EE201/MSE207 Lecture 16

Variational principle (Ch. 7)

Only Sec. 7.1

Theorem: For an arbitrary $|\psi\rangle$, the ground state energy E_g satisfies inequality

$$E_g \le \langle\psi|\hat{H}|\psi\rangle = \langle\hat{H}\rangle$$

Proof is simple. Let us expand $|\psi\rangle = \sum_n c_n|\psi_n\rangle$. Then since $E_n \ge E_g$, we get

$$\langle\hat{H}\rangle = \sum_n |c_n|^2 E_n \ge E_g \sum_n |c_n|^2 = E_g$$

This theorem can be useful to estimate E_g (or at least to find an upper bound)

Idea: Use trial wavefunctions $|\psi\rangle$ with many adjustable parameters and minimize $\langle\hat{H}\rangle$. Hopefully $\min\langle\hat{H}\rangle$ is close to E_g.

Extensions of this method can also be used to find $|\psi_g\rangle$,
first-excited state energy and wavefunction (using subspace orthogonal to $|\psi_g\rangle$),
second-excited state, etc.

EE201/MSE207 Lecture 16

Band structure (back to Ch. 5)

Band structure for electrons is a consequence of a periodic potential in a lattice (due to periodic arrangement of atoms).

For simplicity let us consider 1D case

$V(x+a)=V(x)$ (periodic with lattice constant a)

Bloch's theorem: If $V(x+a)=V(a)$, then for an eigenstate of energy

$$\boxed{\psi(x+a)=e^{iKa}\,\psi(x)}$$ (almost periodic, "quasimomentum" $\hbar K$)

Therefore $\psi(x)=e^{iKx}\tilde{\psi}(x)$ with periodic $\tilde{\psi}(x)$, $\tilde{\psi}(x+a)=\tilde{\psi}(x)$

Proof

Introduce displacement operator $\widehat{D}$, so that $\widehat{D}f(x)=f(x+a)$.

It commutes with Hamiltonian, $\left[\widehat{D},\widehat{H}\right]=0$, therefore common eigenfunctions.

$\psi(x+a)=\lambda\,\psi(x)$ If $|\lambda|\neq 1$, then ψ would increase or decrease exponentially

Therefore $|\lambda|=1$, can denote $\lambda=e^{iKa}$.

Periodic boundary condition for Bloch's theorem

$$V(x+a) = V(a) \quad \Rightarrow \quad \psi(x+a) = e^{iKa}\,\psi(x)$$

Usually people use periodic boundary condition in using Bloch's theorem

$\psi(x+Na) = \psi(x)$ for $N \ggg 1$ atoms in a (1D) sample

Why? Because it does not matter, but makes calculations simpler

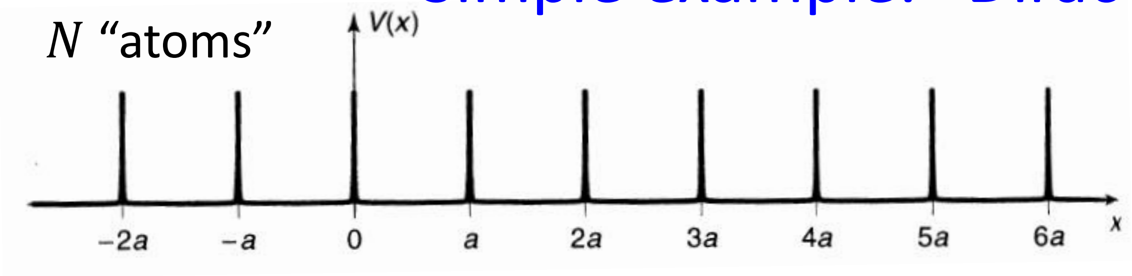
Then $K = \dfrac{2\pi n}{Na}, \qquad n = 0, \pm 1, \pm 2, \ldots$

This gives N different values of K (the same e^{iKa} if $\Delta n = N$):
N states in a band for N atoms

Since N is very large, K is almost continuous.

