How does nanosize influence the electron band gap?

There is a distinct difference the band structure of matter in conductors, semiconductors and insulators. The region available for electrons to occupy is called 'bands' indicating wider freedom for movement of electrons within a given band.
Figure below explains the formation of these bands as matter grows from atoms (or molecules) to nanoparticles to bulk matter.
In bulk matter, the bands are actually formed by the merger of bunch of adjacent energy levels of numerous atoms or molecules. As the particle size gets finer and reaches the nanoscale where every particle is made up of only finite number of atoms, the number of overlapping orbitals or energy levels decreases and the width of the band starts to narrow. As an extreme case, a single atom (or molecule) will have very discrete energy levels that are represented by single lines.

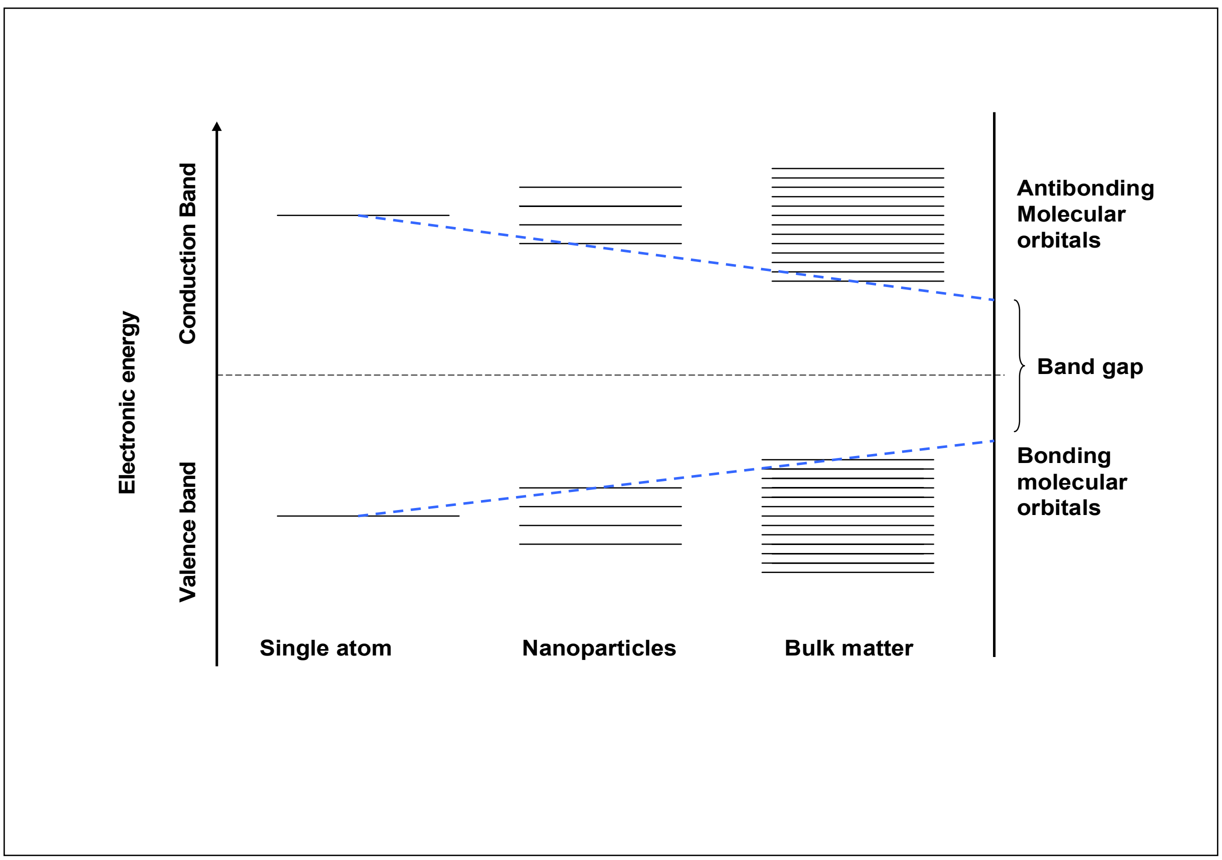

Figure: Band gap change in nanoparticles

As can be seen from Figure, the gap between the valence and the conduction bands increases with the decreasing particle size. This explains why the nanoparticles have wider band gap than the corresponding bulk matter. The band gap is the region forbidden for the electrons. The larger the forbidden region, the greater the restriction on the movement of electrons. Hence nanoparticles exhibit lower electrical conductivity. There is also a shift the absorption spectrum towards low wavelength blue region or UV region.

Nanosize zinc oxide and carbon nanotubes can be seen as examples of this concept. Nanosize zinc oxide has wider band gap and blue shift in absorption spectrum. Bulk graphite shows excellent electrical conductivity, while its nanophase variant, the carbon nanotubes, shows a band gap and semiconductor like behavior. In case of carbon nanotubes, the band gap is dependent on geometrical shape features like elliptical nature and twists.