Origin of the energy band structure

in periodic lattices; “molecular orbital” and “electron wave diffraction” reasoning.

July 1, 2021

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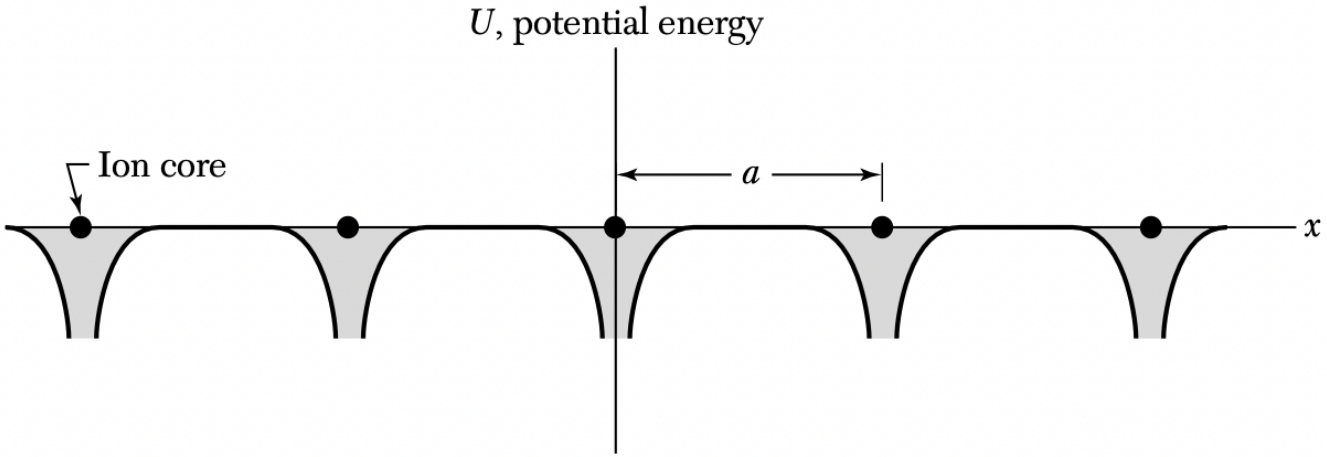
- So the energy bands are given from the periodicity



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- At the edge of the first Brillouin zone band gap occurs.
- The wavefunctions at $k = \pm\frac{\pi}{a}$ are not the traveling waves $\exp(i\frac{\pi x}{a})$ or $\exp(-i\frac{\pi x}{a})$ of free electrons. These are standing waves.

Origin of the band gaps: "electron wave diffraction" reasoning

- Hence, the time-independent state is represented by standing waves. We can form two different standing waves from the two traveling waves:

$$\begin{aligned} \psi(+) &= \exp(i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a) \\ \psi(-) &= \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a) \end{aligned} \tag{1}$$

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- The two standing waves $\psi(+) and \psi(-)$ pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap

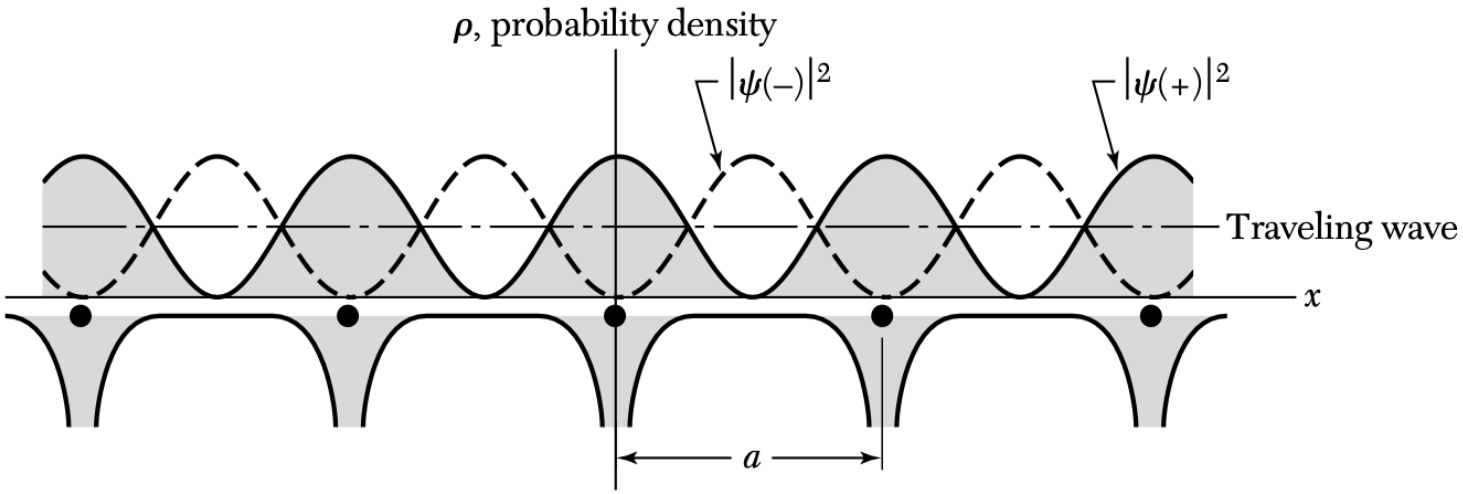

Figure 1: The probability density on y axis is $\rho = \psi^*\psi = |\psi|^2$

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- When we calculate the average or expectation values of the potential energy over these three charge distributions, we find that the potential energy of $\rho(+)$ is lower than that of the traveling wave (because you put in the same point $+$ and $-$ charges that cancel out each others), whereas the potential energy of $\rho(-)$ is higher than the traveling wave.

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- We have an energy gap of width E_g if the energies of $\rho(+)$ and $\rho(-)$ differ by Eg

