

Size and Shape Dependent Intra-Band Energy Spacing in Metal Nanoparticles

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Abstract: A simplified model is developed to account for particle size and shape-dependent spacing between the discrete energy levels ($\Delta\epsilon$) in metal nanoparticles using the free-electron theory approach. The input parameters for this method are valency, number of atoms, the volume of nanoparticle, and the effective mass of the electron. It is considered that the electrons are confined in a small space which causes quantization of allowed energy states. Metal nanoparticles having the valency ranging between one and five e.g. Au, Mg, Al, Fe, and Nb have been considered for calculation. The calculated results show that the value of $\Delta\epsilon$ increases with decreasing particle size. Based on the model, it is predicted that the particle shape, as well as valency and effective mass of the electron, can also affect the spacing between the energy levels of nanoparticles.

Keywords: nanoparticles; nano-size; free-electron theory; shape dependent; size dependent; metals

1. Introduction

The last few years have witnessed an increasing interest in nanoscale materials that has resulted in a new realm of physical, chemical as well as biological phenomena. The tremendous interest in nano-systems comes from the fact that at the nanometer scale the physical, chemical, biological, etc. properties of these materials not only depend on their structure but also on their sizes that has culminated into new branch of nanoscience and technology *i.e.* nanoelectronics, bionanotechnology, etc. It is observed that they behave differently from those of the corresponding bulk metals mainly due to surface effect and quantum size effect^[1-6] where the dimensions of the nanoparticles are comparable to the mean free path and/or the de Broglie wavelength of the electrons. Furthermore, the different properties of nanomaterials are considered due to their electronic structure and the contribution of conduction electrons, which arises due to the presence of a large number of atoms at the surface while the contribution of bound electrons is assumed to be independent of size. In the case of microscale metals, the electrons of the constituent atoms can move freely inside the specimen. When the size is reduced to the nanoscale, owing to the presence of a limited number of conduction electrons they are confined to a small region, which causes quantization in their allowed energy states. This manifests itself in

the form of changes in different properties at the nanoscale. Besides, it is observed that nanoscale materials exhibit shape-dependent properties too^[3] because nanoparticles of different shapes have differences in the exposed surfaces, which lead to differences in atomic distribution across the nanoparticle surface. It, in turn, affects the rate kinetics of electron transfer. However, the effect of shape and size on the spacing between the discrete energy levels of nanoparticles using the free-electron theory has not yet carried out. Accordingly, a simplified and comprehensive model to estimate the particle size-dependent spacing between the discrete energy levels ($\Delta\epsilon$) in metal nanoparticles (Au, Mg, Al, Fe, and Nb) using the free electron theory approach has been presented in this work. In this model, valency, the number of atoms, the volume of nanoparticle, and the effective mass of electron have taken as the input parameters.

2. Theoretical Section

On the basis of free electron theory, the average energy of an electron is given by

$$\bar{E} = \frac{3}{5}E_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right] \quad (1)$$

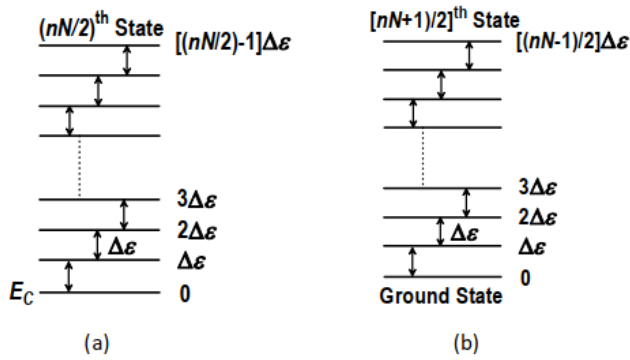


Fig. 1. Energy level diagram at conduction band for metal nanoparticle (a) for even values of either n or N and (b) for odd values of both n and N . Here E_C denotes the bottom edge of the conduction band.

