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Application of the LCAO method for energy band calculation in nanocrystals

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ABSTRACT

On the basis of the LCAO method, the energy band width of a conduction electron in a one dimensional crystal is found to be 4γ. The quantity γ is a measure of overlapping interactions among the atomic orbitals of a conduction electron. In the present work, this method is applied to a copper (f.c.c.) nanocrystal of size equal to 10a (a being the lattice constant) to see the nature of dependence of γ on the nanocrystal size. It is found that γ increases inversely as the size of nanocrystals. This agrees well with the observation that the energy band widths in nanocrystals are wider compared to those of the corresponding bulk materials.

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KEYWORDS

Nanocrystals;
Atomic orbital;
Overlapping interaction;
Energy band gap.

INTRODUCTION

According to LCAO method the energy eigen value of a conduction electron in a crystalline solid is given by[1]

$$E(\vec{k}) = E_0 - \alpha - \gamma \sum_m e^{i\vec{k}.(\vec{R}_j - \vec{R}_m)} \quad (1)$$

E_0 is the atomic energy, γ and α are two positive quantities defined by

$$\alpha = -\int \varphi^*(\vec{r} - \vec{R}_j) V(\vec{r} - \vec{R}_j) \varphi(\vec{r} - \vec{R}_j) d\tau$$

$$\gamma = -\int \varphi^*(\vec{r} - \vec{R}_m) V'(\vec{r} - \vec{R}_j) \varphi(\vec{r} - \vec{R}_j) d\tau$$

$V(\vec{r} - \vec{R}_j)$ is the lattice potential and $V'(\vec{r} - \vec{R}_j)$ is the lattice potential minus the corresponding atomic potential experienced by a conduction electron at a position $\vec{r}$ in the vicinity of the jth lattice site. The quantity α does not include any overlapping interaction between the atomic orbitals, while γ is a measure of the overlapping interactions.

In an f.c.c. 3D crystal, one obtains from Eq. 1 the width of an energy band given by

$$E_{bottom} = E_0 - \alpha - 12\gamma$$

$$E_{top} = E_0 - \alpha$$

Hence energy band width is

$$E_{top} - E_{bottom} = 12\gamma$$

In an one dimensional crystal,[1]

$$E_{top} = E_0 - \alpha + 2\gamma \quad \left(\text{for } k_x = +\pi/a\right)$$

$$E_{bottom} = E_0 - \alpha - 2\gamma \quad \left(\text{for } k_x = -\pi/a\right)$$

Hence energy band width is

$$E_{top} - E_{bottom} = 4\gamma$$

Therefore, according to this model, the energy band width increases only when γ increases. With the help of some basic calculations, an attempt is made in this present work to evaluate γ for a 10a size one dimensional copper nanocrystal and then to compare the results with the already available observational data.

RESULTS AND DISCUSSION

Figure 1 depicts the evaluated atomic potential of a singly charged, i.e. monovalent copper atom. For copper, $a = 3.61\times10^{-10}$ m. Figure 2 essentially represents the overlapping interactions of the atomic potentials in the lattice of the cooper nanocrystal. The total lattice potential (attractive) of a 10a monovalent copper nanocrystal is given by

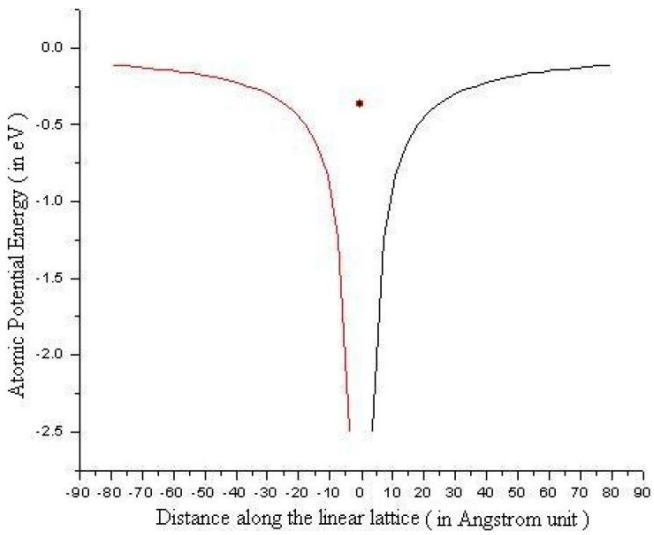

Figure 1 : Atomic potential of a conduction electron with respect to a singly charged copper atom.

