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FIRST-PRINCIPLE CALCULATION OF ELECTRONS CHARGE DENSITY IN THE DIAMOND–STRUCTURE SEMICONDUCTOR CRYSTALS

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ABSTRACT

A computational study of the total electrons charge density in the diamond-structure semiconductor crystals has been performed. In a typical modern electronic structure calculation, the charge density is obtained from a certain density functional, however, the charge density in this work was obtained from first principles. It is assumed that the one-electron Bloch functions for the crystals will not very seriously differ from the wave functions in the atomic systems, therefore, they are represented by the well known normalized Slater atomic orbital for multi-electron atoms and ions. Since the spherical harmonics are expressed in the spherical coordinate system, all the calculations are done in this system. The wave functions and the total electron charge densities are calculated along the [l00], [010], and [00l] directions for the state k=0. The atomic system of units is used throughout the calculations. i.e. distances are expresPsed in unit of the Bohr radius, and charges in unit of the electronic charge. It has been found that in each crystal, the total electrons charge density along the [100] and [010] directions are equal, however, the charge densities at a given distance from the center of the cell along [001] and [100] directions are not exactly equal; the density along [100] been always higher. This shows that the potentials arising from the electrons are not spherically symmetric. The results are presented and discussed.

Keywords: Density Functional Theory, Energy Band Calculation

INTRODUCTION

Semiconductors have played a major role in the current technological revolution. The enormous advances in electronics and computer science were made possible by a better understanding of the properties of semiconductors. For roughly the past ninety years, a major aspiration of condensed matter physics has been to explain and predict the properties of solids knowing only the identities of the constituent atoms (Balkanski and Wallis, 2000). Recently, this goal has been realized for many semiconductor properties. The successes are best illustrated by the progress made in understanding the electronic and optical properties of semiconductors (Seeger, 2004).

In a crystal, there are of the order of 10^{24} particles per cm^3, and these interact with each other. It is very obvious that the Hamiltonian describing a typical crystal is highly complicated and an accurate solution of the energy eigenvalue problem for a solid is very difficult if not impossible. Several simplifications and approximations are necessary before a useful scheme can be obtained for calculating or predicting the properties of solids (Dornald, 2003).

Since the pioneering work in electronic structure calculation by Wigner and Seitz (1933, 1934) and Slater (1934) there has been a proliferation of interest and techniques in the field. At present there are many methods of energy structure calculation some of which are: Free-Electron Approximation, Nearly-Free-Electron Approximation, Cellular Method, Augmented Plane Wave Method, Scattering Matrix and Green's Function Method, Orthorgonolized Plane Wave Method, Pseudopotential Method, Green's Function Cellular Method, and Density Functional Theory Method (Patrick and Emily, 2008 and James *et al*, 2008).

Density Functional Theory (DFT) is a powerful tool use to investigate the electronic structure of many-body systems, in particular molecules and condensed phases. DFT is among the most popular and versatile methods available in condensed matter physics. Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendants are based on a complicated wave function. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic quantity (Kieron, 2007). This work is primarily concerned with the calculations of the electronic charge density in the diamond-structure semiconductor. However, before such a calculation can be done the electronic wave functions must be known, therefore, these wave functions are also calculated. Knowledge of the electronic charge distribution in insulators is essential for a complete description of the nature of the chemical bond in such materials. The most significant progress in this direction was made by Walter and Cohen (1971) using the pseudopotential method. In particular they have calculated the charge densities for several diamond and zinc-blende type semiconductors using wave functions derived from pseudo-potential band-structure calculations. However, in this work the charge density is obtained directly from the electronic wave function, calculated from first-principles. Fundamentally, the input to the charge density calculations in this work are the lattice constant of the crystal and the atomic number of the constituent atom.

A brief description of the diamond-structure lattice, a comprehensive account of the calculation of the electronic wave functions and the calculated functions are presented in section 2. The procedure of obtaining the charge density, and the variation of the charge density within the Wigner-Sietz cell are treated in section 3.

The Normalized Slater Orbitals

The diamond lattice may be considered as being made up of two face-centered cubic (FCC) lattices displaced from one another by one-quarter of a body diagonal. Each atom has four nearest neighbors at a distance $a_{lat}(3/4)^{1/2}$, where a_{lat} is the lattice constant, arranged at the comers of a regular tetrahedron (Jan and Andreas, 2002). Geometrically, the diamond structure is described as a simple cubic with basis vectors (Marvin, 1975).