where E_F and T are respectively the Fermi energy and temperature. At room temperature, the quantity $(K_B T / E_F)^2$ is negligibly small. Therefore, for practical purposes, one can write

$$\bar{E} = \frac{3}{5} E_F \tag{2}$$

The quantum size effect is well known for metal nanoparticles. In the case of metals, the conduction band is half filled and the density of energy levels is high enough so that a noticeable separation in energy levels within the conduction band is observed. If the size of the metal nanoparticle is made small enough, the continuous density of electronic states is broken up into discrete energy levels (Figs. 1a and 1b). This happens when the energy band spacing becomes greater than the thermal energy, $K_B T$, and thus below the temperature T , metals start exhibiting non-metallic properties. Further, it is supposed that the spectra of nanoparticles be equispaced and the energy spacing $\Delta\epsilon$ between energy levels depend on the Fermi energy (E_F) of the metal and on the number of conduction electrons η and can be estimated as $\Delta\epsilon = E_F / \eta$.^[4] However, the value of η ($= nN$) is depending upon the valency n and the number of atoms N in the metal. Therefore, the total energy of η electrons shall be nNE . Since the spacing between the discrete energy levels be equispaced it shall have $nN/2$ (for even values of either n or N) and $(nN + 1)/2$ (for odd values of both n and N) discrete levels (Fig. 1a and 1b). This is due to the fact that electrons are considered to be fermions, and according to Pauli's exclusion principle, only two electrons can occupy a single discrete level. The total energy of nN electrons shall therefore be equal to $0 + \Delta\epsilon + 2\Delta\epsilon + \dots + (nN/2 - 1) \Delta\epsilon$ (for even values of either n or N) and $0 + \Delta\epsilon + 2\Delta\epsilon + \dots + (nN - 1) \Delta\epsilon/2$ (for odd values of both n and N). Therefore, for odd values of both n and N , we have

$$\Delta\epsilon = \frac{8nN\bar{E}}{(nN-1)(nN+1)} \tag{3}$$

Using eqn. (2), we have

$$\Delta\epsilon = \frac{24}{5} \cdot \frac{nNE_F}{(nN-1)(nN+1)} \tag{4}$$

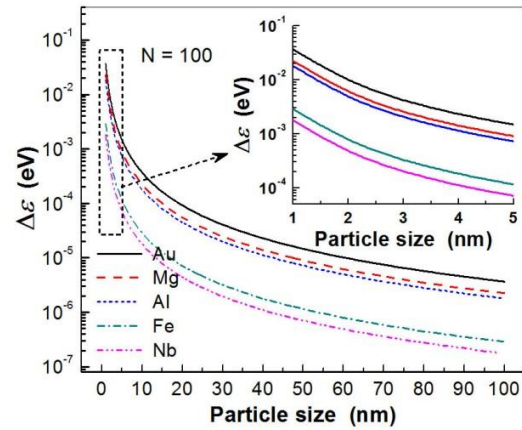


Fig. 2. The spacing between the discrete energy levels of different nanoparticles depending on their particle size. Inset: Enlarged view particle size (≤ 5 nm) dependent $\Delta\epsilon$ of different nanoparticles.

Now, the Fermi energy of electrons is given as^[7,8]

$$E_F = \frac{\hbar^2}{2m_e^*} \left(\frac{3\eta}{8\pi V_s} \right)^{2/3} \tag{5}$$

Here, m_e^* is the effective mass of the electron. Using eqs. (4) and (5), we have an expression for $\Delta\epsilon$ in case of odd values of both n and N

$$\Delta\epsilon = \frac{3^{5/3}}{5\pi^{2/3}} \cdot \frac{\hbar^2}{m_e^*} \cdot \frac{(nN)^{2/3}}{V_s^{2/3}} \cdot \frac{nN}{(nN+1)(nN-1)} \tag{6}$$

Where V_s is the volume of different nanoparticles having different (sphere, cube, cylinder, disk, regular tetrahedron, etc.) shapes. According to expression (6), the values of $\Delta\epsilon$ depends on m_e^* , n , N and V_s . Furthermore, for even values of either n or N , we have an expression for $\Delta\epsilon$ shall be

$$\Delta\epsilon = \frac{8\bar{E}}{(nN-2)} \tag{7}$$

Using eqns. (2) and (5), we have an expression for $\Delta\epsilon$ can be obtained as

$$\Delta\epsilon = \frac{3^{5/3}}{5\pi^{2/3}} \cdot \frac{\hbar^2}{m_e^*} \cdot \frac{(nN)^{2/3}}{V_s^{2/3}} \cdot \frac{1}{(nN-2)} \tag{8}$$

