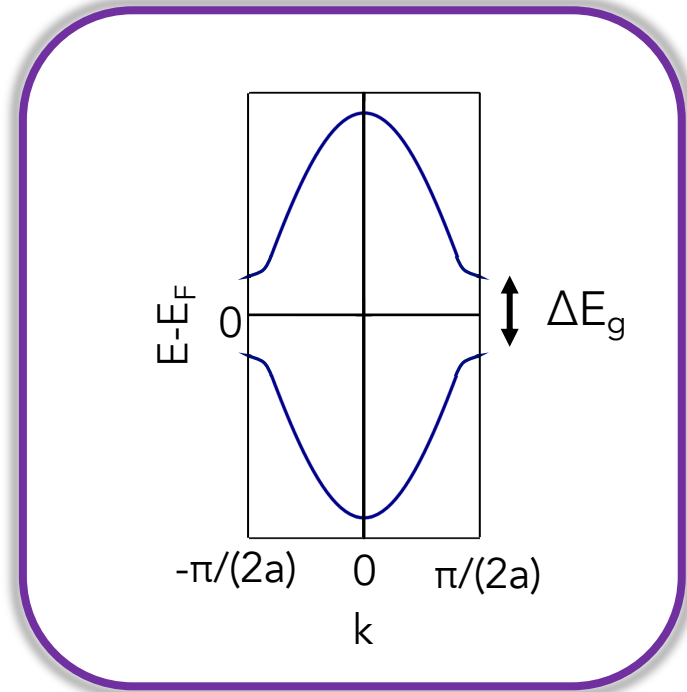
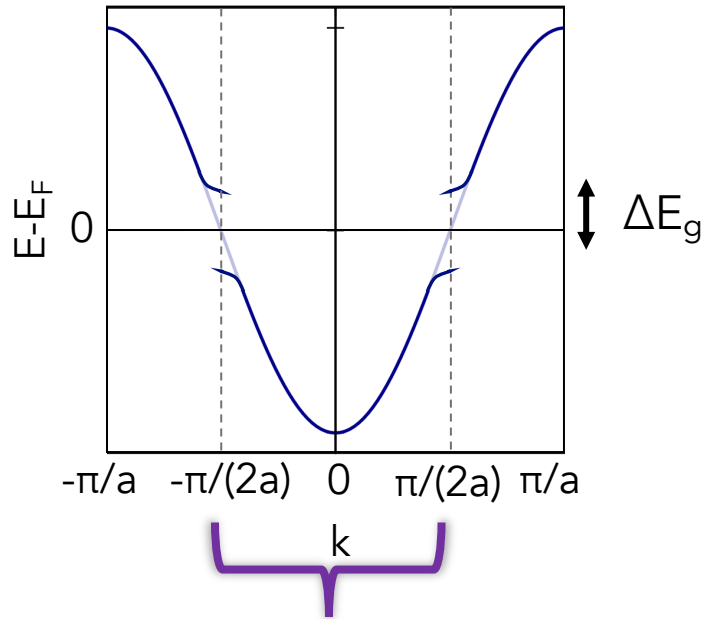


1D Su-Schrieffer-Heeger (SSH) model

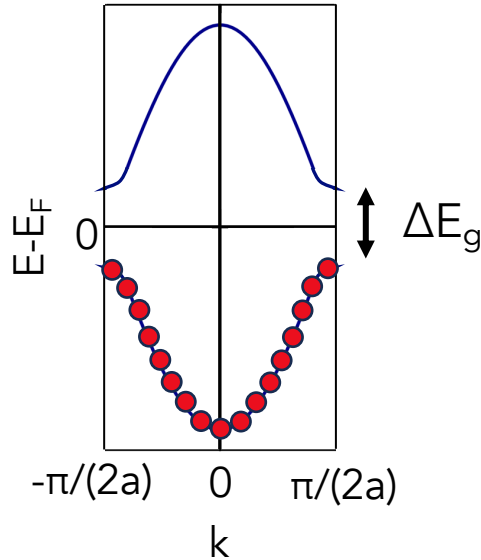
1D chain with *alternating* nearest-neighbor hopping



