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DEFECT STATES IN SOLIDS AND DENSITY FUNCTIONAL THEORY

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Defect States in Solids

and

Density Functional Theory

by

Pinchus M. Laufer

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1984

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Abstract

**Impurity States in Solids
and
Density Functional Theory**

by

Pinchus M. Laufer

Adviser: Professor Joseph B. Krieger This work is divided into three sections: (1) In the first section we have investigated the basis dependence of calculated energy eigenvalues of gap states, introduced by ideal vacancies and surfaces, in the tight binding (orbital removal) method by employing a Green's function analysis. We find that (a) if Wannier functions are employed there are no ideal vacancy or surface gap states; (b) if atomic orbitals are used, no ideal vacancy gap states exist in the limit as the number of orbitals on the atom to be removed approaches infinity, although (c) spurious solutions for finite band models can exist. We find the reason for these results is that the orbital removal method is not equivalent to removing the potential of the removed atom. Thus, if the size of the basis is allowed to increase without limit, the orbital removal method yields the same energy eigenvalues as the Hamiltonian of the unperturbed system. This result is independent of the method used to solve the eigenvalue equation.

(2) In the second section we develop a generalized effective mass equation to deal with rapidly varying perturbations. (Our analysis is

limited to a single non-degenerate band.) We apply this formalism to calculate the binding energy of an impurity and then a vacancy within the exactly soluble Kronig-Penney model. In each case our formalism shows a considerable improvement over the results of a standard EMT calculation. In the case of the impurity, for a small but rapidly varying perturbation, the generalized form yields the exact result, while EMT never achieves more than 25% of the correct energy. For the vacancy as well the results of our formalism are clearly superior although here it is clear that for large perturbations the one band formalism is inadequate.

(3) In the third section we present an exactly soluble model system of two interacting electrons attracted to a common force center by a harmonic oscillator potential. This model is used to test the appropriateness of various approximation schemes for the $v_{xc}[n(r)]$ and $E_{xc}[n(r)]$. In addition, we show analytically that the exact Kohn-Sham eigenvalue for the highest occupied orbital equals the difference between the ground states of the two and one particle systems. Our analysis leads us to conclude that (a) Single particle (Kohn-Sham) energy eigenvalues may be poor even if the corresponding total energies are approximated very well. (b) The functionals for correlation energies and potentials are inadequate. (c) Although the exchange energy functionals (including correction terms) yield good energies, the corresponding potential functions are much worse.

ולא הביישן למד,

אבות פרק ב׳ משנה ה׳

....nor can a bashful man learn

Tractate Avoth (2:5)

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Chapter I

Chapter One - Critique of Tight Binding Orbital Removal Method

In the last few years there has been considerable interest in calculating the electronic states introduced in the band gaps of semiconductor crystals by vacancies and surfaces. Excellent reviews of the various methods have been published by Pantelides[1] for vacancy state calculations and by Pollman[2] for surface state calculations. In this chapter we critically examine the tight binding orbital removal method as applied to both problems[3,4]. The application of this method, employing a Green's function analysis, has been generalized and extended to the study of the electrical properties of interfaces[5] and superlattices[6] and has become an important technique in semiconductor calculations.

1.1 The Tight Binding Method

The general problem which we wish to solve is $H\psi = E\psi$ in the case of a perturbation in an otherwise perfect crystal. We approach this by first obtaining a description of the perfect crystal band structure.

Let $\phi_\alpha(\bar{r})$ be the atomic-like basis functions centered at $\bar{r} = 0$, then in order to get a solution which satisfies the Bloch condition we create a new set of basis states

$$\chi^{\nu}_{\alpha\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{j} e^{i\vec{k}\cdot(\vec{R}_j+\vec{t}_\nu)} \phi_\alpha(\vec{r}-\vec{R}_j-\vec{t}_\nu) \qquad (1)$$

where R_j is the j^{th} lattice vector; α denotes the orbital type; ν is the location of the ν^{th} atom in the unit cell and N is the number of Bravais lattice points in the bulk. Then the Bloch function ψ^0_{nk} may be written

$$\psi^0_{n\bar{k}}(\bar{r}) = \Sigma_{\alpha\nu} C^n_{\alpha\nu} \chi^\nu_{\alpha\bar{k}}(\bar{r}) \qquad (2)$$

$$H^0\psi^0_{n\bar{k}}(\bar{r}) = E^0_{n\bar{k}}(\bar{r}) \qquad (3)$$

yielding

$$\sum_{\alpha,\nu} \left\{ \langle \chi^{\nu'}_{\alpha'\vec{k}} | H^0 | \chi^{\nu}_{\alpha\vec{k}} \rangle - E^0_{n\vec{k}} \langle \chi^{\nu'}_{\alpha\vec{k}} | \chi^{\nu}_{\alpha\vec{k}} \rangle \right\} C^n_{\alpha\nu}(\vec{k}) = 0$$

or

$$\det \left\| \langle \chi^{\nu'}_{\alpha'\vec{k}} | H^0 | \chi^{\nu}_{\alpha\vec{k}} \rangle - E^0_{n\vec{k}} \langle \chi^{\nu'}_{\alpha'\vec{k}} | \chi^{\nu}_{\alpha k} \rangle \right\| = 0 \qquad (4)$$

which could be solved for each individual k to yield E^0_{nk}. The matrix elements which appear in (1) can be reduced to matrix elements involving the atomiclike basis ϕ_α and a sum over lattice sites.

$$\langle \chi^{\nu'}_{\alpha' k} | \chi^{\nu}_{\alpha k} \rangle = \delta_{\alpha\alpha'} \delta_{\nu\nu'}$$

$$\langle \chi^{\nu'}_{\alpha' k} | H^0 | \chi^{\nu}_{\alpha k} \rangle = \frac{1}{N} \langle \sum_j e^{i\vec{k}\cdot(\vec{R}_j+\vec{\tau}_{\nu'})} \phi_{\alpha'}(\vec{r}-\vec{R}_j-\vec{\tau}_{\nu'}) | H^0 | \sum_\ell e^{i\vec{k}\cdot(\vec{R}_\ell+\vec{\tau}_\nu)} \phi_\alpha(\vec{r}-\vec{R}_\ell-\vec{\tau}_\nu)$$

$$= \frac{1}{N} \sum_{j,\ell} e^{i\vec{k}\cdot(\vec{R}_\ell-\vec{R}_j)} e^{i\vec{k}\cdot(\vec{\tau}_\nu-\vec{\tau}_{\nu'})} \langle \phi_{\alpha'}(\vec{r}-\vec{R}_j-\vec{\tau}_{\nu'}) | H^0 | \phi_\alpha(\vec{r}-\vec{R}_\ell-\vec{\tau}_\nu) \rangle$$

$$= \sum_{j''} e^{i\vec{k}\cdot\vec{R}_{j''}} e^{i\vec{k}\cdot(\vec{\tau}_\nu-\vec{\tau}_{\nu'})} \langle \phi_{\alpha'}(\vec{r}-\vec{\tau}_{\nu'}) | H^0 | \phi_\alpha(\vec{r}-\vec{R}_{j''}-\vec{\tau}_\nu) \rangle$$

Let $\vec{\tau}_{\nu\nu'} = \vec{\tau}_\nu - \vec{\tau}_{\nu'}$

$$= \sum_j e^{i\vec{k}\cdot(\vec{R}_j+\vec{\tau}_{\nu\nu'})} \langle \phi_{\alpha'}(\vec{r}) | H^0 | \phi_\alpha(\vec{r}-\vec{R}_j-\vec{\tau}_{\nu\nu'}) \rangle \tag{5}$$

For localized ϕ_α we expect that as the distance between centers increases the size of the matrix element of H^0 decreases. Thus the number of "integrals" $\langle\phi_{\alpha'}(r)|H^0|\phi_\alpha(r - R_j - \tau_\nu)\rangle$ depends on how many neighbors are considered before neglecting the remaining contributions.

Rather than actually constructing the ϕ_α and computing the matrix elements, we can approach this problem from the opposite end. Since we know the energy band structure from optical data we can treat the matrix elements as free parameters and choose values which will best fit the known features of the band structure. This approach is known as the empirical tight-binding method.

1.2 Generalized Koster Slater Method

The basis for the method is the early work of Koster and Slater[7], who showed that the electronic energy levels introduced in the band gaps by a localized perturbation could be calculated from a knowledge of the Green's function for the perfect crystal and the matrix elements of the potential, both calculated in the Wannier representation. Moreover, the rank of the determinant required for the calculation of the energy eigenvalues was shown to be equal to the rank of the nonzero elements of the perturbing potential matrix in this representation.

Further amplification of this method has been given by Callaway[8] and calculations of the electronic states in the band gap have been performed for the vacancy[9] and divacancy[10] of Si in the Wannier representation. The calculations turned out to be difficult because of the complexity inherent in calculating the Wannier functions and few subsequent calculations have been performed in this representation[11].

However, Lannoo and Lenglart[12] observed that the Green's-function method is not limited to employing Wannier functions as a basis, but can be applied using some other localized basis set as well. We present the generalized Koster Slater method along with its derivation in this section.

Given any complete orthonormal set of functions $\{\phi_\alpha\}$ we can expand any wavefunction $\psi = \Sigma_\alpha C_\alpha \phi_\alpha$ (6)

We are interested in finding the bound states, in the energy gap, induced by a general perturbation. That is we wish to solve for the eigenstates of $H\psi = E\psi$ where $H = H^0 + V$,

H^0 - the perfect crystal Hamiltonian,

V - the perturbation potential

The method (based on Koster-Slater) proceeds as follows,

$$(H^0 + V)\psi = E\psi$$

$$(E - H^0)\psi = V\psi$$

Define $$G^0(E) = (E - H^0)^{-1}$$

then $$\psi = G^0(E)V\psi$$

or $$[1 - G^0(E)V]\psi = 0 \qquad (7)$$

Using a complete orthonormal set $\{\phi_\alpha\}$,

$$\Sigma_\alpha[\delta_{\alpha\alpha'} - \Sigma_{\alpha''}G^0(E)_{\alpha'\alpha''} V_{\alpha''\alpha}]C_\alpha = 0$$

$$\det ||\delta_{\alpha\alpha'} - \Sigma_{\alpha''}G^0(E)_{\alpha'\alpha''} V_{\alpha''\alpha}|| = 0 \qquad (8)$$

for non-trivial expansion coefficients C_α.

$$G^0_{\alpha\alpha'}(E) = \int\phi^*_\alpha(E - H^0)^{-1}\phi_{\alpha'}d\tau \qquad (9)$$

Let |nk> be the eigenstates of H^0; then we can expand the above in some more convenient manner.

$$G^{0}_{\alpha\alpha'}(E) = \sum_{n,\vec{k}} \frac{\langle\alpha|n\vec{k}\rangle\langle n\vec{k}|\alpha'\rangle}{E - E^{0}_{n\vec{k}}} \qquad (10)$$

where E^0_{nk} is the n^{th} energy band function.

If instead of a C-O-N set $\{\phi_\alpha\}$ we only have a limited number of basis functions which are not complete, we still want to write

$$\psi = \Sigma_\alpha{}' \, C_\alpha \phi_\alpha$$

and fit the C_α, variationally to get the best result. This leads to the identical equation for the C_α : $Det(1 - G^0V) = 0$ except that now the solution is variational - not exact.

At this stage the Green's function method is just as unwieldly as solving $H\psi = E\psi$, but under the following conditions, which are just those in which tight binding is usually employed, it yields a vast improvement over other methods by dramatically reducing the rank of the matrix equation.

If (1) the $\{\phi_\alpha\}$ are chosen as a localized set

and

(2) V, the perturbing potential, has a finite range

then since $\langle\phi_\alpha|V|\phi_{\alpha'}\rangle \neq 0$ only if ϕ_α, $\phi_{\alpha'}$ and V overlap, there is only a small number of matrix elements V which are non-zero.

Thus V can be written schematically as

$$V = \begin{pmatrix} V & 0 \\ 0 & 0 \end{pmatrix} \quad (11a)$$

and

$$G^0(E) = \begin{pmatrix} G^0_{11}(E) & G^0_{12}(E) \\ G^0_{21}(E) & G^0_{22}(E) \end{pmatrix} \quad (11b)$$

and thus

$$1 - G^0(E)V = \begin{pmatrix} 1 - G^0_{11}(E)V & 0 \\ - G^0_{21}(E)V & 1 \end{pmatrix} \quad (11c)$$

and $\mathrm{Det}(1 - G^0(E)V) = \mathrm{Det}(1 - G^0_{11}V)$ reducing the size of our problem to the order of the overlap of V, ϕ_α and $\phi_{\alpha'}$.

The Green's function method is exactly equivalent to solving the problem through the Schroedinger equation. Thus it provides a useful analytical tool for studying the implications of approximations introduced in the solution of the problem.

It is also worth noting that this can be done for many different perturbing potentials V with little additional effort. This is because $G^0_{\alpha\alpha'}(E)$ need only be calculated once, since it is depends solely upon the properties of the perfect crystal. Thus the only changes are in the matrix elements of V.

In solving $H\psi = E\psi$ we are led to $Det(H - E) = 0$, which is of large rank even in the case of localized perturbations. If Wannier functions are used as a basis, the rank of $(H - E)$ is equal to the number of sites included times the number of bands. Since the number of sites depends on the extent of the wavefunction - which can be quite extended even for highly localized perturbations - the matrix is still of considerable rank.

However, the Green's function method which yields $Det(1 - G^0V) = 0$ is limited by the size of V. Thus if V is localized we need only the number of bands times the number of sites over which the perturbation extends. This causes a vast reduction in the size of the determinantal equation to be solved.

1.3 The Ideal Vacancy

1.3.1 Definition and Background

In the empirical tight binding method (ETBM) a linear combination of atomic orbitals (LCAO) band structure is performed treating the matrix elements of the Hamiltonian as parameters to be fit to known energy bands[13].

The ideal vacancy is then defined by removing an atom from the perfect crystal leaving all other atoms at the same positions. The Hamiltonian matrix elements between orbitals centered on the atom to be removed and all other basis states of the system are removed, while the basis states centered on all other sites are retained, and all their Hamiltonian matrix elements are assumed unaltered.

We shall refer to this procedure as the orbital removal method since the resulting Hamiltonian matrix from which the eigenvectors and eigenvalues of the vacancy state are derived is identical to the Hamiltonian matrix that would be obtained if the orbitals on the central atom were removed from the basis set and no other changes were made in the Hamiltonian matrix.

The orbital removal method has been employed in a variety of calculational techniques. Cluster calculations have been performed using this method to investigate the vacancy in diamond[14]. However, it was found that even clusters of 71 atoms were not large enough to contain the wave function sufficiently so as to eliminate undesirable surface-vacancy interactions which introduce uncertainty in the determination of the bound state energy levels. An alternative technique to deal with the difficulties inherent in the cluster calculations is to impose periodic boundary conditions, which correspond to an infinite crystal with a superlattice of defects[15]. This technique then leads to the necessity of performing the calculations for a supercell which must be considerably larger than the unit cell of the host material in order to decrease the dispersion of the vacancy 'band'. Similarly, calculations of ideal surface states have been performed employing the orbital removal method on finite slabs[16] as well as employing transfer matrix techniques[17].

Bernholc and Pantelides[3] further developed the Green's function technique in the case of the ideal vacancy as defined above. They showed (and we will reproduce this in greater detail) that in an arbitrary localized representation the gap states introduced by the vacancy are given by the zeros of $G^0_{\alpha\alpha}$ where G^0 is the perfect crystal Hamiltonian and α, α' are the atomiclike orbitals on the atom to be removed.

For our Green's function formalism we need to know the form of the perturbation V, which is simply $H - H^0$, but this requires H be cast in a form of the same rank as H^0.

$$H^0 = \begin{pmatrix} H^0_{11} & H^0_{12} & H^0_{13} & \cdots & H^0_{1n} \\ H^0_{21} & H^0_{22} & \cdots & & H^0_{2n} \\ \vdots & & & & \vdots \end{pmatrix}$$

which can be written as

$$H^0 = \begin{pmatrix} H^0_X & H^0_A \\ H^0_A & H^0_B \end{pmatrix}$$

where H^0_X represents $\langle\alpha|H|\alpha'\rangle$ when α and α' are orbitals centered on atom X, the atom which is to be removed in creating the vacancy. H^0_B then represents the block of matrix elements on the remaining atoms, while H_A^0 is the overlap of H^0 between orbitals on atom "X" and all other atoms.

In accordance with the orbital removal definition of a vacancy given above we can get the Hamiltonian for the perturbed problem by eliminating the rows and columns containing orbitals centered on atom "X" from the matrix.

i.e. $$H = \begin{pmatrix} H_X^0 & H_A^0 \\ H_A^0 & H_B^0 \end{pmatrix} = H_B^0$$

However, this new matrix H_B^0 is of inappropriate rank for the calculations at hand. Thus we seek a matrix of the same rank of H^0 which will yield the same eigenvalue spectrum as H_B^0 (which is of lesser rank).

