A Study for CNDO Efficiency for Band Structure Calculations of IV-Covalent Materials: (Sn, Ge, Si and C)

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Summary

Lattice constant, cohesive energy, direct band gap and valence band width had been calculated for grey tin by using (CNDO-LUC) method, then we had been making a comparison with experimental and other workers results for (C, Si, Ge and Sn) with zinc-blende structure in order to study the efficiency of this method. The results had showed that this method is good for lattice constant and bad for other properties all at the same time.

I. Introduction

The semiempirical methods gave us a privilege of no long time for getting results, because it had been adopted many approximations as compared with other ab-initio and numerical methods, according to that it is used in many fields (Harker and Larkins 1979, Freund and Hohlneicher 1979, Schmid and Brodbek 1985, Vogl *et al.* 1983) and for along time even in the last years (Marshed 2006, Mijbil 2006, Hassan 2001), as well as papers about had been published (Thiel 2002). Nevertheless these approximations led to inaccurate data in some aspects which became a disadvantage (Dorestt and White 2000), for this reason we made this research in order to measure the efficiency of CNDO (Complete Neglect of Differential Overlap) as one among the primary semiempirical methods, that presented by (Pople *et al.* 1965) in which he neglected many electron-electron interactions and focused on both valence electrons and nuclei as a core of the atom (with the other electrons) (Pople and Beveridge 1970). Here LUC approximation (Large Unit Cell) or (Supercell) (Bredow 2000) is used in order to minimize the size of BZ (Brillion Zone) and so to diminish the number of the special points in which the aspects of the crystal such as band structure could be calculated (Rogan and Lagos 2001, Chadi and Cohen 1973).

We have firstly studied how CNDO method practically and mathematically work, and see how its parameter the orbital exponent (ξ), bonding parameter (β), *s*-shell electronegativity (*EES*) and *p*-shell elecronegativity (*EEP*) could be changed and how this change may effect on the results, and secondly we have calculated the lattice constant, cohesive energy valence band width and the direct band gap for the semimetal grey tin (α-Sn) (Myles *et al.* 2001, Cuenya *et al.* 2002) which has 50 electrons, exist at atmospheric pressure (Akdim *et al.* 2002, Mujica *et al.* 2003) and under 13^{o}C with diamond structure (Khan *et al.*1996, Cuenya *et al.* 2001), and compared our results with the experimental and other workers used the same method for the substance and other materials which are (Sn, C, Si and Ge) of the same diamond structure.

II. Method

II.1. Mathematically

According to LCAO approximation (Linear Combination of Atomic Orbitals) and LUC with eight atoms, and STO (Slater Type Orbital) for atomic orbitals of the form:

$$\Psi(r,\theta,\varphi) = Nr^{n^*-1}\exp(-\xi r)Y(\theta,\varphi) \tag{1}$$

Where:
$\Psi(r,\theta,\varphi)$ is Slater type orbital. r,θ,φ are the polar spherical coordinates of the atom. N is the normalization constant. n^* is the effective principal quantum number. $Y(\theta,\varphi)$ is the spherical harmonics (Daudal *et al.* 2000).

According to that Fock-matrix element (F_{ss}) and the total energy (E) can be calculated as (Pople and Beveridge 1970):

$$F_{ss} = -EES + \left[0.5(1-P_{ss}) - Q_A\right]\gamma_{AA} + \sum_{B(\neq A)} Q_B\gamma_{AB} \tag{2}$$

$$F_{sp} = \beta_{AB}S_{sp} - 0.5P_{sp}\gamma_{AB} \tag{3}$$

$$E = 0.5\sum_{sp}\left[P_{sp}\left(H_{sp}-F_{sp}\right)\right] + \sum_{A<B} Z_A Z_B R_{AB}^{-1} \tag{4}$$

and the final result with LUC approach (Harker and Larkins 1979) is:

$$F_{ss}(0) = -EES + 0.5\gamma_{AA}^{oo} - \sum_B Q_B(0)\sum_v \gamma_{AB}^{ov} + \sum_{v\neq o}\beta_{AB}^{ov}S_{os,vp} - 0.5\sum_v P_{ss}(0)\gamma_{AA}^{ov}f(x) \tag{5}$$

$$F_{sp}(0) = \sum_v \beta_{AB}^{ov}S_{os,vp} - 0.5P_{ps}(0)\sum_v \gamma_{AB}^{ov}f(x) \tag{6}$$

$$E = 0.5\sum_{sp} P_{sp}(0)\left[F_{sp}(0)+H_{sp}(0)\right] + 0.5\sum_A\sum_B Z_A Z_B R_{AB}^{-1} \tag{7}$$

Where:
$f(x)$ it is Szymanski enhancement function. o is a LUC. v is the other LUCs.

II.2. Practically

1. We had used a computer program which is composed by the researcher [M. A. Abdulsattar] to calculate the properties of gery tin, and it was written with (Fortran Power Station) language and work on (PC IV).
2. We had changed the four parameters of the CNDO method ξ, β_{AB}, *EES* and *EEP* in arbitrary way until we get an amount of the lattice constant very near to the experimental value with the minimum value of the total energy of the crystal.

3. Then we measure the values of the cohesive energy and all the energies of the electronic band.
4. If the values of energies were in agreement with the experiment then we would stop and fix the parameters.
5. If the values of the energies were bad we should change the parameters again until getting the closest values to the experiments.

The chart below shows the simple steps of CNDO method work practically, and parameters of our work and others for grey tin, silicon, diamond and germanium are listed in table (1)

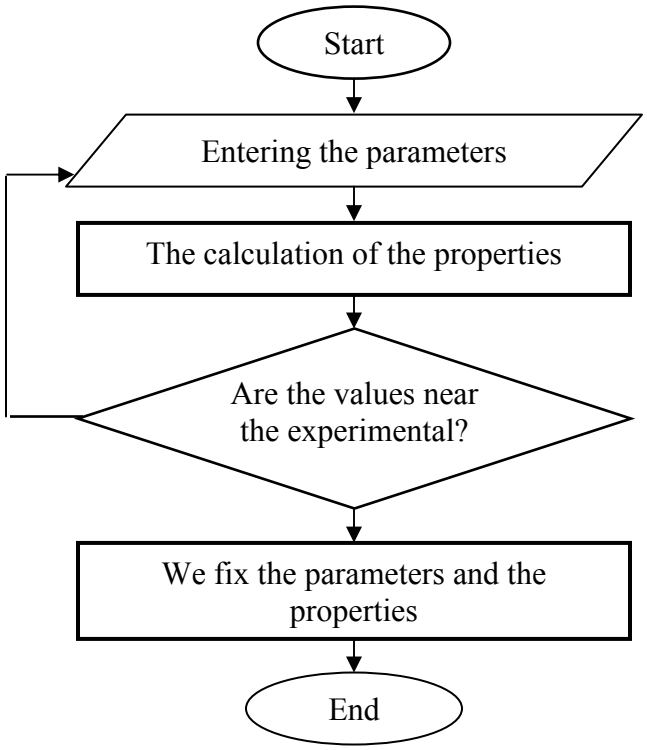

Figure (1); Shows the simple steps of CNDO method for bands calculations.