ENERGY DENSITY FUNCTIONAL THEORY IN DOPED SEMICONDUCTORS

by

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DECLARATION

I hereby affirm that this thesis has been composed by myself and that it is a record of my research work. It has not been accepted in any previous application for a higher degree. All the sources of information are specially acknowledged by means of references.

Abali
Signature

23/9/86
Date

CERTIFICATION

This Thesis entitled "Energy Density Functional Theory in doped Semiconductors" by Adah Ijachi Amali meets the regulations governing the award of the degree of M.Sc. Physics of Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.

Chairman, Supervisory Committee — Date

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ABSTRACTS

The Thomas-Ferni (TF) method and its refinement, the Thomas-Fermi-Dirac (TFD) approach have been widely employed in the literature to study screening in both metals and semiconductors, but only for homogeneous and isotropic model solids (i.e. within the Local density approximation). The frontier of static dielectric screening theory in semiconductors is here extended further to account for exchange-correlation and inhomogeneity within the framework of the energy density functional formalism. In particular, the reciprocal space formulation of Langreth and Mehl is used to give exchange-correlation a nonlocal description. The resulting nonlocal TFD equation is linearized to obtain a closed analytical expression for the spatial dielectric function and the range of validity is investigated. It is shown that the spatial dielectric function still has a simple analytical form but the constants appearing in it have many body effects incorporated. The present nonlocal Thomas-Fermi-Dirac theory (TFD-NLDA) is more effective at reducing attractive potentials than all previous linear or nonlinear screening theories based on the TF method.

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CHAPTER 1

I N T R O D U C T I O N

The study of the response of semiconductors to a static point charge impurity has attracted considerable attention in time past. This response which consists of a rearrangement of the valence electrons and the shielding of the bare impurity potential is effectively described by the dielectric function. The dielectric function serves as a simple unifying concept for all the theories of the electron gas. A knowledge of it permits one to obtain directly properties of an interacting electron system like ground state energy, response to an external potential, phonon dispersion spectra, optical absorption coefficient, pseudopotential form factors etc. Until recently, analytical expressions have been found for the dielectric function only in momentum space ($\underline{k}$-space) and then Fourier transformed to obtain the corresponding spatial dielectric function $\varepsilon(\underline{r})$. (Penn, 1962; Srinivasan 1969; Walter and Cohen, 1970: Bassani et al, 1974). Apart from the fact that the first step involved cumbersome computations, the method did not lend itself to the nonlinear treatment of dielectric response as a result of the intrinsic linearity of the Fourier transform.

Only a few years ago, however, Resta (1977) used an r-space approach to develop a general theory of screening in semi-conductors in which the Thomas-Fermi screening equation (Thomas, 1927; Fermi, 1928) was explicity solved to obtain a

is an unphysical one and the theory runs into problems, for instance, in ion-core regions where electrons are bound (Meyer and Young, 1970). The basic TF equation mentioned above is equivalent to the Euler-Lagrange equation arising from a variation of the Hohenberg-Kohn-Sham [HKS] functional subject to the constraint on the total number of particles.

The TF screening theory in semiconductors can be straighforwardly generalized to any local bare impurity pseudo potential. In particular, it has been suggested that for more refined impurity calculations, the pseudo potential approach could be adopted instead of using a purely Coulombic impurity potential (Cornolti and Resta, 1978). Of recent, the pseudopotential approach has been used to compute cohesive energy and charge-density form factors of beryllium and the results have further confirmed the Langreth and Mehl's reciprocal space formulation as an approximation scheme superior to the LDA (Von Barth and Pedroza, 1985).

HKS define the non-coulombic part of their energy functional in terms of kinetic and exchange-correlation energy functionals as

$$G[n] = T_s[n] + E_{xc}[n]$$

All the many-body effects of a system are incorporated in these two functionals. In the Kohn-Sham [KS] scheme, the quasiparticle kinectic energy is given an exact treatment and an attempt is made to expand the exchange-correlation functional $E_{xc}[n]$ as a gradient series in terms of density. The accuracy of the scheme depends on how well $E_{xc}[n]$ is known in terms of its functional dependence on the density $n(\underline{r})$. Another version of the gradient expansion method involves expanding both $T_{xc}[n]$ and $E_{xc}[n]$.

linearized equation. This dielectric function is seen to have the same form as that obtained by Resta but differs only in terms of the constants appearing in it.

Chapter 4 presents numerical results for silicon, diamond and germanium in the linear approximation and investigates its range of validity. The results confirm earlier findings that inclusion of exchange-correlation and inhomogeneity corrections in the TF theory lead progressively to more effective screening.

CHAPTER 2

ENERGY DENSITY FUNCTIONAL THEORY

2.1 The total energy of an N-particle system.

In many problems involving atoms, molecules and solids, one is interested in calculating ground state energies and electron density distributions from which in turn all other equilibrium properties can be obtained. Each of the systems mentioned above involves a many-body problem for which no exact solutions are possible in quantum mechanics. The Schrodinger equation given below provides, in principle, the usual tool for solving completely the problem of particles or systems of particles in quantum mechanics.

$$H\Psi = E\Psi \qquad 2.1.1$$

The wavefunction Ψ which describes the whole system is a function of all the dynamical coordinates of all the particles. This means that the Schrodinger equation is in many variables and does not seperate into independent equations in each variable.

The zero approximation usually made in tackling these many-body problems is to put them in one-body form. In doing this, it is assumed that the Schrodinger equation is seperable, and that each particle can be represented by its own wavefunction which is a function of the coordinates of that particle only (Raimes, 1961).

The electrons around which the discussion of these many-body problems center, fall under the category of Fermions,

which are identical and indistinguishable Quantum particles possessing half integral spin and occupancy of zero or one per particle state. They are represented by antisymmetric wavefunctions usually written as Slater determinants of the single particle wavefunctions. The Slater determinant for an N-body system is given by:

$$\Psi(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_\alpha(\underline{r}_1) \ldots\ldots\ldots & \psi_\alpha(\underline{r}_N) \\ \psi_\beta(\underline{r}_1) \ldots\ldots\ldots & \psi_\beta(\underline{r}_N) \\ \psi_\gamma(\underline{r}_1) \ldots\ldots\ldots & \psi_\gamma(\underline{r}_N) \\ \ldots\ldots\ldots\ldots\ldots & \ldots\ldots \\ \psi_\mu(\underline{r}_1) \ldots\ldots\ldots & \psi_\mu(\underline{r}_N) \end{vmatrix} \qquad 2.1.2$$

where the subscripts refer to the quantum states of the particles and $\underline{r}_1, \underline{r}_2 \ldots\ldots, \underline{r}_N$, specify both spatial and spin coordinates. The Slater determinant is antisymmetric with respect to the interchange of any two rows.

A further simplification of the many body problem is to assume that the lattice of ions which is found in real systems is replaced by a uniform positive background. This model is called a Jellium model (Pines, 1962) and its Hamiltonian is written as:

$$H = \sum_i^N \frac{-1}{2} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{r_{ij}} + Z \sum_i^N \frac{1}{|\underline{r} - \underline{r}_i|} \qquad 2.1.3$$

The total energy of the system is calculated as the expectation value of this Hamiltonian.

$$E = \langle \Psi \mid H \mid \Psi \rangle \qquad 2.1.4$$

This expectation value involves integration over spatial coordinates as well as summation over discrete coordinates. In evaluating the total energy, the more cumbersome configuration space representation in which Slater determinants or antisymmetrized products of single-particle wavefunctions are employed is avoided in favour of the method of second quantization. This method (also called occupation number representation) in which interaction processes between particles are solely interpreted in terms of annihilation and creation of particles, provides a simple and compact approach to solving the many-body problem. In this approach, use is still made of single particle wavefunctions, but occupation numbers rather than coordinates become the dynamical variable.

The N x N Slater determinant is written as a state vector in Fock space using Dirac's notation as:

$$\Psi(1, 2, \ldots, N) = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2), \ldots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) \ldots & \psi_2(N) \\ \vdots & \vdots & \vdots \\ \psi_N(1) & \psi_N(2) \ldots & \psi_N(N) \end{vmatrix}$$

$$= |\psi_1\ \psi_2 \ldots \psi_N\rangle \qquad 2.1.5$$

In second quantization, the wavefunctions are quantized and become field operators and the classical operators become second quantized:

$\psi(\underline{r}) \longrightarrow \hat{\psi}(\underline{r})$, Quantized field operator.

$H \longrightarrow \mathbb{H}$, Second Quantized operator.

For each particle wavefunction ψ_α, a corresponding creation operator a_α^+ and an annihilation operator a_α can be defined. So that the quantized field operators can be defined in terms of them as:

$$\hat{\psi}(\underline{r}) = \Sigma_\alpha \psi_\alpha(\underline{r}) a \qquad 2.1.6$$

$$\hat{\psi}^+(\underline{r}) = \Sigma_\alpha \psi_\alpha^*(\underline{r}) a_\alpha \qquad 2.1.7$$

products of these operators have uniquely defined properties, two of which are of immediate relevance to our problem[++]

$$\langle \hat{\psi}^+(\underline{r}) \psi(\underline{r}') \rangle = \langle a_\alpha^+ a_\beta \rangle = \gamma_\sigma(\underline{r}' | \underline{r}) \qquad 2.1.8$$

$$\langle \hat{\psi}^+(\underline{r}_1) \hat{\psi}^+(\underline{r}_2') \hat{\psi}(\underline{r}_2') \hat{\psi}(\underline{r}_1') \rangle = \langle a_\alpha^+ a_\beta^+ a_\lambda a_\gamma \rangle =$$

$$= \Gamma_\sigma(\underline{r}_1' \underline{r}_2' \mid \underline{r}_1 \underline{r}_2) \qquad 2.1.9$$

Equations 2.1.8 and 2.1.9 define the one-particle and two particle density matrices respectively, with σ designating the spin state and the subscripts α, β, λ and γ the quantum states. These two matrices are related as

$$\Gamma_\sigma(\underline{r}_1' \ \underline{r}_2' | \underline{r}_1 \ \underline{r}_2) = \tfrac{1}{2} \begin{vmatrix} \gamma_\sigma(\underline{r}_1 | \underline{r}_1') & \gamma_\sigma(\underline{r}_1 | \underline{r}_2') \\ \gamma_\sigma(\underline{r}_2 | \underline{r}_1') & \gamma_\sigma(\underline{r}_2 | \underline{r}_2') \end{vmatrix} \qquad 2.1.10$$

[++]A more detailed treatment of the present discussion and the equations that follow is available in Longuet-Higgins (1966)

in the coulomb field of the nucleus and of the other electrons respectively. In second quantized form, we write this Hamiltonian as:

$$\mathbb{H} = \mathbb{T} + \mathbb{V} + \mathbb{U} \qquad 2.1.15$$

where

$$\mathbb{T} = \frac{-1}{2} \int \hat{\psi}^{+}(\underline{r}') \nabla^2_{\underline{r}'} \hat{\psi}(\underline{r}') d\underline{r}' \qquad 2.1.16$$

and its expectation value, is,

$$\langle \mathbb{T} \rangle = \frac{-1}{2} \int \nabla^2 \gamma(r|r')|_{r'=r} dr \qquad 2.1.17$$

Similarly

$$\mathbb{V} = \int \hat{\psi}^{+}(\underline{r}) V(\underline{r}) \hat{\psi}(\underline{r}) d\underline{r} \qquad 2.1.18$$

$$\langle \mathbb{V} \rangle = \int V(\underline{r}) n(\underline{r}) d\underline{r} \qquad 2.1.19$$

where $V(r) = \frac{-Z}{|\underline{R} - \underline{r}|}$

$$\mathbb{U} = \tfrac{1}{2} \int \hat{\psi}^{+}(\underline{r}_1) \hat{\psi}^{+}(\underline{r}_2) U_{12} \hat{\psi}(\underline{r}_1) \hat{\psi}(\underline{r}_2) d\underline{r}_1 d\underline{r}_2 \qquad 2.1.20$$

$$\langle \mathbb{U} \rangle = \int U_{12} \Gamma(\underline{r}_1 \underline{r}_2 | \underline{r}_1 \underline{r}_2) d\underline{r}_1 d\underline{r}_2 \qquad 2.1.21$$

or

$$\langle \mathbb{U} \rangle = \frac{1}{2} \int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} n(\underline{r}_1) n(\underline{r}_2) - \frac{1}{4} \int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} \gamma(r_1|r_2) \gamma(r_2|r_1) \qquad 2.1.22$$

where we have used $U_{12} = \dfrac{1}{|\underline{r}_1 - \underline{r}_2|}$

The first term of equation 2.1.22 corresponds to the direct term while the second is the Exchange term arising from the antisymmetric nature of electron wavefunctions.