One choice consistent with the definition is

$$H^{(1)} = \begin{pmatrix} E_0 I & 0 \\ 0 & H_B^0 \end{pmatrix} \qquad \text{I has rank of } H_X^0$$

This clearly has the same spectrum as H_B^0 with an additional n-fold degenerate occurrence of E_0. V would depend on the size of H_A^0 in this instance.

A second choice which is more advantageous for manipulations is:

$$H^{(2)} = \begin{pmatrix} H_X^0 + E_0 I & H_A^0 \\ H_A^0 & H_B^0 \end{pmatrix}$$

We claim that in the limit that $E_0 \rightarrow \infty$ the eigenvalue spectrum is the same as for H_B^0, and thus it is valid for our purposes.

Then

$$V = H^{(2)} - H^0 = \begin{pmatrix} E_0 I & 0 \\ 0 & 0 \end{pmatrix}$$

which would be very easy to handle.

As this is an important point we shall pause here to prove the equivalence of the eigenvalue spectra.

Proof:

$$H^{(2)} = \begin{pmatrix} H_X^0 + E_0 I & H_A^0 \\ H_A^0 & H_B^0 \end{pmatrix}$$

$$\text{Det} \begin{pmatrix} H_X^0 + E_0 I - \lambda I & H_A^0 \\ H_A^0 & H_B^0 - \lambda I \end{pmatrix} = 0$$

is solved for λ_i to get the spectrum. If H_X^0 is of rank $n_0 \times n_0$, proceed by factoring E_0 out of each of the first n_0 rows, and dividing both sides of the resultant equation by $(E_0)^n$,

$$(E_0)^n \, \text{Det} \begin{pmatrix} E_0^{-1} \left[H_X^0 + (E_0 - \lambda) I \right] & H_A^0 / E_0 \\ H_A^0 & H_B^0 - \lambda I \end{pmatrix} = 0$$

If we collect terms in orders of E_0 (or more simply let $E_0 \to \infty$ first), we see that the term which has all the diagonal elements of the upper left-hand block is the highest power of E_0. This is the only term which survives as $E_0 \to \infty$. Thus

$$\text{Det} = \left[\prod_{\alpha=1}^{n} \left(1 + \frac{H^0_{X\alpha\alpha} - \lambda}{E_0} \right) \right] \text{Det} \left(H_B^0 - \lambda I \right) = 0$$

The second part just reproduces the spectrum of H_B^0 and the first part is equal to 1 in the limit as $E_0 \to \infty$. Q.E.D.

Now

$$V = \begin{pmatrix} E_0 I & 0 \\ 0 & 0 \end{pmatrix}$$

and we must take $\lim E_0 \to \infty$

$Det(1 - G^0 V) = 0$ was the condition for finding the bound state energy. Thus $Det(1 - G^0_{11}(E)V) = Det(1 - E_0 G^0_{11}(E))$; where $G^0_{11}(E)$ has dimensions $n \times n$. Dividing by E_0^{-1} gives

$$Det\,(E_0^{-1} - G^0_{11}(E)) = 0$$

and taking $\lim E_0 \to \infty \implies Det(G^0_{11}(E)) = 0$

Thus for the case of the ideal vacancy defined by the orbital removal method we need only solve

$$Det(G^0_{11}(E)) = 0, \qquad (12)$$

where $G^0_{11}(E)$ is the block corresponding to the atom which is being removed.

Furthermore, Bernholc and Pantelides[3] proceed to point out that if an sp^3 basis is used, as is quite common in these calculations, then by symmetry the s and p orbitals on the central atom do not mix, from which it follows that there are no off-diagonal elements of G^0_{11}.

Thus $Det\,G^0_{11}(E) = 0$ reduces to $\Pi_\alpha G^0_{\alpha\alpha}(E) = 0$ where α labels the orbitals on the atom under consideration. States of A_1 symmetry are given by the zeros of G^0_{ss} and states of T_2 symmetry are given by the zeros of G^0_{pp}. For Si, they find a bound state of T_2 symmetry 0.27 eV above the valence-band edge using the tight-binding parametrization of the best energy bands obtained by Pandey and Phillips[18]. Earlier calculations of this quantity by Callaway[9] and Hughes using the Koster-Slater method in the Wannier representation yielded no gap states unless the vacancy potential was made stronger than the negative of the atomic potential that was removed. Kauffer et al.[19], employing an identical definition of the ideal vacancy as given in Ref. 3 but using a different parametrization of the energy bands, find a bound state 0.12 eV above the valence-band edge.

Calculations of the Si vacancy states directly employing the vacancy potential have also been performed. Louie et al.[20], employing a periodically spaced vacancy in a pseudopotential calculation which involved the self-consistently determined potential near the defect, find a bound state at approximately 0.5 eV above the valence-band edge. More recently, other calculations directly employing the vacancy potential have been performed by Bernholc, Lipari, and Pantelides[21] and by Baraff and Schluter[22], who find the unrelaxed vacancy state 0.76 and 0.7 eV above the valence band, respectively. When self-consistency is included the eigenvalue is lowered by about 0.1 eV[21]. In comparing the results of Refs. 3 and 21, Bernholc et al.[16] speculate that the level obtained in the tight-binding method is too low because the conduction bands are not adequately represented by the tight-binding parameters. Support for this argument has been given by Papaconstantopoulos and Economou,[23] who used 20 adjustable parameters in an sp^3 basis which include first-, second-, and third-neighbor interactions to fit a band structure obtained from a pseudopotential calculation. Performing the same calculation given in Ref. 3 they find a bound state of T_2 symmetry 0.75 eV above the top of the valence band.

In applying the orbital-removal method, certain questions naturally arise[24] which have not previously been systematically studied. One such question is whether the calculated binding energy of a vacancy state (or a surface state) depends on the choice of localized basis states used to parametrize the Hamiltonian matrix. That is, would the set of basis states we could employ - s, p, etc., atomiclike orbitals, Wannier functions or the true atomic orbitals - affect the value obtained for the energy. In each case the matrix elements appearing in the Hamiltonian will be different but can correspond to the same energy-band eigenvalues. Recent work by Das Sarma and Madhukar[25] has shown that for three different choices of tight-binding parameters such that the fitting of the energy bands appears "equally good", the A_1 vacancy energy levels for GaAs calculated by this method are significantly different, essentially covering the entire band gap. Similar variations are found for the other vacancy states as well. A second question involves the convergence of the solutions for gap states as the number of orbitals and hence the number of bands is increased, i.e., can spurious solutions exist for gap states in a finite-band approximation which will disappear (merge into the bands) as the number of bands is increased.

Our analysis[24] is based on the Green's-function technique developed by Bernholc and Pantelides[3] As we have already stated, this technique is exactly equivalent to finding the eigenvalues and eigenfunctions of the vacancy states in the orbital-removal method as defined above. Moreover, the Green's-function method provides a useful analytic technique for studying the implications of the definition of the vacancy in the tight-binding method. We wish to stress that our analysis is therefore not a critique of the Green's-function method but rather of the tight-binding method and is equally applicable to whatever technique is employed to solve the Schroedinger equation when the tight-binding definition of the vacancy is employed.

1.3.2 Orbital-Removal Method in the Wannier Representation for Vacancy States

The bound-state energy eigenvalues for ideal vacancy states in the band gaps of the perfect crystal are given by the solutions of

$$\mathrm{Det}\ G^{0}_{\alpha\alpha'}(E) = 0, \tag{13}$$

where $\{\phi_\alpha\}$ denote the orthonormal set of orbitals associated with the atom to be removed creating the vacancy. Here

$$G^0_{\alpha\alpha'} = \sum_{n,\vec{k}} \frac{\langle\alpha|n\vec{k}\rangle\langle n\vec{k}|\alpha'\rangle}{E - E^0_{n\vec{k}}} \qquad (14)$$

where the matrix elements of the perfect-crystal Green's function G^0 are given in terms of the Bloch states of the perfect crystal, $|nk\rangle$, and the corresponding energy bands E^0_{nk}, and the $\{\phi_\alpha\}$ are the set of orbitals which are localized about the site of the atom to be removed.

Case of one atom per unit cell

Suppose the $\{\phi_\alpha\}$ are Wannier functions, $A_n(\vec{r} - \vec{R}_j)$, where

$$A_{nj} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_j}\, \Psi_{n\vec{k}}(\vec{r}) \qquad (15)$$

so

$$\langle A_{n'j} | \Psi_{nk} \rangle = \frac{1}{\sqrt{N}}\, e^{i\vec{k}\cdot\vec{R}_j}\, \delta_{nn'} \qquad (16)$$

Then removing an atom at R_j yields

$$(G^0_{jj})_{n'n''} = \sum_{n,\vec{k}} \frac{\langle A_{n'j}|n\vec{k}\rangle\langle n\vec{k}|A_{n''j}\rangle}{E - E^0_{n\vec{k}}}$$

$$= \frac{1}{N}\, \delta_{n'n''} \sum_{\vec{k}} \frac{1}{E - E^0_{n\vec{k}}} \qquad (17)$$

Thus in this representation $(G^0_{jj})_{n'n''}$ is diagonal, so

$$\text{Det}\, G^0_{jj}(E) = \prod_n \frac{1}{N} \sum_{\vec{k}} \frac{1}{E - E^0_{n\vec{k}}} \qquad (18)$$

and the solutions of Eq. (13) are the solutions of

$$\frac{1}{N} \sum_{\vec{k}} \frac{1}{E - E^0_{n\vec{k}}} = 0 \qquad (19)$$

for some n. But if E is in a band gap, for a given n, $E - E^0_{nk}$ always has the same sign for all k. Therefore there are no solutions of Eq. (19) in the band gaps. The discussion above is also valid for removing an entire cell of a crystal with more than one atom per unit cell and so leads to the result that there are no gap states for the divacancy of Si or Ge, etc., predicted by this calculation.

We observe, however, that in the Kronig-Penney model, the removal of one "atom", i.e., one delta function, can be treated exactly. It is well known that in such a model one gap state is introduced between every two successive bands[26], which is a counter-example to the result given by Eq. (19).

We also note that in the empirical tight-binding method, it is not necessary to know the functional form of the Wannier functions. In this method the matrix elements of the Hamiltonian between localized atomiclike orbitals are adjusted to reproduce the band structure obtained from other methods. If the Wannier functions are taken as this set of localized orbitals then the matrix elements of the unperturbed Hamiltonian are given by $\langle A_{n'j'}|H^0|A_{nj}\rangle = \varepsilon_{n,j-j'}\delta_{n,n'}$ where

$$\epsilon_{n,j} = \frac{1}{N} \sum_{\vec{k}} \epsilon_n(\vec{k})\, e^{-i\vec{k}\cdot\vec{R}_j}$$

Thus for any given band structure $\varepsilon_n(k)$ we can make the eigenvalues of the empirical Hamiltonian approximate $\varepsilon_n(k)$ as closely as we desire with the resulting Bloch states satisfying Eq. (16) exactly, from which Eq. (19) immediately follows.

It can, of course, be argued that such localized states, i.e., Wannier functions, are not the true atomic orbitals that should be removed but rather a combination of many orbitals - not only from the atom to be removed, but from other atoms as well. However, the same argument can be made as well in the cases in which this method has been employed. In such cases the orthonormal set of atomiclike functions that are removed are constructed, using Lowdin's[13,27] method, by taking linear combinations of the atomic orbitals from different atoms in different cells. This is necessary because the actual atomic orbitals on two atoms will not in general be orthogonal to each other. When this orthogonalization process is completely carried out the resulting atomiclike orbitals include contributions from essentially all atomic orbitals in the system. It thus appears that if unambiguous results are to be obtained, the orbitals that should be removed are the true atomic orbitals related to the removed atom rather than some set which has been obtained by taking linear combinations of orbitals which include contributions from other atoms.

1.3.3 Orbital-Removal Method Using Atomic Orbitals

We consider the basis functions $\{\phi_{\alpha j}\}$ to be the true atomic orbitals where j denotes the j^{th} atom in the crystal. Then since orbitals on the same atomic site are eigenfunctions of the same atomic Hamiltonian we can take

$$\langle \phi_{\alpha j} | \phi_{\alpha' j} \rangle = \delta_{\alpha\alpha'} \tag{20}$$

but

$$\langle \phi_{\alpha j} | \phi_{\alpha' j'} \rangle \neq 0, \qquad j \neq j' \tag{21}$$

Employing the same arguments as Bernholc and Pantelides (see the Appendix) it can be shown that in the orbital-removal method the energy levels in the band gaps introduced by the ideal vacancy are given by the solutions of

$$\text{Det}\, \tilde{G}^0_{11} = 0 \tag{22}$$

where

$$\tilde{G}^0 = S^{-1} G^0 S^{-1} \tag{23}$$

and S is the overlap matrix, i.e.,

$$S_{\alpha j, \alpha' j'} = \langle \phi_{\alpha j} | \phi_{\alpha' j'} \rangle \tag{24}$$

It follows from Eq. (20) that

$$S = \begin{pmatrix} I & S_{12} \\ S_{21} & I \end{pmatrix} \tag{25}$$

It is convenient to take linear combinations of the $\{\phi_{\alpha j}\}$ to form a set $\{\phi'_{\alpha j}\}$ such that

$$\phi'_{\alpha 0} = \phi_{\alpha 0}$$

and (26)

$$\langle \phi_{\alpha 0} | \phi_{\alpha' j'} \rangle = \delta_{\alpha\alpha'} \delta_{jj'}$$

where j = 0 denotes the atom to be removed. Thus the orbitals on the atom to be removed are still the atomic orbitals and in this representation S has the form

$$S = \begin{pmatrix} I & 0 \\ 0 & S_{22} \end{pmatrix} \qquad (27)$$

Then

$$S^{-1} = \begin{pmatrix} I & 0 \\ 0 & S_{22}^{-1} \end{pmatrix} \qquad (28)$$

and it follows from Eqs. (23) and (28) that

$$\tilde{G}^0_{11} = G^0_{11} \qquad (29)$$

with matrix elements

$$\tilde{G}^0_{\alpha\alpha'} = G^0_{\alpha\alpha'} = \sum_{n,\vec{k}} \frac{\langle \alpha | n\vec{k} \rangle \langle n\vec{k} | \alpha' \rangle}{E - E^0_{n\vec{k}}} \qquad (30)$$

where α, α' are orthonormal atomic orbitals on the $j = 0$ atom. In a finite-band approximation there will be r orbitals $\alpha = 1, \ldots, r$. We can make a unitary transformation to another set of r orthonormal functions A' without changing the value of the determinant, i.e.,

$$\text{Det } G^{0'} = \text{Det } UG^0U^+ = \text{Det } UU^+ \text{Det } G^0 = \text{Det } G^0. \qquad (31)$$

We choose the A'_α as follows. Let A'_1 be that linear combination of the $\phi_{\alpha 0}$ which gives the maximum overlap with the Wannier function A_1 belonging to the lowest energy band and centered in the cell of the atom $j = 0$. Similarly, let A_2' be that linear combination of the $\phi_{\alpha 0}$ which is orthogonal to A_1' and gives the maximum overlap with the Wannier function A_2 belonging to the next highest energy band, etc. For any finite set of r atomic orbitals these functions cannot, in general, be made identical to the Wannier functions. However, as r increases the fit can be made better until in the limit as $r \to \infty$, $A'_n \to A_n$ for $n \leq r$ because the $\{\phi_{\alpha 0}\}$ then span a complete set for any square integrable function since they are the eigenfunctions of an atomic Hamiltonian.

Thus in the limit of large r

$$\langle A'_\alpha | nk \rangle \to \langle A_\alpha | nk \rangle = N^{-\frac{1}{2}} \delta_{\alpha n}, \qquad n \leq r \qquad (32)$$

For one atom per cell there are only r bands if there are r orbitals taken as the basis on each atom. Then the contribution from these higher-lying bands to $G^0_{\alpha\alpha'}(E)$ is

$$G^{0(r)}_{\alpha\alpha'}(E) = \sum_{n>r,\vec{k}} \frac{\langle\alpha|n\vec{k}\rangle\langle n\vec{k}|\alpha'\rangle}{E - E^0_{n\vec{k}}} \qquad (33)$$

However, as $r \to \infty$ $E_{nk} \to \infty$ for $n \geq r$ and since there are a finite number of such bands and the matrix elements appearing in $G^{0\,(r)}_{\alpha\alpha'}$ are non-singular we have that for any finite energy E,

$$G^{0(r)}_{\alpha\alpha'} \to 0 \quad \text{as } r \to \infty \qquad (34)$$

Substituting the results of Eqs. (30) - (34) into Eq. (22) yields a diagonal matrix with the resulting eigenvalue equation

$$\frac{1}{N} \sum_{\vec{k}} \frac{1}{E - E^0_{n\vec{k}}} = 0 \qquad (35)$$

which has no solution for E in an energy gap. Equation (35) results only in the limit $r \to \infty$. This result is also obtained if any complete set of basis functions is employed and is not limited to the use of the true atomic orbitals. In a finite-band model solutions for E can exist in the energy gaps (as shown in the following section) depending on the choice of basis functions, but Eq. (35) implies that these solutions will disappear (the energy level will move into a band) when a complete set of basis functions is employed.