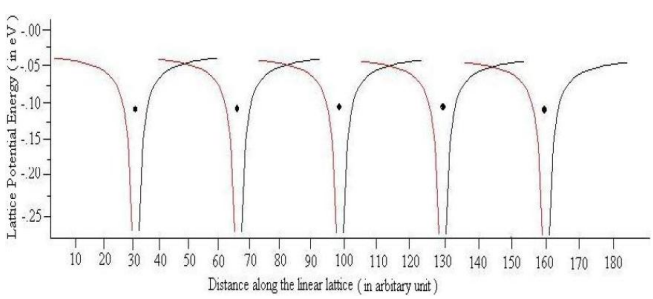

Figure 2 : Lattice potential experienced by a conduction electron in a monoatomic copper lattice. (Dots represent lattice sites)

$$V(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{q^+.(-e)}{a}\sum_1^{10}\frac{1}{n},\ \left(q^{+1} \equiv 1e\right)$$

$$= -\frac{9\times10^9\times1.6\times10^{-19}\times1.6\times10^{-19}}{3.61\times10^{-10}}\times2.98968\quad eV$$

$$= -11.93\ eV, \qquad (2)$$

in the unit of the dielectric constant of copper crystal ε = 1. This lattice potential is obtained by superposition of the atomic potentials corresponding to lattice site numbers 1, 2, 3, ……, 10 at the position of the lattice site number 1.

Let X_1, X_2, X_3……X_{10} denote the lattice potential minus the corresponding atomic potential, respectively, experienced by a conduction electron when it is in the vicinity of lattice site numbers 1, 2, 3, ……10 in the general expression

$$V'(\vec{r}-\vec{R}_j) = -V(\vec{r}) - \left\{-V(\vec{r}-\vec{R}_j)\right\} \qquad (3)$$

It may be noted that the potential experienced by a conduction electron in the vicinity of the lattice site number 1 inside the 10a size copper nanocrystal is

$$V(\vec{r}-\vec{R}_1) = \frac{1}{4\pi\varepsilon_0}\times\frac{(+q).(-e)}{a} = -3.98\ e\ V \qquad (4)$$

In this calculation, it is assumed that the conduction electron is one lattice constant away from a lattice site at its nearest approach. Accordingly, under the same assumption

$$V(\vec{r}-\vec{R}_2) = -\frac{3.98}{2}eV, V(\vec{r}-\vec{R}_3) = -\frac{3.98}{3}eV,$$

$$....., V(\vec{r}-\vec{R}_{10}) = -\frac{3.98}{10}eV \qquad (5)$$

It is seen that when a conduction electron approaches a positively charged lattice site to a distance

TABLE 1 : Evaluated values of X_n.

X_n	in eV
$X_{1/4}$	-3.99
$X_{1/2}$	+3.97
X_1	+7.946
X_2	+10.231
X_3	+10.599
X_4	+10.931
X_5	+11.13
X_6	+11.26
X_7	+11.357
X_8	+11.4285
X_9	+11.483
X_{10}	+11.528

of a/2.997, $V'(\vec{r}-\vec{R}_J)$ becomes equal to zero. As shown in TABLE 1 at a distance of approach equal to a/4, $V'(\vec{r}-\vec{R}_j)$ becomes negative, which implies a repulsive potential in the scheme of energy measurement as explained here after.

With respect to some suitably assigned reference level of energy measurement (which is taken to be the $V(\vec{r})=0$ level), it is seen from Figures 1 and 2 and also from Eqs. 2, 3, 4, 5 that as the number of lattice sites in the nanocrystal increases, the corresponding lattice potential approaches the reference level $\{V(\vec{r})=0\}$ progressively. In this scheme of energy measurement, the lattice potential $V(\vec{r}-\vec{R}_j)$ is less than $V(\vec{r})$ for all values of the lattice site number j. In the stated scheme of energy measurement, the Eq. 3 should be rewritten as

$$\mathbf{V'(\vec{r}-\vec{R}_j)=V(\vec{r})-V(\vec{r}-\vec{R}_j)}$$
$$\mathbf{=X_n} \qquad \textbf{(6)}$$

Keeping this consideration in mind, the values of X_n except that for $X_{1/4}$ become positive. In TABLE 1, the values of X_n are listed.