Here the values of V_s for different shaped nanoparticles are given as $V_s = (4/3)\pi r^3$; for spherical nanoparticles {radius r ($= d/2$) where d is the particle diameter}

$V_s = a^3$; for cubic nanoparticles (a is the edge length)

$V_s = \pi r^2 l$; for cylindrical nanoparticles { r ($= d/2$) is radius and d is the particle diameter and l is the length with ($l \gg d$)}

$V_s = \pi r^2 l$; for disk like nanoparticles { r ($= d/2$) is radius and d is the particle diameter and l is the thickness with ($l \ll d$)}

$V_s = (\sqrt{2}/12)a^3$; for regular tetrahedron nanoparticles (a is the edge length).

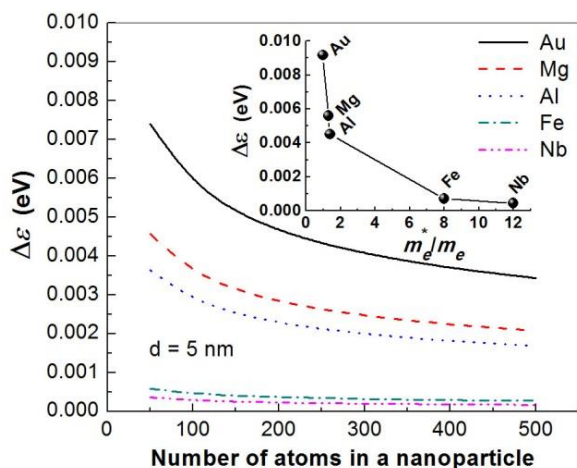


Fig. 3. The spacing between the discrete energy levels of different nanoparticles depending on the number of atoms in a nanoparticle having the size of 5 nm. Inset: dependence of $\Delta\varepsilon$ on effective mass of electron for different nanoparticle having the size of 2 nm.

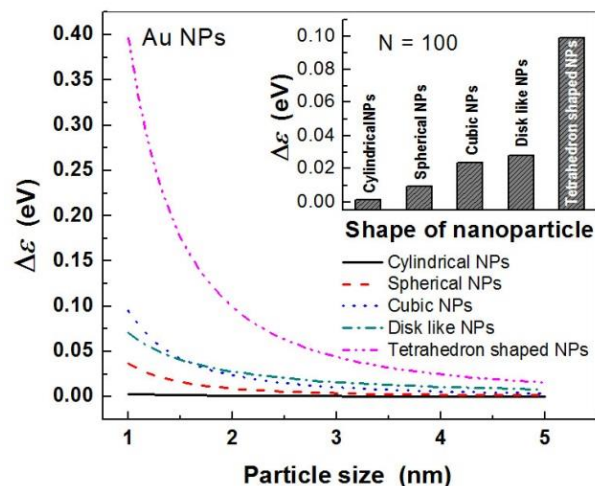


Fig. 4. The spacing between the discrete energy levels of Au nanoparticles depending on their particle size with different shapes with $N = 100$. Inset: Shape dependent $\Delta\varepsilon$ for Au nanoparticle having the size of 2 nm.

3. Results and Discussions

Fig. 2 shows the particle size-dependent $\Delta\varepsilon$ of different metal (Au, Mg, Al, Fe, and Nb) nanoparticles having the valency lying between 1 and 5. The values of m_e^* for different metals were taken from Ashcroft and Mermin^[7] and Kittel^[8] and the results are shown in Fig. 2 are for spherical nanoparticles consisting of 100 atoms in them. It is observed that the value of $\Delta\varepsilon$ decreases with increasing particle size as well as valency. This effect is more prominent for the particles below 5 nm size (inset Fig. 2), which is due to the localization of the energy levels *i.e.* quantum sizing effect.^[9,10] Further, when the particle size is larger than 100 nm, the value of $\Delta\varepsilon$ seems to be constant - bulk value. This indicates that the boundary value for the size effect is ~ 100 nm. When the particle size is large enough, the size effect on its $\Delta\varepsilon$ value can, therefore, be neglected.