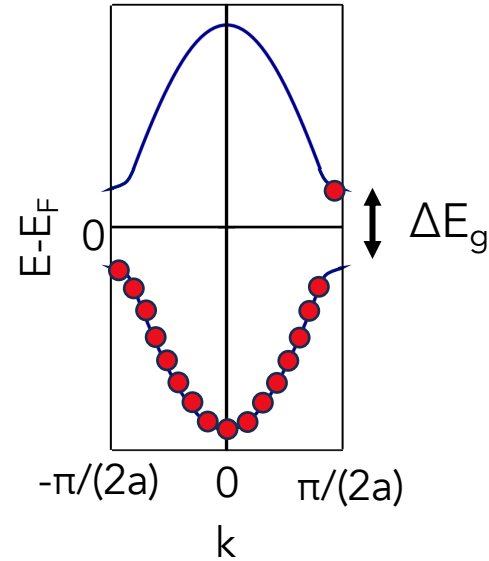
Band folding to 1st Brillouin zone $\rightarrow$ multiple bands



Electron Filling – Insulator



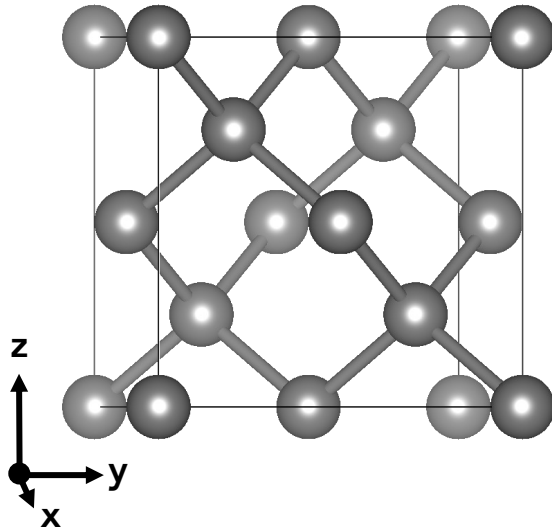
Electrons fill up to Fermi Energy (E_F)
Filled bands do not conduct



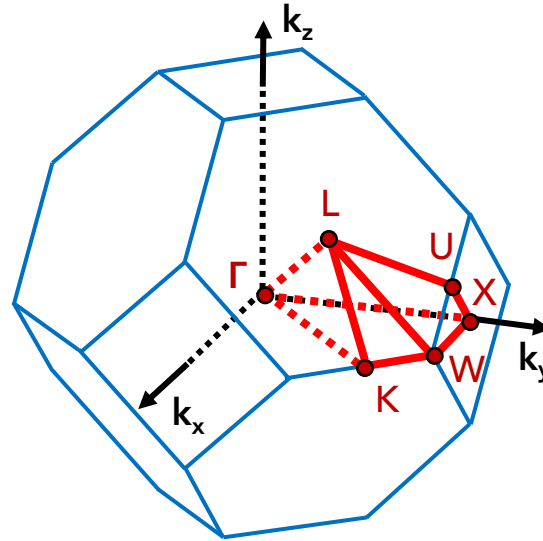
Insulator: Finite amount of energy (ΔE_g) required to excite electron to conduction state

