Tight-binding description

Solids - well localized "atomic" orbitals + electrons hopping between them.

\[
\langle \vec{r} | \vec{R} \rangle_{\text{at}} = \phi_{\text{at}}(\vec{r} - \vec{R}) \quad \phi_{\text{at}}: \text{atomic orbitals}
\]

- Simplest case: H-crystal - only one s-orbital per atom

= diagonalize \( \hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \) in subset \( \{ | \vec{R} \rangle_{\text{at}} \} \)

"Problem": atomic orbitals at different sites not orthogonal (overlaps): \( \langle \vec{R}' | \vec{R} \rangle_{\text{at}} \neq \delta_{\vec{R}\vec{R}'} \)

= construct \( | \vec{R} \rangle = \sum_{\vec{R}'} U_{\vec{R} \vec{R}'} | \vec{R}' \rangle_{\text{at}} \) (will suitable choice of \( U \) ) another basis with \( \langle \vec{R}' | \vec{R} \rangle = \delta_{\vec{R}\vec{R}'} \)

\( \Rightarrow \) Wannier basis

- When atomic orbitals are well localized \( \langle \vec{R} | \vec{R} \rangle_{\text{at}} \sim \sim e^{-||\vec{R} - \vec{R}'||^2/\sigma^2} \), also WF will be localized.
• Representation of Hamiltonian

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \]

\[ \hat{H} = \sum_{R,R'} \left( \frac{\langle R | \hat{H} | R' \rangle}{\hbar_{R-R'}} \right) \langle R | \hat{H} | R' \rangle \]

Matrix element for tunneling between Wannier orbitals

• If Wannier orbitals are well localized, \( \hbar_{R-R'} \) falls off exponentially.

Simplest approximation:

\[ \hbar_{R-R'} = \begin{cases} 
\epsilon & \text{if } R=R' \\
-J & \text{if } R,R' \text{ nearest neighbors} \\
0 & \text{else}
\end{cases} \]

• Band structure:

\[ |\Psi_k\rangle = \frac{1}{\sqrt{V}} \sum_{R} e^{i\mathbf{k}\cdot\mathbf{r}} |R\rangle \]

\[ \text{check: } \Psi_k(r) = e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ \frac{1}{\sqrt{V}} \sum_{R} \mathcal{W}(r-R) e^{i\mathbf{k}\cdot(R-r)} \right\} \]

\( \hat{H} \) is diagonalized by the Bloch functions

\[ |\Psi_k\rangle = \frac{1}{\sqrt{V}} \sum_{R} e^{i\mathbf{k}\cdot\mathbf{r}} |R\rangle \]

\[ \hat{H} |\Psi_k\rangle = \frac{1}{\sqrt{V}} \sum_{R} e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ \epsilon |R\rangle - J |\mathbf{r}+\mathbf{a}_1\rangle - J |\mathbf{r}+\mathbf{a}_2\rangle \\
- J |\mathbf{r}+\mathbf{a}_2\rangle - J |\mathbf{r}+\mathbf{a}_1\rangle \right\} \]
\[ H | \psi_n \rangle = \left[ \epsilon - 2 \int \cos(k_x a) - 2 \int \cos(k_y a) \right] | \psi \rangle \]
3) Screening in dielectrics & metals

**Solid:** Long-ranged Coulomb interaction screened by mobile charges (last!)

\[ \Rightarrow \text{effectively short-ranged interaction between charges} \]

\[ \phi(r) = \frac{q}{r} \]

"bare charge"

Motivation:

- relation to dielectric response \( \Rightarrow \) optical conductivity
- understand effective interactions between (quasi)particles in the solid (e.g., attractive interactions which lead to superconductivity)
- response functions \( \equiv \) excitation spectrum, collective excitations

**Macroscopic description**

Maxwell: (cgs)

\[ \nabla \times \mathbf{E} = \frac{4\pi}{c} \mathbf{J} \]

\[ \nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{J} + \frac{4\pi}{c} \frac{\partial \mathbf{E}}{\partial t} \]

\[ \nabla \cdot \mathbf{B} = 0 \]

\[ \mathbf{S}_{ij} \] : microscopic charges, currents: "external & induced"
Macroscopic Maxwell equations:

\[ \nabla \cdot \mathbf{D} = 4\pi \rho_{\text{ext}} \]
\[ \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J}_{\text{ext}} + \frac{4\pi}{c} \frac{\partial \mathbf{D}}{\partial t} \]

\( \mathbf{D} = \varepsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H} \)