Fig. 3 illustrates the dependence of $\Delta\varepsilon$ on the number of atoms in a nanoparticle for spherical shaped Au, Mg, Al, Fe, and Nb nanoparticles of 5 nm diameters. The value of $\Delta\varepsilon$ for different nanoparticles is found to decrease upon the increasing number of atoms in a nanoparticle. Also, it can be seen that energy spacing $\Delta\varepsilon$ decreases with the increase in the value of m_e^* (inset of Fig. 3).

To illustrate the shape-dependent values of $\Delta\varepsilon$, Au nanoparticles have been taken as an example. Accordingly, Fig. 4 shows the particle size-dependent $\Delta\varepsilon$ of Au nanoparticles of 2 nm size having different (spherical, cubic, cylindrical disk, and regular tetrahedron) shapes with fixed $N (=100)$ atoms. It is found that the values of $\Delta\varepsilon$ decrease with increasing particle size in all the cases. This observation clearly indicates a shift from metallic character to non-metallic (insulator) behavior upon downsizing. The inset of Figure 4 indicates the shape-dependent $\Delta\varepsilon$ for Au nanoparticle. It can be seen that the value of $\Delta\varepsilon$ is maximum in case of regular tetrahedron shaped nanoparticles while it is minimum for cylindrically shaped nanoparticles and follow the structure sequence tetrahedron \rightarrow disk \rightarrow cubic \rightarrow spherical below 2 nm and above which it follows tetrahedron \rightarrow cubic \rightarrow disk \rightarrow spherical. These observations clearly

consolidate the idea of the pronounced shape and size-dependent properties in nanoscale materials.

4. Conclusions

In summary, a simplified model is developed for the size- and shape-dependent intra-band energy spacing of metal (Au, Mg, Al, Fe, and Nb) nanoparticles having different valency based on the free electron theory. The model predicts an increase in intra-band energy spacing with the decreasing size of nanoparticles. This effect is more prominent for the particles below 5 nm size, which is due to the localization of the energy levels *i.e.* quantum sizing effect. Also, it is demonstrated that the shape of nanoparticles, as well as the effective mass of the electron, play an important role in deciding the value of spacing between energy levels.

Conflicts of Interest

The authors declare no conflict of interest.

References

- Mohazzabi P.; Mansoori G.A. Why Nanosystems and Macroscopic Systems Behave Differently. *Int. J. Nanosci. Nanotechnol.*, 2005, **1**, 53–60. [[Link](#)]
- Schmid G. Nanoparticles: From Theory to Application, Wiley VCH, Weinheim. 2004.
- Kimura K. The Effect of Shape and Size on the Electronic Properties of Ultrafine Metallic Particles. *Phase Trans.: Multinational J.*, 1990, **24-26**, 493–527. [[CrossRef](#)]
- Halperin W.P. Quantum Size Effects in Metal Particles. *Rev. Mod. Phys.*, 1986, **58**, 533–606. [[Link](#)]
- Marzke R.F. Quantum Size Effects in Small Metallic Particles. *Catalysis Rev.: Sci. Eng.* 1979, **19**, 43–65. [[CrossRef](#)]
- Kubo R. Electronic Properties of Metallic Fine Particles. *J. Phys. Soc. Jpn.*, 1962, **17**, 975–986. [[CrossRef](#)]

- 7 Ashcroft N.W.; Mermin N.D. *Solid State Physics*, Holt-Saunders International Editions: Science: Physics, Holt, Rinehart and Winston Publ. 1976.
- 8 Kittel C. *Introduction to Solid State Physics*, 16th Edn. Wiley-India, New Delhi, 2011.
- 9 Cottey A.A. Band Theory of the Quantum Size Effect for a Simple Model. *J. Phys. C: Solid State Phys.*, 1971, **4**, 1734–1738. [\[Link\]](#)
- 10 Grassian V.H. When Size Really Matters: Size-Dependent Properties and Surface Chemistry of Metal And Metal Oxide Nanoparticles in Gas and Liquid Phase Environments. *J. Phys. Chem. C*, 2008, **112**, 1830–1831. [\[CrossRef\]](#)



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