Electronic Structure of 3D Crystals

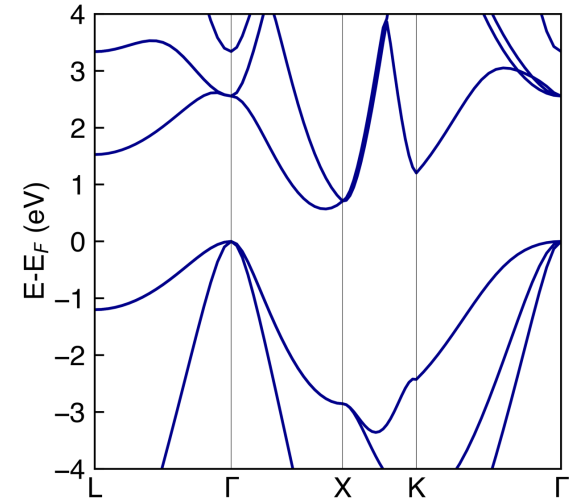
Crystal Structure
Real Space



Brillouin Zone
Reciprocal Space



Band Structure
Electronic Eigenenergies
in Reciprocal Space



Hohenberg-Kohn Theorem

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

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

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

Hohenberg-Kohn Theorem

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

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

Positions/types of ions

Universal

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

Kohn-Sham Density Functional Theory

Kohn-Sham Density Functional Theory (DFT)

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

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

Kohn-Sham Density Functional Theory

Kohn-Sham Density Functional Theory (DFT)

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

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

Single-particle kinetic energy

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

Kohn-Sham Density Functional Theory

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Single-particle kinetic energy

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

Hartree energy

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

Kohn-Sham Density Functional Theory

Kohn-Sham Density Functional Theory (DFT)

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

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

Single-particle kinetic energy

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

Hartree energy

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

Exchange-correlation energy

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

$$E_{xc}[\rho(\mathbf{r})] = ???$$

Reciprocal Space for Periodic Systems

Bloch functions

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

$\mathbf{k} \in 1^{\text{st}}$ Brillouin zone (reciprocal space unit cell)
 $n \in \mathbb{Z}^+$: band index

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

$$\mathbf{R} = n_1 \vec{\mathbf{a}}_1 + n_2 \vec{\mathbf{a}}_2 + n_3 \vec{\mathbf{a}}_3$$

$n_i \in \mathbb{Z}$

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$\mathbf{G} = m_1 \vec{\mathbf{b}}_1 + m_2 \vec{\mathbf{b}}_2 + m_3 \vec{\mathbf{b}}_3$$

$m_i \in \mathbb{Z}$

Plane wave basis convenient for periodic systems

Bloch functions

$$\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk}(\mathbf{r})$$

Plane-wave basis functions

$$\psi_{nk}(\mathbf{r}) = \sum_{\mathbf{G}} c_{Gnk} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

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

n : band index

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

Kohn-Sham Density Functional Theory

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

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

Turns into N 1-electron Schrödinger equations

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

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

DFT Eigenvalues

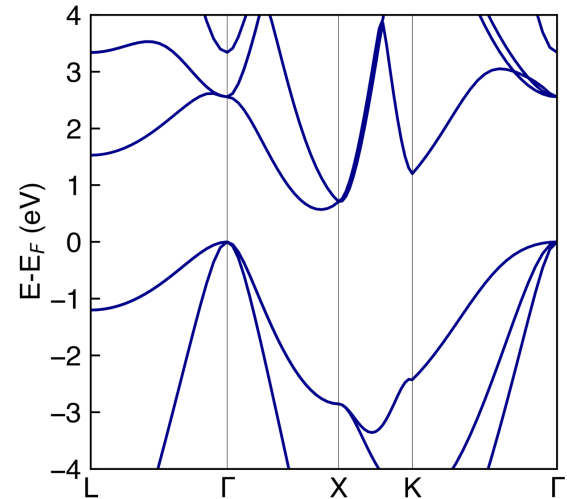
$$\left[-\frac{1}{2}\nabla^2 + \sum_A \frac{Z_A e^2}{|\mathbf{r} - \mathbf{R}_A|} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}[\rho]}{\delta \rho} \right] \psi_{nk}^{KS} = \left[-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{XC}[\rho] \right] \psi_{nk}^{KS}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