Origin of the band gaps: "electron wave diffraction" reasoning

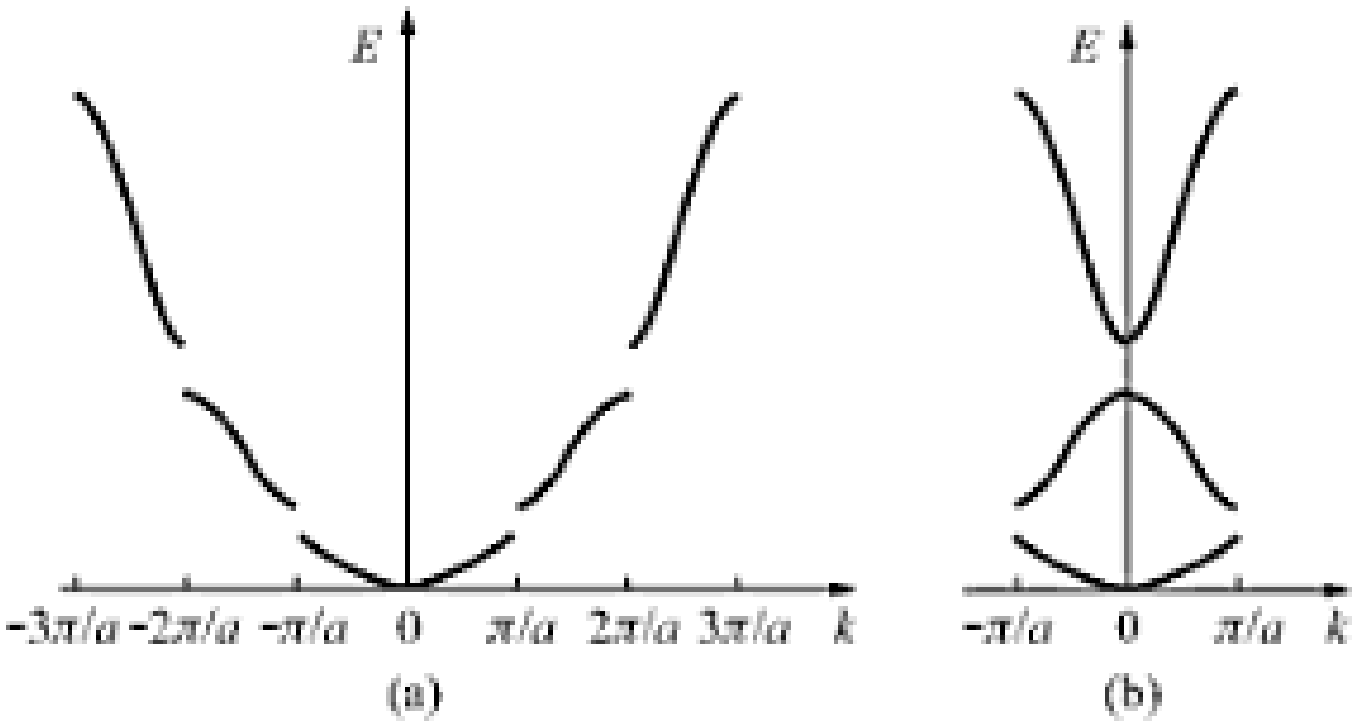

Figure 2: Energy band gaps

Origin of the band gaps: Molecular orbital reasoning

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- We first review the argument used to explain the energy structure of a covalent bond. Consider two identical hydrogen atoms so far apart that there is no interaction whatsoever between them. Further suppose that the electron in each atom is in the same ground state: a 1s electron with an energy of -13.6 eV (ignore spin).

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- When the hydrogen atoms are brought closer together, the individual wave functions of the electrons overlap and, by the exclusion principle, can no longer be in the same quantum state, which splits the original equivalent energy levels into two different energy levels.

Origin of the band gaps: Molecular orbital reasoning

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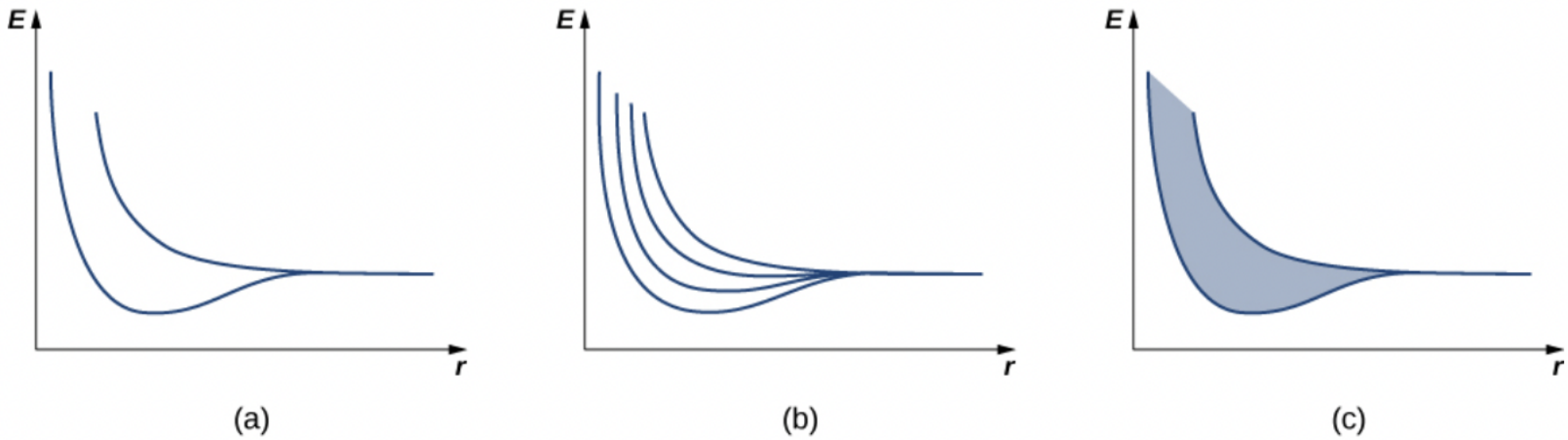

Figure 3: The dependence of energy-level splitting on the average distance between (a) two atoms, (b) four atoms, and (c) a large number of atoms. For a large number of electrons, a continuous band of energies is produced.