The total energy of the fermion system under consideration is then written as:

$$E = \langle \mathbb{H} \rangle = \langle \mathbb{T} \rangle + \langle \mathbb{V} \rangle + \langle \mathbb{U} \rangle \qquad 2.1.23$$

or

$$E = \frac{-1}{2} \int \nabla^2 \gamma (\underline{r} | \underline{r}') \Big|_{\underline{r}'=\underline{r}} d\underline{r} + \int V(\underline{r}) n(\underline{r}) d\underline{r}$$

$$+ \frac{1}{2} \int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} n(\underline{r}_1) n(\underline{r}_2) - \frac{1}{4} \int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} \gamma(\underline{r}_1 | \underline{r}_2) \gamma(\underline{r}_2 | \underline{r}_1) \qquad 2.1.24$$

This result was first obtained by Dirac (1930) and it shows clearly that the total energy of a many-electron system can be written as a functional of its density and external potential.

$$E = E[n, V]$$

It is later shown in the Hohenberg and Kohn formalisim that the potential V(r) is infact a unique functional of density, which then means that the energy is a unique functional of density.

$$E = E[n]$$

In line with the above expression there have been many attempts to formulate the problem of inhomogeneous interacting electron gas with the total electron density as the basic variable rather than the wave function (Hodges, 1973).

2.2 The Hohenberg-Kohn-Sham formalism [HKS]

Hohenberg and Kohn [HK] (1964) and Kohn and Sham [KS] (1965) put forward a general theory for the treatment of inhomogeneous electron gases in their ground state commonly referred to as the Density-Functional Formalism. The central quantity in this theory is the electron density, and the theory establishes that the ground state energy and consequently all ground state properties of any system are functionals only of the density.

Hohenberg and Kohn considered a system of electrons in its ground state (assumed for simplicity to be nondegenerate) moving in a static external potential $V(r)$. In the previous section it was shown that the energy of such a system can be expressed as,

$$E = E[n, V] \qquad 2.2.1$$

but in their Density functional formalism, Hohenberg and Kohn went on to show by a formal proof (Uniqueness theorem) that V itself (apart from an additive constant) is a unique functional of density (this proof is shown in Appendix A).

$$E = E[n] \qquad 2.2.2$$

The formal statement of the HK formalism then follows that the ground state energy of a many electron system is a universal functional of the electron density.

HK define an energy functional

$$E_v[n] = \int v(r)n(\underline{r})d\underline{r} + F[n] \qquad 2.2.3$$

where

$$F[n] = \langle \Psi | (T + U) | \Psi \rangle \qquad 2.2.4$$

The correct ground state density $n(\underline{r})$ (having spatial integral equal to N) associated with $v(\underline{r})$ gives $E_v[n]$ equal to the ground state energy E_N, so that for any density n' other than the ground state density,

$$E_N < E_v[n'] \qquad 2.2.5$$

A variation of $E_v[n]$ about the correct ground state density vanishes,

$$\delta E_v[n] = 0 \qquad 2.2.6$$

subject of course, to the condition that all densities considered satisfy

$$\int n(\underline{r})d\underline{r} = N \qquad 2.2.7$$

The expression for the total energy 2.1.24 is rewritten with electrostatic terms separated as

$$E_v[n] = \int v(\underline{r})n(\underline{r})d\underline{r} + \tfrac{1}{2}\int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}d\underline{r}' + G[n] \qquad 2.2.8$$

$G[n]$ contains the kinetic and exchange terms.
The electrostatic potential of the system is

$$\phi(\underline{r}) = V(\underline{r}) + \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' \qquad 2.2.9$$

If V(r) is regarded as being due to a distribution of positive charge of number density $n_+(r)$, then

$$\phi(r) = \int \frac{n(r') - n_+(r')}{|\underline{r} - \underline{r}'|} dr' \qquad 2.2.10$$

The potential satisfies the poisson equation

$$\nabla^2 \phi(r) = -4\pi [n(r) - n_+(r)] \qquad 2.2.11$$

In doing the variation of $E_V[n]$ subject to the constraint on the total number of particles, we define a Lagrange parameter μ such that for the correct density,

$$\frac{\delta E_V[n]}{\delta n} = \mu \qquad 2.2.12$$

or

$$\delta E_V - \mu \delta n = 0$$

$$\delta [E_V[n] - \mu \int n(\underline{r}) d\underline{r}] = 0 \qquad 2.2.13$$

Equation 2.2.8 is rewritten as

$$E_V[n] = \int \phi(\underline{r}) n(r) d\underline{r} + G[n] \qquad 2.2.14$$

$$\therefore \frac{\delta E_V[n]}{\delta n} = \phi(r) + \frac{\delta G[n]}{\delta n} = \mu \qquad 2.2.15$$

or

$$\phi(\underline{r}) + \frac{\delta G[n]}{\delta n} = \mu \qquad 2.2.16$$

For large N, μ is equal to the chemical potential and at absolute zero of temperature, chemical potential is equal to the Fermi energy, E_F.

The major task in any many-electron system is the determination of the functional $G[n]$. In the HK approach an expression is sought for $G[n]$ in two regions of approximation, namely in the regions of nearly constant and slowly varying densities. A combination of the results in these two approximation regions yields an expression for the formal gradient expansion.

$$G[n] = \int d\underline{r}\left\{g^{(o)}(n(r)) + g^{(2)}(n(r))\left|\vec{\nabla} n(r)\right|^2 + \ldots\right\}$$

where $g^{(o)}$ and $g^{(2)}$ are functions of n representing kinetic and exchange-correlation energy densities. This expression is valid in principle for a system in which the density non uniformity is both small and slowly varying. As a practical calculational tool for real systems, however, Kohn and Sham propose the self-consistent scheme.

As a starting point, a non-interacting system of N electrons moving in a static external potential $V_s(\underline{r})$, is considered. In analogy to equation 2.2.16, one can write

$$V_s(r) + \frac{\delta T_s[n]}{\delta n(\underline{r})} = \mu_s \qquad 2.2.17$$

The new set of Schrodinger equations to be solved for the exact density distribution is then,

$$\left\{-\frac{1}{2}\nabla_i^2 + V_{eff}(\underline{r})\right\}\psi_i(\underline{r}) = \varepsilon_i\psi_i(\underline{r}) \qquad 2.2.23$$

The ground state energy corresponding to this density may be found from equations 2.2.8 and 2.2.21, with

$$T_s[n] = \sum_{i=1}^{N}\varepsilon_i - \int V_{eff}(\underline{r})n(\underline{r})d\underline{r} \qquad 2.2.24$$

All the complexity of the many body problem is contained in the functional $E_{xc}[n]$

For the case in which the density is slowly varying, Kohn and Sham expand $E_{xc}[n]$ as

$$E_{xc}[n] = \int d\underline{r}\ \left\{\epsilon_{xc}(n(\underline{r}))n(\underline{r}) + \epsilon_{xc}^{(2)}(n(\underline{r})|\vec{\nabla}\ n(r)|^2 + \ldots\right\} \qquad 2.2.25$$

The most frequently used approximation is to neglect the gradient terms;

i.e.

$$E_{xc}[n] = \int d\underline{r}\ \epsilon_{xc}(n(r))n(\underline{r}) \qquad 2.2.26$$

so that

$$V_{eff}(\underline{r}) = \phi(\underline{r}) + \mu_{xc}(n(r)) \qquad 2.2.27$$

where

$$\mu_{xc} = \frac{d}{dn}\left[n\varepsilon_{xc}(n)\right] \qquad 2.2.28$$

is just the exchange correlation part of the chemical potential of a uniform electron gas of density n.

This approximation is good for two cases: that of very slowly varying density, because the omitted gradient terms are small, and that of very high density [$r_s << 1$], since in this limit the exchange and correlation is much smaller than the kinectic energy.

Rather than using equation 2.2.24 to calculate $T_s[n]$, a second approach to the gradient expansion is to expand both $T_s[n]$ and $E_{xc}[n]$ in a gradient series so that the solution of Schrodinger's equation is avoided (Hodges, 1973).

$$T_s[n] = \frac{3}{10}\int(3\pi^2 n)^{\frac{2}{3}} n d\underline{r} + \tfrac{1}{2}\int t^{(2)}(n)|\vec{\nabla} n|^2 dr + \ldots \qquad 2.2.29$$

$$E_{xc}[n] = \int \varepsilon_{xc}(n)\, n d\underline{r} + \tfrac{1}{2}\int g^{(2)}_{xc}|\vec{\nabla} n|^2 d\underline{r} + \ldots \qquad 2.2.30$$

$g^{(2)}$ and $t^{(2)}$ are unknown functions of n and ε_{xc} is the exchange-correlation energy density of a uniform electron gas.

In the region of slowly varying density where low order gradient expansion is applicable, Hodges (1973) expands the kinetic energy as

$$T_s[n] = T_o[n] + T_2[n] + T_4[n] + \ldots \qquad 2.2.31$$

$$T_o[n] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}\int n^{5/3}(\underline{r}) d\underline{r} \qquad 2.2.32$$

$$T_2[n] = \frac{1}{72}\int \frac{|\vec{\nabla} n(r)|^2}{n(\underline{r})} d\underline{r} \qquad 2.2.33$$

$$T_4[n] = \frac{(3\pi^2)^{-\frac{2}{3}}}{540} \int d\underline{r}\; n(\underline{r})^{\frac{1}{3}} \left[\frac{\nabla^2 n(r)}{n(\underline{r})} + \alpha(\nabla n(r))^2 \frac{\nabla n(r)}{n^3(r)} + \beta'\left(\frac{\nabla n(\underline{r})}{n(\underline{r})} \right) \right] \qquad (2.2.34)$$

$T_o[n]$ = Thomas-Fermi term

$T_2[n]$ = Corrected Weiszacker term

$T_4[n]$ = Contributions from non-linear theory.

$\alpha = -9/8$

$\beta' = 1/3$

The adequacy of gradient expansion representation of the exchange-correlation functional is still a subject of investigation. Equation 2.2.30 is rewritten by Wang and Rasolt (1976) as

$$E_{xc}[n] = \int d\underline{r}\; [A_{xc}(n(\underline{r})) + B_{xc}(n(\underline{r}))|\vec{\nabla} n(\underline{r})|^2 + \ldots] \quad 2.2\,35$$

where $A_{xc}(n(\underline{r})) = n(\underline{r})\; \epsilon_{xc}(n(\underline{r}))$

as given by Hedin and Lundquist (1969) is found to be fairly accurate for metallic densities.

B_{xc} has so far been evaluated only in the high density limit*, but this has been done separately as B_c (Ma and Breuckner, 1968) and B_x (Sham, 1971). Calculations done by Tong and Sham (1966) however show that inclusion of the term B_c worsens agreement with empirically determined correlation energy.

*It has been extended to metallic densities by Geldart & Rasolt (1975, 1976).

The correlation energy they calculate is about a factor of 2 too large for small atoms, but better for larger atoms. They conclude that gradient contributions misrepresent E_{xc} presumably because the electronic density in atoms has too rapid a spatial variation near the nucleus.

Another important point is that since A_{xc} and B_{xc} were determined from the electron gas system which is a continuum of states, their accuracy in Real systems with discrete states is in question.

Before concluding this section it is worth mentioning that works of different authors (Lang and Sham, 1975; Kleinman, 1974) have raised important questions as to how physically meaningful it is to separate A_{xc} and B_{xc} into their individual exchange and correlation parts. This is more so, since exchange and correlation are basically of the same origin.

2.3 The Local density Approximation (LDA)

There are numerous approximate methods of solving many-body problems. These include perturbation theory, Hartree-Fock, collective variable method etc., but we restrict this treatment to methods having density as the basic variable. The different formulations of the problem fall into two wide classes; namely, the LOCAL-DENSITY APPROXIMATION and the NON-LOCAL DENSITY APPROXIMATION (NLDA).

In this section, we discuss the local density approximation with particular emphasis on its simplest form; the statistical Thomas-Fermi model. The concept of LDA is based on the theory of the uniform electron gas system where the density as well as the potential under which particles move are given global interpretations. It is assumed that what happens in any region of space within the system is independent of what goes on elsewhere within the system.

2.3.1 Statistical Thomas-Fermi model (TF).

This is a semiclassical model with the basic assumption being that electrons surrounding the nucleus of an atom can be treated as a system of degenerate, non-interacting electron gas at absolute zero of temperature. The electrons fill all the cells in phase-space below a certain energy level (the Fermi energy, E_F) and all remaining cells above this level are unoccupied. It is also assumed that we are dealing with closed shell systems (i.e. there are no unpaired electrons). By making these kinds of assumption the following factors are automatically ignored;

(i) Exchange effects due to repulsion among electrons of like spin arising from the pauli exclusion principle.