$$\hat{\mathbf{b}}_1 = \frac{1}{2}\left(\hat{\mathbf{a}}_x + \hat{\mathbf{a}}_y\right), \quad \hat{\mathbf{b}}_2 = \frac{1}{2}\left(\hat{\mathbf{a}}_x + \hat{\mathbf{a}}_z\right), \quad \hat{\mathbf{b}}_3 = \frac{1}{2}\left(\hat{\mathbf{a}}_y + \hat{\mathbf{a}}_z\right) \qquad [2.1]$$

which describe points on the faces of the unit cube and

$$\begin{aligned} \hat{\mathbf{b}}_4 &= \frac{1}{4}\left(\hat{\mathbf{a}}_x + \hat{\mathbf{a}}_y + \hat{\mathbf{a}}_z\right), \quad \hat{\mathbf{b}}_5 = \frac{1}{4}\left(3\hat{\mathbf{a}}_x + 3\hat{\mathbf{a}}_y + \hat{\mathbf{a}}_z\right), \\ \hat{\mathbf{b}}_6 &= \frac{1}{4}\left(3\hat{\mathbf{a}}_x + \hat{\mathbf{a}}_y + 3\hat{\mathbf{a}}_z\right), \quad \hat{\mathbf{b}}_7 = \frac{1}{4}\left(\hat{\mathbf{a}}_x + 3\hat{\mathbf{a}}_y + 3\hat{\mathbf{a}}_z\right), \end{aligned} \qquad [2.2]$$

which designate the internal points. In Equations [2.1] and [2.2] the $\mathbf{a}_j$'s are the primitive vectors of the direct lattice. Table 1, below lists some elements which exhibit the diamond structure. The nearest neighbor distance, d is calculated from the appropriate lattice constant at 20ºC and is expressed in the Bohr radius, a_0 (Babaji, 1999).

Table 1: **Some Parameters of Semiconductors with the Diamond structure.**

Element	**Nearest Neighbor Distance, d (a_0)**	**Radius of Inscribed Sphere, r_{in} (a_0)**	**Radius of Circumscribed Sphere, R (a_0)**
Carbon	2.903032661	1.451516331	3.652902660
Silicon	4.434022000	2.217011000	5.579374000
Germanium	4.613878530	2.306939265	5.805669834
α – Tin	5.293751049	2.646875525	6.661157328

The charge density at the point **r**, ρ(**r**) is given by

$$\rho(\mathbf{r}) = \sum_j \left|\Psi_j\right|^2, \qquad [2.3]$$

where Ψ_j is the wave function of the j^th electron.

The one-electron function for an electron in an atomic system can be obtained numerically with the Hartree-Fock method (Hartree, 1957a) or analytically with Roothan's Self-eonsistent-Field (SCF) method (Breene, 1958). The usefulness of functions simpler than the Hartree-Fock functions was recognized long ago, (Lowdin, 1953 and Slater, 1951). They both made use of a single exponential function to describe an atomic orbital. In this work, the atomic orbitals employed are the Slater atomic orbitals for multi-electron atoms and ions given by Mcweeny (1979) as:

$$\Phi_n\left(\vec{r},\theta,\varphi\right) = A r^{n^*-1} \exp\left(\frac{-Z_{eff}\vec{r}}{n^*}\right) Y_{l,m}\left(\theta,\varphi\right), \qquad [2.4]$$

Where $Y_{l,m}\left(\theta,\varphi\right)$ is the real spherical harmonics, n is the principal quantum number, n* is the effective principal quantum number, A is a normalization constant, and Z_{eff} is the effective nuclear charge and is given by

$$Z_{eff} = Z - \sigma, \qquad [2.5]$$

where σ is the screening constant.

It is a fact (Huag and Koch, 1992) that the one-electron wave functions in crystals, Ψ_j are given by the Bloch theorem

$$\Psi_{\lambda,k}\left(\mathbf{r}\right) = \exp\left(i\mathbf{k}\bullet\mathbf{r}\right) u_{\lambda,k}\left(\mathbf{r},\right), \qquad [2.6]$$

where λ is the energy eigenvalue, **k** is the wave vector, and u is the Bloch function and is required to have the full translational symmetry of the lattice, i.e.

$$u_{\lambda,k}\left(\mathbf{r}\right) = u_{\lambda,k}\left(\mathbf{r}+\mathbf{R}\right), \qquad [2.7]$$

for any direct lattice point vector **R**. It is assumed here that the Bloch functions in the crystal will not very seriously differ from the atomic orbitals in the atomic system, in fact even in practically and accurate calculations in solids the atomic orbitals are used as a first approximation (John and Stefan, 2003).

Therefore, the normalized Slater orbitals, Eq. [2.4] were used for the various u_j.
The radial component of the Slater orbital is given by

$$R_n(\mathbf{r}) = A\mathbf{r}^b \exp(-t\,\mathbf{r}), \qquad [2.8]$$

where

$$b = n^* - 1, \quad \text{and} \quad t = \frac{Z_{eff}}{n^*}. \qquad [2.9]$$

To calculate R(**r**), n^* and σ must be known. There are several rules proposed for the calculation of these quantities and can be found in the work of Slater (1955). These rules were used to calculate n^* and σ and then the various radial factors R(**r**) in α — tin. However, in the case of C, Si and Ge the various R(**r**) were calculated using the values of Z_{eff} reported by Clementi and Raimondi (1963).

The real spherical harmonics, $Y_{l,m}(\theta,\varphi)$ are the angular component of the Slater orbitals. In this work, the expressions for the real spherical harmonics given in appendix A of Mcglynn *et.al* (1972) were used.
Since the spherical harmonics are expressed in the spherical coordinate system all calculations are done in this system. It should be noted that by virtue of the real spherical harmonics, the Slater atomic orbitals are directional. In view of this fact, and also in line with the general practice in electronic structure calculations, the charge density is computed along a well defined direction. To simplify the calculations the directions considered are: $\theta=\varphi=0^\circ$ i.e. [001]; $\theta=90^\circ,\ \varphi=0^\circ$ i.e. [100]; and $\theta=0^\circ,\ \varphi=90^\circ$ i.e. [010].

