Lecture 14: Solid State Paradox

For the solid states the infinitely high potential barrier stands as a valid approximation for the electronic stationary behavior; however, this is equivalently to state that electrons are "free" outside the barrier, and evolving as stationary waves, with trial paradigmatic two-parameter trigonometric 1D form:

$$\psi_k(A,x) = A\sin(kx)$$

with the associate free electronic Hamiltonian:

$$\hat{H}_k = -\frac{\hbar^2}{2m_0}\partial_x^2 .$$

Note that if one would like to consider the Hamiltonian with some potential that mimics the infinite barrier in asymptotic limit, i.e. as is the case of $|x/a|^\alpha, \alpha \to \infty$, with a - the width of the free barrier, will soon conclude that the corresponding term in energy is not divergent in a very narrow domain, namely for $a \in [\lambda/2, \lambda/12]$ that is in obvious contradiction with forming of stationary waves in the well; therefore the only acceptable Hamiltonian in the case of infinite well is that restricted to the kinetic term only.

Unfolding the ordinary variational procedure, one starts with imposing the normalization condition on the trial wave-function:

$$1 = \int_0^a \psi_k^* \psi_k dx = A^2 \int_0^a \sin^2(kx) dx = \frac{A^2}{2}\int_0^a [1-\cos(2kx)]dx = \frac{A^2}{2}\left[a - \frac{1}{2k}\sin(2ka)\right],$$

assisting the two constants' relationship in the form:

$$A = \sqrt{\frac{2}{a - \frac{1}{2k}\sin(2ka)}} = \sqrt{\frac{2}{a}}\sqrt{\frac{1}{1-\frac{\sin(2ka)}{2ka}}}$$

On the other side, the energy computation with the *A* constant expression, i.e. in the normalization condition of the wave-function, yields the paradoxical result:

$$E_k = \int_0^a \psi_k^* \hat{H}_k \psi_k dx$$

$$= A^2 k^2 \frac{\hbar^2}{2m_0}\int_0^a \sin^2(kx) dx = A^2 k^2 \frac{\hbar^2}{2m_0}\frac{1}{2}\left[a - \frac{1}{2k}\sin(2ka)\right] = \frac{\hbar^2 k^2}{2m_0}$$

since being in accordance with de Broglie quantization provides through variation

$$0 = \partial_k E_k = k\frac{\hbar^2}{m_0}$$

the solution

$$k = 0$$

that produces the infinite amplitude in the above expression:

$$\lim_{k\to 0} A = \sqrt{\frac{2}{a}}\sqrt{\frac{1}{1-\lim\limits_{k\to 0}\frac{\sin(2ka)}{2ka}}} = \sqrt{\frac{2}{a}}\sqrt{\frac{1}{1-1}} = \infty\,,$$

and consequently the “strange” couple of eigen-solutions:

$$\begin{cases}\psi_{k=0}(x) = \infty\cdot 0 = ?\\ E_{k=0} = 0\end{cases}$$

leaving with the idea that electrons in the fundamental (ground) solid state are “hidden”: they have no observable energy (or zero energy) although they may have an un-determinate existence by means of the “associate” wave-function.

However, beside the fact that we made the first encounter with the “quantum hidden state” realization, the present paradox is solved by invoking other quantum postulate, namely that of wave-function continuity at the extremities of the infinite well:

$$\psi_k(x=a) = \psi_k(x>a)$$

that may be regarded also as a sort of wave-function variational principle

$$\delta\psi_k\big|_{x=a} = 0$$

at the domain existence limit; explicitly looks as

$$A\sin(ka) = 0$$

from where follows the entire spectra of k - quantification

$$k = \frac{\pi}{a}n\,,\ n = 1,2,\ldots$$

with excluded zero (or ground state, or hidden state) solution above.

In these conditions the amplitude of the eigen-function will be proportional with the square root of the inverse of the well’s width

$$A = \sqrt{\frac{2}{a}} \, ,$$

while the couple of finite and non-zero, eigen-solution of the electronic movement in the solid states (modeled as an infinite well) take the consecrated (already proved) forms:

$$\begin{cases} \psi_k(x) = \sqrt{\dfrac{2}{a}} \sin\left(n\pi \dfrac{x}{a}\right) \\ E_k = \dfrac{\hbar^2 \pi^2}{2m_0 a^2} n^2 \end{cases}$$

Yet, the case of solid states reveals the important idea that electronic behavior is at least forbidden in their truly ground state, or it happens in a hidden manner – this may be the quantum state that when approached to allow the super-conductivity phenomena; equivalently, one can say that since electrons in solid state are normally situated in “excited” states this may be the natural basic explanation for their propensity for conduction and metallic properties.

Nevertheless, for the moment we remain with idea that, in a way or other, the variational principle (for energy or wave-function) are the necessary and sufficient requisites in order to solve the quantum eigen-problems for the ground or near ground sates.