(ii) Correlation correction due to coulomb repulsion among electrons of opposite spin.

(iii) the inhomogeneity due to atomic shell structure.

(iv) Relativistic effects which arise at finite temperatures.

Before writing down the TF equations, a brief discussion of the conditions of validity of the TF method would be necessary.

In any system, we can readily identify characteristic lengths like nearest neighbour distance, Bohr radii, de Broglie wavelength, Debye screening length, etc., over which microscopic and macroscopic quantities vary. An electron at the Fermi surface, for example, is characterized by a wave-vector k_F and a de Broglie wave length λ

$$\text{where } \lambda = \frac{2\pi}{k_F} \qquad 2.3.1$$

In the TF approximation, this wave-length is taken to be small compared to the characteristic size of inhomogeneities which occur within the system. The effective potential under which the electrons move, and which determines the extent of inhomogeneity of the system varies only slowly over this characteristic wavelength. A condition of validity for the TF approximation is then written as:

$$\left| \frac{d\lambda(\underline{r})}{d\underline{r}} \right| \ll 1 \qquad 2.3.2$$

This relation imposes the condition that the electron density, as well as the potential under which electrons move, be necessarily slowly varying functions in space. As a result of this, their gradients are neglected. The TF method is also particularly suitable for treatment of systems with high density.

The energy functional of Hohenberg and Kohn is

$$E_V[n] = -\frac{1}{2}\int \nabla^2 \gamma(\underline{r}'|\underline{r})\Big|_{\underline{r}'=\underline{r}} d\underline{r} + \int V(\underline{r})n(\underline{r})d\underline{r}$$

$$+ \frac{1}{2}\int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1-\underline{r}_2|} n(\underline{r}_1)n(\underline{r}_2) - \frac{1}{4}\int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1-\underline{r}_2|} \gamma(\underline{r}_1|\underline{r}_2)\gamma(\underline{r}_2|\underline{r}_1)$$

The TF approximation involves the neglect of the last term, and a plane wave representation for the electron gas, such that

$$\gamma(\underline{r}|\underline{r}') = \frac{2}{\pi}\sum_{k<k_F} e^{-i\underline{k}.\underline{r}} e^{i\underline{k}.\underline{r}'} \qquad 2.3.3$$

The energy functional then becomes

$$E_V[n] = -\frac{1}{\pi}\sum_{k<k_F}\int \nabla^2 e^{i\underline{k}.(\underline{r}-\underline{r}')}\Big|_{\underline{r}'=\underline{r}} d\underline{r}$$

$$+ \int V(\underline{r})n(\underline{r})d\underline{r} + \frac{1}{2}\int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1-\underline{r}_2|} n(\underline{r}_1)n(\underline{r}_2) \qquad 2.3.4$$

The first term of equation 2.3.4 is easily evaluated to give the kinetic energy of a free electron gas.

$$T_o[n] = \frac{3}{10}\int (3\pi^2 n)^{\frac{2}{3}} n d\underline{r} \qquad 2.3.4$$

The electrostatic potential of the system is given by 2.2.9 and 2.2.10;

$$\phi(r) = V(r) + \int \frac{n(\underline{r}')}{|\underline{r}-\underline{r}'|} d\underline{r}'$$

OR

$$\phi(r) = \int \frac{n(\underline{r}') - n_+(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}'$$

Using these results, we write

$$E_V[n] = \frac{3}{10}\int (3\pi^2 n)^{\frac{2}{3}} n d\underline{r} + \int \phi(\underline{r}) n d\underline{r}. \qquad 2.3.5$$

In order to do arbritrary variations of this functional subject to constraint on total number of particles, we introduce the Lagrange parameter μ, such that

$$\frac{\delta E_V[n]}{\delta n(\underline{r})} = \phi(r) + \frac{1}{2}(3\pi^2)^{\frac{2}{3}} n^{\frac{2}{3}} = \mu \qquad 2.3.6$$

or

$$\delta E_V[n] - \mu \delta n(\underline{r}) = 0$$

$$\delta\{E_V[n] - \mu \int n(\underline{r}) d\underline{r}\} = 0 \qquad 2.3.7$$

$$\delta\{E_V[n] - \mu N[n]\} = 0 \qquad 2.3.8$$

where

$$N[n] \equiv \int n(\underline{r}) d\underline{r} = N \qquad 2.3.9$$

From 2.3.6

$$\phi(\underline{r}) + \frac{1}{2}(3\pi^2)^{\frac{2}{3}} n(\underline{r})^{\frac{2}{3}} = \mu \qquad 2.3.10$$

$$n(\underline{r}) = \frac{1}{3\pi^2}\{2[\mu - \phi(\underline{r})]\}^{3/2} \qquad 2.3.11$$

The potential $\phi(\underline{r})$ as defined by 2.2.11 satisfies the Possion equation, hence

$$-\nabla^2 \phi(\underline{r}) = \frac{2^{7/2}}{3\pi}\{[\mu - \phi(r)]\}^{3/2} + 4\pi n_+(r)$$

As has been seen through the above equation the Thomas-Fermi theory is the simplest approximation to the formalism of Hohenberg, Kohn and Sham. In its original form it is an application of the ideas of free-electron gas approximation to a many-electron system in which the potential is not constant. This is done by requiring that the density n and radius of Fermi sphere k_F defined for the former (i.e. free electron system) become functions of $\underline{r}$; so that in analogy to the equation

$$n = \frac{k_F^3}{3\pi^2} ,$$

we can write

$$n(\underline{r}) = \frac{k_F^3(r)}{3\pi^2}$$

The conditions on the TF-theory make it more suitable for metals than other system like atoms and surfaces. The requirement of slowly varying density is not satisfied near the nucleus of an atom, neither is the high density requirement met at large distances in the atom. However, in atoms as Z increases the high density region expands and the assumption of the theory is more nearly satisfied (Elyashar and Koelling, 1977). An additional point arises in the case of insulators and semiconductors which suffer from low density regions, meaning that the applicability of the theory would be doubtful.

It has however been argued that, besides the existence of impurities in most real insulators, the semiconductors in which we are interested are covalent crystals and possess a spatial electronic charge distribution which is rather similar to metals. This is because there are valence electrons in the interestitial region corresponding to covalent bonds, although localised in certain preferred directions (Ashcroft, 1976). Neglecting anisotropic effects, the TF theory can therefore be used for semiconductors with minor modifications and appropriate boundary conditions. (Ambladh & Von Barth, 1984).

2.4 The Weighted density (Gunnarsson et al, Alonso and Girifalco).

and

The Mean Weighted density Schemes (Gunnarsson and Jones)

This is one of the approximation schemes that fall within the class of non local density approximations. It leans on an isotropic behaviour of the electron correlation and attempts an improvement of the spherical average of the exchange-correlation hole. It is to be understood as a means of approximating the exchange-correlatio n charge density using a rather simple modification of the correlation factor for the uniform (homogeneous)

electron gas that conserves the total exchange charge, gives the proper depth of exchange hole, vanishes at large distances from the center of the hole and reduces to the homogeneous gas form when the electron density is constant.

We start by introducing the concepts of exchange and correlation holes and correlation factor.
The exchange-correlation functional $E_{xc}[n]$ of the density functional theory is

$$E_{xc}[n] = \frac{1}{4}\int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1-\underline{r}_2|}\Gamma(\underline{r}_1\underline{r}_2|\underline{r}_1\underline{r}_2) \qquad 2.4.1$$

$\Gamma(\underline{r}_1\underline{r}_2|\underline{r}_1\underline{r}_2) \equiv \Gamma(\underline{r}_1, \underline{r}_2)$ is the two particle density matrix and can be written in terms of one particle and joint density matrices as

$$2\Gamma(\underline{r}_1,\underline{r}_2) = n(\underline{r}_1)n(\underline{r}_2) - \tfrac{1}{2}\gamma(\underline{r}_1|\underline{r}_2)\gamma(\underline{r}_2|\underline{r}_1) \qquad 2.4.2$$

If it is assumed that the motion of one electron is independent of the instantaneous positions of the others, then we should have

$$2\Gamma(\underline{r}_1,\underline{r}_2) = n(\underline{r}_1)n(\underline{r}_2) \qquad 2.4.3$$

i.e. a multiplicative law for the simultaneous occurrence of two independent events.
The antisymmetry of the wavefunction would however not allow this. Hence in general, there is correlation between the motion of any two of the particles, so that

$$2\Gamma(\underline{r}_1, \underline{r}_2) = n(\underline{r}_1)n(\underline{r}_2) + C(\underline{r}_1,\underline{r}_2) \qquad 2.4.4$$

where $C(\underline{r}_1,\underline{r}_2)$ describes the departure from quasi-independence due to correlation.

It is convenient to write

$$2\Gamma(\underline{r}_1,\underline{r}_2) = n(\underline{r}_1)n(\underline{r}_2)\ [1 + g(\underline{r}_1, \underline{r}_2)] \qquad 2.4.5$$

where $g(\underline{r}_1,\underline{r}_2)$ is the correlation factor. From elementary probability theory, the conditional probability of finding a particle at $\underline{r}_2$ when one is known to be at $\underline{r}_1$ is then

$$\frac{2\Gamma(\underline{r}_1,\underline{r}_2)}{n(\underline{r}_1)} = n(\underline{r}_2)\ [1 + g(\underline{r}_1, \underline{r}_2)] \qquad 2.4.6$$

The presence of a particle at $\underline{r}_1$ therefore changes the probability of finding a particle at a second point $\underline{r}_2$ by a fractional amount $g(\underline{r}_1,\underline{r}_2)$ and an absolute amount $n(\underline{r}_2)g(\underline{r}_1,\underline{r}_2)$,

Mutual repulsion between the particles result in a correlation factor which is negative for $\underline{r}_2 \cdots\rightarrow \underline{r}_1$; this therefore creates a 'hole' of depth $n(\underline{r}_2)g(\underline{r}_1,\underline{r}_2)$ around any point where a particle already exists. (CORRELATION HOLE).

If spin is introduced into the above expression, we can argue qualitatively that even for non interacting particles, there is a (like-spin) correlation hole arising merely from the antisymmetry of the wave function. This is called FERMI or EXCHANGE HOLE.

The total conditional probability (for like-spin) gives a SUM RULE;

$$\int n(\underline{r}_2) g(\underline{r}_1, \underline{r}_2) d\underline{r}_2 = -1 \qquad 2.4.7$$

i.e. when a particle is known to be at $\underline{r}_1$ in a particular spin state, the probability of finding a second particle somewhere in the same spin state is reduced by unity.

The weighted density scheme which was due separately to Gunnarsson et al (1977) and Alonso and Girifalco (1978) is an attempt to introduce nonlocality into the exchange-correlation energy functional. This is done by replacing the correlation factor g by its form for the homogeneous electron gas g_h and the density $n(\underline{r}_1)$ by some average $\tilde{n}(\underline{r}_1)$.

$$g(\underline{r}_1, \underline{r}_2) \equiv g(\underline{r}_1, \underline{r}_2 ; n(\underline{r}_1)) = g_h(\underline{r}_1, \underline{r}_2; \tilde{n}(\underline{r}_1)) \qquad 2.4.8$$

where the homogeneous electron gas result (March, 1967) is,

$$g_h(\underline{r}_1, \underline{r}_2; \tilde{n}(\underline{r}_1)) = -\frac{9}{2}\left\{ \frac{\sin k_F r_{12} - k_F r_{12} \cos k_F r_{12}}{(k_F r_{12})^3} \right\}$$

$$k_F = \left[3\pi^2 \tilde{n}(\underline{r}_1)\right]^{\frac{1}{3}}$$

$$r_{12} = |\underline{r}_1 - \underline{r}_2|$$

$\tilde{n}(\underline{r}_1)$ is determined as a kind of average over the exchange hole. Using the above approximation, the exchange-correlation functional is then written as

$$E_{xc}[n] = \frac{1}{2} \int \frac{d\underline{r}_1 d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} n(\underline{r}_1) n(\underline{r}_2) g_h(\underline{r}_1 \underline{r}_2; \tilde{n}(\underline{r}_1)) \qquad 2.4.10$$

The exchange-correlation hole around an electron should contain exactly one electron, and it is described by the quantity

$$n_{xc}(\underline{r}_1,\underline{r}_2) = n(\underline{r}_2)g_h(\underline{r}_1,\underline{r}_2;\ \bar{n}(\underline{r}_1)) \qquad 2.4.11$$

and satisfies the sum rule

$$\int n_{xc}(\underline{r}_1,\underline{r}_2)d\underline{r}_2 = -1. \qquad 2.4.12$$

The weighted density approximation results in substantial improvement of the exchange energy of atoms, but gives poor correlation energies.