The values of the real spherical harmonics calculated along the three directions are given in Table 2. It is obvious that the Slater orbitals must vanish if their associated real spherical harmonics is zero. As can be seen from Table 2, there are equal number of non-zero orbitals along the [100] and [010] directions. Also the number of orbitals along the [001] is lower than along the [100] and [010] directions. The calculated normalized Slater orbitals along these directions for the various atoms are given in Table 3.

Table 2: Values of the Real Spherical Harmonics.

l	m	[100] direction	[001] direction	[010] direction
0	0	(1/4п)$^{1/2}$	(1/4 п)$^{1/2}$	(1/4 п)$^{1/2}$
1	0	0	(3/4 п)$^{1/2}$	0
1	1	(3/4 п)$^{1/2}$	0	0
1	-1	0	0	(3/4 п)$^{1/2}$
2	0	-(5/16 п)$^{1/2}$	2(5/16 п)$^{1/2}$	-(5/16 п)$^{1/2}$
2	1	0	0	0
2	-1	0	0	0
2	2	0	0	0
2	-2	(15/8 п)$^{1/2}$	0	-(15/8 п)$^{1/2}$
3	0	0	2(7/16 п)$^{1/2}$	0
3	1	-(21/16 п)$^{1/2}$	0	0
3	-1	0	0	-(21/16 п)$^{1/2}$
3	2	0	0	0
3	-2	0	0	0
3	3	(35/16 п)$^{1/2}$	0	0
3	-3	0	0	-(35/16 п)$^{1/2}$
4	0	3(9/256 п)$^{1/2}$	8(9/256 п)$^{1/2}$	3(9/256 п)$^{1/2}$
4	1	0	0	0
4	-1	0	0	0
4	2	-60/8(18/1440п)$^{1/2}$	0	0
4	-2	0	0	-60/8(18/1440п)$^{1/2}$
4	3	0	0	0
4	-3	0	0	0
4	4	105(9/80640 п)$^{1/2}$	0	0
4	-4	0	0	105(9/80640 п)$^{1/2}$
5	0	0	(11/4 п)$^{1/2}$	0
5	1	15/18(264/1440 п)$^{1/2}$	0	
5	-1	0	0	15/18(264/1440 п)$^{1/2}$
5	2	0	0	0
5	-2	0	0	0
5	3	-420/8(22/80640 п)$^{1/2}$	0	0
5	-3	0	0	-420/8(22/80640 п)$^{1/2}$
5	4	0	0	0
5	-4	0	0	0

Table 2 continue

l	m	[100] direction	[001] direction	[010] direction
5	5	$945(11/2\ п\times10!)^{1/2}$	0	0
5	-5	0	0	$945(11/2\ п\times10!)^{1/2}$
6	0	$-15/48(13/4\ п)^{1/2}$	$(13/4\ п)^{1/2}$	$-15/48(13/4\ п)^{1/2}$
6	1	0	0	0
6	-1	0	0	0
6	2	$630/48(312/80640\ п)^{1/2}$	0	0
6	-2	0	0	$630/48(312/80640\ п)^{1/2}$
6	3	0	0	0
6	-3	0	0	0
6	4	$-22680/48(26/7257600п)^{1/2}$	0	0
6	-4	0	0	$-22680/48(26/7257600п)^{1/2}$
6	5	0	0	0
6	-5	0	0	0
6	6	$498960/48(13/2\ п\times12!)^{1/2}$	0	0
6	-6	0	0	$498960/48(13/2\ п\times12!)^{1/2}$

Table 3.1a: The Normalized Slater Orbitals of Carbon Along the [100] Direction.

Orbital Type	Normalized Slater Function
1s	$[(5.6727)^3/п\ ]^{1/2}\ \exp(-5.6727\ x)\ (1/4п)^{1/2}$
2s	$[(3.2166)\ )^5/96п]^{1/2}\ x\ \exp(-1.6083\ x\ )\ (1/4п)^{1/2}$
$2p_x$	$[(3.1358)^5\ /32п\ ]^{1/2}\ x\ \exp(-1.5679\ x\ )\ (3/4п)^{1/2}$

Table 3.1b: The Normalized Slater Orbitals of Carbon along the [001) Direction.

Orbital Type	Normalized Slater Function
1s	$[(5.6727)^3/п\ ]^{1/2}\ \exp(-5.6727\ z)\ (1/4п)^{1/2}$
2s	$[(3.2166)\ )^5/96п]^{1/2}\ z\ \exp(-1.6083\ z\ )\ (1/4п)^{1/2}$
$2p_z$	$[(3.1358)^5\ /32п\ ]^{1/2}\ z\ \exp(-1.5679\ z\ )\ (3/4п)^{1/2}$

Table 3.2a: The Normalized Slater Orbitals of Silicon along the [100] Direction.