1.3.4 Vacancy States in a Finite Band Model

The sensitivity of the calculated energy eigenvalues to the choice of basis functions can most easily be seen in a two-band model. If we take two orthonormal orbitals per unit cell ϕ_1 and ϕ_2, the eigenvalue-eigenvector equation for the energy bands and Bloch functions can be written

$$\Sigma_j A_{ij} C_j = EC_i, \tag{36}$$

where

$$A_{ij}(k) = \langle \chi_i | H^0 | \chi_j \rangle \tag{37}$$

$$\psi_{n\vec{k}} = \Sigma_i C_i^{(n)}(\vec{\kappa}) \chi_i(\vec{r},\vec{\kappa}), \tag{38}$$

and χ_i is the Bloch sum arising from the ϕ_i orbital.

Taking only two orbitals per unit cell results in Eq. (36) being a 2 × 2 matrix equation which can be solved analytically for the energy bands and the Bloch functions. Employing these results we find

$$\langle \phi_i | G^0 | \phi_j \rangle = \begin{pmatrix} \frac{1}{N} \sum \frac{E - A_{22}}{(E - E^0_{1k})(E - E^0_{2k})} & \frac{1}{N} \sum \frac{A_{12}}{(E - E^0_{1k})(E - E^0_{2k})} \\ \frac{1}{N} \sum \frac{A_{21}}{(E - E^0_{1k})(E - E^0_{2k})} & \frac{1}{N} \sum \frac{E - A_{11}}{(E - E^0_{1k})(E - E^0_{2k})} \end{pmatrix} \tag{39}$$

If we take $\phi_n = A_n$, the Wannier function belonging to the n^{th} band for n = 1, 2, then

$$\chi_{n,\vec{k}} = \psi_{n,\vec{k}} = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \tag{40}$$

and

$$A_{nn'} = E^0_{n\vec{k}} \delta_{nn'} \tag{41}$$

Substituting Eqs. (40) and (41) into Eq. (39) yields

$$\langle\phi_i|G^0|\phi_j\rangle = \begin{pmatrix} \frac{1}{N}\sum \frac{1}{E - E^0_{1k}} & 0 \\ 0 & \frac{1}{N}\sum \frac{1}{E - E^0_{2k}} \end{pmatrix} \qquad (42)$$

which is just a special case of the result obtained previously, yielding no vacancy states in the gap.

However, if instead of Eq. (40) we take

$$\chi_{n,\vec{k}} = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{r}} u_{no}(\vec{r}) \quad , \qquad n = 1, 2 \qquad (43)$$

corresponding to atomiclike orbitals

$$\phi_{n,\ell} = \phi_n(\vec{r}-\vec{\ell}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{\ell}} \chi_{n,\vec{k}}$$

$$= \frac{1}{\sqrt{N}} u_{no}(\vec{r}) \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}-\vec{\ell})} \qquad (44)$$

then, as with the case of Wannier functions, the functions $\phi_n(\vec{r} - \vec{\ell})$ are localized[28] about the cell ℓ and satisfy

$$\langle\phi_{n\ell}|\phi_{n'\ell'}\rangle = \delta_{nn'}\delta_{\ell\ell'} \qquad (45)$$

Then

$$A_{nn} = \epsilon_n + \frac{\hbar^2 k^2}{2m} \quad , \qquad n = 1, 2 \qquad (46)$$

where

$$H^0 u_{no} = \epsilon_n u_{no} \qquad (47)$$

and

$$A_{nn'} = \frac{\hbar}{m} \vec{k} \cdot \vec{p}_{nn'} \quad , n \neq n' \tag{48}$$

where

$$\vec{p}_{nn'} = \langle u_{n0} | \vec{p} | u_{n'0} \rangle \tag{49}$$

Substituting Eqs. (45) through (48) into Eq. (39) we see immediately that the off-diagonal terms in G^0 are zero because A_{12} is odd in k and E_{1k} and E_{2k} are both even and

$$G^0_{11} = \sum_{\vec{k}} \frac{E - \epsilon_2 - \frac{\hbar^2 k^2}{2m}}{(E - E^0_{1k})(E - E^0_{2k})} \tag{50}$$

$$G^0_{22} = \sum_{\vec{k}} \frac{E - \epsilon_1 - \frac{\hbar^2 k^2}{2m}}{(E - E^0_{1k})(E - E^0_{2k})} \tag{51}$$

with

$$E_{\frac{1}{2}} = \frac{\hbar^2 k^2}{2m} + \frac{(\epsilon_1 + \epsilon_2) \pm [(\epsilon_1 - \epsilon_2)^2 + 4 |\vec{k} \cdot \vec{p}_{12}|^2]^{1/2}}{2} \tag{52}$$

If the two orbitals refer to two different atoms in the unit cell, then the eigenvalues for states in the gap are given by $G^0_{11} = 0$ if atom 1 is removed or $G^0_{22} = 0$ if atom 2 is removed. In either case $(E - E_{1k})(E - E_{2k}) < 0$ for E in the gap. Then for any E in the gap $E - (\varepsilon_1 + h^2k^2/2m) \leq 0$ because $(E_1)_{min} = \varepsilon_1$ so $G^0_{22} \neq 0$ for such E. However, the term $E - (\varepsilon_2 + h^2k^2/2m)$ can change sign for E in the gap, so removing atom 1 (i.e., the one associated with the conduction band) can lead to gap states. A more careful analysis shows that for sufficiently large p_{12}, the energy of this vacancy state can be made as close to the top of the valence band as desired, and as p_{12} is decreased the energy of this state can be made to rise to the bottom of the conduction band. In addition, if the two orbitals refer to the same atom (there is thus one atom per unit cell) then the condition for a gap state is

$$\text{Det } G^0 = 0 = G^0_{11} G^0_{22} \tag{53}$$

so the above analysis still obtains, i.e., depending on the magnitude of p_{12} there can be a gap state corresponding to $G^0_{11} = 0$. Thus the results depend on the choice of localized orbitals describing the atomiclike states to be removed. If Wannier functions are employed there will be no gap states, but with another similar - but not identical - choice of a localized basis set we can obtain gap states in a finite-band model even though the energy bands in both cases are the same.

1.4 Discussion of Assumptions in Ideal Vacancy Calculations

The results of Section 3 lead to the conclusion that either there are no gap states introduced in a crystal by an ideal vacancy, i.e., that some relaxation must be assumed if any gap states are to exist, or there is some fundamental problem with the orbital-removal method. However, since it can be shown that in the Kronig-Penney model gap states exist even if there is no relaxation, we examine the latter possibility.

There are two fundamental assumptions from which Eq. (13) directly follows. The first asserts that when an atom is removed from a perfect crystal all the other atoms retain their original positions. This essentially defines the ideal vacancy and, although it may not be true in practice, yields a well defined problem that can fruitfully be used as a starting point for vacancy calculations.

The second assumption is that the atomiclike orbitals are retained on all other atoms and their interactions are assumed unaltered. However, the matrix elements of the full Hamiltonian between any two orbitals (in the single-particle approximation) depend in principle on the potential throughout the solid and not merely on the contribution of these two atoms to the crystal potential. Thus this assumption is not equivalent to asserting that each atom continues to make the same contribution to the crystal potential as it did originally (except of course for the vacancy atom); rather, it is equivalent to assuming that the crystal potential has not changed at all anywhere within the solid. For example, the second assumption requires that the matrix elements of the potential between orbitals from atoms adjacent to, but on opposite sides of, the vacancy be unchanged. This clearly cannot be true except when all interactions other than those from nearest neighbors are neglected. Even in the case of nearest-neighbor interactions only, the matrix elements of the potential between states on a single atom adjacent to the vacancy will change because these states will partially overlap the vacancy site.

This point is most simply illustrated by the following model calculation. We first observe that the orbital-removal method is not restricted to a crystal but can be applied to any multi-atom system provided that the Bloch states in the Green's function are replaced by the complete set of quantum states q, with energy E_q, of the unperturbed system. Here q denotes all the quantum numbers associated with a given state. Equation (13) then is valid for states not degenerate with any E_q with

$$G^{0}_{\alpha\alpha'} = \sum_{q} \frac{\langle\alpha|q\rangle\langle q|\alpha'\rangle}{E - E_q} \tag{54}$$

Consider two identical atoms separated by a finite distance. For simplicity we take one orbital on each atom ϕ_1 and ϕ_2, both of which are eigenfunctions of the Hamiltonian of the isolated atom, and assume they are orthonormal for the given separation distance. It is then trivial to calculate the Green's function given by Eq. (54). The resulting eigenvalue when atom 1 is removed is then obtained from $G^0_{11}(E) = 0$ which results in

$$E = \varepsilon + \langle\phi_2|V_1|\phi_2\rangle \tag{55}$$

with wave function $\psi = \phi_2$, where ε is the eigenvalue for the isolated atom and V_1 is the potential due to the presence of atom 1. We thus see that even though atom 1 has been removed, its contribution through the potential, V_1, remains and leads to an incorrect energy eigenvalue for an electron in the presence of the remaining atom even though the wave function is correct.

An even simpler way of seeing that this must happen is to first recall that the eigenvalues obtained from setting the determinant of the appropriate block of the Green's function equal to zero are identical to the eigenvalues obtained from the Hamiltonian matrix when all rows and columns involving matrix elements with the removed orbitals are eliminated. In our two atom, one orbital per atom model the initial Hamiltonian matrix is only 2 x 2, i.e.,

$$H^0 = \begin{pmatrix} H^0_{11} & H^0_{12} \\ H^0_{21} & H^0_{22} \end{pmatrix} \tag{56}$$

and removing the matrix elements involving ϕ_1 immediately yields

$$E = H^0_{22} = \langle\phi_2|(p^2/2m + V_2) + V_1|\phi_2\rangle$$

$$= \varepsilon + \langle\phi_2|V_1|\phi_2\rangle \qquad (57)$$

as obtained from the Green's-function calculation.

Moreover, it is clear that if we assume a continually larger set of orbitals as a basis on each atom, the Hamiltonian matrix still has the form given by Eq. (56) with the H_{ij} each being a matrix containing matrix elements of the full Hamiltonian between orbitals on atom i with orbitals on atom j. If we proceed to calculate the eigenvalues for the isolated atom 2 by the orbital removal method, i.e., set the matrix elements involving atom 1 equal to zero, then the matrices H^0_{11}, H^0_{12} and H^0_{21} are removed and the resulting Hamiltonian matrix is given by H^0_{22}; the resulting Hamiltonian matrix is then composed of matrix elements of the full Hamiltonian $H^0 = p^2/2m + V_1 + V_2$ between all states of the isolated atom 2. Then since the atomic orbitals on isolated atom 2 span a complete set for any square integrable function, as the number of these orbitals increases without limit, the eigenvalues of the Hamiltonian matrix approach the eigenvalues of $H^0 = p^2/2m + V_1 + V_2$ of which Eq. (55) is the first approximation, and not the eigenvalues of $H = p^2/2m + V_2$; thus, we see the "ghost" potential, V_1, continues to contribute as if atom 1 were still present.

This is also what happens in the case of the ideal vacancy in an otherwise perfect crystal. The orbital-removal method yields the same eigenvalues as obtained from setting to zero the matrix elements involving the orbitals from the atom to be removed but not modifying the other elements. Thus the other elements of the Hamiltonian matrix involve matrix elements of the full Hamiltonian including the potential of the atom that was removed. Then, as the number of orbitals is allowed to approach infinity and the set becomes complete, the resulting eigenvalues become those of the perfect crystal with no vacancy present. This is the reason why in Section 3 we found no gap states when we allowed the number of orbitals to approach infinity and assumed completeness of the set of orbitals.

Thus, although the orbital-removal method is very appealing, it cannot be correct because it does not actually change the potential from that of the perfect crystal. At best it will result in spurious results for a finite-band model as indicated by Eq. (56) for the two-atom problem and these solutions must ultimately converge to the band energies of the perfect crystal when the method is made fully convergent. Since the cluster calculation[14] employing the orbital-removal method is an approximation to treating the vacancy in an infinite crystal, it too suffers from the same defect as well as do other non-Green's-function techniques employing the tight-binding (orbital-removal) definition of the vacancy.[15-17]

Nothing stated above, however, should be construed as implying that the original Koster-Slater method is incorrect. When this latter method is employed in the case of a vacancy, orbitals are not removed but rather the crystal Hamiltonian is perturbed by adding a term that represents the change in the potential due to the removal of the atom. Recall, that in the Green's-function approach[7] this yields

$$(I - G^0 U)\psi = 0, \tag{58}$$

and the energy eigenvalues are given by

$$\mathrm{Det}\ (I - G^0 U) = 0. \tag{59}$$

where U is the perturbation potential, G^0 is the Green's function for the unperturbed Hamiltonian, and ψ is the wave function for the electron state.

In the two-atom model discussed above $U = -V_1$ for the removal of atom 1. We have exactly solved the preceding equations assuming only one atomic orbital on each atom where each orbital is the true atomic state in the absence of the other atom. We find for the ground state

$$E = \varepsilon$$

and

$$\psi = \phi_2 \qquad \text{exactly.}$$

Thus, unlike the orbital-removal method, the original Koster-Slater method yields the exact result both for the energy and the wave function when the perturbation created by the vacancy is treated correctly.

In other words, a correct quantum mechanical calculation concerning the effects of removing an atom can not be obtained by merely reducing the size of the basis set without making any other changes in the Hamiltonian matrix (which is what is done in the orbital removal method) but requires the incorporation of the change in the potential caused by the removal of an atom.

The assumption that the orbitals on the atom to be removed may be eliminated from the basis set (thus ensuring that the calculated vacancy eigenfunction will have zero overlap with these orbitals) has recently been criticized by Pena and Mattis[29]. They argue that just as an impurity atom, the vacancy contributes its own set of orbitals, these orbitals being linearly independent of the set of states belonging to the neighboring atoms and the rest of the crystal. This view is necessary mathematically to obtain a complete set of states as well as to make the connection between the pseudopotential and LCAO methods. They illustrate this point for the case of a halogen vacancy in sodium chloride where a pseudopotential calculation of the vacancy state yields a bound state having considerable amplitude at the vacancy site which would not be reproduced by an LCAO calculation using atomic orbitals centered on the neighboring atoms exclusively.

An even simpler example is given by the vacancy states in the Kronig-Penney model of a one dimensional periodic array of delta function potentials. Since the Schroedinger equation for a one dimensional potential has two linearly independent solutions for a given energy, then for E in the band gap the solutions for the perfect crystal are two states satisfying Bloch's theorem but with complex k. When a vacancy is created by removing one of the delta functions, these states still satisfy the Schroedinger equation to the left and right of the point where the delta function has been removed. The vacancy state is then obtained by matching the logarithmic derivative of these functions that decay as the distance to the vacancy becomes large. The resulting vacancy state is then strongly peaked at the vacancy site. Numerical examples are provided by Saxon and Hutner[30] who find for a typical case that the probability density at the vacancy site is more than twice as large as that on the nearest neighbor.

Thus, even if the potential is treated correctly the exclusion of the on-site orbitals from the basis set cannot, in general, be expected to yield the correct result because the wave function may have significant overlap with the orbitals on the "central" atom.

1.5 Implications for Surface State Calculations

The orbital removal method has been extended to the problem of surface state calculations. In this case two non-interacting surfaces are created by the removal of atomic planes. If only nearest neighbor interactions are included, one plane of atoms is removed; if next nearest neighbor interactions are included, two planes are removed, and so on. Since this method is equivalent to creating a "planar vacancy" or a "multiplanar vacancy" by the orbital-removal method without taking into consideration any change in the matrix elements of the Hamiltonian between orbitals on atoms that are not removed, it must suffer from the same difficulties as the orbital-removal method in the vacancy calculation.