To remedy this, Gunnarson and Jones proposed the MODIFIED WEIGHTED DENSITY (MWD) in which the correlation function g_h for the homogeneous electron gas is replaced by a simple analytical function $\bar{g}(\underline{r},n)$.

$\bar{g}(\underline{r}, n)$ is chosen to give;

(i) the correct sum rule

$$\int n\bar{g}(\underline{r}, n)d\underline{r} = -1 \qquad 2.4.13$$

(ii) the correct exchange-correlation energy $E_{xc}^{LDA}[n]$ for a homogeneous system

$$E_{xc}^{LDA}[n] = \tfrac{1}{2}\int V_{xc}(r)\ n_{xc}\ d\underline{r} \qquad 2.4.14$$

They chose for a metal surface, the form

$$\bar{g}(\underline{r},n) = C\{1 - \exp(-\lambda r)^5\} \qquad 2.4.15$$

where C and λ depend on the density n which reproduces the correct assymptotic behaviour of the functional far outside the metal surface.

In order to model the correct long-range behaviour in other systems, one would require different analytic forms of $\bar{g}$.

Pedroza (1984) has added that $\bar{g}(\underline{r}, n)$ be ≥ -1 for all densities in order to obtain good results. Other analytic forms for $\bar{g}$ proposed by the same author include,

$$\bar{g}_1(\underline{r}, n) = (a + br) \exp(-cr^2) \qquad 2\,4.16$$

and

$$\bar{g}_2(\underline{r}, n) = (a + br) \exp(-cr). \qquad 2.4.17$$

These both properly tend to zero at large $\underline{r}$. a, b, c, are functions of density, chosen so that the sum rule is satisfied.

The mean weighted density (MWD) scheme approximate the exchange-correlation energy functional as,

$$E_{xc}[n] = \tfrac{1}{2} \int \frac{d\underline{r}_1 \, d\underline{r}_2}{|\underline{r}_1 - \underline{r}_2|} \, n(\underline{r}_1) n(\underline{r}_2) \bar{g}(|\underline{r}_1 - \underline{r}_2|; \bar{n}(\underline{r}_1)). \qquad 2.4.18$$

The exchange-correlation potential $V_{xc}(\underline{r})$ is then defined by

$$V_{xc}(\underline{r}) = \delta E_{xc}[n] / \delta n(\underline{r}). \qquad 2.4.19$$

2.5 The 'Single q' approximation (Langreth and Mehl)

The work of Langreth and Mehl (1981; 1983; 1984) focuses on a description of exchange-correlation energy beyond the local density approximation in reciprocal space. It provides a workable calculational scheme for inclusion of effects of exchange and correlation in non uniform systems like atoms, molecules, solids, surfaces etc. The true exchange-correlation functional is discussed as a simple function of a multitude of wave vectors and it is argued qualitatively that there is only one of these in addition to k_F(the local Fermi wave vector) which is important.

They started by writing the exchange-correlation energy of a nonuniform system as

$$E_{xc}[k_F] = \frac{e^2}{4\pi^3} \int d^3r \, k_F^4 \, W[k_F] \qquad 2.5.1$$

where

$$k_F \equiv k_F(\underline{r}) = [3\pi^2 n(\underline{r})]^{\frac{1}{3}}$$

is the local Fermi wavevector and W is a dimensionless quantity of the order of unity given by

$$W[k_F] = W_{LDA}(k_F) + \delta W \qquad 2.5.2$$

W_{LDA} is the LDA result

$$W_{LDA}(k_F) = -\left(1 + \frac{\varepsilon_c}{\varepsilon_x}\right) \qquad 2.5.3$$

ε_c and ε_x are local values of correlation and exchange energies per particle respectively.

$$\varepsilon_x = \frac{-3k_F}{4\pi} \qquad 2.5.4$$

W is the deviation from the local approximation. In this scheme W is to be thought of as a function of a presumably infinite number of variables q_0, $q_1 \ldots q_n \ldots$ determined from k_F.

These wave vectors can be taken as inverse lengths; the first q_o being taken as k_F. Going beyond the LDA amounts to identifying which inverse lengths(other than k_F) derivable from a density destribution have the greatest effect on the systems exchange-correlation energy.

In relation to density variation, the most important lengths are those which define the scale over which the density varies; some examples include;

(i) planar metallic surfaces, where in addition to k_F^{-1}, the next most important length must be the width (or healing length) of the surface layer.

(ii) In a tightly bound orbital in an atom or molecule or solid this length must be the size of the orbital.

(iii) In a slowly varying valence state such as in a solid, it presumably can be related to the derivative of the density.

As already mentioned, the first basic assumption of this scheme is that there is just one length ξ for each $\underline{r}$, which characterizes the scale over which the density varies.

$$q_1 \approx q_3 \approx q_4 = \ldots\ldots = \xi^{-1} \equiv q \qquad 2.5.5$$

The value of q is such that the validity criterion of the LDA is $q \ll k_F$ and $\frac{q^2}{k_F^2}$ is the fractional correction to the LDA. The approximation $q \ll k_F$ is reasonable in the examples given above.

Equation 2.5.2 can then be rewritten incorporating the fractional correction to the LDA explicity as;

$$W[k_F] \quad W(k_F, q) \equiv W_{LDA}(k_F) + Z(k_F, q) \frac{q^2}{k_F^2} \qquad 2.5.6$$

where

Z is a dimensionless quantity of the order of unity.

The simplest reasonable form of q chosen is

$$q(\underline{r}) \equiv \frac{1}{\xi} = \frac{|\vec{\nabla} k_F(\underline{r})|}{2k_F(\underline{r})} \qquad 2.5.7$$

For sufficiently slowly varying disturbances, this gives exact results when substituted into equation 2.5.6. By exact, it is meant that previous gradient expansion results due to Resolt and Geldart (1975; 1976), Ma and Brueckner (1968) Langreth and Perdew (1980) are reproduced if q is set to zero in $Z(k_F, q)$ and it is expanded.

It is also argued that this choice of q is reasonable because we are dealing with systems in or nearly in equilibrium under their own internal forces resulting from Coulombic interaction and density variations with length Scales that are grossly inconsistent with this q probably do not occur in such systems.

To determine the form of Z, a wave vector decomposition of E_{xc} is first done.

$$E_{xc}(\underline{k}) = \int \frac{d^3k}{(2\pi)^3} V(\underline{k})\tilde{S}(\underline{k}, n) \qquad 2.5.7$$

where

$V(\underline{k}) = \frac{4\pi}{K^2}$ is the coulomb potential in Fourier space.

$$\tilde{S}(\underline{k}, n) = 1 + \tfrac{1}{2}\int n(\underline{r})n(\underline{r}')\{\tilde{g}(\underline{r}, \underline{r}') - 1\}e^{i\underline{k}\cdot(\underline{r}-\underline{r}')}d^3rd^3r'$$

where

$g(\underline{r}, \underline{r}')$ is the pair correlation function

Equation 2.5.7 is rewritten as:

$$E_{xc}(\underline{k}, n) = E_{xc}^{LDA}(\underline{k}, n) + \frac{1}{2\pi k^2}\int d^3r k_F^2 Z_{xc}(k_F, q; k)q^2 \qquad 2.5.8$$

Here,

$$Z_{xc}(k_F, q) = \int_0^\infty d\underline{k}\ Z_{xc}(k_F, q; k) \qquad 2.5.9$$

where

$Z_{xc}(k_F, q; k)$ is the wave vector decomposition of $Z_{xc}(k_F, q)$.

For small q which represents the most important contribution to Z, they split Z into Z_c and Z_x (contributions to correlation and exchange energies) and investigate the variation of these over 3-wave vector scales.

This idea was due to Nozieres and Pines (1958) who showed that it is useful in the calculation of the energy of an infinite (Bulk) electron gas to decompose the correlation energy into a sum of fluctuations over different wave vectors, and to use one approximation for small wave vector and another for large.

By a set of subtle arguments, Langreth and Mehl arrive at forms for Z_c and Z_x as,

$$Z_c(k_F, q) = \int_0^\infty d\underline{k}\, Z_c(k_F, q;k)$$
$$= Z_c(k_F,0) - \int_0^{k_c} d\underline{k}\, Z_c(k_F, o;k)$$
$$= 2 - \int_o^{k_c} \frac{4\sqrt{3}}{k_{FT}} \exp\left(\frac{-2\sqrt{3}k}{K_{FT}}\right) dk$$

or

$$Z_c(k_F, q) = 2 \exp\left(\frac{-2\sqrt{3}}{K_{FT}} k_c\right) \qquad 2.5.10$$

where k_{FT} is the Thomas-Fermi wave vector given as

$$k_{FT} = \left(\frac{\Pi}{4} a_o k_F^3\right)^{\frac{1}{2}}$$
$$k_c = 6fq$$
$$Z_x(k_F, q;k) = Z_x(k_F, 0;k) \text{ for all } q$$

and

$$Z_x(k_F, q) = -\frac{7}{9} \qquad 2.5.11$$

The nonlocal contribution to E_{xc} is then

$$E_{xc}^{NL} = -\frac{e^2}{16\Pi^3} \int d^3r |\vec{\nabla} k_F(\underline{r})|^2 \left\{2\exp\left(\frac{-2\sqrt{3}}{K_{FT}} k_c\right) - \frac{7}{9}\right\} \qquad 2.5.12$$

putting n as the basic variable instead of k_F, gives the total exchange-correlation energy as:

$$E_{xc}[n] = E_{xc}^{LDA}[n] + a\int d^3r \frac{|\nabla n(\underline{r})|^2}{|n(\underline{r})|^{4/3}} (2e^{-F} - 7/9)$$

where

$$F = b|\vec{\nabla} n(\underline{r})| / [n(\underline{r})]^{7/6} \qquad 2.5.14$$

$$a = \pi / [16(3\pi^2)^{4/3}] = 2.1435 \times 10^{-3} \qquad 2.5.15$$

$$b = (9\pi)^{1/6} f = 1.745f \qquad 2.5.16$$

f is an adjustable parameter

f ~ 0.13 for surfaces

f ~ 0.17 for atoms

and

f ~ 0.15 for solids

We will adopt this last value in our treatment.

The full expression for the exchange-correlation functional $E_{xc}[n]$ is

$$E_{xc}[n] = A\int d^3r[n(r)]^{4/3} + a\int d^3r \frac{|\vec{\nabla} n(r)|^2}{[n(r)]^{4/3}} (2e^{-F} - 7/9) \qquad 2.5.17$$

To bring out more explicitly the 'single q' approximation character we would rewrite $E_{xc}[n]$ as,

$$E_{xc}[n] = E_{xc}[n;q] \qquad 2.5.18$$

so that

$$E_{xc}[n;q] = E_{xc}[n;k_F] + E_{xc}[n;q_T] \qquad 2.5.19$$

corresponds to local and nonlocal contributions to the exchange-correlation functional respectively.

Equation 2.5.17 is then written as

$$E_{xc}[n;q] = A\int d^3r[n(r)]^{4/3} + a\int d^3r \frac{|\vec{\nabla} n(\underline{r})|^2}{[n(\underline{r})]^{4/3}} (2e^{-F} - 7/9) \qquad 2.5.20$$

where

$$A = -\frac{3}{4}\frac{(3\pi^2)^{\frac{1}{3}}}{\pi}\beta \qquad 2.5.21$$

β, being the correlation enhancement factor for the local term given by Hedin and Lundquist (1971) as,

$$\beta = 1 + Cx\ln(1 + 1/x) \qquad 2.5.22$$

$$x = \frac{0.0914}{k_F} \quad , \quad C = 0.7734$$

One can calculate a non-local exchange-correlation contribution to the kinetic energy. This contribution, $t_{xc}(n;q)$, is given by the same authors to be

$$t_{xc}(n;q) = -\frac{8d|\vec{\nabla} n|^2}{n^{7/3}}(2e^{-F} - 7/9) + 7ab\frac{|\vec{\nabla} n|^3}{n^{7/2}}e^{-F} \quad 2.5.28$$

Its contribution to the chemical potential is

$$\mu_{t_{xc}}(n;q) = \frac{d}{dn}[nt_{xc}(n;q)] \quad 2.5.29$$

This idea of exchange-correlation contribution to kinetic energy is in line with our earlier argument that any non locality in kinetic energy will be closely related to nonlocality in exchange-correlation energy. We have however not included t_{xc} in the present calculation as its effect is still being investigated.