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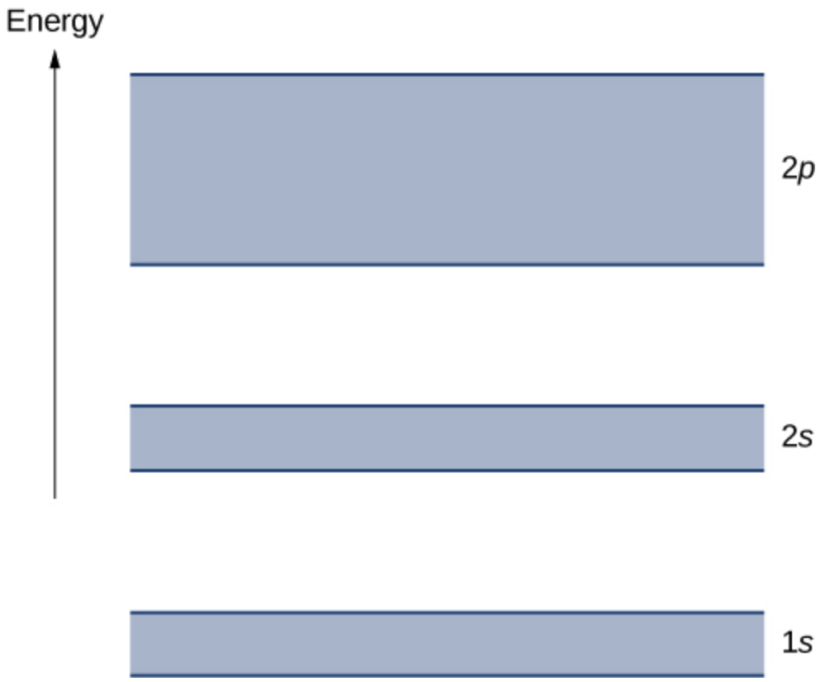

Figure 4: The allowed states of energy and wave number are still technically quantized, but for large numbers of atoms, these states are so close together that they are consider to be continuous or "in the continuum."

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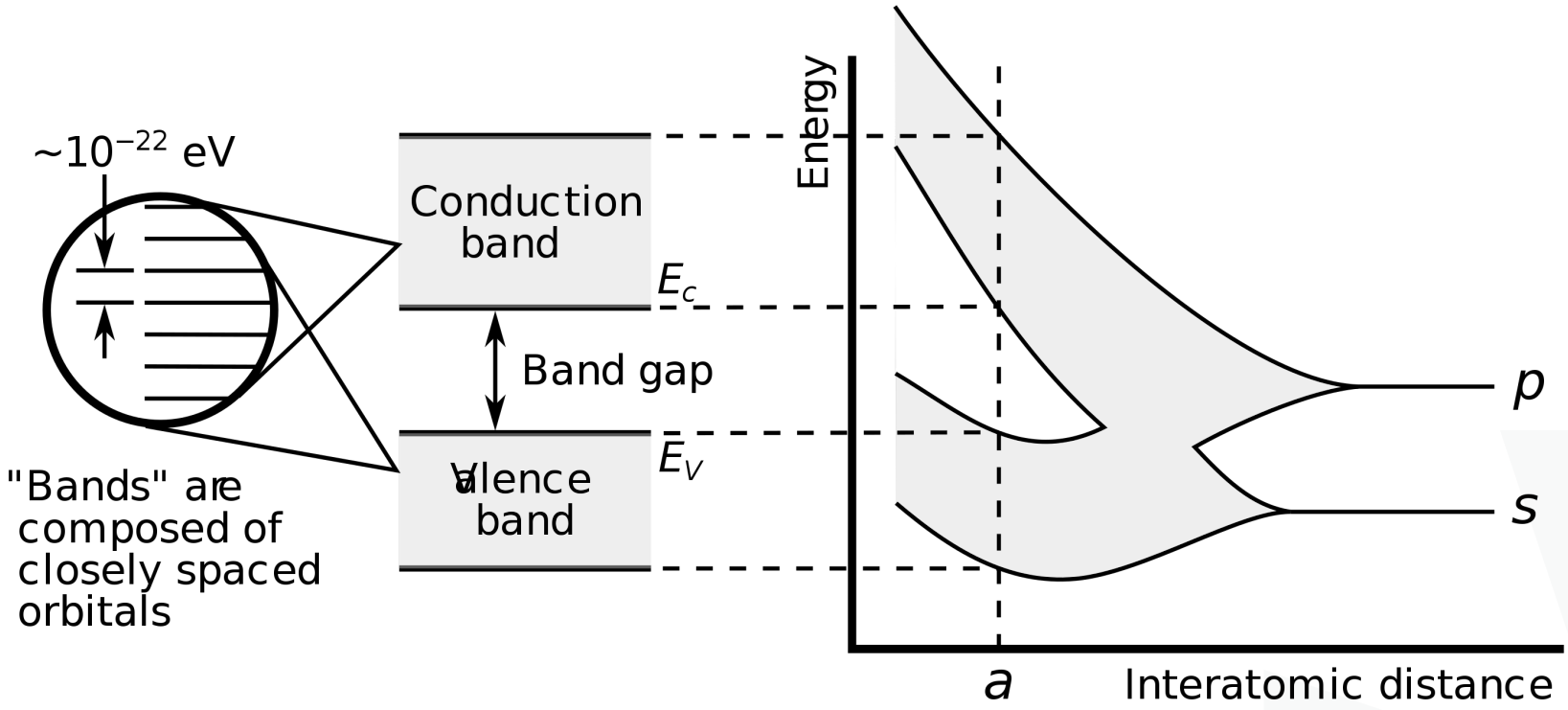