DFT band structure usually plots of ε_{nk}^{KS}

ε_{nk}^{KS} obtained from DFT are:

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

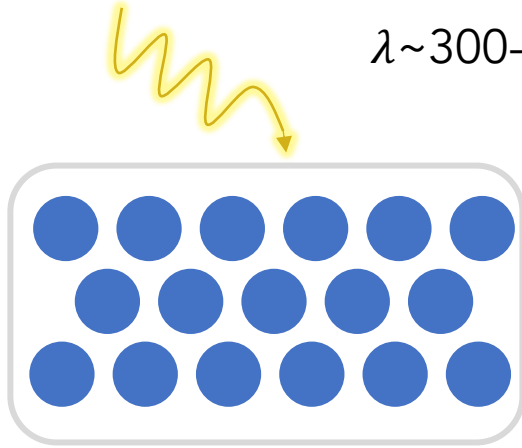
Still produce qualitatively good band structures!



Note About Optical Energy Transitions

Visible Light

$\lambda \sim 300\text{-}700\text{nm}$ ($3000\text{-}7000 \text{ \AA}$)



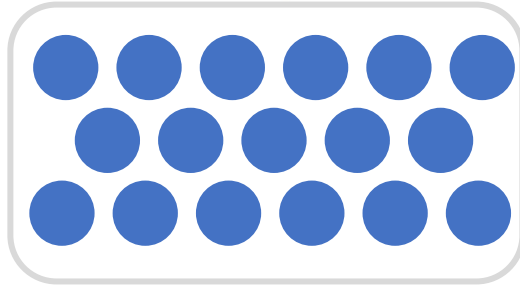
Crystal Structure

$a \sim 1\text{-}10\text{\AA}$

Note About Optical Energy Transitions

Visible Light

$\lambda \sim 300\text{-}700\text{nm}$ ($3000\text{-}7000 \text{ \AA}$)

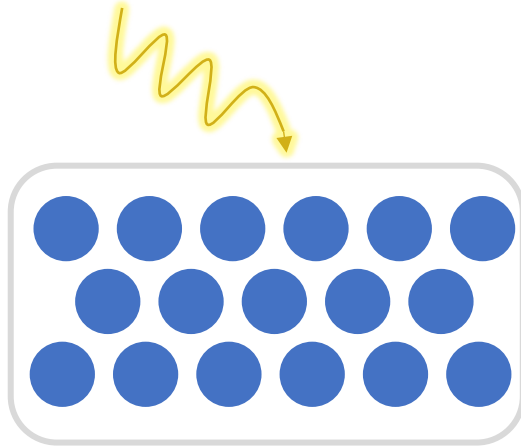


Crystal Structure

$a \sim 1\text{-}10\text{\AA}$

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

Note About Optical Energy Transitions



Visible Light

Wavelength $\lambda \sim 300\text{-}700\text{ nm}$ ($3000\text{-}7000\text{ \AA}$)

$$k = \frac{2\pi}{\lambda} \quad k_{\text{visible light}} \sim 10^{-3}\text{-}10^{-4}\text{ \AA}^{-1}$$

Crystal

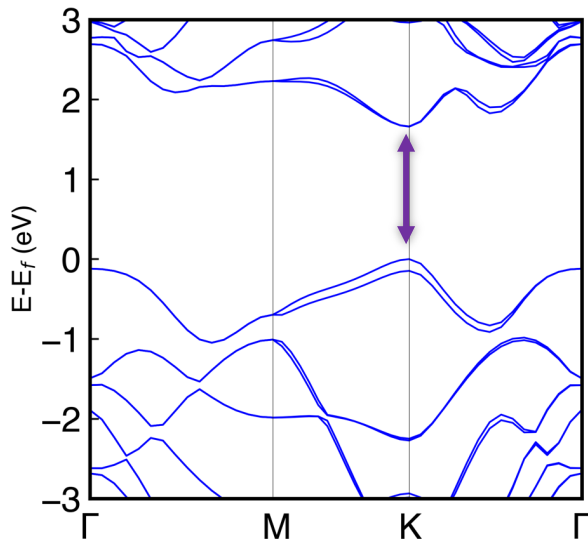
Unit cell length scale: $a \sim 1\text{-}10\text{ \AA}$