Simple example: “Dirac comb”

N “atoms”



Dirac comb:

$$V(x) = \alpha \sum_{j=1}^{N} \delta(x - ja)$$

(wrapped around)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\,\psi(x)$$

$$0 < x < a \;\Rightarrow\; \psi(x) = A\sin(kx) + B\cos(kx), \quad k = \sqrt{2mE}/\hbar$$

From Bloch’s theorem we know that

at $-a < x < 0, \quad \psi(x) = e^{-iKa}[A\sin(k(x+a)) + B\cos(k(x+a))]$

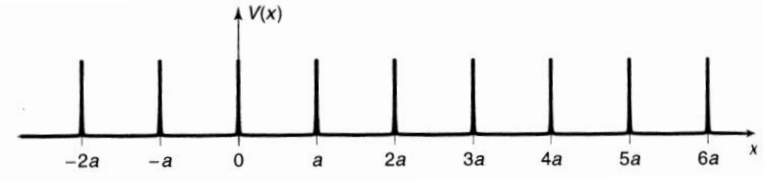
$$\begin{cases} \psi(0+0) = \psi(0-0) \quad \Rightarrow \quad B = e^{-iKa}\,[A\sin(ka) + B\cos(ka)] \\ \psi'(0+0) - \psi'(0-0) = (2m\alpha/\hbar^2)\,\psi(0) \end{cases}$$

$$\Rightarrow \quad kA - e^{-iKa}[kA\cos(ka) - kB\sin(ka)\,] = (2m\alpha/\hbar^2)\,B$$

From these two equations we find (eliminating A and B)

$$\cos(Ka) = \cos(ka) + \frac{m\alpha a}{\hbar^2}\frac{\sin(ka)}{ka}$$

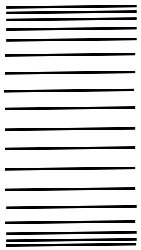
Dirac comb (cont.)



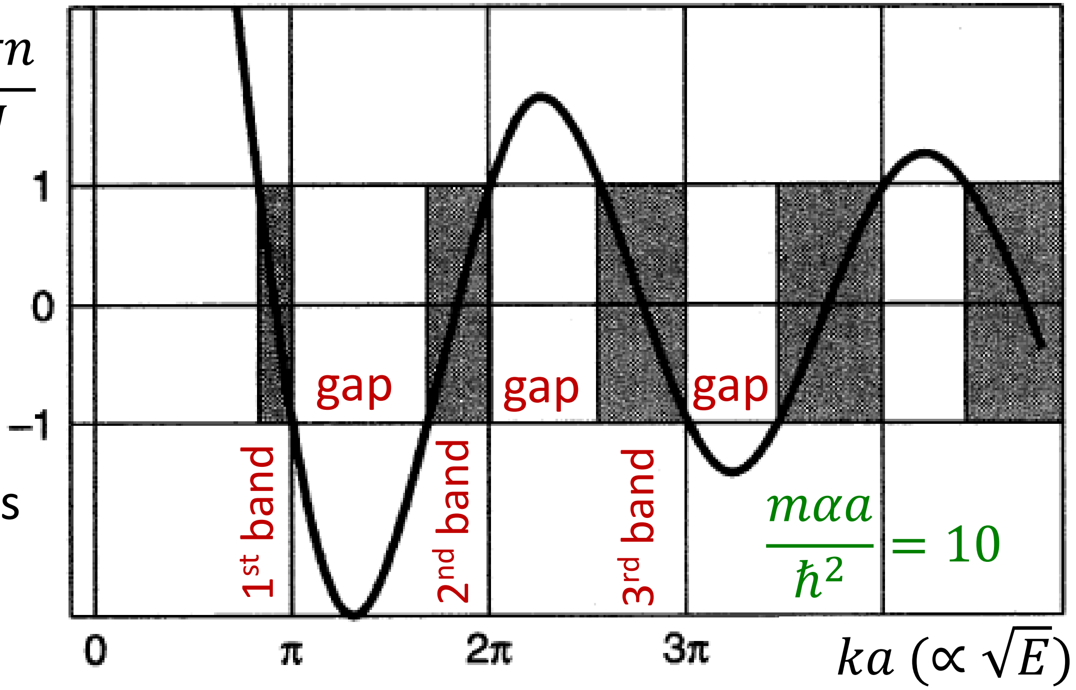
$$V(x) = \alpha \sum_{j=1}^{N} \delta(x - ja)$$