We can show this directly by demonstrating that as in the case of the vacancy calculation there are no surface-state energy eigenvalues in the band gaps when Wannier functions are employed as the localized atomiclike orbitals. For simplicity we consider the case of one atom per unit surface cell. Then, employing the orbital removal method the energy eigenvalues, E(q), for surface states in the energy band gaps are given by the solutions of[4]

$$\mathrm{Det}\ ||G^0_{\ell\ell'}(E,q)|| = 0, \qquad (60)$$

where $G^0_{\ell\ell'}$ is the Green's function in the layer-orbital representation, i.e.,

$$G^0_{\ell\ell'}(E,q) = \langle\phi_q^{\alpha m}|G^0|\phi_q^{\alpha m'}\rangle, \qquad (61)$$

where ℓ is a composite subscript for the orbital α on the atomic plane m, and ℓ,ℓ' in Eq. (60) run only over those layers to be removed creating the two non-interacting surfaces. Here the layer orbitals $\phi_q^{\alpha m}$ are defined by[4]

$$\phi_q^{\alpha,m} = N_2^{\frac{1}{2}} \Sigma_j e^{i\vec{q}\cdot\vec{\rho}_j^m} \phi_\alpha(\vec{r} - \vec{\rho}_j^m), \tag{62}$$

where ρ_j^m are the two-dimensional lattice vectors connecting sites occupied by the atoms with orbital type α on the m^{th} lattice plane and q is a vector in the two-dimensional Brillouin zone defined by a surface cell. Let

$$\phi_\alpha(\vec{r} - \vec{\rho}_j^m) = A_\alpha(\vec{r} - \vec{\rho}_j^m).$$

Then the layer orbitals can be written

$$A_q^{\alpha,m} = \frac{1}{\sqrt{N_2}} \sum_j e^{i\vec{q}\cdot\vec{\rho}_j^m} A_\alpha(\vec{r} - \vec{\rho}_j^m) \tag{63}$$

and

$$\psi_{n,\vec{k}} = \frac{1}{\sqrt{N}} \sum_{j,m} e^{i\vec{k}\cdot\vec{\rho}_j^m} A_n(\vec{r} - \vec{\rho}_j^m) \tag{64}$$

so

$$\langle \psi_{n,\vec{k}} | A_q^{\alpha,m} \rangle = \sqrt{\frac{N_2}{N}} \, e^{-imk_\perp a} \, \delta_{n\alpha} \, \delta_{qk_\parallel} \tag{65}$$

where we have used $\vec{\rho}_j^m = \vec{\rho}_j + m\vec{a}$ and $k_\parallel$ is the projection of $\vec{k}$ on the surface, while $k_\perp$ is the projection of $\vec{k}$ on a. Then

$$G^0_{\ell\ell'}(E,\vec{q}) = \sum_{n,\vec{k}} \frac{\langle A_{\vec{q}}^{\alpha,m} | n\vec{k}\rangle \langle n\vec{k} | A_{\vec{q}}^{\alpha',m'}\rangle}{E - E_{n\vec{k}}}$$

$$= \frac{N_2}{N} \sum_{k_\perp} \frac{e^{2k_\perp a(m'-m)}}{E - E_\alpha(\vec{q},k_\perp)} \delta_{\alpha\alpha'} \qquad (66)$$

which is diagonal in band index so Eq. (60) becomes $\Pi_\alpha \det G^{0\,\alpha\,\alpha}_{mm'} = 0$ where $G^{0\,\alpha\,\alpha'}_{mm'}$ are the elements of G^0 belonging to band α.

When only one layer is to be removed (i.e., nearest-neighbor interactions only) $m = m' = 1$ so $G^{0\,\alpha\alpha}_{mm'}$ is a 1×1 matrix and the eigenvalue condition is

$$\frac{N_2}{N} \sum_{k_\perp} \frac{1}{E - E_\alpha(\vec{q},k_\perp)} = 0 \qquad (67)$$

which yields no gap solutions.

If we must remove two layers (i.e., next-nearest-neighbor interactions), then $G^{0\,\alpha\alpha}_{mm'}$ is a 2×2 matrix, and the eigenvalue condition is

$$\det G^{0\alpha\alpha}_{mm'} = \left(\frac{N_2}{N}\right)^2 \begin{vmatrix} \sum_{k_\perp} \frac{1}{E - E_\alpha(\vec{q},k_\perp)} & \sum_{k_\perp} \frac{e^{2k_\perp a}}{E - E_\alpha(\vec{q},k_\perp)} \\ \sum_{k_\perp} \frac{e^{-2k_\perp a}}{E - E_\alpha(\vec{q},k_\perp)} & \sum_{k_\perp} \frac{1}{E - E_\alpha(\vec{q},k_\perp)} \end{vmatrix}$$

$$= 0$$

or

$$\left| \sum_{k_\perp} \frac{1}{E - E_\alpha(\vec{q}, k_\perp)} \right|^2 - \left| \sum_{k_\perp} \frac{e^{ik_\perp a}}{E - E_\alpha(\vec{q}, k_\perp)} \right|^2 = 0 \qquad (68)$$

But for E in an energy band gap $E - E_\alpha$ always has the same sign for a given α so the first term is always larger than the second. Thus for the case of next-nearest-neighbor interactions there are no gap states.

In general, if we have a Hamiltonian with n nearest-neighbor interactions we can remove n layers to decouple the two solids to create two non-interacting ideal surfaces. Since $G^0_{\ell\ell}(E,q)$ is diagonal in band index in the Wannier representation, the ideal surface-state energy spectrum is obtainable from the zeros of $\det G^{0\,\alpha\alpha}_{mm'} = 0$ where, for a given α, $G^{0\,\alpha\alpha}_{mm'}$ has rank n. For $n > 2$ it is difficult to proceed as above to show no solutions exist in the gap by direct evaluation of the determinant.

Consider the case where we take an infinite solid in all directions and take the limit

$$\frac{N_2}{N} \sum_{k_\perp} \longrightarrow \frac{a}{2\pi} \int dk_\perp$$

Then

$$G^{0\alpha\alpha}_{mm'} = \frac{a}{2\pi} \int f_{\alpha\vec{q}}(k_\perp)\, e^{-ik_\perp a(m-m')}\, dk_\perp \qquad (69)$$

where

$$f_{\alpha \vec{q}}(k_\perp) = \frac{1}{E - E_\alpha(\vec{q}, k_\perp)} \tag{70}$$

For interactions between n nearest neighbors we can decouple the two solids to create two noninteracting surfaces by removing any number of layers greater or equal to n. If we let the number of layers removed become increasingly large, i.e., m, m' = M >> n, then $G^{0\,\alpha\,\alpha'}_{mm'}$ looks the same as the Hamiltonian matrix in the Wannier representation of a one dimensional problem with energy-band function $f_{\alpha\vec{q}}(k_\perp)$, i.e., if $f_{\alpha\vec{q}}(k_\perp)$ is the energy-band function of some Hamiltonian h, then in terms of Wannier functions $\bar{A}_{\alpha m}$,

$$\langle \bar{A}_{\alpha m} | h | \bar{A}_{\alpha m'} \rangle = f_{\alpha q, m'-m},$$

where

$$f_{\alpha, q, m} = \frac{a}{2\pi} \int f_{\alpha q}(k_\perp) e^{-ik_\perp a m} dk_\perp .$$

In the limit of large M. the matrix representation of h in the Wannier representation can be diagonalized by a unitary transformation to a Bloch representation

$$\text{Det}\, G^{0\;\alpha\alpha}_{mm'} = \text{Det}\, \bar{G}^{0\;\alpha\alpha}_{ii'} = \Pi_i \bar{G}^{0\;\alpha\alpha}_{ii} ,$$

where $\bar{G}^{0\;\alpha\alpha}_{ii}$ is the i^{th} eigenvalue of $\bar{G}^{0\,\alpha\,\alpha}_{mm'}$ but since $G^{0\,\alpha\,\alpha}_{mm'}$ is the Hamiltonian matrix of h with eigenvalues $f_{\alpha\vec{q}}(k_\perp)$, we have

$$\bar{G}^{0\alpha\alpha}_{ii'} = \frac{1}{E - E_\alpha(\vec{q}, k_\perp)} \delta_{ii'} \tag{71}$$

so Det $G^{0\,\alpha\,\alpha}_{mm'}$ can never be equal to zero for E in the band gap.

Despite the results above for vacancy states and surface states, the orbital-removal method may be applicable to problems involving overlayers, heterojunctions, and superlattices. This is due to the fact that in these cases not only is a plane or planes of atoms removed, but they are replaced by another set of atoms having interactions with the other atoms in the crystal and thus the potential is actually changed. The analysis of the last two sections however, suggests that if accurate quantitative results are to be obtained, the matrix elements of the Hamiltonian between states that are near the removed layers must be adjusted to take account of the change in potential due to the existence of the interface.

Appendix A

Green's-Function Method With A Nonorthogonal Basis

Let $\{\phi_\alpha\}$ be a complete set of functions with overlap matrix

$$S_{\alpha\alpha'} = \langle\phi_\alpha|\phi_{\alpha'}\rangle .$$

The Schroedinger equation for the energy and eigenfunction of a state in a band gap can be written

$$[1 - G^0(E)V] = 0, \qquad \text{(A1)}$$

where V is the perturbation potential on the unperturbed Hamiltonian H^0 and $G^0 = (E = H^0)^{-1}$. Since the set $\{\phi_\alpha\}$ is complete we may expand ψ in terms of its elements:

$$\psi = \Sigma_{\alpha'} C_{\alpha'}\phi_{\alpha'} \qquad \text{(A2)}$$

Substituting Eq. (A2) into Eq. (A1), multiplying both sides of the resultant equation by ϕ^*_α, and integrating yields

$$\sum_{\alpha'} [S_{\alpha\alpha'} - (G^0V)_{\alpha\alpha'}] C_{\alpha'} = 0 \qquad \text{(A3)}$$

If the $\{\phi_\alpha\}$ were a complete orthonormal set, then

$$\sum_{\alpha''} |\alpha''\rangle\langle\alpha''| = \mathbb{1}$$

from which it immediately follows that

$$(G^\circ V)_{\alpha\alpha'} = \sum_{\alpha''} G^\circ_{\alpha\alpha''} V_{\alpha''\alpha'}$$

In general, for a nonorthonormal set $\{\phi_\alpha\}$,

$$\mathbb{1} = \sum_{\beta,\gamma} |\phi_\gamma\rangle\langle\phi_\beta| (S^{-1})_{\gamma\beta} \qquad \text{(A4)}$$

Equation (A4) follows from noting that since $\{\phi_\alpha\}$ is complete,

$$|f\rangle = \sum_\alpha f_\alpha |\phi_\alpha\rangle$$

Therefore,

$$\langle\phi_\beta|f\rangle = \sum_\alpha f_\alpha S_{\beta\alpha}$$

and multiplying by S^{-1} and summing over β gives

$$\sum_\beta S^{-1}_{\gamma\beta} \langle\phi_\beta|f\rangle = \sum_{\alpha,\beta} f_\alpha S^{-1}_{\gamma\beta} S_{\beta\alpha} = \sum_\alpha f_\alpha S_{\gamma\alpha} = f_\gamma$$

Therefore

$$|f\rangle = \sum_\gamma f_\gamma |\phi_\gamma\rangle = \sum_{\gamma,\beta} S^{-1}_{\gamma\beta} |\phi_\alpha\rangle\langle\phi_\beta|f\rangle$$

from which Eq. (A4) immediately follows.

Using Eq. (A4) we obtain

$$(G^{\circ}V)_{\alpha\alpha'} = \sum_{\beta,\gamma} G^{\circ}_{\alpha\beta} \, (S^{-1})_{\beta\gamma} \, V_{\gamma\alpha'} \tag{A5}$$

and substituting (A5) into Eq. (A3) and multiplying both sides of Eq. (A3) by $(S^{-1})_{\delta\alpha}$ and summing over α yields

$$\sum_{\alpha'} \Big(\delta_{\delta\alpha'} - \sum_{\alpha,\beta,\gamma} S^{-1}_{\delta\alpha} \, G^{\circ}_{\alpha\beta} \, S^{-1}_{\beta\gamma} \, V_{\gamma\alpha'} \Big) C_{\alpha'} = 0$$

which has nontrivial solutions if and only if

$$\det \Big\| \delta_{\alpha\alpha'} - \sum_{\alpha''} \bar{G}^{\circ}_{\alpha\alpha''} V_{\alpha''\alpha'} \Big\| = 0 \tag{A6}$$

where

$$\bar{G}^{\circ}_{\alpha\alpha''} \equiv \sum_{\beta,\gamma} S^{-1}_{\alpha\beta} \, G^{\circ}_{\beta\gamma} \, S^{-1}_{\gamma\alpha''} \tag{A7}$$

We may now proceed in exactly the same manner as given in Ref. 3, i.e., we write for a potential having only a finite number of nonzero matrix elements with the basis states $\{\phi_\alpha\}$,

$$V = \begin{pmatrix} V & 0 \\ 0 & 0 \end{pmatrix}$$

and partition $\bar{G}^0$ so that it is written

$$\bar{G}^0 = \begin{pmatrix} \bar{G}^0_{11} & \bar{G}^0_{12} \\ \bar{G}^0_{21} & \bar{G}^0_{22} \end{pmatrix}$$

It then follows that

$$\mathrm{Det}\ ||I - \bar{G}^0 V|| = \mathrm{Det}\ ||I - \bar{G}^0_{11} V|| \qquad \text{(A8)}$$

Again using the arguments of Ref. 3, the eigenvalues of the Hamiltonian for which all the matrix elements with orbitals on the atom to be removed are set equal to zero are the same as those obtained by $V = E_0 I$ and letting $E_0 \rightarrow \infty$. We obtain from Eqs. (A6) and (A8)

$$\mathrm{Det}\ ||\bar{G}^0_{11}|| = 0. \qquad \text{(A9)}$$

Chapter II

Chapter Two - Generalized Effective Mass Theory

2.1 Introduction

The results of the previous chapter leave us without a simplified method with which to approach the impurity or defect problem. At this stage we would be compelled to perform a full scale calculation of Det(1 - G^0(E)V) = 0 to find the binding energy.

It has been suggested[1] that the vacancy in Si may be treated by the Kohn-Luttinger effective mass theory (EMT). This was based on the observation that the k vector decomposition of the wavefunction (as calculated within a Green's function formalism using self-consistent techniques) is comprised almost entirely of Bloch functions with k values near the nearby band extrema.

The three valence bands degenerate at k = 0 contribute 79.6% of the wavefunction of the Si vacancy while the next nearest band, the lowest lying conduction band, contributes an additional 10.9%. This prompted Pantelides, Lipari and Bernholc[1] (PLB) to attempt a calculation of the Si vacancy energy and wavefunction within the EMT using the three valence bands.

Although the value obtained for E_b (0.9eV as compared to 0.8eV using a non self-consistent Green's function calculation) was quite good, they noted that the corresponding wavefunction did not have the correct structure. While " . . . the Green's-function theoretic wavefunction has a dangling-hybrid-like character the EMT wavefunction does not. Instead, it looks like a bonding function with maximum amplitude in the region where the vacancy potential is large."

In addition, the inclusion of Umklapp terms in the calculation of the energy added a correction (~2eV) of greater magnitude than the first order term, which precluded any possibility of a vacancy bound state in the energy gap.

PLB argue that inclusion of conduction band Bloch functions, (which are antibonding in nature) would rectify this problem. If the EMT included the conduction bands as well, then the maximum of the vacancy wavefunction would be shifted away from the vacancy site, thus lowering the value of the potential matrix elements $\langle\psi_{n\vec{K}}|V|\psi_{n'\vec{K}'}\rangle$ used in calculating the additional energy due to Umklapp corrections.

The good values for the energy levels obtained in EMT are due to cancellations of large corrections - Umklapp which increases the potential matrix elements and inclusion of conduction bands which would decrease them.

As is well known, effective mass theory is based upon the assumption that we are dealing with a weak, slowly varying perturbation potential and thus a wavefunction which is strongly peaked about a band extremum.

However, the vacancy hardly qualifies as a slowly varying potential, so it is not surprising that neither the wavefunction nor the energy with Umklapp terms included turn out correctly.

Although a direct application of EMT leads to results which are inconclusive at best, the observation made by PLB is an important one. Since the wavefunction is comprised to a great extent of Bloch functions with $\bar{\kappa}$ value belonging to nearby band extrema, it suggests that an extension of EMT may be made to include this class of potential as well.

This led us to enquire into the nature of EMT and whether we could make a successful generalization to encompass perturbations such as defects, and to include the rapid variation of the potential near the ionic core of impurities. That is, can we modify the theory to enable us to treat the case of rapidly varying potentials.

2.2 Effective Mass Equations for Envelope Wavefunctions

The first successful derivation of an effective mass Schroedinger equation that is capable of deriving both energy eigenvalues and eigenfunctions using envelope wavefunctions was given by Luttinger and Kohn[2].

They showed that if the perturbing potential, $V(\bar{r})$, was slowly varying in space over the unit cell of the crystal, and one assumed that the wavefunction was mainly composed of a superposition of Bloch waves from near the band extremum, then through second order in the expansion of $\varepsilon_n(\vec{\kappa})$, the eigenvalue-eigenfunction equation can be written (assuming an extremum at $\vec{\kappa} = 0$)

$$[\varepsilon_n(-i\nabla) + U(\vec{r})]F_n(\vec{r}) = EF_n(\vec{r}) \tag{1}$$

where

$$F_n(\vec{r}) = \Omega^{-\frac{1}{2}}\Sigma_{\vec{\kappa}} e^{i\vec{\kappa}\cdot\vec{r}} C_n(\vec{\kappa}) \tag{2}$$

and the wavefunction $\psi(\vec{r})$ is given by

$$\psi(\vec{r}) = \Omega^{-\frac{1}{2}}\Sigma_{\vec{\kappa}} \; C_n(\vec{\kappa}) e^{i\vec{\kappa}\vec{r}} \phi_{no}(\vec{r}) \tag{3}$$

$$= F_n(\vec{r})\phi_{no}(\vec{r}) \tag{4}$$

Thus far we have considered the effective mass theory for potentials that vary slowly over the dimensions of several unit cells of the crystal. This formalism, however, is often employed to calculate the energy levels of donors and acceptors in semiconductors in which case the potential ~ 1/r, i.e., a singularity at the position of the ionized impurity. Faulkner[3] has shown that the excited states of such a system can be quantitatively described by the effective mass theory for the envelope function discussed above, but discrepancies appear when the ground state of the system is considered. This is as to be expected since the ground state envelope function is greatest in the region of the potential singularity and it is there that corrections to the simple theory given above are most likely to be important.