Note: linear response relations in general non-local in space and time tensor \( \mathbf{D}_\alpha (\mathbf{r}, t) = \int d\mathbf{r}' \varepsilon_{\alpha\beta} (\mathbf{r}-\mathbf{r}', t-t') \mathbf{E}_\beta (\mathbf{r}', t') \)

\( \to \) Fourier:

\[ \mathbf{D}(\mathbf{q}, \omega) = \int d^3 q' \int d\omega' e^{i\mathbf{q}\cdot\mathbf{q}'} \mathbf{D}(\mathbf{q}', \omega) \]

\[ \mathbf{D}(\mathbf{q}, \omega) = \frac{\mathcal{D}(\mathbf{q}, \omega)}{\varepsilon(\mathbf{q}, \omega)} \mathbf{E}(\mathbf{q}, \omega) \]

Interpretation of dielectric function \( \varepsilon \)

Consider some "bare" potential due to "external" charge density:

\[ -\nabla^2 \phi_{\text{ext}} = 4\pi \rho_{\text{ext}} \]

\[ \nabla \cdot \mathbf{D} = \nabla (\varepsilon \mathbf{E}) = \varepsilon \nabla \phi = -\varepsilon \nabla^2 \phi \]

\[ \Rightarrow \phi(\mathbf{q}, \omega) = \frac{\phi_{\text{ext}}(\mathbf{q}, \omega)}{\varepsilon(\mathbf{q}, \omega)} \]
=\) phenomenologically describes screening

Relation to conductivity:

\[
\nabla \times \mathbf{B} = \frac{\mu_0}{c} \mathbf{j}_{\text{ext}} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}
\]

Nonmagnetic material: \( \mathbf{j}_{\text{ext}} = 0 \)

\[
\nabla \times \mathbf{E} = -\frac{i\omega}{c} \mathbf{D}
\quad \text{(Fourier:} \ \frac{\partial}{\partial t} \rightarrow -i\omega \text{)}
\]

\[
= -\frac{i\omega}{c} \mathbf{E}
\]

Microscopic: \( \mathbf{j} = \text{induced current} \)

\[
\nabla \times \mathbf{B} = \frac{\mu_0}{c} \mathbf{j} - \frac{i\omega}{c} \mathbf{E}
\]

\[
\quad \sigma \mathbf{E} \quad \text{definition of conductivity}
\]

\[
= -\frac{i\omega}{c} \left( 1 + i \frac{\mu_0 \sigma(\omega)}{c} \right) \mathbf{E}
\]

Compare with \( \Box \):

\[
\varepsilon(\omega) = 1 + i \frac{\mu_0 \sigma(\omega)}{c}
\quad \left( 1 + i \frac{\sigma}{c} \text{ in SI units} \right)
\]

Optical response: measurement at \( q = 0 \)

(\( \lambda_{\text{visible}} \gg \text{atomic spacing} \))

Relation to charge response function:

Define \( \delta n = X \delta V_{\text{ext}} \)

Response of density to external potential
Energy \quad (S = -e \delta n, \quad V = -e \phi)

Poisson: \quad \phi = \frac{N_{\text{el}}}{q^2} (S_{\text{ext}} + S_{\text{induced}})

\frac{1}{\varepsilon(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} X(q, \omega)

Usually difficult to compute \(X = \frac{\delta n}{\delta V_{\text{ext}}}\) for

interacting many-particle system.

Often used: mean-field (random phase) approximation

\(RPA\)

\(\delta n = X \delta V_{\text{ext}} = X_{\text{free}} (\delta V_{\text{ext}} + \delta V_{\text{ind}})\)

Response of interacting electrons to external potential

\(\approx\) response \(X_{\text{free}}\) of non-interacting electrons

to full potential (external + induced)

with \(\delta V_{\text{ind}} = -e \phi_{\text{ind}} = \frac{4\pi e^2}{q^2} \delta n\)

\(\Rightarrow \delta n = X_{\text{free}} (\delta V_{\text{ext}} + \frac{4\pi e^2}{q^2} \delta n)\)

\(\Rightarrow \delta n = X_{\text{RPA}} \delta V_{\text{ext}} \quad \text{with} \quad X_{\text{RPA}}(q, \omega) = \frac{X_{\text{free}}(q, \omega)}{1 - \frac{4\pi e^2}{q^2} X_{\text{free}}(q, \omega)}\)
Implications of denominator (see below)

- Pole at \( \omega > 0 \): collective excitations
- Pole at \( \omega = 0 \): Instability (charge-density wave, \( @ q \omega \)) etc.

\[ \text{Static screening: Thomas-Fermi model} \]

Simplest model for \( X_{\text{free}} \):

Density \( n(r_0) \) at given point \( r_0 \) \( \approx \)