$$\cos(Ka) = \cos(ka) + \frac{m\alpha a}{\hbar^2}\frac{\sin(ka)}{ka}$$

$$Ka = \frac{2\pi n}{N}$$

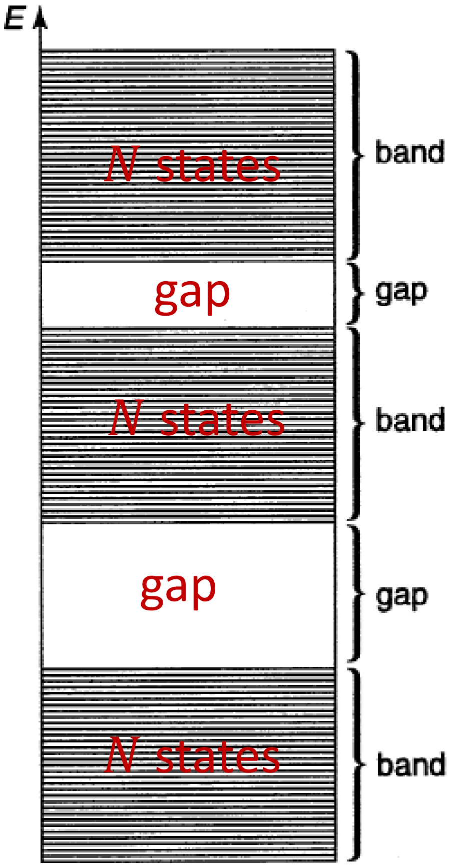


N states



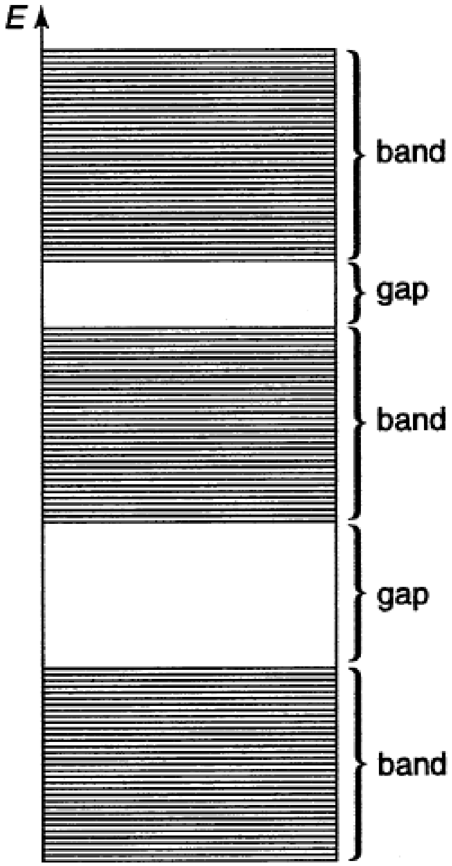
$$\frac{m\alpha a}{\hbar^2} = 10$$

Gaps become smaller, eventually continuum



N states per band
(× 2 spin)

Bands



N states per band
(× 2 spin)

Gaps become smaller, eventually continuum

If one electron per atom ($q = 1$), then half a band is filled (good conductor)

If $q = 2$, then one band is filled completely (insulator or semiconductor; cannot slightly excite electrons)

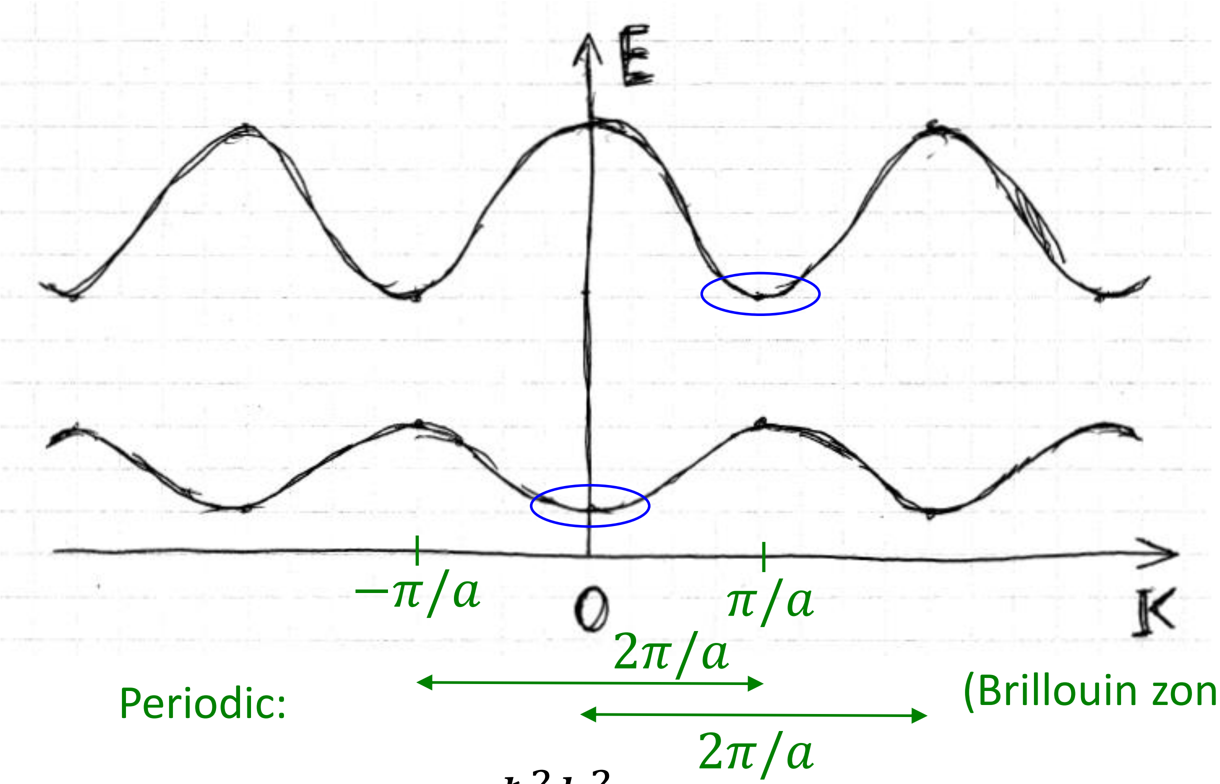
If $q = 3$, then 1.5 bands are filled (good conductor)

