

1. Periodic vs. non-periodic boundary conditions and the 1-D free electron gas

Consider a one dimensional free electron gas. Assume there are no inter-particle interactions and so the energy of a particle is strictly kinetic. The energy eigenvalues determined using the time-independent Schrodinger equation are slightly different depending on the boundary conditions one utilizes. Assuming that $\psi(0) = \psi(L) = 0$ (particle-in-a-box boundary conditions) for an infinite square well of width L , the solutions of the time-independent Schrodinger equation are $\psi(x) = A \sin(x)$, where A is the normalization constant and $k = \frac{n\pi}{L}$ where $n = 1, 2, 3, \dots$. On the other hand, assuming periodic boundary conditions $\psi(0) = \psi(L)$ (not necessarily 0), the solutions of the Schrodinger equation are $\psi(x) = Ae^{ikx}$ where $k = \frac{2\pi n}{L}$ where $n = 0, \pm 1, \pm 2, \dots$. At first glance, one seems to be getting different answers since the energy levels that the free electrons occupy depend on the boundary conditions. However, the important point is that the use of periodic boundary conditions should not affect the properties of a system containing a large number of particles (macroscopic system). As an example, calculate - in the limit of a large number of electrons - the total energy of a 1-D system of free electrons

$$E = \sum_i \frac{\hbar^2 k_i^2}{2m}$$

at $T=0$ K using both periodic and non-periodic boundary conditions and observe that it is the same.