We are interested in extending the EMT to enable us to treat rapidly varying potentials which are weak in the sense that the binding energies for the states they produce is small. That is, E_b as measured as a distance from the nearest band edge is a small fraction of the energy band gap. (This criterion is satisfied for donor and acceptor states in semiconductors.) In this situation it is reasonable to assume that the wavefunction for this state can be described adequately by restricting ourselves to a superposition of Bloch states from a small region of $\vec{k}$ space around the band extremum of the nearest band. (Assuming for simplicity a non-degenerate band structure.)

We can thus neglect the effect of band mixing in deriving an expansion for the wavefunction and calculate the corrections to the EMT using an envelope function belonging to only one band.

Although all of this is easily extended to a time dependent potential as well (with the restriction that it have no high frequency components) we will restrict our discussion to the time independent case.

Let $\Psi(\vec{r}) = \Sigma_{\vec{K}} C_n(\vec{K}) \phi_{n\vec{K}}(\vec{r})$ where $\phi_{n\vec{K}}(\vec{r})$ are Bloch functions of quasimomentum $\vec{K}$ in band n, the nearest band. If V is the perturbation on the perfect crystal periodic potential, then:

$$(H^0 + V)\Psi(\vec{r}) = \varepsilon \Psi(\vec{r}) \tag{5}$$

and

$$H^0 \phi_{n\vec{K}}(\vec{r}) = \varepsilon_n(\vec{K}) \phi_{n\vec{K}}(\vec{r}) \tag{6}$$

where $\varepsilon_n(\vec{K})$ is the n^{th} energy band function.

Recall:

$$\langle \phi_{n\vec{K}} | \phi_{n'\vec{K}'} \rangle = \delta_{nn'} \delta_{\vec{K}\vec{K}'} \tag{7}$$

and

$$\phi_{n\vec{K}} = \Omega^{-\frac{1}{2}} e^{i\vec{K}\vec{r}} U_{n\vec{K}}(\vec{r}) \tag{8}$$

thus

$$\int |U_{n\vec{K}}|^2 \, d\vec{r} = \Omega \tag{9}$$

Then:

$$\Psi(\vec{r}) = (1/\Omega) \Sigma_{\vec{K}} C_n(\vec{K}) U_{n\vec{K}}(\vec{r}) e^{i\vec{K}\vec{r}} \tag{10}$$

$$\langle \Psi | H | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle = \langle \Psi | H^0 + V | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle$$

$$= (1/\Omega) \Sigma_{\vec{K},\vec{K}'} C_n^*(\vec{K}) C_n(\vec{K}') \langle e^{i\vec{K}\vec{r}} U_{n\vec{K}}(\vec{r}) | H | e^{i\vec{K}'\vec{r}} U_{n\vec{K}'}(\vec{r}) \rangle$$
$$- (\lambda/\Omega) \Sigma_{\vec{K},\vec{K}'} C_n^*(\vec{K}) C_n(\vec{K}') \langle e^{i\vec{K}\vec{r}} U_{n\vec{K}}(\vec{r}) | e^{i\vec{K}'\vec{r}} U_{n\vec{K}'}(\vec{r}) \rangle$$

$$= \Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \varepsilon_n(\vec{\kappa}') \delta_{\vec{\kappa}\vec{\kappa}'} - \lambda \Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \delta_{\vec{\kappa}\vec{\kappa}'} + (1/\Omega) \Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}}(\vec{r}) | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}'}(\vec{r}) \rangle \quad (11)$$

If one assumes the $C_n(\vec{\kappa})$ are peaked about the band extremum, then in the sum over $\vec{\kappa}$ and $\vec{\kappa}'$, which contains terms of the form $C_n(\vec{\kappa}')C_n(\vec{\kappa})$, we can to a good approximation replace

$$\Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}'} \rangle$$

by

$$\Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}_o} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}_o}) \rangle \quad (12)$$

i.e., $\langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}'} \rangle \implies \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}_o} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}'_o} \rangle$ in the final term of equation (11). This would be exact if the periodic part ofthe Bloch function $U_{n\vec{\kappa}}(\vec{r})$ were independent of $\vec{\kappa}$ (as is the case for plane waves).

Variation of $\langle\Psi|H|\Psi\rangle$ subject to the normalization, $\langle\Psi|\Psi\rangle$ being constant yields:

$$\delta\{\langle\Psi|H|\Psi\rangle - \lambda\langle\Psi|\Psi\rangle\} = 0 \quad (13)$$

or using (12)

$$\delta\{\Sigma_{\vec{\kappa}} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}) [\varepsilon_n(\vec{\kappa}) - \lambda] + (1/\Omega) \Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \times \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}_o} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}_o} \rangle\} = 0$$

$$= \Sigma_{\vec{\kappa}}\{C_n(\vec{\kappa})[\varepsilon_n(\vec{\kappa})-\lambda] + (1/\Omega)\Sigma_{\vec{\kappa}'}C_n(\vec{\kappa}')\langle e^{i\vec{\kappa}\vec{r}}U_{n\vec{\kappa}_o}|V|e^{i\vec{\kappa}'\vec{r}}U_{n\vec{\kappa}_o}\rangle\} \times \delta C_n^*(\vec{\kappa}) + \text{C.C.} = 0$$

==>

$$[\varepsilon_n(\vec{\kappa})-\lambda]C_n(\vec{\kappa}) + (1/\Omega)\Sigma_{\vec{\kappa}'}C_n(\vec{\kappa}')\langle e^{i\vec{\kappa}\vec{r}}U_{n\vec{\kappa}_o}|V|e^{i\vec{\kappa}'\vec{r}}U_{n\vec{\kappa}_o}\rangle = 0 \qquad (14)$$

Multiply by $e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'}$ and sum over $\vec{\kappa}$:

$$\Sigma_{\vec{\kappa}}[\varepsilon_n(\vec{\kappa})-\lambda]C_n(\vec{\kappa})e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'} + (1/\Omega)\Sigma_{\vec{\kappa},\vec{\kappa}'}C_n(\vec{\kappa}')e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'} \times\langle e^{i\vec{\kappa}\vec{r}}U_{n\vec{\kappa}_o}|V|e^{i\vec{\kappa}'\vec{r}}U_{n\vec{\kappa}_o}\rangle = 0$$

or

$$\Sigma_{\vec{\kappa}}[\varepsilon_n(\vec{\kappa})-\lambda]C_n(\vec{\kappa})e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'} + (1/\Omega)\Sigma_{\vec{\kappa},\vec{\kappa}'}\int C_n(\vec{\kappa}')e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'} \times e^{i(\vec{\kappa}'-\vec{\kappa})\vec{r}}|U_{n\vec{\kappa}_o}(\vec{r})|^2V(\vec{r})d\vec{r} = 0$$

Define

$$F_n(\vec{r}') = \Omega^{-\frac{1}{2}}\Sigma_{\vec{\kappa}}C_n(\vec{\kappa})e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'} \qquad (15)$$

and using[4]

$$\varepsilon_n(-i\nabla)[e^{i\vec{\kappa}\vec{r}}] = \varepsilon_n(\vec{\kappa})e^{i\vec{\kappa}\vec{r}}$$

we obtain:

$$\varepsilon_n(\vec{\kappa}_o-i\nabla')F_n(\vec{r}') + (1/\Omega)\int\Sigma_{\vec{\kappa}}\{F_n(\vec{r})e^{i(\vec{\kappa}-\vec{\kappa}_o)(\vec{r}'-\vec{r})} \times V(\vec{r})|U_{n\vec{\kappa}_o}(\vec{r})|^2d\vec{r} = \lambda F_n(\vec{r}')$$

$$\Delta(\vec{r}'-\vec{r}) = \Omega^{-1}\Sigma'_{\vec{\kappa}\in 1^{st}\,\text{B.Z.}}e^{i(\vec{\kappa}-\vec{\kappa}_o)(\vec{r}'-\vec{r})} \qquad (16)$$

thus

$$\varepsilon_n(\vec{\kappa}_o-i\nabla)F_n(\vec{r}) + \int F_n(\vec{r}')V(\vec{r}')|U_{n\vec{\kappa}_o}(\vec{r}')|^2\Delta(\vec{r}-\vec{r}')d\vec{r}' = \lambda F_n(\vec{r}) \qquad (17)$$

where $F_n(\vec{r})$ is the envelope wavefunction, and the generalized effective mass wavefunction is given by:

$$\Psi = F_n(\vec{r})\phi_{n\vec{\kappa}_o}(\vec{r}) = \Omega^{-\frac{1}{2}} e^{i\vec{\kappa}_o\vec{r}} U_{n\vec{\kappa}_o}(\vec{r})$$

$$= \Omega^{-\frac{1}{2}} \Sigma_{\vec{\kappa}} C_n(\vec{\kappa}) e^{i\vec{\kappa}_o\vec{r}} U_{n\vec{\kappa}_o}(\vec{r})$$

Multiplying equation (14) by $C_n^*(\vec{\kappa})$ and summing over $\vec{\kappa}$ yields:

$$\Sigma_{\vec{\kappa}} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}) \varepsilon_n(\vec{\kappa}) + \Sigma_{\vec{\kappa},\vec{\kappa}'} C_n^*(\vec{\kappa}) C_n(\vec{\kappa}') \langle e^{i\vec{\kappa}\vec{r}} U_{n\vec{\kappa}_o} | V | e^{i\vec{\kappa}'\vec{r}} U_{n\vec{\kappa}_o} \rangle$$

$$= \lambda \Sigma_{\vec{\kappa}} C_n^*(\vec{\kappa}) C_n(\vec{\kappa})$$

or

$$\langle \Psi | H | \Psi \rangle = \lambda \langle \Psi | \Psi \rangle = \lambda$$

thus

$$\lambda = E$$

and

$$\varepsilon_n(\vec{\kappa}_o - i\nabla) F_n(\vec{r}) + \int F_n(\vec{r}') V(\vec{r}') |U_{n\vec{\kappa}_o}(\vec{r}')|^2 \Delta(\vec{r}-\vec{r}') d\vec{r}' = E \times F_n(\vec{r}) \qquad (18)$$

Although the wavefunction may be in error by $O(\delta)$ (since we have included only one band) it follows from the variational principle that the energy will be in error by only $O(\delta^2)$.

The function $\Delta(\vec{r} - \vec{r}')$ is a delta function-like expression which is strongly peaked for $\vec{r} = \vec{r}'$ and has a width of order a lattice vector[2]. Since by hypothesis the $C_n(\vec{\kappa})$ are strongly peaked near $\vec{\kappa} = \vec{\kappa}_o$, the envelope function $F_n(\vec{r})$ will be slowly varying (it has only long wavelength fourier components) and so can be considered approximately constant over the range where $\Delta(\vec{r} - \vec{r}')$ is appreciable. Therefore, Equ. (18) can be approximated by

$$\varepsilon_n(\vec{\kappa}_o - i\nabla)F(\vec{r}) + \int V(\vec{r}')|U_{n\vec{\kappa}_o}(\vec{r}')|^2\Delta(\vec{r}-\vec{r}')d\vec{r}'F(\vec{r}) = E\times F(\vec{r}) \qquad (19)$$

Equation (19) represents the time independent version of the results of Resca and Resta[5] for the differential equation satisfied by the envelope function. It is equivalent to the usual effective mass equation except that the effective potential is

$$V_{eff}(\vec{r}) = \int V(\vec{r}')|U_{n\vec{\kappa}_o}(\vec{r}')|^2\Delta(\vec{r} - \vec{r}')d\vec{r}' \qquad (20)$$

In the regions of space in which $V(\vec{r})$ is slowly varying we would like to show that this reduces to the usual effective mass equation, i.e. $V_{eff}(\vec{r}) = V(\vec{r})$. Since $\Delta(\vec{r}' - \vec{r})$ is sharply peaked about $\vec{r} = \vec{r}'$ and $V(\vec{r})$ is slowly varying, $V(\vec{r}')$ can be evaluated at $\vec{r}' = \vec{r}$ and removed from the integral thus:

$$\int|U_{nk_o}(\vec{r}')|^2\Delta(\vec{r}-\vec{r}')V(\vec{r}')d\vec{r}' = V(\vec{r})\int|U_{nk_o}(\vec{r}')|^2\Delta(\vec{r}-\vec{r}')d\vec{r}'$$

$$= (V(\vec{r})/\Omega)\int|U_{nk_o}(\vec{r}')|^2\sum_{\substack{\vec{\kappa}\varepsilon 1^{st} \\ B.Z.}} e^{i(\vec{\kappa}-\vec{\kappa}_o)(\vec{r}-\vec{r}')}d\vec{r}'$$

$$= (V(\vec{r})/\Omega)\sum_{\substack{\vec{\kappa}\varepsilon 1^{st} \\ B.Z.}} e^{i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}}\int e^{-i(\vec{\kappa}-\vec{\kappa}_o)\vec{r}'}|U_{nk_o}(\vec{r}')|^2d\vec{r}' \qquad (21)$$

The integral is just the Fourier transform of $|U_{n\vec{\kappa}_o}(\vec{r})|^2$ for each k-value within the first Brillouin zone.

But $U_{no}(\vec{r})$ is just the cell periodic part of the Bloch function at $\vec{\kappa} = \vec{\kappa}_o$, and thus has the periodicity of the lattice.

Therefore the only $\vec{\kappa}$ values for which the Fourier transform is non-zero are where $\vec{\kappa} - \vec{\kappa}_o$ is equal to a reciprocallattice vector. But if the sum is restricted to the first Brillouin zone the only reciprocal lattice vector contained in the sum is when $\vec{\kappa} - \vec{\kappa}_o = 0$.

Thus

$$V_{eff}(\vec{r}) = V(\vec{r})\Omega^{-1}\int |U_{n\vec{\kappa}_o}(\vec{r}')|^2 d\vec{r}' \tag{22}$$

and given the normalization of the $U_{n\vec{\kappa}_o}$ to a unit volume we finally arrive at the desired result,

$$V_{eff}(\vec{r}) = V(\vec{r}) \tag{23}$$

under the conditions normally employed in EMT.

Thus Equ. (19) reduces to the usual effective mass equation in the spatial regions in which $V(\vec{r})$ is slowly varying. However, in regions of rapid variation the potential function is modulated by the variation of the periodic part of the Bloch function at the band extremum as given by Equ. (20).

Resca and Resta claim that the use of the many valley generalization of Equ. (19) resolves the existing discrepancies between theory and experiment for the ground state of donors in silicon. However, since they employed a spherical effective mass approximation for the conduction band minima which in fact is significantly anisotropic having $m_{\parallel}/m_{\perp} \simeq 5$, their results may not be considered a definitive test of the improvement that Equ. (19) makes over Equ. (1), the standard effective mass equation.

We note that while Resca et.al.[5] employ the approximation

$$\phi_{\bar{K}}(\bar{r}) \simeq e^{i(\bar{K}-\bar{K}_o)\bar{r}}\phi_{\bar{K}_o}(\bar{r})$$

our derivation relies only on the strongly peaked character of the $C_n(\bar{K})$. The approximation above is equivalent to saying that the periodic part of the Bloch function is essentially constant throughout the Brillouin zone.

We employ the Kronig-Penney model as a guide in this work since it is an exactly soluble case of a rapidly varying potential. The probability density for a typical "vacancy" in the Kronig-Penney model is given in Figure 1. We observe that this has periodic maxima which are steadily declining in magnitude.

This suggests that it may be possible to treat this problem in the EMT where the solution will turn out to be an envelope function times a Bloch function of fixed k value and thus a specific periodicity in real space. The probability density for a delta function impurity, i.e. the depth of the particular "well" is not the same as those of the background, shows similar behavior. In fact the vacancy is just a special case in which the strength of the impurity is zero.

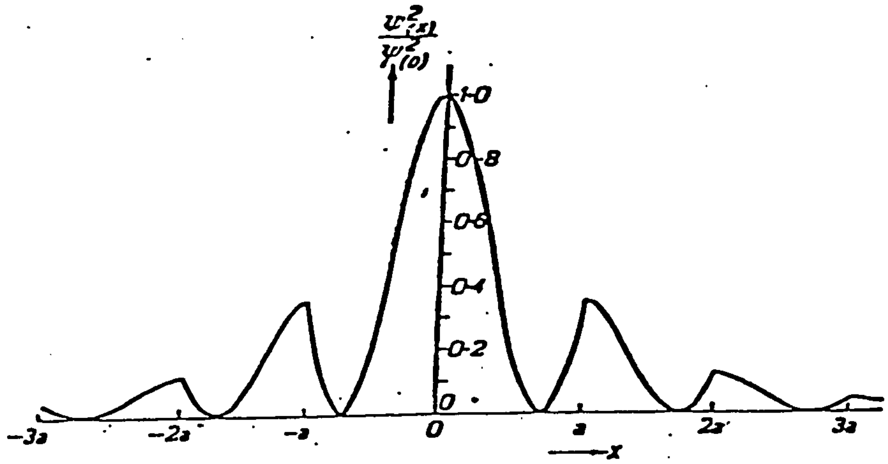


Fig. 1. Probability function associated with an extra energy level due to a single defect lattice point.