Orbital Type	Normalized Slater Function
Is	$[(13.5745)^3/п\ ]^{1/2}\ \exp(-13.5745\ x\ )\ (1/4п)^{1/2}$
2s	$[(9.020)^5\ /96\ п]^{1/2}\ x \exp(-4.5100\ x\ )\ (1/4п)^{1/2}$
$2P_x$	$[(9.9450)^5\ /32\ п]^{1/2}\ x\ \exp(-4.9725\ x)\ (3/4п)^{1/2}$
3s	$[2(4.9032)^7\ /5\ п\times 3^9]^{1/2}\ x^2\ \exp(-1.6344\ x\ )\ (1/4\ п)^{1/2}$
$3p_x$	$[2(4.2852)^7\ /5\ п\times 3^8]^{1/2}\ x^2\ \exp(-1.4284\ x\ )\ (3/4\ п)^{1/2}$

Table 3.2b: The Normalized Slater Orbitals of Silicon along the [001] Direction.

Orbital Type	Normalized Slater Function
Is	$[(13.5745)^3/п\ ]^{1/2}\ \exp(-13.5745\ z\ )\ (1/4п)^{1/2}$
2s	$[(9.020)^5\ /96\ п]^{1/2}\ z \exp(-4.5100\ z\ )\ (1/4п)^{1/2}$
$2P_z$	$[(9.9450)^5\ /32\ п]^{1/2}\ z\ \exp(-4.9725\ z)\ (3/4п)^{1/2}$
3s	$[2(4.9032)^7\ /5\ п\times 3^9]^{1/2}\ z^2\ \exp(-1.6344\ z\ )\ (1/4\ п)^{1/2}$

Table 3.3a: The Normalized Slater Orbitals of Germanium Along the [100] Direction.

Orbital Type	Normalized Slater Function
Is	$[(31.2937)^3 / \pi\ ]^{1/2} \exp(-31.2937\, x)\ (1/4\, \pi)^{1/2}$
2s	$[(23.3648)^5 / 96\, \pi]^{1/2}\ x\ \exp(-1l.6824\, x)\ (l/4\, \pi)^{1/2}$
$2p_x$	$[(28.0822)^5 / 32\, \pi]^{1/2}\ x\ \exp(-14.041l\, x)\ (3/4\, \pi)^{1/2}$
3s	$[2(17.7897)^7 / 5\, \pi \times 3^9]^{1/2}\ x^2 \exp(-5.9299\, x)\ (l/4\, \pi)^{1/2}$
$3p_x$	$[2(l7.0136)^7\ / 5\pi \times 3^8)^{1/2}\ x^2 \exp(-5.6712\, x)\ (3/4\, \pi)^{1/2}$
$3\,d_z^2$	$[(16.2513)^7 / 2\pi \times 3^8]^{1/2}\ 1/3^{1/2}\ x^2\ \exp(-5.4171\, x)\ (5/16\, \pi)^{1/2}$
$3\,d_{x^2-y^2}$	$[(16.2513)^7 / 2\pi \times 3^8]^{1/2}\ x^2\ \exp(-5.4171\, x)\ (15/16\, \pi)^{1/2}$
4s	$[2^{6.4}(7.4403)^{8.4} / 3.7^{8.4}\ \pi \times \Gamma(8.4)]^{1/2}\ x^{2.7} \exp(-2.0109\, x)\ (1/4\, \pi)^{1/2}$
$4p_x$	$[3 \times 2^{6.4}(6.2719)^{8.4} / 3.7^{8.4}\, \pi \times \Gamma(8.4)]^{1/2}\ x^{2.7} \exp(-1.6951\, x)\ (1/4\, \pi)^{1/2}$

Table 3.3b: The Normalized Slater Orbitals of Germanium along the [001] Direction.

Orbital Type	Normalized Slater Function
Is	$[(31.2937)^3 / \pi\ ]^{1/2} \exp(-31.2937\, z)\ (1/4\, \pi)^{1/2}$
2s	$[(23.3648)^5 / 96\, \pi]^{1/2}\ z\ \exp(-1l.6824\, z)\ (l/4\, \pi)^{1/2}$
$2p_z$	$[(28.0822)^5 / 32\, \pi]^{1/2}\ z\ \exp(-14.041l\, z)\ (3/4\, \pi)^{1/2}$
3s	$[2(17.7897)^7 / 5\, \pi \times 3^9]^{1/2}\ z^2 \exp(-5.9299\, z)\ (l/4\, \pi)^{1/2}$
$3p_z$	$[2(l7.0136)^7\ / 5\pi \times 3^8)^{1/2}\ z^2 \exp(-5.6712\, z)\ (3/4\, \pi)^{1/2}$
$3\,d_z^2$	$[2(16.2513)^7 / 2\pi \times 3^8]^{1/2}\ 1/3^{1/2}\ z^2\ \exp(-5.4171\, z)\ (5/16\, \pi)^{1/2}$
4s	$[2^{6.4}(7.4403)^{8.4} / 3.7^{8.4}\ \pi \times \Gamma(8.4)]^{1/2}\ z^{2.7} \exp(-2.0109\, z)\ (1/4\, \pi)^{1/2}$

Table 3.4a: The Normalized Slater Orbitals of α-Tin along the [100] Direction.