Brillouin zone length scale" $\frac{2\pi}{a} \sim 1\text{-}10^{-1}\text{ \AA}^{-1}$

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

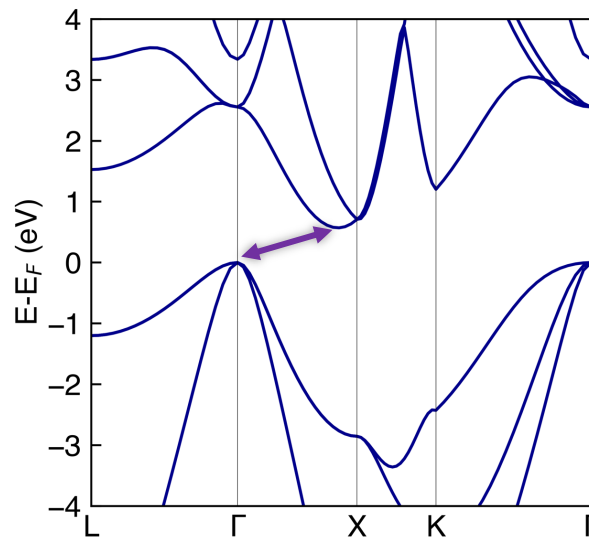
Lowest energy excitation (fundamental band gap) ...

Direct Gap
(monolayer MoS₂)



...can be optically excited

Indirect Gap
(silicon)



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

Magnetism

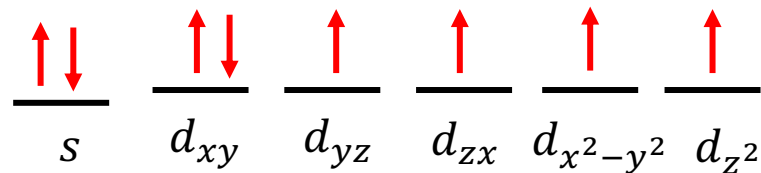
Magnetic elements

period	group																18		
1	1*																	2	
1	1	H																	He
2	3	4																	10
2	Li	Be																	Ne
3	11	12																	18
3	Na	Mg																	Ar
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	
lanthanoid series 6			58	59	60	61	62	63	64	65	66	67	68	69	70	71			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
actinoid series 7			90	91	92	93	94	95	96	97	98	99	100	101	102	103			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

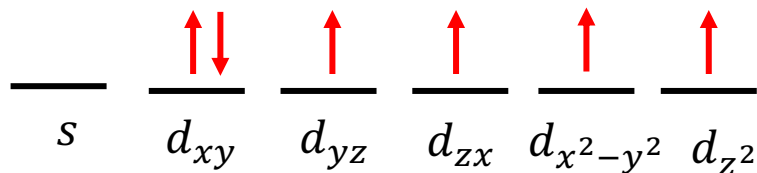
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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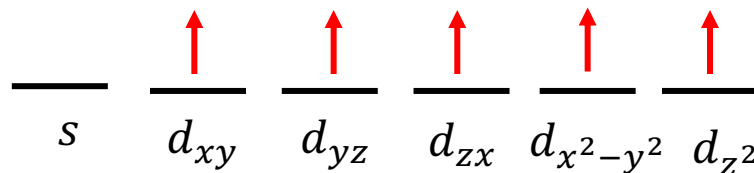
Different numbers of up-spin and down-spin electrons