Equation 2.5.25 can be rewritten as:.

$$\mu_{xc}(n;q) = \frac{-(3\pi^2 n)^{\frac{1}{3}}}{\Pi}\beta - \frac{4}{3}a\frac{|\vec{\nabla} n|^2}{n^{8/3}}\cdot n^{\frac{1}{3}}(2e^{-F} - 7/9) + \frac{7}{3}a\frac{|\vec{\nabla} n|^2}{n^{8/3}}\cdot n^{\frac{1}{3}}\cdot\frac{b|\vec{\nabla} n|}{n^{7/6}}e^{-F}$$

making use of the substitutions;

$$q = \frac{|\vec{\nabla} n|}{6n}, \quad k_F = (3\pi^2 n)^{\frac{1}{3}}$$

$$\delta = \frac{q^2}{k_F^2} = \frac{|\vec{\nabla} n|^2}{36(3\pi^2)^{2/3} n^{8/3}}$$

$$\frac{|\nabla n|^2}{n^{8/3}} = 36(3\pi^2)^{2/3}\delta$$

$$a = \frac{\pi}{16(3\pi^2)^{4/3}}$$

$$a \frac{|\vec{\nabla} n|}{n^{8/3}} \cdot n^{\frac{1}{3}} = \frac{3k_F}{4\pi}\delta$$

$$\frac{b|\vec{\nabla} n|}{n^{7/6}} = F$$

μ_{xc} becomes

$$\mu_{xc}(n;q) = -\frac{k_F}{\pi}\left[\beta + \delta(2e^{-F} - 7/9 - 7/4Fe^{-F})\right] \qquad 2.5.30$$

or

$$\mu_{xc}(n;q) = -\frac{k_F}{\pi}\left[\beta + g\,\delta\right] \qquad 2.5.31$$

where

$$2e^{-F} - 7/9 - 7/4Fe^{-F}$$

At absolute zero of temperature, the chemical potential gives the Fermi energy. The total energy is a sum of kinetic and exchange-correlation contributions, therefore

$$E_F = \frac{k_F^2}{2}(1 - \delta) - \frac{k_F}{\pi}(\beta + g\delta) \qquad 2\,5.32$$

The parameters δ, β and g are defined as

$$\delta = \frac{q^2(r)}{k_F^2(r)} \qquad 2.5.33$$

$$\beta = 1 + cx \ln(1 + 1/x) \qquad 2.5.34$$

$$g = 2e^{-F} - 7/9 - 7/4Fe^{-F} \qquad 2.5.35$$

where

$$x = \frac{0.0914}{k_F(r)} \qquad 2.5.36$$

$$c = 0.7734 \qquad 2.5.37$$

and

$$F = \frac{b|\vec{\nabla} n(\underline{r})|}{n(\underline{r})^{7/6}} = 6fq(\underline{r})(3\pi/k_F(r))^{\frac{1}{2}} \qquad 2.5.38$$

CHAPTER 3

DIELECTRIC SCREENING

3.1 Dielectric function

The concept of dielectric function can be formulated by considering the response of an electron gas to the presence of an impurity point charge. The presence of the impurity causes a polarization of the medium which results in the screening of the coulomb interaction between the impurity and the electrons. The screening of a charge disturbance in a real system is of two kinds (Friedel, 1954; Noziers and Pines, 1958).

The first corresponds to the influence of the intraband transitions. In this case the electrons are free to respond spatially to the perturbation and so alter the potential of an external charge Z from Z/r to $Z/r \exp(-\alpha r)$ where α depends on the density of the medium and represents inverse lengths of the order of interparticle spacing for some solids.

The second corresponds to the influence of inter band transitions (the case where electrons do not respond spatially) which reduce the potential from Z/r to $Z/r\epsilon$, where ϵ is the dielectric function . This case describes more the response of insulators and semiconductors in presence of impurity, while the first case refers to metals. In the vicinity of the impurity, the expression for the screened impurity potential is very complicated and depends on the

type of impurity. Generally speaking, the treatment of dielectric response falls into two classes (linear and nonlinear response), and in each case, the results obtained are different for positive and negative charged impurities. Within the framework of the electron gas model, a positively charged impurity, like a proton, for example, would provide a very strong perturbing potential to the electron gas resulting in a large and rapidly varying electron pile up around the impurity. The problem would then require a treatment that is nonlinear as well as non-local. (Friedel, 1952; Ambladh et al, 1976).

A negative charged impurity on the other hand gives rise to additional complication by creating a coulomb hole around itself, within which electrons are forbidden to exist. This again demands nonlinear treatment as well as a redefinition of some of the usual boundary conditions. A linear response theory is useful only when the impurity charge is sufficiently weak so as to produce only linear response within the electron gas.

In real solids it is assumed that core states of the atoms comprising the solid are sufficiently tightly bound so that local field corrections are of little significance; in other words dielectric screening involves all the valence electrons and is comparatively insensitive to the details of the band structure (Ehrenreich and Cohen, 1959; Penn, 1962).

Most of the early work on impurity screening was done for metals using the Thomas-Fermi method (Mott, 1936) in the treatment of a homogeneous and isotropic degenerate electron gas model (Friedel, 1954; Alfred and March, 1955; 1956; March, 1957). Since this model is a system of continuous states, more nearly suited to metals, questions obviously arise as to how adequate a tool, the Thomas-Fermi method is, in the treatment of other systems like insulators and semiconductors which suffer from depleted state density in the gap. It is however argued that the covalent crystals in which we are here interested have appreciable electronic charge density residing between the ions (forming so-called covalent bonds). These electrons involved in the covalent bonds are loosely bound and rather than being strongly localized in the neighbourhood of the ion cores, they are localized in the vicinity of the lines joining each ion to its nearest neighbours. This means that covalent crystals have a spatial electronic distribution that is not very much different from metals, and with adequate account of nonlocality and isotropy taken the TF method would be a useful tool in treatment of such systems. (Ashcroft, 1976)

In Gaussian units, the electric displacement is related to charge density as

$$\nabla . \underline{D} = 4\pi\rho \qquad 3\,1.1$$

If we consider a cubic semiconductor crystal in presence of an electric field $\underline{E}$ parallel to $\underline{k}$, then the static longitudinal wavevector dependent dielectric function $\epsilon(\underline{k})$ which describes the response of the crystal to this field is found from

$$\underline{D}e^{i\underline{k}\cdot\underline{r}} = \epsilon(\underline{k})\underline{E}e^{i\underline{k}\cdot\underline{r}}$$

This field and the charge density generating it satisfy poisson's equation;

$$\vec{\nabla}\cdot\underline{D} = \vec{\nabla}\cdot(\epsilon\underline{E}) = \epsilon\vec{\nabla}\cdot\underline{E} = 4\pi\rho \qquad 3.1.2$$

using $\underline{E} = -\vec{\nabla}V$ in this equation, we get,

$$\epsilon\nabla^2 V = -4\pi\rho$$

In Fourier space, the potential becomes

$$V(\underline{k}) = \frac{4\pi\rho(\underline{k})}{k^2\epsilon(\underline{k})} \qquad 3.1.4$$

This is rewritten in terms of the unscreened impurity potential as

$$V(\underline{k}) = \frac{V_o(\underline{k})}{\epsilon(\underline{k})} \qquad 3.1.5$$

where

$$V_o(\underline{k}) = \frac{4\pi}{k^2}\rho(\underline{k}) \qquad 3.1.6$$

The above expression for $V(\underline{k})$ is a consequence of the assumption that the unscreened potential is local. It should be noted that in general V and ρ are functions of time and hence of frequency in $\underline{k}$-space, but since for

most applications, we are interested in either static fields or fields varying with phonon frequency, we would neglect frequency dependence in the present treatment. Until recently, all approaches to the problem of dielectric screening in semiconductors were in $\underline{k}$-space (Bassani et al, 1974; Penn, 1962 Srinivasan, 1969; Walter and Cohen, 1970). Besides the cumbersome computations involved, this meant that only linear effects could be studied due to the linearity of Fourier transform. Only a few years ago, however, Resta (1977) used an $\underline{r}$-space approach to develop a general theory of screening in semiconductors in which the Thomas-Fermi Screening equation was explicitly solved to obtain a closed analytical expression for the spatial dielectric function $\bar{\varepsilon}(r)$.

Although the TF method has been widely used for metals with appreciable success, Kohn and Sham (1965) have shown that the assumption of homogeneous electron gas leads to inaccurate results. Hohenberg and Kohn (1964) put forward a theorem to the effect that the total energy of an interacting electron-gas in an external potential can be written as a unique functional of the local density (equation 2.2.2). The exact form of this functional which incorporates all the many-body effects is unknown and the TF theory provides the simplest approximation to it. Hence in their formulation

they showed that the TF scheme is equivalent to the Euler-Lagrange equation obtained by constrainted minimization of the unique functional.

There are however several conditions on the theory which make it more appropriate for a metal, as already mentioned, than for other systems like atoms, surfaces, insulators and semiconductors. This leads us to seek corrected versions of the theory with effects of exchange-correlation and nonlocality incorporated. Already there have been several steps in this direction (Scavinsky, 1983; Scarfone, 1984; Elegba and Amali, 1986a,b). The effects of nonlocality are introduced into the present treatment using results based on Langreth and Mehl's reciprocal space formulation of the preceding chapter.

3.2 Calculations.

In the absence of any external disturbance the homogeneous and isotropic model solid has a uniform electron density n_o, given as

$$n_o = \frac{k_F^3}{3\Pi^2} \qquad 3.2.1$$

where k_F (the valence Fermi momentum) is the radius of the spherical region occupied in k-space by the ground state of the system. If a static impurity point-charge of potential

$$V_o(r) = \pm Z/r \qquad 3.2.2$$

(Spherical symmetry is assumed throughout this chapter)

is introduced into the system, there is a redistribution of charges resulting in $V_o(r)$ being screened to give an effective screened potential $V(r)$. Also the electrons in the vicinity of the charge impurity will take on various values of kinetic energy depending on the potential they 'feel'.

We shall first of all take the case where the charge impurity is positive in which case, an excess of negative charges will be created around it. In a region about any point r, we can define a local Fermi energy $E_F(r)$. An equilibrium condition for no diffusion of electrons is reached where

$$E_F(r) + V(r) = E_F + V(R) \qquad 3\ 2.3$$

here, R is the screening radius beyond which $V(r)$ has the Coulomb form screened by the static macroscopic dielectric constant $\varepsilon(o)$. $V(R)$ is a constant and E_F is the ambient Fermi energy.

The TF theory assumes that equation 3.2.1 holds even for a nonuniform system.

$$n(r) = \frac{k_F^3(r)}{3\Pi^2} \qquad 3.2.4$$

The displaced electron density is related to the screened potential by the oisson equation.

$$-\nabla^2 V(r) = 4\Pi\left[n(r) - n_o\right] \qquad 3.2.5$$

We proceed to establish a general solution to this equation within the framework of the Thomas-Fermi-Dirac theory using the expression of $E_F(r)$ obtained in Eq 2.5.32 which has the effects of inhomogeneity incorporated. As a first systematic improvement we use a reduced version of $E_F(r)$ which excludes exchange-correlation contribution to kinetic energy

$$E_F(r) = \frac{k_F^2(r)}{2}(1-\delta) - \frac{k_F(r)}{\Pi}\{\beta + g\delta\} \qquad 3.2.5$$

where δ, β and g are given by equations 2.5.33, 2.5.34 and 2.5.35 respectively.

Our main approximation in this work is to give the parameters δ, β and g global interpretations, although in principle, it is seen from their definitions that they are functions of position $\underline{r}$.

Introducing an exchange parameter γ defined as

$$\gamma = \frac{1}{2^{\frac{1}{2}}\Pi} \qquad 3.2.6$$

we rewrite equation 3 2.5 as

$$E_F(r) = \frac{k_F^2(r)}{2}(1-\delta) - k_F(r)\,2^{\frac{1}{2}}\gamma(\beta + g\delta)$$

This gives

$$k_F(r) = \frac{2^{\frac{1}{2}}\gamma(\beta + g\delta) \pm \sqrt{2\gamma^2(\beta + g\delta)^2 + 2(1-\delta)E_F(r)}}{(1-\delta)}$$

using $E_F(r) = E_F + V(R) - V(r)$ from equation 3.2.3, we get

$$k_F(r) = \frac{2^{\frac{1}{2}}}{(1-\delta)}\left\{\gamma(\beta + g\delta) + \sqrt{\gamma^2(\beta + g\delta)^2 + (1-\delta)\left[E_F + V(R) - V(r)\right]}\right\}$$

This is a generalization of all earlier results obtained by Resta (1977) and Scarfone (1984).