Density of homogeneous electron gas in potential \( V = V(r_0) \) ("local density approximation")

Homogeneous electron gas: \( (n_F(x) = \frac{1}{e^{\frac{x}{k_B T}} + 1} \text{ Fermi}) \)

\[ n(V) = \int \frac{d^3k}{(2\pi)^3} \text{ } n_F \left( \frac{\hbar^2 k^2}{2m} + V - \mu \right) \]

\[ \Rightarrow X_{\text{free}} \approx -\frac{\partial n}{\partial \mu} \text{ Thomas-Fermi} \]

Note: \( \frac{\partial n}{\partial \mu} \) = Compressibility
\[ \varepsilon = \frac{1}{1 + \frac{4\pi e^2}{q^2} \varepsilon_{\text{free}}} \]

\[ \varepsilon = 1 - \frac{4\pi e^2}{q^2} \varepsilon_{\text{free}} \]

Thomas-Fermi

Define Thomas-Fermi wave vector

\[ k_{TF}^2 = \frac{4\pi e^2}{\hbar^2} \frac{\partial n}{\partial \mu} \Rightarrow \varepsilon_{TF} = 1 + \frac{k_{TF}^2}{q^2} \]

at \( T = 0 \):

\[ n = \int \frac{d^3k}{(2\pi)^3} \quad \text{with} \quad \frac{\hbar^2 k_{TF}^2}{2m} = \mu \]

\[ k_{TF}^2 = \frac{4\pi e^2}{\hbar^2} k_f = \frac{1}{k_{TF}} = \Theta(\text{few } \text{Å}) \text{ for typical densities of mobile electrons in metals} \]

Screamed potential of extra point charge (impurity atom, defect in crystal, ...)

\[ \phi(x) = \frac{4\pi e}{q^2} \cdot \frac{1}{\varepsilon(x)} = \frac{4\pi e Q}{k_{TF}^2 + q^2} \]
\[ \phi(r) = \frac{Q}{r} e^{-r/k_{TF}} \]

Yukawa potential

screening length \( \kappa_{TF} \)

more accurate: \( \chi_{\text{free}}(q) \) exact response of homogeneous electron gas: Lindhard theory

\[
\chi_{\text{free}}(q, \omega = 0) = -\frac{2m}{\hbar^2} \frac{k_F}{\pi^2} \left\{ 1 - \frac{S}{\pi} \left( 1 - \frac{q^2}{2S} \right) \ln \left| \frac{S^2 + q^2}{S^2} \right| \right\}
\]

\[
\chi_{\text{free}}(q, \omega = 0) = -\frac{2m}{\hbar^2} \frac{1}{2\pi} \left\{ 1 - (1 - \frac{q^2}{2S}) \Theta(q^2 - 2S) \right\}
\]

\[
\chi_{\text{free}}(q, \omega = 0) = -\frac{2m}{\hbar^2} \frac{1}{2\pi q} \left\{ \ln \left| \frac{S^2 + q^2}{S^2} \right| \right\}
\]

\( = \) more and more singular at \( |q| = 2k_F \)

for lower \( d \) \( (= \) instability for \( d = 1 \) \)

\( \rightarrow \) interference effects (Friedel oscillations)

\[ \ln d = 3 @ T = 0 : \quad \phi(r) = c \frac{\cos(2k_F r)}{r^2} \]

\[ \phi \]

\[ + \]

\[ - \]
Dynamic (frequency-dependent) screening

- Some general properties of response functions
  
  Linear response \( \hat{H} = \hat{H}_0 + \hat{A} \cdot f(t) \)
  
  (e.g., \( \hat{A} = e n \) density, \( f = \text{ext} \))
  
  \[ \langle \hat{A}(t) \rangle = \int dt' X(t-t') A(t') \]

1) Causality: \( X(t) = 0 \text{ for } t < 0 \)

   \[ X(t) = \lim_{\delta \to 0} X(\omega + i\delta) = \lim_{\delta \to 0} \int dt X(t)e^{i(\omega + i\delta)t} \]

   Meaning: response to perturbation \( f(t) = f(\omega)e^{-i\omega t} \)

   \( \rightarrow \text{adiabatic switch on of field} \)

2) Analytic properties

   \( X(\omega) \) analytic for \( \text{Im} \omega > 0 \),

   \( X(\pm i\omega) \rightarrow 0 \text{ for } |\omega| \rightarrow \infty \),

   imply relation between \( \text{Re} \) and \( \text{Im} \)

   \[ X'(\omega + i\delta) = \frac{d}{d\omega} \int d\omega' \frac{X''(\omega + i\delta)}{\omega' - \omega} \]

   \[ X''(\omega + i\delta) = -\frac{d}{d\omega} \int d\omega' \frac{X'(\omega + i\delta)}{\omega' - \omega} \]

   \[ \text{Kramers-Kronig relation} \]