Neutral Atomic Fe

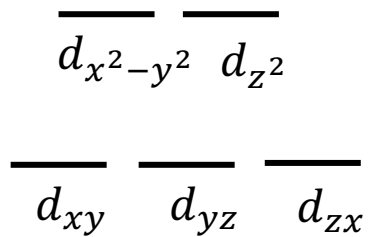
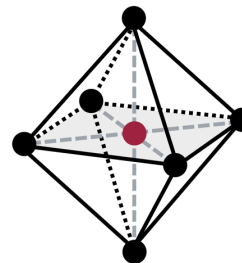


Atomic Fe^{2+}



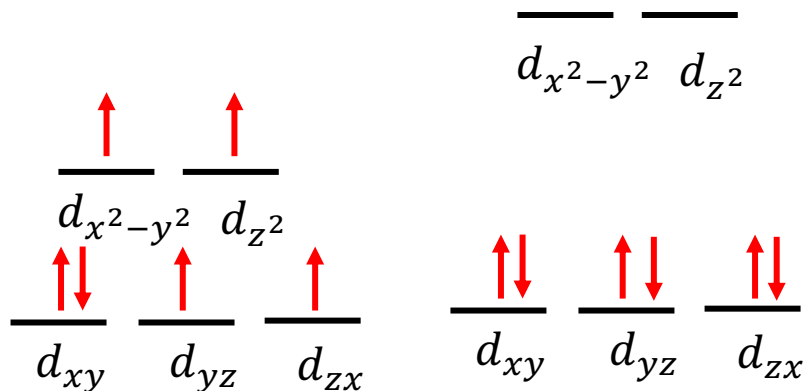
Atomic Fe^{3+}

Octahedral Crystal Field Splitting



Octahedral Crystal Field Splitting

d_{xy}

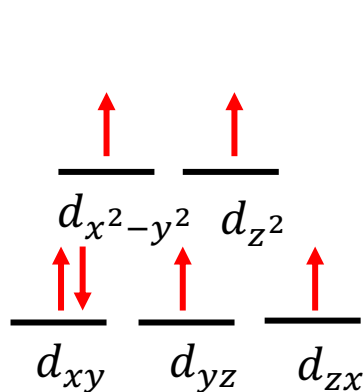


Octahedral Fe^{2+}
(High spin)

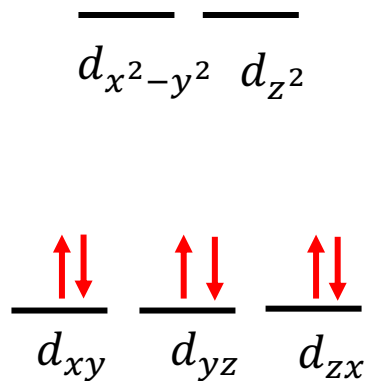
Octahedral Fe^{2+}
(Low spin)

Octahedral Crystal Field Splitting

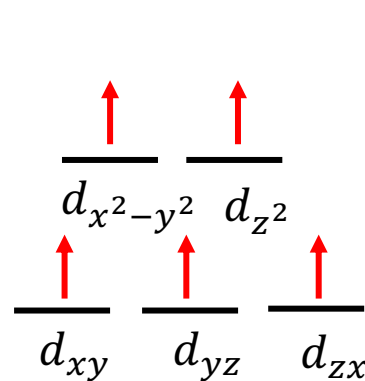
d_{xy}



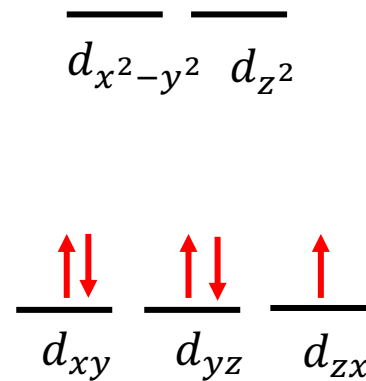
Octahedral Fe^{2+}
(High spin)