The linearized Poisson equation can be solved in spherical coordinates:

$$\frac{d^2V(r)}{dr^2} + \frac{2}{r}\frac{dV(r)}{dr} - Q^2V(r) = -Q^2V(R) \qquad 3.2.24$$

The homogeneous equation

$$\frac{r^2d^2V(r)}{dr^2} + 2r\frac{dV(r)}{dr} - Q^2r^2V(r) = 0 \qquad 3.2.25$$

is equivalent to the transformed Bessel's equation. Since the potential is a real quantity, we take the real part of the solution to this equation, which is

$$V(r) = -\frac{1}{r}\left\{\alpha e^{Qr} + \beta e^{-Qr}\right\} \qquad 3.2.26$$

where α and β are real constants. If the point charge impurity is of multiplicity Z,

$$V(r) = -\frac{Z}{r}\left\{\alpha e^{Qr} + \beta e^{-Qr}\right\} \qquad 3.2.27$$

The particular integral is $V(R)$, so the general solution becomes

$$V(r) = -\frac{Z}{r}\left\{\alpha e^{Qr} + \beta e^{-Qr}\right\} + V(R) \qquad 3.2.28$$

In the case of dielectric screening in metals, the potential is completely screened only at infinity and tends to the Coulomb form at the origin;

$$\therefore \quad V(r) = \frac{e^{-Qr}}{r} \quad \text{for metals} \qquad 3.2.29$$

The boundary conditions used to describe incomplete screening in semiconductors are:-

$$\lim_{r \to 0}[rV(r)] = \lim_{r \to 0}[rV_o(r)] = -Z$$

and

$$V(R) = \frac{V_o(R)}{\epsilon(o)} = \frac{-Z}{\epsilon(o)R} \qquad 3.2.31$$

where

$$V_o(r) = \frac{-Z}{r} \qquad 3.2.32$$

using these conditons in the expression for V(r), we get

$$\alpha + \beta = 1 \qquad 3.2.33$$

and

$$\alpha = -\beta e^{-2QR} \qquad 3.2.34$$

From these two equations,

$$\beta(1 - e^{-2QR}) = 1$$

or

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$$\beta = \frac{1}{1 - e^{-2QR}} \qquad 3.2.35$$

and

$$\alpha = -\frac{e^{-2QR}}{1 - e^{-2QR}} \qquad 3.2.36$$

equation 3.2.28 is then rewritten as

$$V(r) = \frac{-Z}{r}\left\{ - \frac{e^{+Qr-2QR}}{1-e^{-2QR}} + \frac{e^{-Qr}}{1-e^{-2QR}}\right\} + V(R)$$

$$= -\frac{Z}{r}\left\{\frac{e^{-Qr}}{e^{-QR}(e^{QR}-e^{-QR})} - \frac{e^{Qr-2QR}}{e^{-QR}(e^{QR}-e^{-QR})}\right\} + V(R)$$

$$= \frac{-Z}{r}\left\{\frac{e^{QR-Qr} - e^{-(QR-Qr)}}{e^{QR} - e^{-QR}}\right\} + V(R)$$

$$= \frac{-Z}{r}\,\frac{\sinh Q(R-r)}{\sinh QR} + V(R)$$

$$V(r) = \frac{-Z}{r}\,\frac{\sinh Q(R-r)}{\sinh QR} + V(R) \qquad r < R \qquad 3.2.37$$

The spatial dielectric function $\bar{\varepsilon}(r)$ which characterizes the response of the semiconductor to a static impurity point charge Z at $r = 0$, is conventionally defined as

$$\bar{\varepsilon}(r) = \frac{V_o(r)}{V(r)} \qquad r \leq R \qquad 3.2.38$$

where $V_o(r)$ and $V(r)$ are unscreened and screened potentials respectively. The screened impurity potential beyond the screening radius R is

$$V(r) = \frac{V_o(r)}{\varepsilon(o)} \qquad r \geq R \qquad 3.2.39$$

where $\varepsilon(o)$ is the static dielectric constant. At the screening radius R,

$$V(R) = \frac{-Z}{\varepsilon(o)R} \qquad 3.2.40$$

so that

$$V(r) = -\frac{Z}{r}\,\frac{\sinh Q(R-r)}{\sinh QR} - \frac{Z}{\varepsilon(o)R} \qquad 3.2.41$$

using the condition that there is continuity of the electric field

$$\underline{E} = -\dot{\nabla}V \qquad 3.2.42$$

for $r \leq R$

$$E(r) = \frac{Z}{r^2}\,\frac{\sinh Q(R-r)}{\sinh QR} + \frac{ZQ}{r}\,\frac{\cosh Q(R-r)}{\sinh QR}$$

and for $r > R$

$$E(r) = \frac{Z}{\varepsilon(o)r^2}$$

so that

$$\frac{Z}{\varepsilon(o)R^2} = \frac{Z}{R^2}\,\frac{\sinh Q(R-R)}{\sinh QR} + \frac{ZQ}{R}\,\frac{\cosh Q(R-R)}{\sinh QR}$$

$$= \frac{1}{R}\,\frac{ZQ}{\sinh QR}$$

or

$$\frac{\sinh QR}{QR} = \varepsilon(o) \qquad 3.2.43$$

From this equation one obtains the screening radius. The definition of the spatial dielectric function is

$$\bar{\epsilon}(r) = \frac{V_o(r)}{V(r)} = \frac{-Z}{rV(r)} \qquad r \leq R$$

putting V(r) from 3.2.41 into this equation we get,

$$\bar{\epsilon}(r) = \frac{-Z}{r} \Big/ \left[\frac{-Z}{r} \frac{\sinh Q(R-r)}{\sinh QR} - \frac{Z}{\epsilon(o)R}\right]$$

$$= \frac{-Z}{r} \Big/ \left[\frac{-Z \sinh Q(R-r)}{rQR\epsilon(o)} - \frac{Z}{\epsilon(o)R}\right]$$

$$= \frac{1}{\frac{1}{QR\epsilon(o)}\left[\sinh Q(R-r) + Qr\right]}$$

or

$$\bar{\epsilon}(r) = \frac{QR\epsilon(o)}{\sinh Q(R-r) + Qr} \qquad r \leq R \qquad 3.2.44$$

In the region $r \geq R$, $\bar{\epsilon}(r)$ simply reduces to its static value $\epsilon(o)$ i e.

$$\bar{\epsilon}(r) = \epsilon(o) \qquad r \geq R$$

In general, the Thomas-Fermi equation comes out in a nonlinear form and as mentioned earlier most problems involving impurity screening give rise to nonlinear response and hence would be better treated with the nonlinear theory.

The non linear Poisson equation (incorporating effects of nonlocality) obtained in the last section is,

$$-\nabla^2 V(r) = 4\pi\left[n(r) - n_o\right]$$

or

$$-\nabla^2 V(r) = \frac{2^{7/2}}{3\pi(1-\delta)^3}\left[\left\{\left[\gamma(\beta+\delta g)+\left[\gamma^2(\beta+g\delta)^2+(1-\delta)\left[E_F+V(R)-V(r)\right]\right]^{\frac{1}{2}}\right\}^3 - \left\{\gamma(\beta+\delta g)+\left[\gamma^2(\beta+g\delta)^2+(1-\delta)E_F\right]^{\frac{1}{2}}\right\}^3\right] \quad 3.2.45$$

obtaining the self-consistent screened potential around an impurity donor or acceptor ion in the semiconductors of interest (diamond, silicon and germanium) involves solving this nonlinear equation numerically. For positive values of Z, the potential satisfies the poisson and Laplace equations for $r \leq R$ and $r \geq R$ respectively. Other conditions include potential tending to the assymptotic values $\frac{Z}{r_c(o)}$ and $\frac{-Z}{r}$ for large and small values of r, respectively; and continuity of the potential and electric field at r = R.

For negative impurity, a region free of any electrons and corresponding to negative kinetic energy called Coulomb hole is created. This means that the Poisson equation 3.2.45 would no longer be valid everywhere. It's region of validity would rather be subject to the constraint

$$E_F(r) = E_F + V(R) - V(r) \geq 0 \quad \text{for } r \geq R_c$$

or

$$V(r) \leq E_F + V(R) \quad , \quad r \geq R_c \qquad 3.2.46$$

The equality holds at $r = R_c$, where R_c is the radius of the Coulomb hole. The Poisson equation is then rewritten differently for three regions of space in the case of negative impurities.

These are:

$$\nabla^2 V(r) = \frac{2^{7/2}}{3\pi(1-\delta)^3}\left[\gamma(\beta+g\delta)+\left\{\gamma^2(\beta+g\delta)^2+(1-\delta)\,E_F\right\}^{\frac{1}{2}}\right]^3,$$

$$\text{for} \quad 0 < r \leq R_c \qquad 3.2.47$$

$$\nabla^2 V(r) = \frac{2^{7/2}}{3\pi(1-\delta)^3}\left[\left[\left\{\gamma(\beta+g\delta)+\left[\gamma^2(\beta+g\delta)^2+(1-\delta)E_F\right]^{\frac{1}{2}}\right\}^3 - \left\{\gamma(\beta+g\delta)+\left[\gamma^2(\beta+g\delta)^2+(1-\delta)\left[E_F+V(R)-V(r)\right]\right]^{\frac{1}{2}}\right\}^3\right]$$

$$\text{for,} \quad R_c \leq r \leq R; \qquad 3.2.48$$

$$\nabla^2 V(r) = 0 \qquad \text{for } R \leq r < \infty \; ; \qquad 3.2.49$$

The boundary conditions on the linear theory also apply to these equations. In the hole region, the solution of equation 3.2.47 is

$$V(r) = \frac{-Z}{r} + \frac{2^{5/2}}{9\pi}\left[\gamma(\beta+g\delta)+\left\{\gamma^2(\beta+g\delta)^2+(1-\delta)\,E_F\right\}^{\frac{1}{2}}\right]^3 r^2 + \alpha \qquad 3.2.50$$

where α is the constant of integration to be determined from the continuity of $V(r)$ at $r = R_c$.

CHAPTER 4

RESULTS AND DISCUSSION

The equations used in the present calculations are basically of Thomas-Fermi origin, but with exchange-correlation and inhomogeneity included. Before proceeding to state our results, we make a brief review of the defects (L.H.Thomas, 1960) of the classical Thomas-Fermi theory and the consequent corrections leading to the present form of its expression. The Thomas-Fermi method in its classical formulation;

(a) overestimates the total energy of systems like atoms.

(b) leads to an infinite density at the nucleus and a fall off like $1/r^6$ at large r contrary to the quantum mechanics prediction of uniform distribution at the center and a smooth exponential fall off at large r.

(c) does not exhibit the important Friedel oscillations of the electron density in presence of impurity and the quantum density oscillations corresponding to shell structure. This is because it is essentially a statistical theory and naturally averages out the shells.

(d) neglects exchange and correlation effects among electrons.

The corrections so far introduced into the TF theory include the following:

(i) The inclusion of Dirac's correction

$$-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int n^{4/3}(\underline{r})d\underline{r}$$

which takes into account exchange. This correction reduces the energy calculated by the TF theory but also gives rise to a discontinuity in the electron density distribution.

(ii) Among the several methods suggested for including correlation (e.g. Slater, Wilson and Wood, 1969; Hedin and Lundquist, 1971), the above expression for exchange is simply multiplied by a factor of β as suggested by Hedin and Lundquist to account for correlation

$$\beta = 1 + Bx\ln(1 + \frac{1}{x})$$

where $x = 0.0914$ and $B = 0.7734$. This method is consistent with our arguement that exchange-correlation is better accounted for by not separating them.

and Gunnarsson and Jones, and the reciprocal space formulation of Langreth and Mehl have been discussed in Chapter 2. The results of the latter are used in the actual calculation.

As already noted, it is desirable that any non-local treatment for E_{xc} be necessarily used for the kinetic energy as well. This is because the kinetic and correlation energies are related through the two particle density matrix, hence any non locality in the kinetic energy would likely be closely related to that of exchange-correlation. Infact, it has been recently shown that there is an additional contribution to kinetic energy arising from exchange-correlation (Bass, 1985 ; Elegba, 1986) as given by equations 2.5.27 and 2 5.30. The effect of this contribution on the present work, is however, still under investigation, hence it is not included in our calculations.

The first step in this calculation is the evaluation of Langreth and Mehl's 'single q' which is given as

$$q = |\vec{\nabla} n|/6n$$

In our approximation we assume a spherical Fermi surface for the semiconductors (diamond. silicon and germanium) under consideration and proceed to calculate the appropriate q using density corresponding to s-orbitals occupied by the valence electrons. These orbitals are 2s, 3s and 4s for

diamond (carbon), silicon and germanium respectively. Also in an effort to keep the calculations simple, the single exponential function has been used to describe an atomic orbital in the self-consistent field (SCF) approach as prescribed by Clementi and Raimondi (1963). Once q is known, the correction to the LDA, δ, arising from the inhomogeneity in density can then be evaluated as

$$\delta = \left(\frac{q}{k_F}\right)^2$$

where q^2 is twice the Weisszacker correction to the kinetic energy.