If $q = 4$, then again insulator or semiconductor

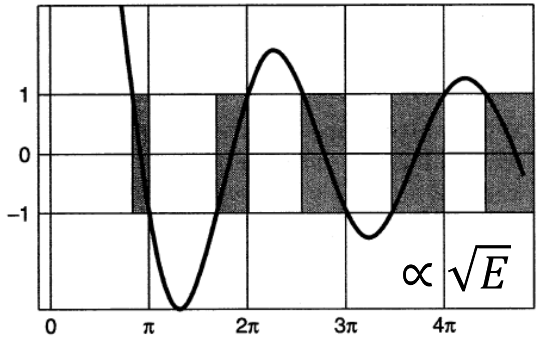
Etc.

Metals usually have $q = 1$

Bands (cont.)



Periodic: (Brillouin zone)



$\cos(Ka) = \ldots$

$\hbar K$ is quasimomentum (behaves as momentum)

For a free particle $E = \dfrac{\hbar^2 k^2}{2m}$

Define effective mass m_{eff} via $\Delta E = \dfrac{\hbar^2 K^2}{2m_{\text{eff}}}$ or even $\Delta E = \dfrac{\hbar^2 (\Delta K)^2}{2m_{\text{eff}}}$

(similar to bands in semiconductors) or even $\dfrac{d^2E}{dK^2} = \dfrac{\hbar^2}{m_{\text{eff}}}$

Quasimomentum $\hbar K$ behaves as momentum

Let us add small force F (e.g., due to electric field acting on electron, $F=-e\mathcal{E}$).

Then $\Delta V=-Fx$ and therefore $E\to E-Fx$ (for the same K).

From Bloch's theorem we know $\psi(x)=e^{iKx}\,\tilde{\psi}_K(x)\propto e^{iKx}$ on the large scale

Adding time dependence, we get (on the large scale)

$$\Psi(x,t)\propto e^{iKx}e^{-i\frac{(E-Fx)t}{\hbar}}=e^{i\left(K+\frac{Ft}{\hbar}\right)x}\,e^{-iEt/\hbar}$$

It means $\quad K\to K+\dfrac{F}{\hbar}\,t \quad\Rightarrow\quad \boxed{\dfrac{d(\hbar K)}{dt}=F}$

We see that $\hbar K$ behaves as momentum (so named quasimomentum)

(for validity of this approach we need very small F)

Actually, significant oversimplification in this approach; this rather a hint.

More rigorously, $\quad e^{i(K+Ft/\hbar)x}e^{(-i/\hbar)\int_0^t E(K+Ft'/\hbar)\,dt'}\,\tilde{\psi}_{K+Ft/\hbar}(x)$

is an approximate solution of SE (straightforward to check).

Also, makes sense for energy change: $\quad Fv_{gr}=\hbar\dfrac{dK}{dt}\,\dfrac{dE}{\hbar\,dK}=\dfrac{dE}{dt}.$

End of material included into the final exam

Following lectures are important,
but not needed for the exam