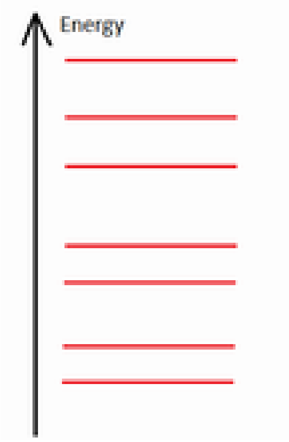
Answer on Question #39673, Chemistry, Physical Chemistry

Question

Can you please explaine to me what's a "quantum size-effect" ?

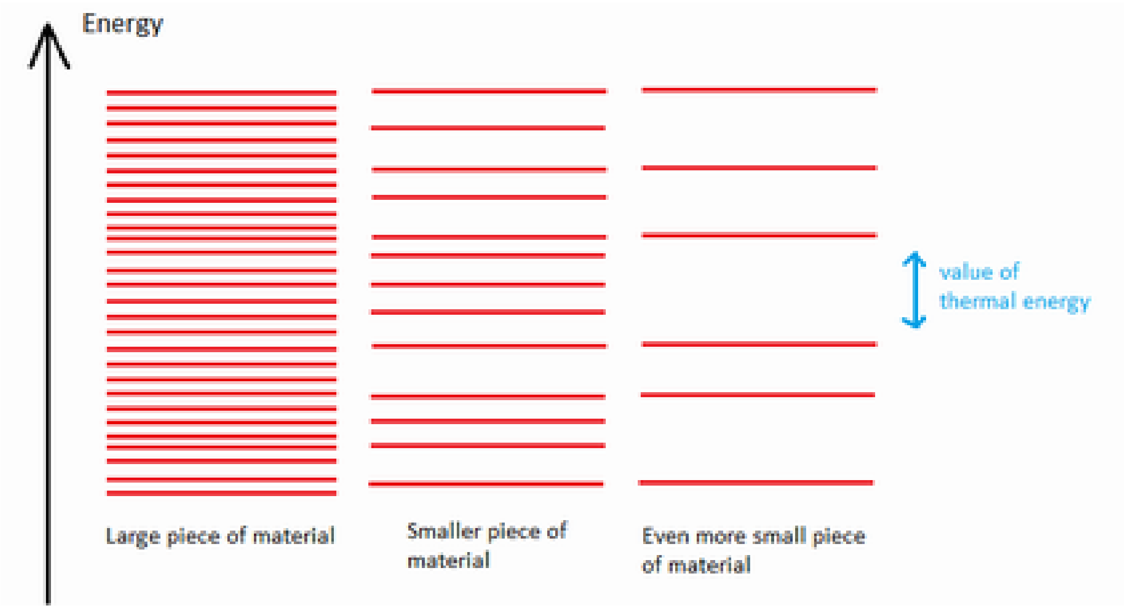
Answer

Any piece of compound contains a number of electrons. Quantum theory applies some restrictions on the value of total (sum of kinetic and potential) energy of a certain electron. Application of these restrictions results in different possible energy levels for the electrons to occupy. In general, any restriction that is applied on a free movement of the electron results in the energy levels become discrete: the total energy cannot be just random. The electron moving freely can have any value of energy; the electron which movement is restricted, e.g., by the size and shape of the crystal, can not - it can have **certain** values of energy. See the picture:



Each red line on a picture represents a certain possible energy level.

The quantum theory gives the next generalization:
the larger the space in which the electron is allowed to move - the denser are the levels situated.
Hence, in a large piece of a material there are many levels that are situated dense to each other, and in a small piece of a material there are fewer levels that are situated far from each other. See the picture:



The next idea is as follows. Electrons can move from one energy level to another, when the system absorbs or releases energy. This exchanged energy must be exactly equal to the difference in energy of the two levels, thus this exchanged energy can have **certain** values. It is said that the energy is absorbed or released in "quanta". And it is obvious that in a large pieces of material the possible energies of these quanta are low, and in a small piece they are high.

Normally, **in a large enough pieces of materials**, the minimum possible energies of quanta (the energy differences between two neighboring levels) are lower than the thermal energy kT (k is the Boltzmann constant, T is the temperature). This fact means that a particular electron can easily "jump" between the levels just because of the thermal fluctuations, and virtually any random value of energy can be divided into a several such "jumps". Hence, **a large piece of material can exchange virtually any quantity of energy with the environment.**

In contrast, **in a small pieces** the energy differences between two neighboring levels can become higher than the thermal energy. That means that the electron will stay on the particular level for a long time (no "thermal jumps"), and it can be moved to the next highest level only if a system receives a quantum with a certain level of energy. **A small piece of material can only exchange quanta of certain, higher than thermal, energy with the environment.**

Any chemical process is accompanied by energy redistribution. Many physical processes are too. And the case of small piece is unique in that way, instead large pieces of different (but large) sizes have similar energy redistribution properties. Now it is clear that for the small pieces the chemical and physical properties will differ from the ones for a bulk material. And this change in properties is referred to as "quantum size effect".

The border size between pieces that are "large" and "small" (from the upmentioned point of view) varies from material to material, but, as a rule, it lies in the range of 20-150 nanometers.