Periodic Potential, Kronig-Penney model

- A very representative and interesting quantum mechanical model that shows how an electron can move inside a periodic crystal is the Kronig-Penney model.

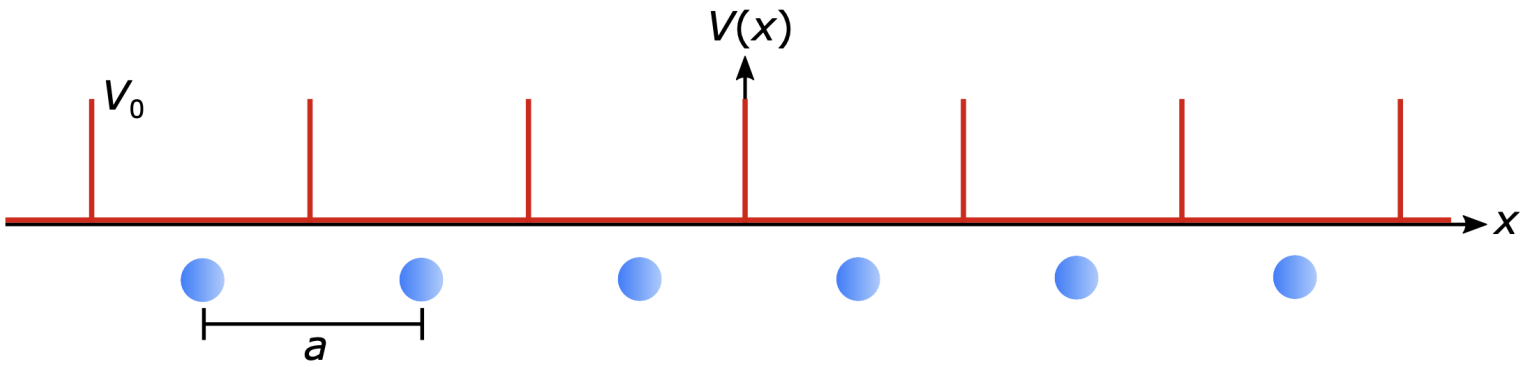

Figure 5: Kronig-Penney model with a periodic potential consisting of delta functions with magnitude V_0 with periodicity a.

Origin of the band gaps: Periodic Potential and Kronig-Penney model

- The Kronig-Penney model is an idealized quantum-mechanical system that describes electron motion in a period array of delta functions with magnitude V_0:

$$U(x) = U_0 \sum_{n=-\infty}^{+\infty} \delta(x - na)$$

where the delta is the dirac delta and a is the lattice constant. The time-independent Schrödinger equation consists:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right) \psi(x) = E\psi(x) \tag{2}$$

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- According to Bloch's theorem, the solution of the Schrödinger equation when the potential is periodic, can be written as:

$$\psi(x) = e^{iqx} u(x) \qquad \text{with } q = n\frac{2\pi}{Na}$$

where $u(x)$ is a periodic function. In fact $u(x) = u(x + a)$.

Origin of the band gaps: Periodic Potential and Kronig-Penney model

- Then imposing the boundary condition for the wave function solution we a trascendental equation:

$$cos(qa) = \frac{2mV_0 a}{\hbar^2} \frac{sin(ka)}{ka} + cos(ka) \tag{3}$$

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- The allowed values of the energy ϵ are given by those satisfying $qa = (\frac{2m\epsilon}{\hbar^2})^{\frac{1}{2}} a$, since the number N of lattice point is big the spectrum of the possible solution is very dense for which that lie under the condition:
$-1 \leq \frac{2mV_0 a}{\hbar^2}\frac{sin(ka)}{ka} + cos(ka) \leq 1$.