<u>Figure 1</u>: Probability Density for a KP Vacancy (P/π = -0.5) From Saxon and Hutner (Reference 6)

2.3 Kronig-Penney Model

$$V_{tot} = \lambda\ \Sigma_{n\neq 0}\delta(x-na) + \lambda'\ \delta(x) \qquad (24)$$

where $\lambda < 0$, an attractive potential. Then:

$$[-\frac{\hbar^2}{2m}\nabla^2 + V_{tot}(x)]\ \Psi(x) = E\Psi(x)$$

$$[\nabla^2 - (2m\lambda/\hbar^2)\Sigma_{n\neq 0}\delta(x-na) - (2m\lambda'/\hbar^2)\delta(x)]\Psi(x) = -(2mE/\hbar^2)\Psi(x)$$

or

$$[\nabla^2 - (2m\lambda/\hbar^2)\Sigma_n\delta(x-na) - 2m(\lambda'-\lambda)/\hbar^2\delta(x)]\Psi(x) = -(2mE/\hbar^2)\Psi(x) \qquad (25)$$

Let $P = m\lambda a/\hbar^2$, $P' = m\lambda' a/\hbar^2$, $p = P' - P$ (26)

$$[\nabla^2 - (2P/a)\Sigma_n\delta(x-na) - (2p/a)\delta(x)]\Psi(x) = -(2mE/\hbar^2)\Psi(x) \qquad (27)$$

$$E = \hbar^2\kappa^2/2m \qquad (28)$$

Saxon and Hutner[6] derive the relationship for the discrete level due to the presence of an impurity in a KP model:

$$\cos(\kappa a) + P\sin(\kappa a)/\kappa a = \pm[1 + p^2(\sin^2\kappa a)/(\kappa a)^2]^{\frac{1}{2}} \qquad (29)$$

[In "perfect crystal" case $P' = P \rightarrow p = 0$, $\cos\kappa a + P\sin\kappa a/\kappa a = \pm 1$ which is just the band edge dispersion relation, and thus does not yield an additional state in the energy gap.]

This transcendental equation is then solved numerically to arbitrary precision to yield $E_{binding}$ of the impurity.

2.4 Kronig Penney Impurity using Effective Mass Theory

If we use the standard EMT for a weak repulsive perturbing potential to attempt a solution of the KP model $V(x) = (\lambda' - \lambda)\ \delta(x)$ where $\lambda', \lambda < 0$ and $\lambda' - \lambda > 0$. Then

$$[-\frac{\hbar^2}{2m_v^*}\frac{d^2}{dx^2} + (\lambda'-\lambda)\delta(x)]F(x) = (E_{emt} - \varepsilon_v)F(x) \qquad (30)$$

is the equation for the envelope function, with m_v^* the effective mass at the top of the valence band; $E_{emt} - \varepsilon_v$, the energy measured from the top of the valence band.

Then since $m_v^* < 0$

$$[-\frac{\hbar^2}{2|m_v^*|}\frac{d^2}{dx^2} - (\lambda'-\lambda)\delta(x)]F(x) = (\varepsilon_v - E_{emt})F(x)$$

which is just the equation for the bound state of a particle of mass $|m_v^*|$ encountering a single attractive spike of magnitude $|\lambda' - \lambda|$.

Using continuity and derivative jump conditions we arrive at the well known solution

$$F(x) = q^{1/2}e^{-q|x|} \quad \text{where } q = |m_v^*|(\lambda'-\lambda)/\hbar^2 > 0 \qquad (31)$$

and

$$E_{emt} - \varepsilon_v = \hbar^2q^2/(2|m_v^*|) = |m_v^*|(\lambda'-\lambda)^2/(2\hbar^2) \qquad (32)$$

Although the behavior of E_b as a function of perturbation strength is correct for small perturbations, i.e., it goes as the square of the potential strength p, the quantitative results of the EMT are poor.

In fact we find in this limit in which the strength of the perturbation is small compared to the background periodic potential that the eigenvalues predicted by the usual effective mass equations are too low by at least a factor of 4 (measured from the top of the valence band) compared to an exact calculation of the energy eigenvalues. This discrepancy increases with the strength of the background although the ratio of the perturbation to the background remains unaltered.

A first attempt at improvement is the inclusion of Umklapp terms

$$E_{emtu} = \langle\Psi|H^0 + V_{pert}|\Psi\rangle \tag{33}$$

where

$$\Psi = \Omega^{-\frac{1}{2}}\Sigma' C_n(k)e^{ikx}U_{nk}(x)$$

Recalling that because of the peaked value of the $C_n(k)$ we can replace $U_{nk}(x)$ by $U_{nk_o}(x)$ in the matrix elements we get:

$$E_{emtu} - \varepsilon_v = |m_v^*|(\lambda'-\lambda)^2/(2\hbar^2) + \langle\Psi|V|\Psi\rangle - \langle F|V|F\rangle$$

$$= |m_v^*|(\lambda'-\lambda)^2/(2\hbar^2) + |m_v^*|(\lambda'-\lambda)^2/\hbar^2|U^{val}(0)|^2 - |m_v^*|(\lambda'-\lambda)^2/\hbar^2$$

$$E_{emtu} - \varepsilon_v = \{|m_v^*|(\lambda'-\lambda)^2/(2\hbar^2)\}[1 + 2\{|U^{val}(0)|^2-1\}] \tag{34}$$

Figure 2 is a plot of the binding energy for a small δ function perturbation calculated within the effective mass approximation as a function of increasing background potential P. For each value of P, p/P = .01 for this calculation. The energy is given as a fraction of the exact binding energy, which can be found by numerical solution of the transcendental equation, and the measure of the background potential is ε_g/E_0 - the energy gap divided by the width of the free electron valence band. $E_0 = \hbar^2\pi^2/(2ma^2)$ which in the KP model is the energy of the minimum of the lowest lying conduction band, irrespective of the strength of the background potential. Thus ε_g is expressed in units normalized such that the energy of the conduction band minimum is 1.

The graph (Figure 2) clearly indicates the great improvement introduced by the Umklapp terms, while at the same time suggesting the inadequacy of this approach. The Umklapp term which should be a small correction in order for the standard EMT to be valid is always at least twice the size of the original term, as reported by PLB in the case of the Si vacancy, and furthermore, even with its inclusion the result starts at 75% of the true value and becomes steadily worse.

This demonstrates that for rapidly varying potentials the Umklapp terms cannot be treated as a perturbation on the envelope wavefunction and energy, but must be included from the start in the eigenvector equation for the wavefunction and energy.

In the following sections we will show that in the limit of weak perturbing potentials the generalized effective mass equation, equation (18), leads to the exact result. Moreover, it is clear why this happens. The use of equation (20) for V_{eff} for a delta function perturbation, essentially results in multiplying the potential by the factor $|U^{val}(0)|^2$ where $U^{val}(0)$ is the cell periodic part of the Bloch function at the top of the valence band evaluated at a lattice site located at x = 0.

In the limit in which the attractive background periodic potential is weak, the Bloch waves near the band extrema closely resemble their forms for the "nearly free electron" approximation. That is $2^{\frac{1}{2}}\cos(kx)$ and $2^{\frac{1}{2}}\sin(kx)$, i.e. the wavefunction for the top of the lower (valence) band has a maximum at the lattice sites because we are dealing with an attractive potential[7]. This yields a factor of $|U^{val}(0)|^2 = 2$, and since the energy eigenvalue is proportional to the square of the strength of the perturbation, this results in a factor of 4 in the energy. Furthermore, for stronger background periodic potential, the valence band wavefunction is even more strongly localized about the lattice site and thus the correction factor increases.

The preceding analysis demonstrates that the observation of PLB that the wavefunction for an electron bound to a vacancy in silicon is mainly composed of Bloch states from the nearby band extrema is not sufficient to employ the multi-band generalization of equation(1) in the calculation of the energy and wavefunction of such states. One must also take into consideration the fact that the potential is rapidly varying over the unit cell and employ the multi-band generalization of equation (19) i.e. the effective potential will depend on a convolution of

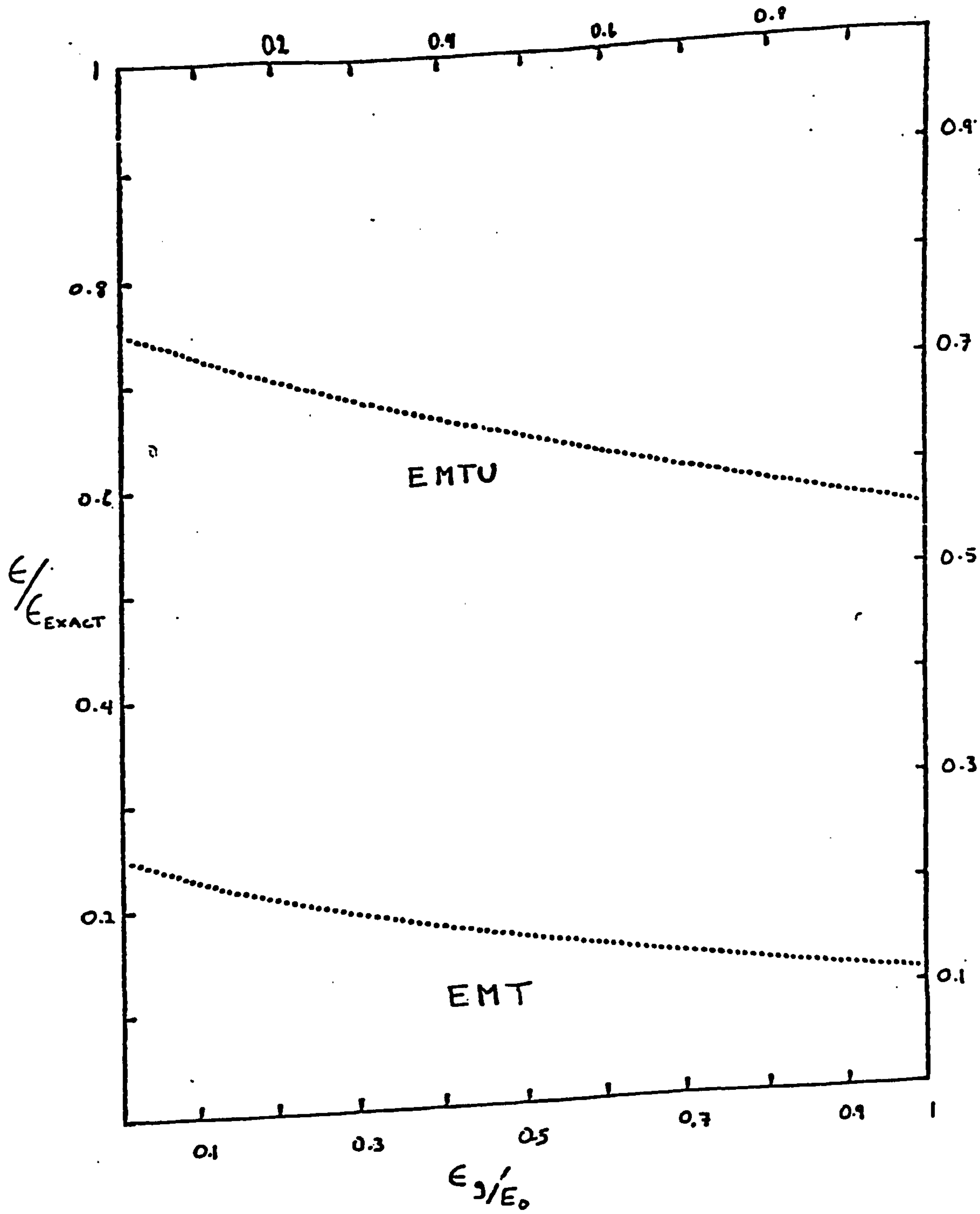


Figure 2: Binding Energies for a KP Defect (p << P) [Calculated/Exact for a Range of Backround Potentials]

the perturbation potential and the Bloch functions at the nearby band extrema. This explains why their final result for the energy eigenvalue employing the effective mass approximation was in such poor agreement with the results of more detailed calculations.

2.5 Kronig Penney Impurity Using Generalized Effective Mass Theory

If we employ the generalized form of the effective mass equation, [equation (19)] for rapidly varying perturbations, the equation for the envelope function is:

$$-\frac{\hbar^2}{2m_v^*}\frac{d^2}{dx^2}F(x) + (\lambda'-\lambda)\int|U^{val}(x')|^2\Delta(x-x')\delta(x')F(x')dx' = (E - \varepsilon_v)F(x) \qquad (35)$$

or

$$-\frac{\hbar^2}{2m_v^*}\frac{d^2}{dx^2}F(x) + (\lambda'-\lambda)|U^{val}(0)|^2\Delta(x)F(0) = (E - \varepsilon_v)F(x)$$

Since $\Delta(x)$ is sharply peaked about $x = 0$ with width $\simeq a$ (the lattice spacing) and for a weak perturbation $F(x)$ will be slowly varying over a lattice constant, we can approximate

$$\Delta(x) \sim \delta(x)$$

and thus

$$V_{eff}(x) = (\lambda'-\lambda)\delta(x)|U_\kappa^{val}(0)|^2 \qquad (36)$$

The potential now includes the effect of the valence band Bloch function at $k = \pi/a$ and therefore can make a considerable difference in the value of the calculated binding energy.

Now by the identical arguments as in the preceding section:

$$F = Ae^{-g|x|} \quad \text{where} \quad g = \{|m_v^*|(\lambda' - \lambda)/(2\hbar^2)\}|U_{\kappa_o}^{val}(0)|^2$$

and

$$E - \varepsilon_v = -\hbar^2 g^2/(2m_v^*) = \{|m_v^*|(\lambda'-\lambda)^2/(2\hbar^2)\}|U_{\kappa_o}^{val}(0)|^4 \qquad (37)$$

In the next section we will calculate the exact result analytically for the case of weak perturbations. In addition, in order to enable a comparison between GEMT and the exact result we will derive expressions for $|m_v^*|/m$ and $|U_{\kappa_o}^{val}(0)|^2$.

2.6 Exact Solution of KP Impurity For Small p

We have the relationship:

$$\cos(\kappa a) + P\sin(\kappa a)/\kappa a = \pm[1 + p^2(\sin^2\kappa a)/(\kappa a)^2]^{\frac{1}{2}} \qquad (29)$$

which gives the exact energy of the impurity in the Kronig Penney model.

In general this must be solved numerically, however for the case of $p << P$ we can derive an expression for E_b which can then be compared with the expressions obtained in approximate theories.

Let $\gamma = \kappa a$

For the band structure we have:

$$\cos\gamma + P\sin\gamma/\gamma = \cos(ka) \qquad (38)$$

then at the top of the valence band where $ka = \pi$, $\gamma = \gamma_o$

$$\cos\gamma_o + P\sin\gamma_o/\gamma_o = -1$$

from which it follows that:

$$P = -\gamma_o \cot(\tfrac{1}{2}\gamma_o) \qquad (39)$$

For small p we expect the energy to be slightly higher than the valence band edge i.e.,

$$E = \hbar^2\gamma^2/(2ma^2)$$

$\gamma = \gamma_o + \delta$ where $\delta << \gamma_o$.

$$F(\gamma) = \cos(\gamma) + P\sin(\gamma)/\gamma = \pm[1 + p^2(\sin^2\gamma)/(\gamma)^2]^{\frac{1}{2}} \qquad (29)$$

So expanding about γ_o yields:

$$F(\gamma) = F(\gamma_o) + (dF/d\gamma)|_{\gamma_o}(\gamma-\gamma_o) = -[1 + p^2(\sin^2\gamma_o)/(\gamma_o)^2]^{\frac{1}{2}} \qquad (40)$$

to order p^2. But $F(\gamma_o) = -1$ (41)

$$F'(\gamma_o) = [P\cos\gamma/\gamma - P\sin\gamma/\gamma^2 - \sin\gamma]_{\gamma=\gamma_o} \qquad (42)$$

using equation (39)

$$F'(\gamma_o) = \cot(\tfrac{1}{2}\gamma_o)[\sin\gamma_o/\gamma_o - 1] \qquad (43)$$

so

$$(\gamma - \gamma_o) = -\tfrac{1}{2}p^2(\sin^2\gamma_o/\gamma_o^2)/F'(\gamma_o)$$

or

$$(\gamma - \gamma_o) = \tfrac{1}{2}p^2(\sin^2\gamma_o/\gamma_o^2)/\{\cot(\tfrac{1}{2}\gamma_o)[1 - \sin\gamma_o/\gamma_o]\} \qquad (44)$$

$$E_b = \frac{\hbar^2}{2ma^2}(\gamma^2-\gamma_o^2) = \frac{\hbar^2}{2ma^2}(\gamma-\gamma_o)(\gamma+\gamma_o) \approx \frac{\hbar^2\gamma_o}{ma^2}(\gamma-\gamma_o)$$

$$E_b = \frac{\gamma_o\hbar^2}{ma^2} \cdot \frac{p^2\sin^2\gamma_o}{2\gamma_o^2\cot(\frac{1}{2}\gamma_o)} \cdot \frac{1}{1-\frac{\sin\gamma_o}{\gamma_o}} \qquad (45)$$

However we would like to compare this to the effective mass results and so we need to eliminate m in favor of m_v^*.