Orbital Type	Normalized Slater Function
Is	$[(49.7)^3 / \pi\ ]^{1/2} \exp(-49.7\, x)\ (1/4\, \pi)^{1/2}$
2s	$[(45.85)^5 / 96\, \pi]^{1/2}\ x\ \exp(-22.9250\, x)\ (l/4\, \pi)^{1/2}$
$2p_x$	$[(45.85)^5 / 32\, \pi]^{1/2}\ x\ \exp(-22.9250\, x)\ (3/4\, \pi)^{1/2}$
3s	$[2(38.75)^7 / 5\, \pi \times 3^9]^{1/2}\ x^2 \exp(-12.9166\, x)\ (l/4\, \pi)^{1/2}$
$3p_x$	$[2(38.75)^7\ / 5\pi \times 3^8)^{1/2}\ x^2 \exp(-12.9166\, x)\ (3/4\, \pi)^{1/2}$
$3\,d_z^2$	$[(28.85)^7 / 2\pi \times 3^8]^{1/2}\ 1/3^{1/2}\ x^2\ \exp(-9.6166\, x)\ (5/16\, \pi)^{1/2}$
$3d_x^z$	$[(28.85)^7 / 2\pi \times 3^8]^{1/2}\ x^2\ \exp(-9.6166\, x)\ (15/16\, \pi)^{1/2}$
4s	$[2^{6.4}(22.25)^{8.4} / 3.7^{8.4}\ \pi \times \Gamma(8.4)]^{1/2}\ x^{2.7} \exp(-6.0135\, x)\ (1/4\, \pi)^{1/2}$
$4p_x$	$[3 \times 2^{6.4}(22.25)^{8.4} / 3.7^{8.4}\, \pi \times \Gamma(8.4)]^{1/2}\ x^{2.7} \exp(-6.0135\, x)\ (3/4\, \pi)^{1/2}$
$4\,d_z^2$	$[15(2)^{4.4}(10.85)^{8.4}\ / 3.7^{8.4}\, \pi\ \Gamma(8.4)]^{1/2}\ x^{2.7}/3^{1/2}\ \exp(-2.9324\, x)\ (5/16\, \pi)^{1/2}$
$4\,d_{x^2-y^2}$	$[15(2)^{4.4}(10.85)^{8.4}\ / 3.7^{8.4}\, \pi\ \Gamma(8.4)]^{1/2}\ x^{2.7}\ \exp(-2.9324\, x)\ (15/8\, \pi)^{1/2}$
5s	$[(5.65)^9 / 35\, \pi\ ]^{1/2}\ (1/1356)]\ x^3\ \exp(-1.4125\, x)\ (l/4\, \pi)^{1/2}$
$5p_x$	$[3(5.65)^9 / 35\, \pi]^{1/2}\ (1/1356)\ x^3\ \exp(-1.4125\, x)\ (3/4\, \pi)^{1/2}$

Table 3.4b: The Normalized Slater Orbitals of α-Tin Along the [001] Direction.

Orbital Type	Normalized Slater Function
Is	$[(49.7)^3/\pi\ ]^{1/2}\exp(-49.7\,z)\,(1/4\,\pi)^{1/2}$
2s	$[(45.85)^5/96\,\pi]^{1/2}\ z\ \exp(-22.9250\,z)\,(l/4\,\pi)^{1/2}$
2p$_x$	$[(45.85)^5/32\,\pi]^{1/2}\ z\ \exp(-22.9250\,z)\,(3/4\,\pi)^{1/2}$
3s	$[2(38.75)^7/5\,\pi\times3^9]^{1/2}\ z^2\exp(-12.9166\,z)\,(l/4\,\pi)^{1/2}$
3p$_x$	$[2(38.75)^7/5\pi\times3^8)^{1/2}\ z^2\exp(-12.9166\,z)\,(3/4\,\pi)^{1/2}$
$3\,\mathrm{d}_z^2$	$[(28.85)^7/2\pi\times3^8]^{1/2}\,1/3^{1/2}\ z^2\ \exp(-9.6166\,z)\ (5/16\,\pi)^{1/2}$
$3\mathrm{d}_x^{z}$	$[(28.85)^7/2\pi\times3^8]^{1/2}\ z^2\ \exp(-9.6166\,x)\ (15/16\,\pi)^{1/2}$
4s	$[2^{6.4}(22.25)^{8.4}/3.7^{8.4}\ \pi\times\Gamma(8.4)]^{1/2}\ z^{2.7}\exp(-6.0135\,z)\ (1/4\,\pi)^{1/2}$
4p$_x$	$[3\times2^{6.4}(22.25)^{8.4}/3.7^{8.4}\,\pi\times\Gamma(8.4)]^{1/2}\ z^{2.7}\exp(-6.0135\,z)\ (3/4\,\pi)^{1/2}$
$4\,\mathrm{d}_z^2$	$[15(2)^{4.4}(10.85)^{8.4}/3.7^{8.4}\,\pi\ \Gamma(8.4)]^{1/2}\ z^{2.7}/3^{1/2}\ \exp(-2.9324\,z)\,(5/16\,\pi)^{1/2}$
$4\,\mathrm{d}_{x^2-y^2}$	$[15(2)^{4.4}(10.85)^{8.4}/3.7^{8.4}\,\pi\ \Gamma(8.4)]^{1/2}\ z^{2.7}\ \exp(-2.9324\,z)\,(15/8\,\pi)^{1/2}$
5s	$[(5.65)^9/35\,\pi\ ]^{1/2}\ (1/1356)]\ z^3\ \exp(-1.4125\,z)\,(l/4\,\pi)^{1/2}$
5p$_x$	$[3(5.65)^9/35\,\pi]^{1/2}\ (1/1356)\ z^3\ \exp(-1.4125\,z)\,(3/4\,\pi)^{1/2}$