Octahedral Fe^{2+}
(Low spin)



Octahedral Fe^{3+}
(High spin)



Octahedral Fe^{3+}
(Low spin)

Spin-polarized charge densities

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

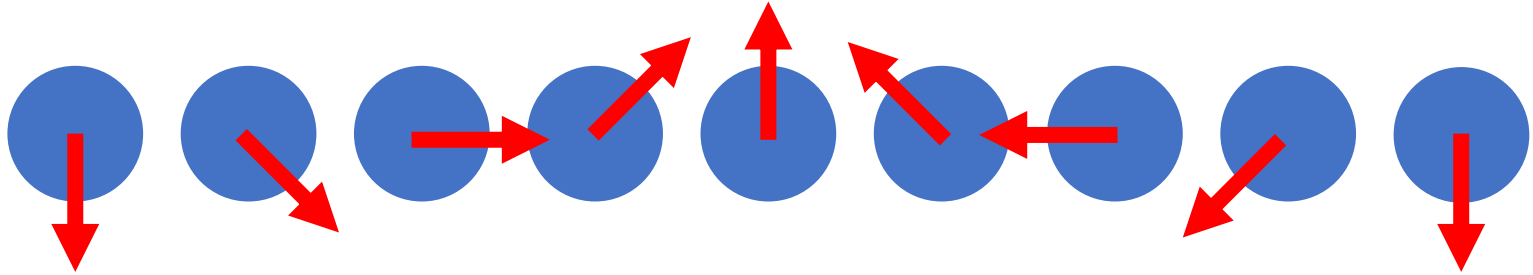
$$\rho \rightarrow \rho_{\uparrow} + \rho_{\downarrow}$$

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

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

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

→ 2x2 matrix $n^{\alpha\beta}(\vec{r})$

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

electron density $\text{Tr}(p) = \sum_{\alpha} p^{\alpha\alpha}(\vec{r}) \equiv n(\vec{r})$

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

↙ external potential

↓

single particle KS equations

$$\sum_{\beta} [-\delta_{\alpha\beta} \nabla^2 + \omega_{\alpha\beta}^{\text{eff}}(\vec{r})] \varphi_{\beta i}(\vec{r}) = \epsilon_i \varphi_{\alpha i}(\vec{r})$$

where $p_{\alpha\beta}(\vec{r}) = \sum_{i \in \text{occ}} \varphi_{\alpha i}(\vec{r}) \varphi_{\beta i}^*(\vec{r})$

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

charge density around an ion

$$q_{\alpha\beta}^{(v)} = \int_{S_v} p_{\alpha\beta}(\vec{r}) d^3r \quad S_v: \text{sphere of pre-defined radius around ion } v$$

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

total energy

$$E = \sum_{i \in \text{occ}} \epsilon_i - \iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r' - \sum_{\alpha} \int d^3r n(\vec{r}) \frac{\partial E_{xc}}{\partial p_{\alpha}} p_{\alpha}(\vec{r})$$

where $p_i = \sum_{\alpha\beta} U_{i\alpha} p_{\alpha\beta} U_{\beta i}^+$ and $q_i^{(v)} \delta_{ij} = \sum_{\alpha\beta} U_{i\alpha}^{(v)} q_{\alpha\beta}^{(v)} U_{\beta j}^{(v)\dagger}$ [some unitary matrix that diagonalizes $p_{\alpha\beta}$]

$$U = \begin{bmatrix} e^{\frac{1}{2}i\phi_r} \cos \frac{1}{2}\theta_r & e^{-\frac{1}{2}i\phi_r} \sin \frac{1}{2}\theta_r \\ -e^{\frac{1}{2}i\phi_r} \sin \frac{1}{2}\theta_r & e^{-\frac{1}{2}i\phi_r} \cos \frac{1}{2}\theta_r \end{bmatrix}$$

where ϕ_r, θ_r define principle axis of magnetic moment at ion r