$$p = m(\lambda'-\lambda)a/\hbar^2$$

Thus

$$E_b = \frac{\hbar^2}{2ma^2\gamma_o^2}\left\{\frac{m(\lambda'-\lambda)a}{\hbar^2}\right\}^2 \frac{\sin^2\gamma_o}{\cot(\frac{\gamma_o}{2})[1-\frac{\sin\gamma_o}{\gamma_o}]}$$

$$= \frac{m(\lambda'-\lambda)^2}{2\gamma_o\hbar^2} \cdot \frac{4\sin^2(\frac{\gamma_o}{2})\cos^2(\frac{\gamma_o}{2})}{\cot(\frac{\gamma_o}{2})[1-\sin\gamma_o/\gamma_o]}$$

$$E_b = \left(\frac{m}{m_v^*}\right)\frac{m_v^*(\lambda'-\lambda)^2}{2\hbar^2\gamma_o}\left[\frac{4\sin^2(\frac{\gamma_o}{2})\cos^2(\frac{\gamma_o}{2})}{\cot(\frac{\gamma_o}{2})[1-\frac{\sin\gamma_o}{\gamma_o}]}\right] \qquad (46)$$

We now use equation (38), the equation which defines the band structure to find m/m_v^*.

$$f(\gamma) = P\sin\gamma/\gamma + \cos\gamma = \cos(ka) \qquad (38)$$

Expand about γ_o, the top of the band , then to lowest order

$$f(\gamma_o) + \frac{\partial f}{\partial \gamma}\Big|_{\gamma_o}(\gamma-\gamma_o) = 1 - \tfrac{1}{2}(ka-\pi)^2$$

$$\Rightarrow \qquad \gamma = \gamma_o + \left[\frac{\partial f}{\partial \gamma}\Big|_{\gamma_o}\right]^{-1} \tfrac{1}{2}(ka-\pi)^2 \qquad (47)$$

$$\varepsilon_v(k) = \frac{\hbar^2\gamma^2}{2ma^2}$$

$$= \frac{\hbar^2}{2ma^2}\left\{ \gamma_o^2 + \left[\frac{\partial f}{\partial \gamma}\Big|_{\gamma_o}\right]^{-1} \gamma_o\,(ka-\pi)^2 + \ldots \right\}$$

$$\frac{1}{m^*}\Big|_{k=\pi/a} = \frac{1}{\hbar^2}\,\frac{\partial^2 \varepsilon_v(k)}{\partial k^2}\Big|_{k=\pi/a} = \frac{1}{2ma^2}\left\{\gamma_1 \cdot 2a^2 \left[\frac{\partial f}{\partial \gamma}\Big|_{\gamma_o}\right]^{-1}\right\}$$

$$= \frac{\gamma_o}{m}\left[\frac{\partial f}{\partial \gamma}\Big|_{\gamma_o}\right]^{-1}$$

So

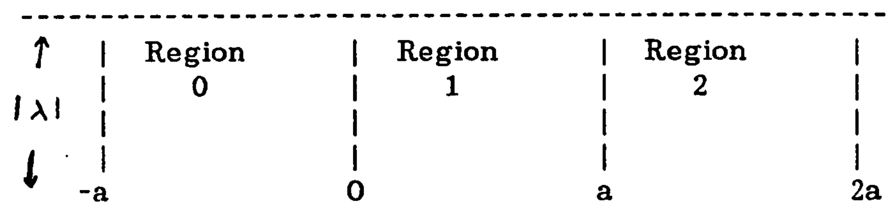
$$\frac{m}{m^*} = \frac{\gamma_o}{\cot\left(\frac{\gamma_o}{2}\right)\left[\frac{\sin\gamma_o}{\gamma_o} - 1\right]} \qquad (48)$$

and

$$E_b = -\frac{m_v^*(\lambda'-\lambda)^2}{2\hbar^2}\left\{\frac{2\sin^2\left(\frac{\gamma_o}{2}\right)}{1-\frac{\sin\gamma_o}{\gamma_o}}\right\}^2 \qquad (49)$$

2.7 Calculation of the Valence Band Bloch Function at the Zone Edge

For a Kronig Penney potential $V = \lambda\Sigma_n \delta(x-na)$, we note that in the regions between the potential spikes, $x \neq na$, the solutions to the Schrodinger equation are just plane waves.



Following the exposition of Gasiorowicz[8]:

$$\phi_o(x) = A_o \sin\kappa x + B_o \cos\kappa x$$

$$\phi_1(x) = A_1 \sin\kappa(x-a) + B_1 \cos\kappa(x-a)$$

Matching the wavefunction at $x = 0$ and using the derivative jump condition (due to δ potential) we get:

(1) $$\phi_o(0) = \phi_1(0)$$

===>

$$B_o = -A_1 \sin\kappa a + B_1 \cos\kappa a \qquad (51)$$

and

(2) $$\phi'_o(-\varepsilon) - \phi'_1(\varepsilon) = 2m\lambda/\hbar^2 \phi(0) = \alpha^2 \phi(0)$$

===>

$$\kappa A_o - [\kappa A_1 \cos\kappa a - \kappa B_1 \sin\kappa a] = \alpha^2 B_o \qquad (52)$$

(3) Periodicity ===> $\phi(x+a) = e^{ika}\phi(x)$

For the valence edge $k = \pi/a$ (zone edge).

$$\phi(x+a) = -\phi(x)$$

a. $\phi(0) = -\phi(a)$ ==> $B_o = -B_1$ (53)

b. $\phi(-\frac{1}{2}a) = -\phi(\frac{1}{2}a)$ ==> $A_o = -A_1$

Substituting equation (53) into equation (51) yields:

$$B_o = A_o \sin\kappa a - B_o \cos\kappa a$$

$$B_o = A_o \sin\kappa a/(1 + \cos\kappa a) = \omega(\kappa)A_o \quad (54)$$

where $\omega = \sin\kappa a/(1 + \cos\kappa a)$. Then from equation (50)

$$\phi^{val}(x) = A_0[\sin\kappa x + \omega(\kappa)\cos\kappa x] \qquad -a \le x \le 0$$

and

$$|\phi^{val}(0)|^2 = |A_o|^2\omega^2(\kappa) \quad (55)$$

where $|A_0|^2$ can be determined from normalization, that is

$$\int_{space}|\phi^{val}(x)|^2dx = 1$$

After some manipulation (which is presented in the appendix) this leads to

$$|U^{val}(0)|^2 = \omega^2|A|^2 = 2\sin^2(\tfrac{1}{2}\kappa a)/(1 - \sin\kappa a/\kappa a) \quad (56)$$

where

$$|A|^2 = \kappa a(1 + \cos\kappa a)/(\kappa a - \sin\kappa a) \quad (57)$$

where κ must be evaluated at the valence edge.

Thus recalling that the exact binding energy was given as:

$$E_b = \frac{|m_v^*|(\lambda'-\lambda)^2}{2\hbar^2}\left\{\frac{2\sin^2\left(\frac{\gamma_0}{2}\right)}{1-\frac{\sin\gamma_0}{\gamma_0}}\right\} \qquad (49)$$

we can rewrite this as follows:

$$E_b = \{|m_v^*|(\lambda'-\lambda)^2/(2\hbar^2)\}|U_{\kappa_0}^{val}(0)|^4 \qquad (50)$$

which is exactly the expression obtained in the generalized effective mass theory [equation (37)].

In figure 2 we do not plot the result for the generalized EMT. The calculation confirmed our analysis that $E_{gemt}/E_{exact} = 1$ for the limiting case of a weak perturbation. Thus we see that for a potential as rapidly varying as the δ function we get the correct binding energy within GEMT provided we restrict ourselves to potentials which are weak.

2.8 Vacancy in the KP Model

The great success of the generalized effective mass theory for rapidly varying though weak potentials suggest that it may be applied to potentials which are stronger as well. As a test of this we investigate a vacancy in the Kronig Penney model, within each of the formalisms previously presented, and compare the results to an exact calculation.

For the vacancy at $x = 0$, $V_{tot} = \lambda\Sigma_{n\neq o}\delta(x-na)$. That is λ', $P' = 0$ ==> $p = -P$ and $\lambda'-\lambda = -\lambda$. Then using the expression for the defect state:

$$\cos\gamma + P\sin\gamma/\gamma = \pm[1 + p^2\sin^2\gamma/\gamma^2]^{\frac{1}{2}} \qquad (29)$$

==>

$$\gamma\tan\gamma = 2P \qquad \text{for the vacancy} \qquad (59)$$

Similarly the band edge is obtained from the expression for the band structure evaluated at the zone edge, $ka = \pi$, which yields:

$$\gamma_o\cot(\tfrac{1}{2}\gamma_o) = -P \qquad (39)$$

and

$$E_b = \hbar^2/(2ma^2)\{\gamma^2 - \gamma_o^2\}$$

For our various emt results we have:

$$E_{emt} - \varepsilon_v = \{\tfrac{1}{2}\lambda^2/\hbar^2\}|m_v^*| \qquad (60)$$

$$E_{emtu} - \varepsilon_v = \{\tfrac{1}{2}\lambda^2/\hbar^2\}|m_v^*|\{4\sin^2(\tfrac{1}{2}\gamma_o)/(1-\sin\gamma_o/\gamma_o) - 1\} \qquad (61)$$

$$E_{gemt} - \varepsilon_v = \{\tfrac{1}{2}\lambda^2/\hbar^2\}|m_v^*|\{2\sin^2(\tfrac{1}{2}\gamma_o)/(1-\sin\gamma_o/\gamma_o)\}^2 \qquad (62)$$

Employing the expression for $|m_v^*|/m$ we can see that if P is given , γ and γ_o may be obtained from equations (59) and (39) which could then be used to calculate E_b for all four cases. We divide out the common factor $\hbar^2/(2ma^2)$ and express the energy as $\gamma^2 - \gamma_o^2$.

1. Exact = $\gamma^2 - \gamma_o^2$

2. $[\gamma^2 - \gamma_o^2]_{emt} = P^2\{ \cot(\frac{1}{2}\gamma_o)(1 - \sin\gamma_o/\gamma_o)/\gamma_o\}$

3. $[\gamma^2 - \gamma_o^2]_{emtu} = [\gamma^2 - \gamma_o^2]_{emt}\{2|U^{val}(0)|^2 - 1\}$

4. $[\gamma^2 - \gamma_o^2]_{gemt} = [\gamma^2 - \gamma_o^2]_{emt} \; |U^{val}(0)|^4$ (63)

where

$$|U^{val}(0)|^2 = 2 \sin^2(\tfrac{1}{2}\gamma_o)/(1 - \sin\gamma_o/\gamma_o)$$

The results of this calculation for values of $-P/\pi$ ranging up to 0.5 are tabulated in Table 1, and presented in Figure 3. For a reason which will be explained later the GEMT which we have been discussing up to this point is listed as GEMT^o in both the figure and the table.

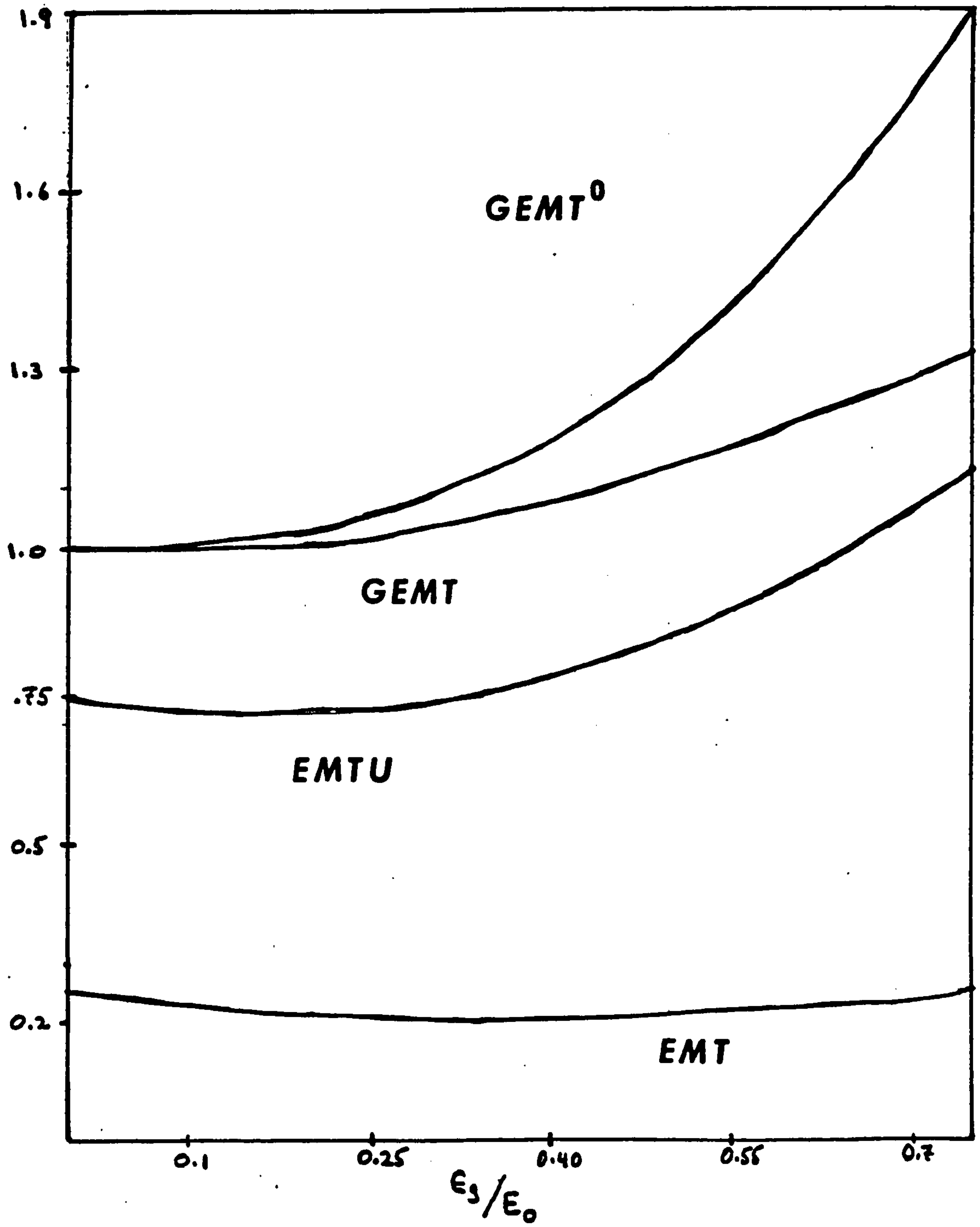
The EMT is clearly inadequate with its predicted binding energy hovering at about 20% of the true value. The inclusion of Umklapp terms as a first order correction (EMTU) looks much more promising until we recall that it is being treated as a perturbative correction on EMT. Then we perceive that it can not be relied upon since it is in fact much greater than the term it is supposed to be correcting. In fact even in the "best" case it is twice the size of the EMT result.

For low background P it seems that GEMT^0 is accurate to ~ 10%. However, with increasing background potential it is also poor. The

$-P/\pi$	EXACT	EMT	EMTU	$GEMT^{o}$	GEMT	ε_G
.10	.001525	.000340	.001109	.001545	.001531	.13147
.15	.005560	.001188	.004040	.005752	.005627	.20042
.20	.01406	.002917	.01034	.01506	.01445	.27161
.25	.02885	.005910	.02182	.03253	.03035	.34511
.30	.05147	.01061	.04078	.06224	.05599	.42100
.35	.08288	.01751	.07009	.1096	.09404	.49936
.40	.1234	.02722	.1133	.1815	.1470	.58026
.45	.1726	.04039	.1750	.2871	.2170	.66378
.50	.2301	.05783	.2605	.4380	.3051	.75000

Table 1: Vacancy Binding Energies in the Various Approximations

(Units Normalized to $(E_{conduction})_{min} = 1$)



<u>Figure</u> <u>3</u>: Binding Energies for a KP Vacancy [Calculated/Exact for a Range of Backround Potentials]

failure of all these techniques for the KP vacancy may be attributed to the strength of the potential, which makes it necessary to use a many band theory to take into account band mixing.

Nevertheless, for semiconductors ε_g/W_v (where W_v is the width of the valence band) is on the order of a few tenths for donor and acceptor states and for this region $GEMT^0$ makes a major improvement over ordinary EMT.

We now investigate the reason for the failure of $GEMT^0$ to provide accurate energies for the vacancy state and whether it can easily be improved upon.

There are two approximations built into our treatment of the vacancy - one, the restriction to only one band is inherent in our derivation of the generalized effective mass equation, while the other, the replacement of $\Delta(x)$ with $\delta(x)$ is made to simplify the calculation.

The replacement of $\Delta(x)$ by $\delta(x)$ is valid provided that F(x), the envelope wavefunction, is relatively constant over the range of $\Delta(x)$. However, for the vacancy, the wavefunction varies considerably over a single cell (see Figure 1), which is the width of $\Delta(x)$. Therefore the GEMT demands a more accurate determination of V_{eff} and what we have previously calculated is merely a first approximation to the GEMT. Thus equation (35) now becomes:

$$\frac{\hbar^2}{2|m_v^*|}\frac{d^2}{dx^2}F(x) - \lambda|U^{val}(0)|^2\Delta(x)F(0) = (E - \varepsilon_v)F(x) \qquad (64)$$

Note that this is still a one band approximation.