Total Electrons Charge Density

From what has been stated in section 2 above, the Bloch functions for the electrons are given by

$$\Psi_j=\exp(i\mathbf{k}.\mathbf{r})\times\mathrm{X} \qquad [3.1]$$

for the jth electron, where X is the normalized Slater orbital function given by $\mathrm{X}=R(\mathbf{r})Y_{l.m}(\theta,\varphi)$ and is tabulated in Table 3. The charge density for the **k**th state of the jth electron in the units employed in this work is given by

$$\rho_j(\mathbf{r},\mathbf{k})=\sum\left|\Psi_{\mathbf{k}}(\mathbf{r})\right|^2. \qquad [3.2]$$

In the calculation of the charge density reported in this paper all the electrons (both core and valence) are taken into consideration in order to enable the result to be used in a DTF calculation and in integrating the Poisson equation for the electron-electron Coulomb interaction in the Diamond-structure semiconductors.

For simplicity, and also for the reason stated above, the sp^3 hybridization of the outermost shell electrons was not considered in calculating the total electron charge density, therefore, it has become necessary to assume a configuration for the two electrons in the p orbitals of the partially occupied outward shell of the atoms. This approximation is quite reasonable in all the crystals considered except may be carbon which in reality has only two core state electrons and four involved in the sp^3 hybridization. The choice of this configuration even though arbitrary must be consistent and has been taken as $p_x^1, p_y^1, p_z^0,$ in all the atoms. The computed charge densities are shown in graphs 1, 2, 3 and 4.

The calculation of the total electron charge density was carried out along the [100], [010], and [00l] directions. It has been found that the total electron charge density along the [100] and [010 directions in each crystal are equal, therefore, only the density along the [100] and [001] directions are given in Figures 1, 2, 3, and 4 which show the variation of the total electrons charge density with the distance from the origin of a Wigner-Seitz cell. It should be noted that in these figures, the distance from the center of the Wigner-Seitz cell is expressed in units of the nearest neighbor distance, d. The charge density has its maximum value at the center of a cell. Also, at the center of the cell, (i.e the origin of the coordinate system employed in the calculations) the density increases with the atomic number Z. As one moves away from the origin, there is a drastic fall in the density.

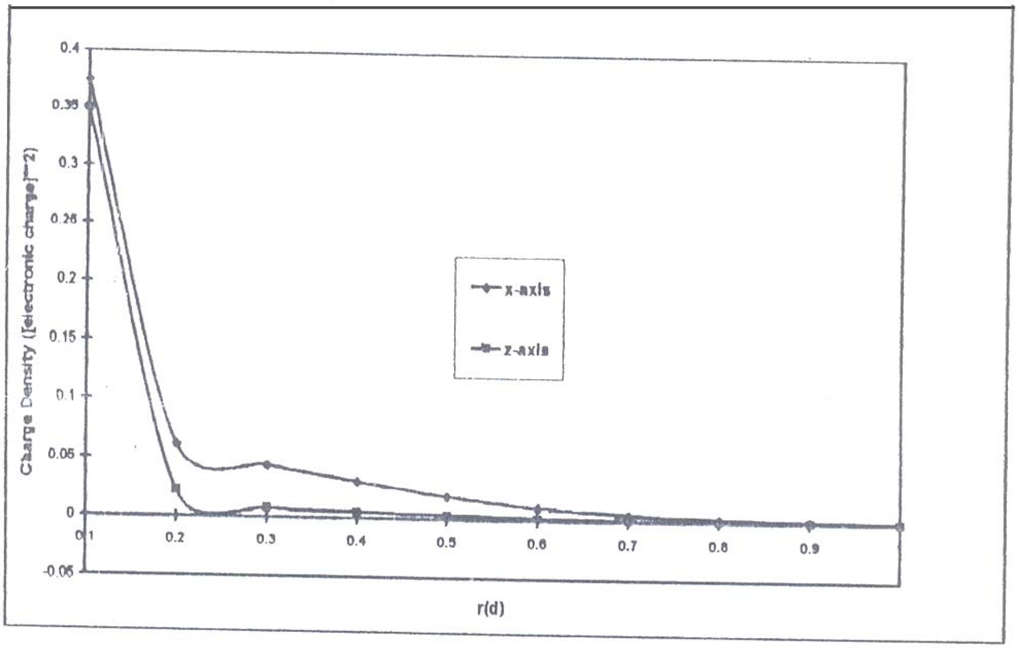

Figure 1. Graph of Charge Density Against Distance From the Center of the Wigner-Seitz Cell of Carbon Crystal