The results obtained in the previous chapter namely equations 3.2.5, 3.2.19, 3.2.24, 3.2.43, and 3.2.44 are applied to study the screening characteristics of the group IV Semiconducting elements, notably silicon and germanium. Diamond is however, included for completness although diamond (carbon) has a relatively large energy gap compared to the others in the group. For each of the elements we have four possible cases;

(i) $\gamma = 0, \quad \delta = 0, \quad$ TF - LDA

(ii) $\gamma = 0, \quad \delta \neq 0 \quad$ TF - NLDA

(iii) $\gamma \neq$, $\quad \delta = 0 \quad$ TFD - LDA

(iv) $\gamma \neq 0, \quad \delta \neq 0 \quad$ TFD - NLDA

This means that for each element four values of the Fermi energy E_F, the screening radius R and the quantity Q corresponding to these four cases above are calculated. The results are displayed in Tables 1, 2, 3 for silicon, Germanium and Diamond respectively. As seen from the last chapter, the linearization process involved a binomial expansion in which the approximation

$$\left| \frac{[V(R) - V(r)](1 - \delta)}{\gamma^2(\beta + g\delta) + (1 - \delta)E_F} \right| << 1$$

was made. This inequality, however does not hold for all values of r between the origin (position of impurity) and the screening radius R. Hence a region of validity of the linearization, given as (R - r) is established in all cases considered using the value of r for which the above inequality becomes an equality. This investigation is done for values of z up to 4. The results of these are also included in Tables 1, 2 and 3.

Finally, making use of equation 3.2.44, the spatial dielectric functions $\bar{\varepsilon}(r)$ for silicon, germanium and diamond are evaluated and displayed in Figs. 1 - 3. A study of the parameters listed in Tables 1, 2, 3 show some important trends with each systematic correction and we go on to discuss these briefly.

Table 1: Results for silicon. Values arising from inclusion of correlation are in parentheses.

	TF-LDA	TF-DLDA	TFD-LDA	TFD -NLDA
Fermi energy E_F	0.461	0.446	0.155(0.100)	0.263(0.167)
Q	1.106	1.315	1.352(1.417)	1.551(1.740)
Screening radius R	4.275	3.593	3.495(3.335)	3.048(3.716)
r(z=1)	0.849	0.932	1.098(1.148)	1.015(1.033)
Region of validity R-r	3.426	2.661	2.397(2.187)	2.033(1.683)
r(z=2)	1.178	1.240	1.420(1.464)	1.300(1.298)
R-r	3.097	2.353	2.075(1.871)	1.748(1.418)
r(z=3)	1.393	1.436	1.620(1.659)	1.477(1.460)
R-r	2.882	2.157	1.875(1.676)	1.571(1.256)
r(z=4)	1.554	1.580	1.766(1.801)	1.606(1.577)
R-r	2.721	2.013	1.729(1.534)	1.442(1.139)

Nearest neighbour distance a (a.u) = 4.44

Static dielectric constant $\epsilon(o)$ = 11.94

Valence Fermi Momentum k_F = 0.96

The first set of results in the tables give values for the Fermi energy E_F. A look at the TFD-LDA entries for E_F suggests that exchange drastically reduces the radius of the Fermi sphere in $\underline{k}$-space from its free electron value. Inhomogeneity acting alone has a mild effect in the same direction, but in presence of exchange, it tends to reduce the effect of exchange. Correlation enhances the effect of exchange. Both exchange and correlation energies arise from correlations in position of electrons with parallel and antiparallel spins respectively. The effect of these correlations is to keep electrons apart, but not enough to permit a free electron behaviour. Any such tendency of electrons staying away from one another gives rise to a reduction in the ground state energy of the system. Subject to the accuracy with which q has been determined, we would deduce from our results that the TFD - LDA value for E_F would be a fair representation of the actual E_F, especially as it has not suffered from the linearization process. This, however, wholely depends on the adequacy of the Langreth and Mehl's formulation as an approximation scheme. The value of E_F for diamond is largest in all cases since diamond (carbon) has a relatively large band gap and the Fermi level is somewhere up the gap.

Table 2. Results for Germanium. Values arising from inclusion of correlation are in parentheses.

	TF-LDA	TF-NLDA	TFD-LDA	TFD-NLDA
Fermi energy E_F	0.480	0.455	0.168(0.113)	0.330(0.230)
Q	1.117	1.531	1.357 (1.421)	1.761(2.046)
Screening radius R	4 560	3.328	3.747(3.583)	2.893(2.489)
r(z=1)	0.827	0.955	1.068(1.116)	0.975(0.953)
Region of validity R-r	3.733	2.373	2.679(2.467)	1.918(1.536)
r(z=2)	1.151	1.238	1.386(1.429)	1.234(1.184)
R-r	3.409	2.090	2.361(2.154)	1.659(1.305)
r(z=3)	1.363	1.415	1.585(1.623)	1.394(1.326)
R-r	3.197	1.913	2.162(1.960)	1.499(1.163)
r(z=4)	1.521	1.545	1.731(1.766)	1.510(1.428)
R-r	3.039	1.783	2.016(1.817)	1.383(1.061)

Nearest neighbour distance a (a.u) = 4.63

Static dielectric constant $\epsilon(o)$ = 16.0

Valence Fermi Momentum k_F = 0.98

Next we consider the values obtained for the screening radius, R, which is the distance from the point charge impurity beyond which the Coulomb form of the impurity potential is screened by the macroscopic dielectric constant $\epsilon(o)$. Inclusion of exchange, non locality and correlation lead progressively to more effectively screened potential with the screening effect greatest in Germanium.

The regions of validity investigated for this linear response theory are the last set of values in Tables 1 - 3. A careful study of the trend in these values show that the region of space about the impurity in which the linearized TFD approximation is meaningless (i.e r) is larger than the linearized TF case. The same is the case for their non local versions. Another feature of the present result is that the regions of validity of the linearization decreases progressively with the inclusion of each correction It is also observed that the region of validity decreases with increasing Z.

As noted previously, earlier workers evaluate dielectric screening function in semiconductors in $\underline{k}$-space and then transform to $\underline{r}$-space. In the TF method of Resta, however, $\bar{\epsilon}(r)$ is first evaluated and then $\epsilon(k)$. It is seen from our results as in previous r-space formulations that $\bar{\epsilon}(r) = \epsilon(o)$ for $r \geq R$, which is in agreement with theory.

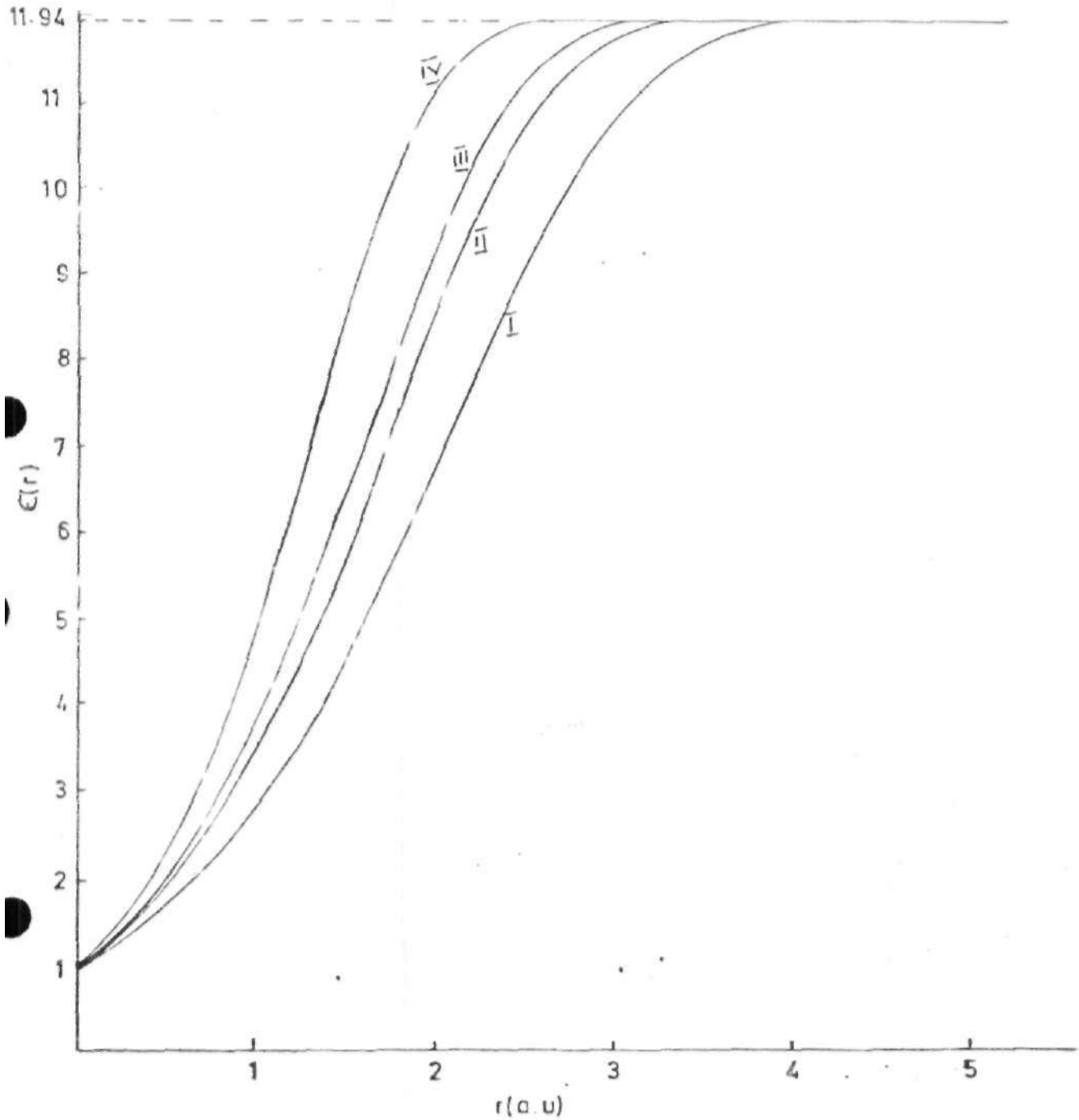
Table 3: Results for diamond. Values arising from inclusion of correlation are in parentheses.

	TF-LDA	TF-NLDA	TFD-LDA	TFD-NLDA
Fermi energy E_F	1.066	1.050	1.601(0.537)	0.674(0.574)
Q	1.363	1.467	1.542(1.572)	1.645(1.704)
Screening radius R	2.756	2.561	2.437(2.390)	2.285(2.205)
r(z=1)	0.484	0.516	0.603(0.622)	0.602(0.625)
Range of Validity R-r	2.272	2.045	1.834(1.768)	1.683(1.580)
r(z=2)	0.710	0.741	0.838(0.856)	0.827(0.849)
R - r	2.046	1.820	1.599(1.534)	1.458(1.356)
r(z=3)	0.863	0.890	0.990(1.008)	0.972(0.912)
R-r	1.893	1.671	1.447(1.382)	1.313(1.293)
r(z=4)	0.980	1.003	1.103(1.120)	1.08(1.098)
R - r	1.776	1.558	1.334(1.270)	1.205(1.107)