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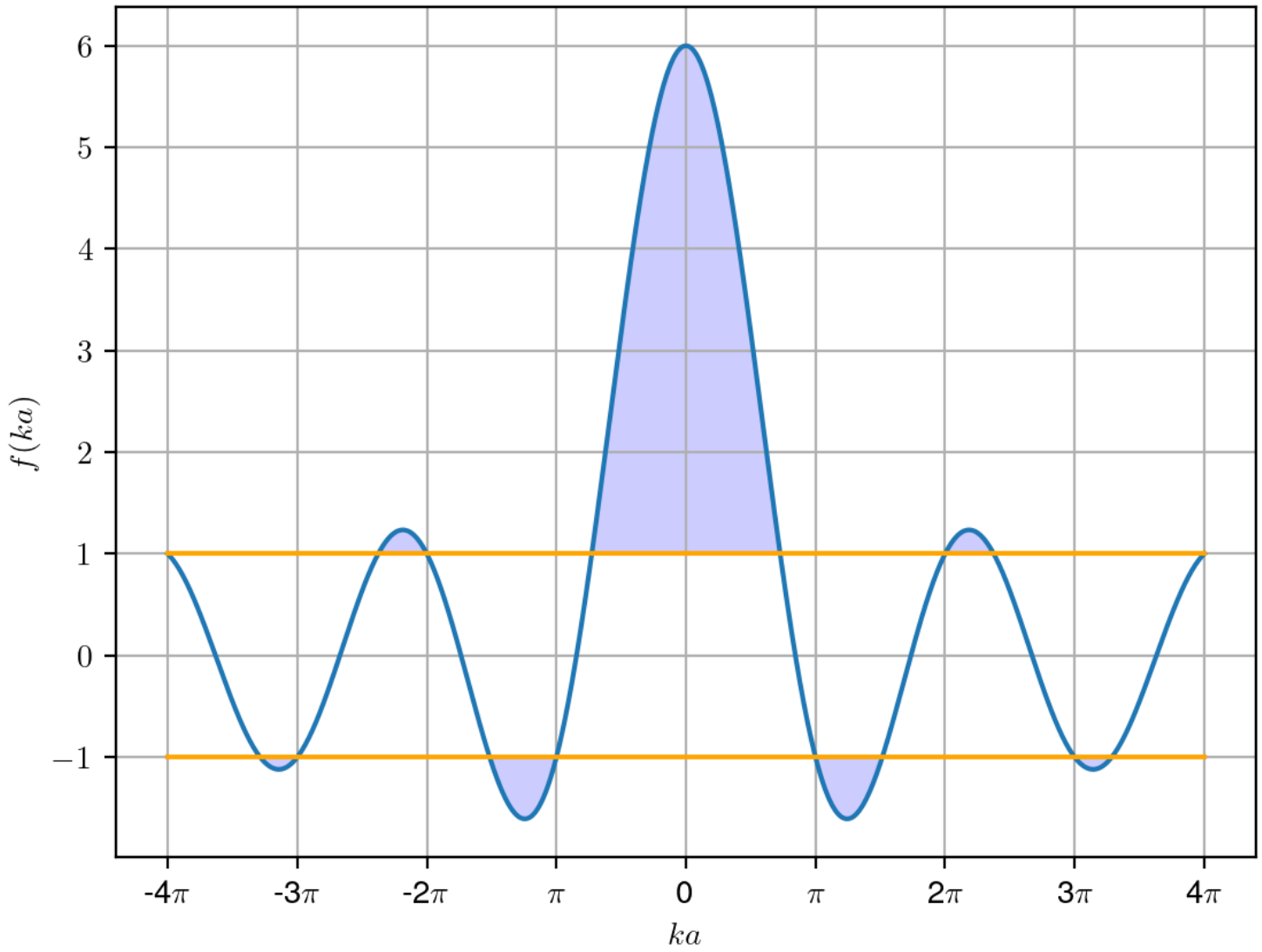

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