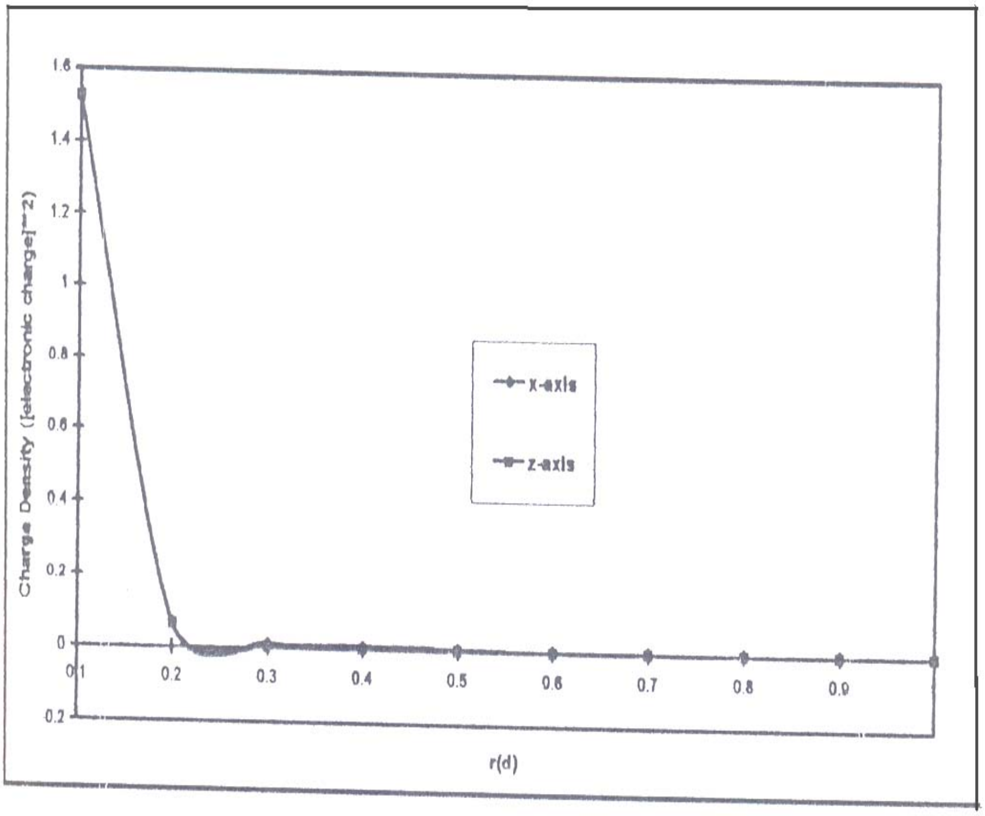

Figure 2. Graph of Charge Density Against Distance From the Center of the Wigner-Seitz Cell of Silicon Crystal

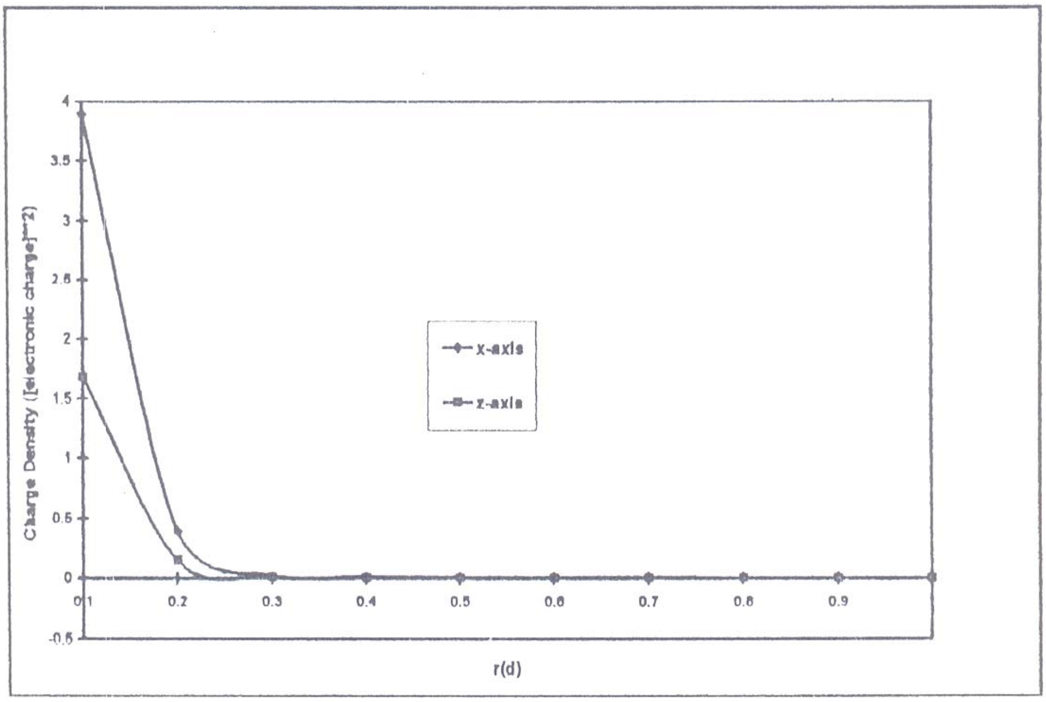

Figure 3. Graph of Charge Density Against Distance From the Center of the Wigner-Seitz Cell of Germanium Crystal