   Example: \( X = \frac{1}{\omega + i\delta} \) \( \Rightarrow \) \( X'' = -\text{Im} \frac{\delta}{\omega}, \omega \neq 0 \)
3) Im $X \rightarrow$ energy absorption

Consider $f(t) = e^{st}(f_{\omega_0} e^{-i\omega t} + f_{\omega_a} e^{i\omega t})$

$E(t) = \langle \hat{H}_0 + \hat{A}f(t) \rangle$

$\frac{dE}{dt} = \langle \frac{d\hat{H}}{dt} \rangle = \frac{df}{dt} \langle \hat{A}(t) \rangle$

\text{Hellmann-Feynman theorem} $X \cdot \dot{f}$

\text{inset:} $X, f$ average over period:

\[
\frac{dE}{dt} = \frac{1}{T} \int_0^T dt \frac{dE}{dt} = -2\omega \chi''(\omega) \frac{f(\omega)}{f(\omega)^2}
\]

\text{Hellmann-Feynman:}

\[
\frac{d}{dt} \langle \psi(\dot{f}) | \hat{f}(\dot{f}) | \psi(\dot{f}) \rangle = \frac{i}{\hbar} \langle \psi(\dot{f}) | \hat{H} | \psi(\dot{f}) \rangle \left\{
\frac{d}{dt} \langle \psi(\dot{f}) | \hat{H} | \psi(\dot{f}) \rangle + \langle \psi | \hat{H} \frac{d\dot{f}}{dt} | \psi \rangle + \langle \psi | \frac{d\hat{H}}{dt} | \psi \rangle \right\} = 0
\]

4) Absorption $\leftrightarrow$ excitation spectrum

\text{Fermi's golden rule} ($T=0$, $\omega_a>0$):

\[
\frac{dE}{dt} = \sum_n V_{0\rightarrow n} (E_f - E_0) \langle n | \hat{A} | 0 \rangle^2 \delta(\omega + E_0 - E_f)
\]
Compare with absorption \( (\omega, \omega \ll 0) \)

\[
X''(\omega + i\delta) = -\pi \sum_n |\langle n | \hat{A} | 0 \rangle|^2 \left[ \delta(\omega + E_n - E_0) - \delta(\omega + E_n - E_0) \right]
\]

\[
\frac{1}{T_0} \sum_n \frac{e^{-\beta E_n} - e^{-\beta E_n}}{Z} |\langle n | \hat{A} | 0 \rangle|^2 \delta(\omega + E_n - E_0)
\]

\[
Z: \text{partition function} \quad Z = \sum_n e^{-\beta E_n}
\]

5) **Fluctuations \leftrightarrow response/dissipation**

Auto correlator

\[
\langle A(t_1) - \langle A \rangle \rangle (A(t_2) - \langle A \rangle) = \langle A(t_1) A(t_2) \rangle - \langle A \rangle^2
\]

\[
C(t_1) = \langle A(t_1) A(t_0) + A(t_0) A(t_1) \rangle
\]

\[
C(\omega) = -2X''(\omega) \coth \left( \frac{\beta \omega}{2} \right)
\]

**Fluctuation-dissipation theorem**

Universal ratio between fluctuations and response

\[
\Rightarrow \text{"thermonotes", fundamentally define thermal equilibrium}
\]
Back to density response: $\chi = \frac{\delta n}{\delta V_{\text{ext}}}$

**Example 1: Oscillator model**

Density $n_0$ of oscillators

$$m \ddot{x} = -m \omega_0^2 x + \frac{\delta V_{\text{ext}}}{\nabla V_{\text{ext}}}$$

$$\ddot{x}(\omega_1^2 - \omega_0^2) = -\frac{1}{m} \nabla V_{\text{ext}}$$

Density: $\delta n/n_0 = -\nabla \cdot \vec{x} = \uparrow$

Fourier: $\delta n/n_0 = -i \vec{q} \cdot \vec{x}$

$$\vec{x} = -\frac{1}{m(\omega_0^2 - \omega^2)} i \vec{q} \cdot \vec{V}_{\text{ext}}$$

$$\implies \delta n = \frac{q^2}{m} \frac{n_0/m}{\omega^2 - \omega_0^2} V_{\text{ext}}$$