It is pertinent to consider the atomic orbitals in their ground state. The orbitals corresponding to a singly ionized copper atom are similar to Hydrogen atom orbitals. These are given by reference[2]

$$\varphi(\vec{r})=e^{-\frac{1}{2}\vec{r}}\,\vec{r}^{\,l}\,L_{n+1}^{2l+1}(\vec{r})$$

where the different symbols have their usual significance. Hence

$$\gamma=-\int\left[\left\{e^{-\frac{1}{2}\vec{r}}\,\vec{r}^{\,l}\,L_{n+1}^{2l+1}(\vec{r})\right\}^{*}V'(\vec{r}-\vec{R}_j)\left\{e^{-\frac{1}{2}\vec{r}}\,\vec{r}^{\,l}\,L_{n+1}^{2l+1}(\vec{r})\right\}\right]d\tau$$

And the value of the normalization integral is

$$\int_0^\infty e^{-\vec{r}}\,\vec{r}^{\,2l}\left[L_{n+1}^{2l+1}(\vec{r})\right]^2\vec{r}^{\,2}\,dr=\frac{2n[(n+l)!]^3}{(n-l-1)!}$$

For an s orbital (l = 0)

$\frac{2n[(n+l)!]^3}{(n-l-1)!}=2$, for n = 1 i.e. ground state orbitals.

Hence $\gamma=-2V'(\vec{r}-\vec{R}_j)$ **(7)**

It may be noted that in the first approximation, effect of all the overlapping interactions is included in $V'(\vec{r}-\vec{R}_j)$ only, and in the light of this approximation, the normalization integral is taken to be independent of $V'(\vec{r}-\vec{R}_j)$.

In TABLE 2 the evaluated values of γ for different nanocrystal sizes containing 2 lattice sites, 3 lattice sites, 4 lattice sites, ...up to10 lattice sites, are given.

TABLE 2 : Evaluated values of γ_n.

$\gamma_n = -2X_n$	in eV
$\gamma_{1/4}$	+ 7.98
$\gamma_{1/2}$	- 7.94
γ_1	-15.892
γ_2	-20.462
γ_3	-21.198
γ_4	-21.862
γ_5	-22.26
γ_6	-22.52
γ_7	-22.714
γ_8	-22.857
γ_9	-22.966
γ_{10}	-23.056

Figure 3 shows the variation of the evaluated γ with nanocrystal sizes. It is quite evident from Figure 3 that as the crystal size decreases the corresponding γ value increases. Hence the energy band width (= 4 γ for a one dimensional Cu nanocrystal) is a function of the size of the nano crystal. To be specific, the band width increases as the size of the nanocrystal decreases. This gives a new approach of theoretical support to the observation that the energy band gap in a nano crystal is inversely proportional to its size[3]. Thus it is seen that the LCAO method can also be applied to the band

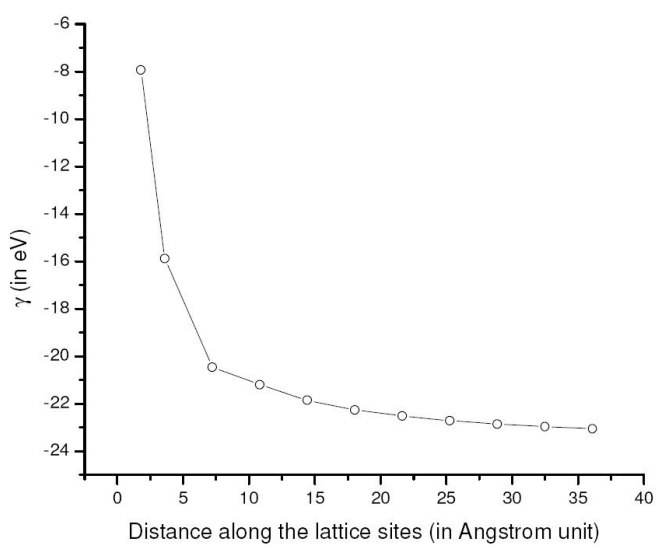

Figure 3 : Dependence of γ on size of copper nanocrystal.

structure studies of nano crystals. Further studies in this line have potential merits.

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REFERENCES

[1] N.F.Mott, H.Jones; 'The Theory of the Properties of Metals and Alloys', 1st Edition, Oxford University Press, Dover, UK **(1958)**.

[2] L.I.Schiff; 'Quantum Mechanics', 1st Edition, McGraw-Hill, New York, USA **(1955)**.

[3] L.Brus; J.Phys.Chem., **90**, 2555 **(1986)**.