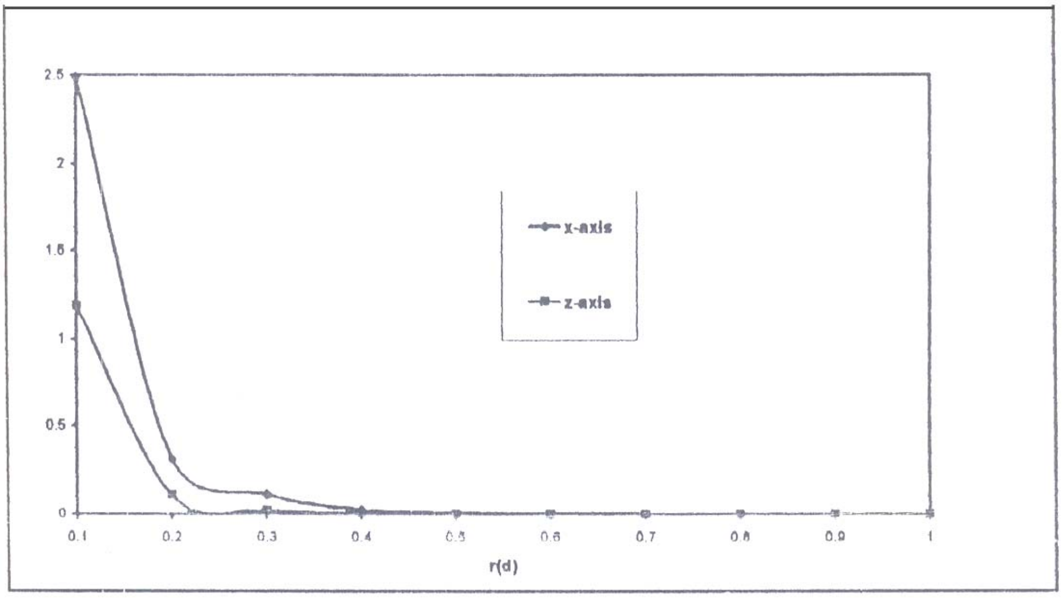

Figure 4. Graph of Charge Density Against Distance From the Center of the Wigner-Seitz Cell of α-Tin Crystal

Table 4: Ratio of the Charge Density at r = 0.5 d to r = 0.0 d in Percentage .

Crystal	[100]	[001]
Carbon	0.21	0.038
Silicon	0.005	0.00095
Germanium	0.00041	0.000074

The closest points on the surface of the cell to its center are at a distance r = 0.5d, while the remotest points are at a distance, R = 1.258d (Babaji, 1999). The ratio of the density at r = 0.5d to that at the origin is given in Table 4. The orbitals of the electrons are highly localized, thus the charge density due to the electrons in a Wigner-Seitz cell is practically zero outside the cell as can be seen from Table 4.

The charge densities, at a given distance from the center of the cell along [001] and [100] directions are not exactly equal, the density along [100] been always higher. This directionality of the charge density is partly due to the assumed electronic configuration of the outermost filled p-orbitals, namely p_x^1, p_y^1, p_z^0. Most importantly, it clearly demonstrates that even with this simple model the Wigner-Seitz potential cells in the diamond-structure semiconductor crystals are not of the muffin-tin form.

CONCLUSION

A first-principle calculation of the electronic wave function and total electrons charge density in the diamond-structure semiconductor crystals has been done. The basic input to all calculations are the lattice constant of the crystal and the atomic number of the constituent atom. The total electrons charge density was calculated along the [100], [010], and [00l] directions. It has been found that the total electrons charge density along the [100] and [010] directions in each crystal are equal. The charge density has its maximum value at the center of a cell. Also, at the center of the cell, (i.e the origin of the coordinate system employed in the calculations) the density increases with the atomic number Z. As one moves away from the origin, there is a drastic fall in the density.

The charge densities at a given distance from the center of the cell along [001] and [100] directions are not exactly equal, the density along [100] been always higher. This directionality of the charge density is partly due to the assumed electronic configuration of the outermost filled p-orbitals, namely p_x^1, p_y^1, p_z^0. Most importantly, it clearly demonstrates that even with this simple model the Wigner-Seitz potential cells in the diamond-structure semiconductor crystals are not of the muffin-tin form. The angular and radial variation of the charge density obtained in this work agrees with that of Eberhard, (2003) and Abdallah *et al* (2006) and it is hoped that the results obtained will be used in a DFT calculation.

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