Nearest neighbour distance a (a.u) = 2.91

Static dielectric constant $\epsilon(o)$ = 5.7

Valence Fermi Momentum k_F = 1.46



FIG·1: Effective Spatial dielectric function for Silicon

GERMANIUM

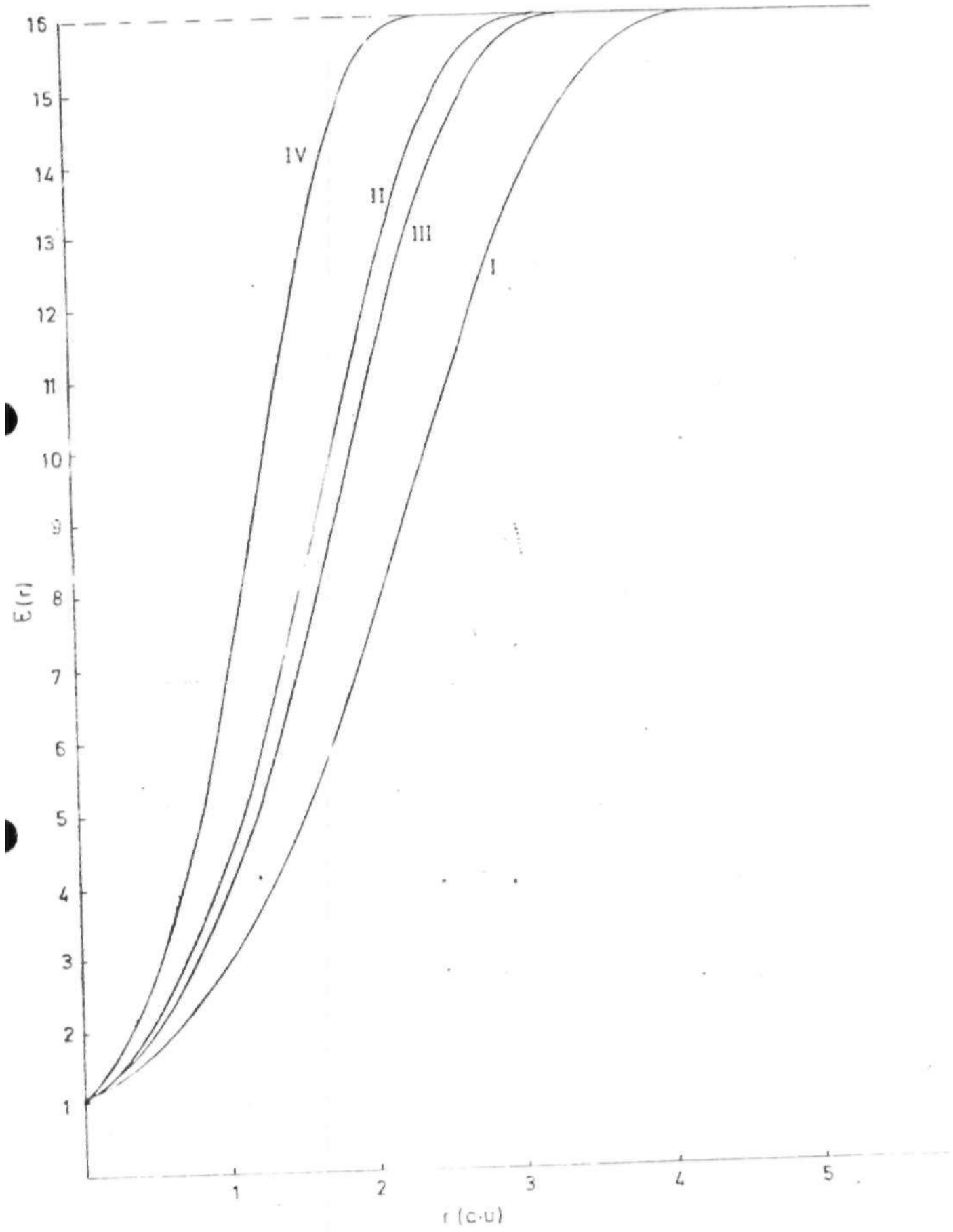


FIG.2: Effective Spatial dielectric function for Germanium

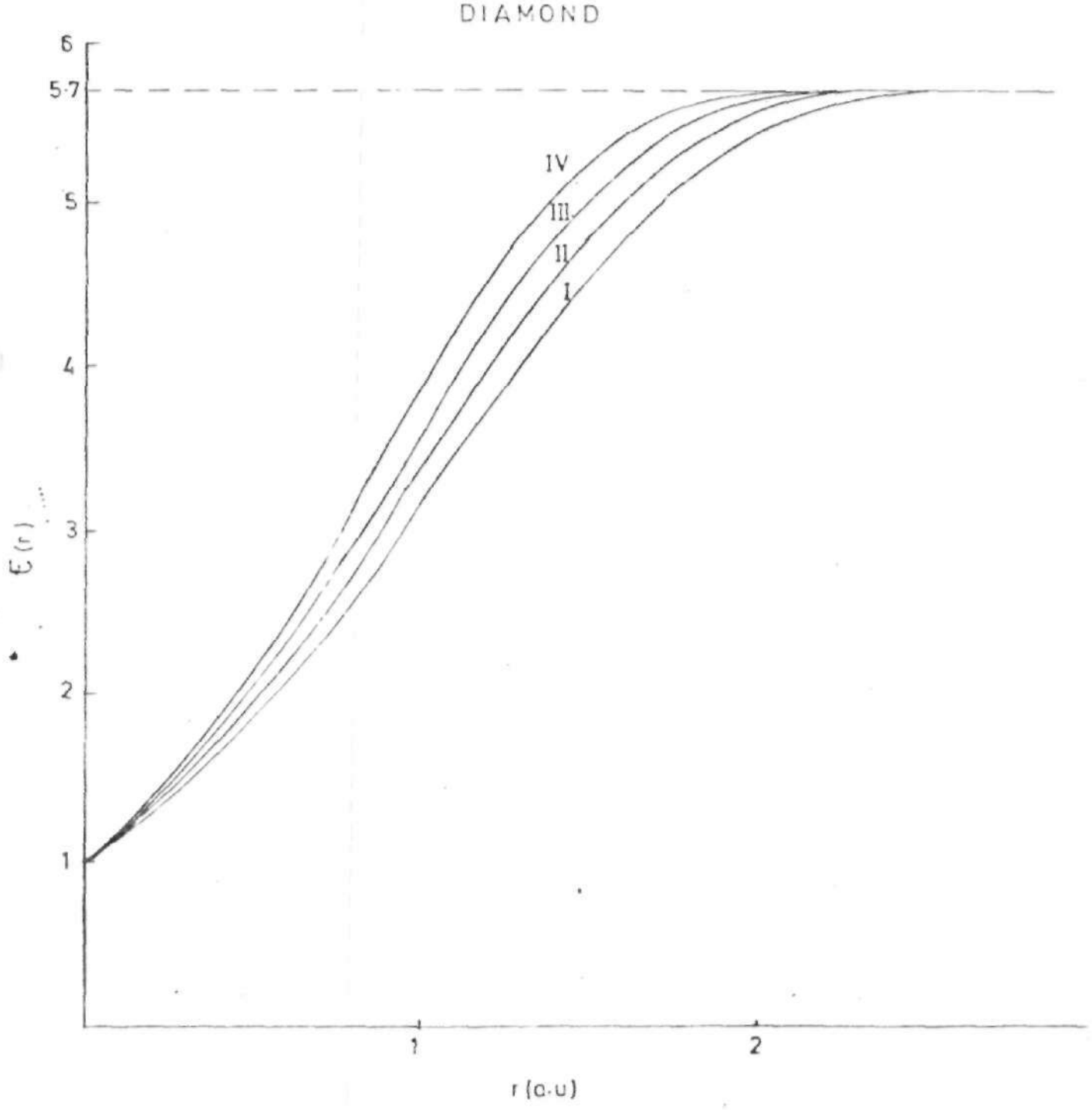


FIG.3: Effective Spatial dielectric function for Diamond

Key to interpretation of curves in Figures 1 - 3 :

Curve	
I	Thomas-Fermi theory in the local density approximation regime (TF-LDA)
II	Thomas-Fermi theory in the non-local density approximation regime (TF-NLDA)
III	Thomas-Fermi-Dirac theory in the local density approximation regime (TFD-LDA), with correlation correction included.
IV	Thomas-Fermi-Dirac theory in the non-local density approximation regime (TFD-NLDA), with correlation correction included.

This is unlike earlier works where $\bar{\varepsilon}(r)$ is only approximately equal to $\varepsilon(o)$ for $r \geq R$. In this respect the TF theory is better than the Penn model and other Penn-based models. The display of $\bar{\varepsilon}(r)$ in Figs. 1-3 show that $\bar{\varepsilon}(r)$ is a smooth monotonic function of r with the TFD-NLDA being the first to attain the maximum value of $\varepsilon(o)$ (i.e. V(r) is most effectively screened). In the case of germanium the inhomogeneity correction alone has a larger screening effect than exchange, as evidenced by the fact that the TF-NLDA version of $\bar{\varepsilon}(r)$ attains maximum faster than TFD-LDA version. This is not the case in the other two semiconductors and may be attributed to the comparatively larger value of the nonlocal parameter δ for germanium.

In the present treatment, we have assumed an essentially static impurity and background charge density. However, for real systems at finite temperature, one would require the dynamic and wave vector dependent dielectric function.

CHAPTER 5

C O N C L U S I O N

We have here developed within the framework of the energy density functional formalism, a linearized TF theory which has the effects of exchange-correlation and inhomogeneity incorporated. The results are a generalization of all earlier ones by Resta (1977) and Scarfone (1984). In particular, it is shown that the spatial dielectric function still has the same simple analytical form but differs from previous ones in the values of the constants appearing in it. The homogeneous and isotropic model solid (corresponding to the LDA) which has been in use up to now, has proved to be a good approximation for linear response of semiconductors despite the anisotropy and inhomogeneity of covalent bonding (Penn, 1962; Walter and Cohen, 1970). This is further confirmed by our results using the fact that the TF-LDA has a greater region of validity in this linearized theory.

Our major result, the TFD-NLDA leads to a more effective screening of the attractive impurity potential than either the linear or non linear TFD results of Scarfone. Although the region of validity of the TFD-NLDA is less than the TF-case, it is nevertheless a correction in the right direction since it has the effects of exchange-correlation and inhomogeneity included. The decreasing region of validity with the systematic inclusion of each correction is probably an indication of the inadequacy of the linear theory for treatment of such systems.

Previous work done on dielectric screening in the range of metallic densities (Almbladh et al., 1976) have confirmed this speculation. It was found that an impurity particle carrying even a unit charge is quite a strong perturbation on an electron gas within the metallic range of densities. This would imply that the potential of a unit charge impurity is strong enough to give rise to bound states in its vicinity (in the case of attractive impurity) thereby invalidating the use of the linear theory. For a negative unit charge impurity, the linear response is found to give a negative electron density near the impurity.

In general, the linear response theory leads to an unreasonable density distribution around the impurity. It is noted that for the theory to work, the induced charge density probably has to be about one order of magnitude smaller than the background charge; In other words the perturbing potential has to be sufficiently weak. In view of the similarity of charge distribution between metals and semiconductors, it is in effect concluded that for the highly charged impurities known to exist in semiconductors, the linear theory is an inadequate tool.

One therefore expects that solving our nonlocal version of the nonlinear poisson equation would provide a better description of dielectric response. This can however be done only numerically. The nonlinear screening theory is presently being investigated with the aim of also throwing more light on the competition between inhomogeneity and exchange-correlation effects in dielectric screening. Based on our earlier

speculation that there is a contribution to kinetic energy arising from exchange-correlation, the effect of such contribution (as calculated by Bass (1985) and Elegba (1986)) on the present screening theory is also being investigated.

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APPENDIX A

Uniqueness Theorem

Let the potential $V(\underline{r})$ have a ground state Ψ which gives rise to the ground state density $n(\underline{r})$, so that the total number of particles is denoted by

$$N = \int n(\underline{r})d\underline{r} \qquad A.1$$

and the corresponding ground state energy as E_N.

Assume that there is another potential $V'(\underline{r})$ having a ground state Ψ' which also gives rise to the same density $n(\underline{r})$, so that,

$$E'_N = \langle\Psi'|H'|\Psi'\rangle \qquad \text{and} \qquad E_N = \langle\Psi|H|\Psi\rangle \qquad A.2 \quad A.3$$

since the ground state Ψ corresponds to the least energy E_N,

$$E_N < \{\langle\Psi'|H'|\Psi'\rangle \ \langle\Psi'|(v - v')|\Psi'\rangle\} = \langle\Psi'|H|\Psi'\rangle \qquad A.4$$

$$E_N < E'_N + \int|v(r) - v'(r)|\, n'(\underline{r})d\underline{r} \qquad A.5$$

but the assumption is that $n(r) = n'(\underline{r})$

$$\therefore \quad E_N < E'_N + \int v(r) - v'(r)\, n(\underline{r})d\underline{r} \qquad A.6$$

Interchanging primed and unprimed quantities, we have

$$E'_N < E_N + \int|v'(r) - v(r)|n(\underline{r})d\underline{r} \qquad A.7$$

Adding A.6 and A.7 leads to the inconsistency.

$$E_N + E'_N < E_N + E'_N \qquad A.8$$

which is resolved only if $n(\underline{r}) \neq n'(\underline{r})$. This implies that $V(\underline{r})$ is a unique functional of $n(\underline{r})$. Since $V(\underline{r})$ fixes H and H through the Schrodinger equation fixes Ψ, it is deduced that another important consequence of this uniqueness theorem is that the ground state wave function Ψ is a unique functional of $n(\underline{r})$.