$\chi_{\text{free}}$

"free": no Coulomb interaction between oscillators, just harmonic potential; OK for low density

$$\chi_{\text{free}} = \frac{q^2 n_0}{m} \left( \frac{1}{\omega - \omega_0} - \frac{1}{\omega + \omega_0} \right) \frac{1}{2\omega_0}$$

Relevant: $\omega \rightarrow \omega + i0^+$ (see above)

$$\text{Im } \chi_{\text{free}}(\omega + i0^+) = -\pi \frac{q^2 n_0}{m} \left[ \delta(\omega - \omega_0) - \delta(\omega + \omega_0) \right]$$

$\rightarrow$ Excitation spectrum: excitation of oscillator quantum $h\omega_0$
\[
\frac{1}{\varepsilon(q,\omega)} = 1 + \frac{\varepsilon_0^2 \varepsilon^2}{q^2} \chi = 1 + \frac{4\pi e^2 n_0 / m}{\omega^2 - \omega_0^2}
\]

\[4\pi e^2 n_0 / m \text{ has unit} \left[ \frac{1}{\text{time}^2} \right]\]

\[4\pi e^2 n_0 / m = \omega_p^2 \quad \omega_p: \text{plasma frequency}\]

\[-\text{Im} \chi = \text{loss} = -\text{Im} \varepsilon^{-1}\]

\[
\frac{1}{\varepsilon} \to 1 \\
\text{for} \quad \omega \to \infty
\]

Screening

for \( \omega \ll \omega_0 \)

unscreened

for \( \omega \gg \omega_0 \)

dielectric loss for \( \omega = \omega_0 \)

Real material (insulator):

dielectrics

loss function: density of state of excitations

\[
\text{=} \text{ only true if all particles are bound} \\
\text{(no fully mobile electrons)}
\]
"unbound" particles \( \omega_0 = 0 \)

(e.g., electrons in metal)

\[
X_{\text{free}} = \frac{q^2}{\omega^2} \frac{n_0/m}{\omega^2} = \text{absorption only at } \omega = 0?
\]

With interaction between particles:

\[
X = \frac{X_{\text{free}}}{1 - \frac{\hbar \omega^2}{q^2} X_{\text{free}}} = \frac{q^2 n_0/m}{\omega^2 \left(1 - \frac{\hbar \omega^2 n_0/m}{\omega^2}\right)}
\]

\[
\omega^2 = \frac{q^2 n_0/m}{\omega^2 - \omega_p^2}
\]

\[
X''(\omega) = -\pi \frac{q^2 n_0/m}{2 \omega_p} \left[ \delta(\omega - \omega_p) - \delta(\omega + \omega_p) \right]
\]

\( \Rightarrow \) new "collective excitation" in system present only due to e-e interaction

- corresponds to long-lived excitation (oscillation) of mobile electrons against positively charged background

\[ \frac{1}{\varepsilon} = \frac{\omega^2}{\omega^2 - \omega_p^2} \xrightarrow{\omega \rightarrow \infty} 0 \]

(complete screening in metals)
Density of particle-hole excitations in solid

For density of good metals: \( \omega \approx \text{several eV} \) => short-ranged (well-screened) interaction OK for low-energy processes.

Note: Form of collective excitation crucially depends on interaction.

What changes when interaction between particles is short-ranged?

\( \phi(r) = \frac{e^{-r/A}}{r} \implies \phi(q) = \frac{4\pi}{q^2 + \frac{1}{A^2}} \)

back to mean-field formula \((\text{RPA})\)
\[ \delta n = X \delta V_{\text{ext}} = X_{\text{free}} (\delta V_{\text{ext}} + \delta V_{\text{ind}}) \]

\[
\text{now: } V_{\text{ind}} = \frac{4 \pi \kappa^2}{\kappa^2 + 1} \delta n
\]

Solution of Poisson Eq. with extra screening.

\[
X = \frac{X_{\text{free}}}{1 - \frac{4 \pi \kappa^2}{(\kappa^2 + 1) X_{\text{free}}}} \to \frac{X_{\text{free}}}{1 - \frac{4 \pi \kappa^2 n_0/m}{\omega^2}}
\]

\[
= \frac{\kappa^2 n_0/m}{\omega^2 - 4 \pi \kappa^2 (n_0/m)^2 \kappa^2}
\]

\[ \Rightarrow \text{now there is a pole at } \omega = C_0/\kappa \]

\[ C_0 = \sqrt{4 \pi \kappa (n_0/m)^2} \]

\[ \omega = \omega_P \]

\[ \Rightarrow \text{sound-like dispersion} \]

\[ \omega = C_0 \]

"Zero Sound" = collective excitation in Fermi system with short-ranged interaction