We now employ the preceding equation to derive the eigenvalue condition for the energy of the bound state introduced by the vacancy in the GEMT formalism. We shall then derive the exact quantization condition for the energy so that we can analyze the differences between the respective expressions and the effect it has on the energy calculation.

Let $f(x) \equiv F(x)/F(0) = (1/\Omega)\Sigma'_k a(k)e^{i(k-k_o)x}$ (65)

then

$$\frac{\hbar^2}{2|m_v^*|}\frac{d^2}{dx^2} f(x) - \lambda|U^{val}(0)|^2\Delta(x)f(0) = (E - \varepsilon_v)f(x)$$

where $f(0) = 1$. Using the definition of $f(x)$ we obtain:

$$a(k) = \frac{|\lambda|\,|U^{val}(0)|^2}{(E-\epsilon_v) + \frac{\hbar^2}{2|m_v^*|}(k-k_o)^2} \quad (66)$$

and thus:

$$f(0) = 1 = (1/\Omega)\Sigma'_k a(k) = (2\pi)^{-1}\int_{B.Z.} a(k)dk$$

or

$$1 = \frac{|\lambda|}{2\pi}|U^{val}(0)|^2 \int_0^{2\pi/a} \frac{dk}{(E-\epsilon_v) + \frac{\hbar^2}{2|m_v^*|}(k-k_o)^2}$$

(67)

Performing the integration we obtain:

$$1 = (2|P|/\pi^2)|U(0)|^2(\omega^{\frac{1}{2}}\theta)^{-1}\tan^{-1}(\omega^{\frac{1}{2}}\zeta/\theta)|_o^1 \qquad (68)$$

where $\theta^2 = (\gamma^2 - \gamma_o^2)/\pi^2$, which is just the binding energy in our scaled units, and $\omega = m/|m_v^*|$

Thus

$$1 = (2|P|/\pi^2)|U(0)|^2(\omega^{\frac{1}{2}}\theta)^{-1}\tan^{-1}(\omega^{\frac{1}{2}}/\theta)$$

or

$$\theta = (2|P|/\pi^2)|U(0)|^2\omega^{-\frac{1}{2}}\tan^{-1}(\omega^{\frac{1}{2}}/\theta) \qquad (69)$$

which can be solved numerically for θ and hence the energy.

We now derive a similar quantization relation for the exact eigenvalue. Recall

$$V_{pert} = -\lambda\delta(x) = |\lambda|\delta(x) \qquad \text{since } \lambda < 0$$

Thus

$$(H^0 + |\lambda|\delta(x))\Psi = E\Psi$$

$$\Psi = \Sigma_{n,k}C_n(k)\phi_{nk}$$

$$\Sigma_{n,k}C_n(k)[\varepsilon_{nk}-E]\phi_{nk}(x) + |\lambda|\delta(x)\Sigma_{n,k}C_{n,k}(k)\phi_{nk}(0) = 0 \qquad (70)$$

Multiplying by $\phi^*_{n'k'}(x)$ and integrating yields:

$$[\varepsilon_{n'k'} - E]C_{n'}(k') + |\lambda|\phi^*_{n'k'}(0)\Sigma_{n,k}C_n(k)\phi_{nk}(0) = 0$$

$$C_{n'}(k') = \frac{|\lambda|\,\phi^*_{n'k'}(0)}{E - \epsilon_{n'k'}}\Sigma_{n,k}C_n(k)\phi_{nk}(0) \qquad (71)$$

Multiply each side by $\phi_{n'k'}(0)$ and sum over n',k'

$$\sum_{n',k'} C_{n'}(k')\phi_{n'k'}(0) = |\lambda| \sum_{n',k'} \frac{C_{n'}(k')|\phi_{n'k'}(0)|^2}{E - \epsilon_{n'k'}} \sum_{nk} C_n(k)\phi_{nk}(0)$$

Dividing through by the expression on the left hand side yields:

$$1 = |\lambda|\Sigma_{n'k'}|\phi_{n'k'}(0)|^2\{E - \varepsilon_{n'k'}\}^{-1} \qquad (72)$$

or

$$1 = (|\lambda|/2\pi|)\Sigma_{n'}\int|U_{n'k'}(0)|^2\{E - \varepsilon_{n'k'}\}^{-1}dk' \qquad (73)$$

The integral expression for GEMT [equation(67)], differs from the exact expression [equation (73)] in three particulars.

(1) The periodic part of the Bloch function is only evaluated at $k = \pi/a$ while in the exact expression $|U_k(0)|^2$ is used and thus it cannot be removed from the integral.

(2) The integral is over all bands in the exact expression as opposed to over only one band in the GEMT expression.

(3) ε_{nk} is replaced by an effective mass expansion about the top of the valence band for the GEMT integral.

That is $\varepsilon_v + \hbar^2(k - k_o)^2/(2m_v^*)$ is used for the energy band structure over the range of integration.

For small enough $|\lambda|$ the energy E is very close to the band edge ε_v. Under these circumstances the major contribution to the integral will come from a small region in k-space about the zone edge $k = \pi/a$. Thus if the limits of integration are extended in both directions to $\pm\infty$ the E which satisfies the relationship would not be appreciably affected. This is equivalent to replacing the sum over one Brillouin zone to a sum over all k. That is

$$\Delta(x) = \Omega^{-1}\Sigma_k e^{i(k-k_o)x} = \delta(x) \qquad (74)$$

However, for λ such that E is far above ε_v, extending the range of integration would affect the value of E necessary to preserve the equality and thus we are not justified in letting $\Delta(x) \dashrightarrow \delta(x)$.

We now show that if the range of integration is extended to include all of k-space, we recover the result of our first approximation to GEMT as previously claimed. Under these circumstances we get:

$$1 = (2|P|/\pi^2)|U(0)|^2(\omega^{\frac{1}{2}}\theta)^{-1}\tan^{-1}(\omega^{\frac{1}{2}}\zeta/\theta)|_o^{\infty} \qquad (75)$$

thus

$$\theta = (|P|/\pi)|U(0)|^2\omega^{-\frac{1}{2}}$$

or

$$\theta^2 = (P^2/\omega\pi^2)|U(0)|^4 \qquad (76)$$

thus

$$[\gamma^2 - \gamma_o^2]_{gemt} = P^2(|m_v^*|/m)|U(0)|^4 \qquad (77)$$

which is identical to the result obtained previously.

It is worth noting that in using the proper GEMT, which is achieved by limiting the range of integration to one Brillouin zone, the change in E is in the correct direction. Recall that our first approximation to GEMT always yielded values of E_b which were greater than the true value. Note that the integrand is positive definite and hence the reduction of the interval of integration implies that for a fixed E, the value of the integral will decrease. Thus the integrand must be increased and this is achieved through lowering E and hence the denominator at each value of k.

If we consider the exact quantization condition for E_b we can determine the effect of omitting the first conduction and all higher lying bands from the calculation. Since the denominator, $E - \varepsilon_{nk}$, is negative for all k in all bands that have been omitted, we can write:

$$1 = \alpha(E) - \beta(E)$$

$\alpha(E), \ \beta(E) > 0$. When we sum over the valence band alone it is equivalent to setting $\beta = 0$, and thus $\alpha(E_1) = 1$. If we now include all other bands,

$$\alpha(E_{exact}) = 1 + \beta(E_{exact}) > 1$$

thus

$$\alpha(E_{exact}) > \alpha(E_1) \implies E_{exact} < E_1$$

thus the energy, E_1, arrived at through ignoring all higher lying bands must be too large.

This is in agreement with our results in both $GEMT^o$ and GEMT. However, standard effective mass theory even with the inclusion of Umklapp corrections underestimates the energy for low background, although for large enough background potentials it eventually yields an overestimate as well. Thus it seems clear that this problem is not within the realm of standard EMT.

Despite the impressive results obtained from the GEMT for both the impurity and vacancy energies, one must be cautious in applying this formalism to a 3-dimensional system. We argued earlier that the singular nature of the energy denominator for systems in which E_b is small guarantees that the major contribution to the integral (sum) accrues from the region near the top of the valence band. However, in three dimensions $d\vec{\kappa} \simeq k^2 dk$ and thus the "singularity" near the band edge is wiped out, while in addition larger $|\vec{\kappa}|$ values contribute proportionally more to the integral since they occupy a larger component of the phase space. Yet under the conditions stated in the work of Resca and Resta, i.e., that the perturbing potential is only a small perturbation on the background,and thus has little effect on the wavefunction which is slowly varying over the range of the perturbation potential,the GEMT should be applicable.

Appendix B

Normalization of the Valence Band Edge Bloch Function

$$\phi^{val}(x) = A_0[\sin\kappa x + \omega(\kappa)\cos\kappa x] \qquad -a \le x \le 0$$

thus

$$|U^{val}(x)|^2 = |A|^2\{\sin\kappa x + \omega(\kappa)\cos\kappa x\}^2 \qquad (B1)$$

where

$$|A|^2 = \Omega|A_0|^2$$

$$|U^{val}(0)|^2 = |A|^2\omega^2(\kappa)$$

and $|A|^2$ can be determined from the normalization of $U(x)$ to a unit volume.

i.e.,

$$(1/a)\int_{-a}^{0}|U^{val}(x)|^2 dx = 1 \qquad (B2)$$

$$= (1/a)|A|^2\int_{-a}^{0}\{\sin^2\kappa x + \omega^2(\kappa)\cos^2\kappa x + 2\omega(\kappa)\sin\kappa x\cos\kappa x\}dx$$

Employing half-angle and double-angle formulae:

$$= (1/a)|A|^2\int_{-a}^{0}\{\tfrac{1}{2}(1-\cos2\kappa x) + \tfrac{1}{2}\omega^2(1 + \cos2\kappa x) + \omega\sin2\kappa x\}dx \qquad (B3)$$

$$= (1/a)|A|^2\int_{-a}^{0}\{\tfrac{1}{2}(\omega^2 + 1) + \tfrac{1}{2}(\omega^2 - 1)\cos2\kappa x + \omega\sin2\kappa x\}dx$$

$$= (1/a)|A|^2\{\tfrac{1}{2}(\omega^2 + 1)a + \tfrac{1}{2}(\omega^2 - 1)\sin 2\kappa a/(2\kappa) - \tfrac{1}{2}(\omega/\kappa)(1-\cos 2\kappa a)\} \quad \text{(B4)}$$

$$\omega^2 = \sin^2\kappa a/(1+\cos\kappa a)^2 = (1-\cos\kappa a)/(1+\cos\kappa a)$$

$$\omega^2 + 1 = 2/(1+\cos\kappa a) \quad \text{(B5)}$$

$$\omega^2 - 1 = -2\cos\kappa a/(1+\cos\kappa a)$$

Thus

$$1 = (1/a)|A|^2\{2\kappa a - \cos\kappa a \times \sin 2\kappa a - \sin\kappa a(1-\cos 2\kappa a)\}/[2\kappa(1+\cos\kappa a)]$$

$$= (1/a)|A|^2\{2\kappa a - 2\sin\kappa a \times \cos^2\kappa a - 2\sin\kappa a \times \sin^2\kappa a\}/[2\kappa(1+\cos\kappa a)]$$

$$= (1/a)|A|^2\{\kappa a - \sin\kappa a\}/[\kappa(1+\cos\kappa a)]$$

Thus

$$|A|^2 = \kappa a(1 + \cos\kappa a)/(\kappa a - \sin\kappa a) \quad \text{(B6)}$$

$$|U^{val}(0)|^2 = \omega^2|A|^2 = \{(1-\cos\kappa a)/(1+\cos\kappa a)\}\kappa a(1+\cos\kappa a)/(\kappa a - \sin\kappa a)$$

$$= (1-\cos\kappa a)/(1 - \sin\kappa a/\kappa a) = 2\sin^2(\tfrac{1}{2}\kappa a)/(1 - \sin\kappa a/\kappa a) \quad \text{(B7)}$$

$$|U^{val}(0)|^2 = 2\sin^2(\tfrac{1}{2}\kappa a)/(1 - \sin\kappa a/\kappa a)$$

Chapter III

The Density Functional Formalism

3.1 Introduction

Ever since the development of quantum mechanics it has been known that the solutions of the appropriate Schrodinger equation provide, from first principles, the basis for understanding the properties of atoms, molecules and solids.

However, for a system containing N electrons, the Schrodinger equation is a 3N dimensional differential equation and consequently our ability to obtain the exact analytic solution is rather limited. Thus even the simplest multi-electron system, the Helium atom, has so far eluded an exact analytic solution.

This state of affairs has led to the development of several approximation methods among whose number are the Thomas-Fermi[1], Hartree[2], Hartree-Fock[3] and configuration interaction[4] techniques.

In the Thomas-Fermi (TF) method, the system of electrons is treated as essentially a continuous liquid of density $n(\bar{r})$ with a kinetic energy density equal to that of a homogeneous electron gas of the local density, $n(\bar{r})$. The original TF theory can be improved to include exchange and correlation effects in terms of local energy densities derived from the homogeneous electron gas results, and it is particularly appealing because it replaces the 3N dimensional wavefunction of the system by a 3 dimensional function, $n(\vec{r})$, as the basic function describing the system. However, the method is inherently flawed in that it replaces a highly non-local quantity, the kinetic energy, by a local function of the density. As a result, the quantum oscillations of charge densities cannot be obtained, and even in cases where the charge densities do not oscillate the comparison of the results of this theory with other more detailed calculations can only be considered approximate.

In the Hartree approximation each electron is considered as moving in the external potential plus the self consistent coulomb field of the other electrons in the system. This method can be derived from the original Schrodinger equation employing the variational principle and assuming a product wavefunction composed of single particle wavefunctions. The Pauli principle is satisfied by allowing only one electron to occupy each electron state. The method leads naturally to an understanding of the shell structure of atoms. However, it neglects electron correlation as well as not satisfying the requirement that the wavefunction be totally anti-symmetric with respect to the interchange of any two electrons, thus neglecting the exchange energy as well.

The latter problem can be handled through the Hartree-Fock (HF) approximation which assumes a trial variational wavefunction in the form of a determinant of single particle wavefunctions. As in the Hartree approximation this leads to a set of coupled differential equations for the ϕ_i (the coupling in the Hartree case arising from the electron density from all other electrons in the self consistent coulomb term) with an aditional non-local exchange contribution. The equations are much more difficult to solve than in the Hartree case, the complexity rapidly increasing with the number of particles in the system. The system of equations may be simplified by approximating the non-local exchange by a local function depending on the electron density, as suggested by Slater[5] who used a particular average obtained from the results of the exchange energy for the uniform electron gas. However, the HF method in either case neglects electron correlation and the replacement of non-local exchage by a local form can at best only be justified a priori in the case of slowly varying electron density. Moreover, it is not entirely obvious which value of the average exchange should be employed[6].

Finally, the configuration interaction (CI) technique circumvents the approximations inherent in the HF method by expanding the wavefunction as a sum of determinantal wavefunctions with undetermined constants, the constants being obtained from employing the variational principle for the energy. As the number of configurations (determinants) in the expansion increases so that the set approaches completeness, the calculated wavefunction should approach the exact wavefunction. This technique therefore takes into consideration exchange and correlation but is very difficult to implement in practice. Its major applications have been on systems containing only a few electrons. For these systems in which CI has been employed, the results obtained are particularly useful in testing the ability of other simple approximation methods to reproduce the highly accurate CI results[7].

Thus the standard approximations employed in multi-electron calculations are either not exact in principle with no apparent method of improving them (TF, H, and HF) or really not practical to employ on systems with a large number of electrons (CI).

More recently, the work of Hohenberg and Kohn[8], and Kohn and Sham[9] heralded a new era in the approach to this problem. In their papers they set forth theorems which dramatically altered the philosophical approach to this problem. They developed a new method of calculating the ground state density and energy eigenvalue. Like TF, this method employs the density instead of the N particle wavefunction as the basic variable describing the system, but unlike TF, it provides a framework which is in principle exact for dealing with the ground state of electronic systems in terms of the electron density.

The remainder of our work is concerned in particular with the ground state of many electron systems. In the following section we give a brief review of the Hohenberg-Kohn-Sham density functional theory and discuss the major difficulty in its implementation.

3.2

We will restrict ourselves to a presentation of the ideas and results (i.e., theorems) of Hohenberg, Kohn and Sham and omit the proofs since they have been reproduced extensively in the literature[10].

Consider the general problem $H\Psi = E\Psi$

where $H = T + v + U$, then in atomic units:

T - the total electron kinetic energy is $-\frac{1}{2}\Sigma_i \nabla_i^2$,

v - the external potential,

U - the electron-electron interaction is $\frac{1}{2}\Sigma'_{i,j}|\vec{r}_{ij}|^{-1}$

Hohenberg and Kohn[8] (HK) showed that:

(1) $v(\vec{r})$ is a unique functional of $n(\vec{r})$ (up to an additive constant) and thus $\Psi_{g.s.}$ and other properties of the ground state are completely and uniquely determined by the electron density $n(\vec{r})$

(2) The ground state energy can be written as follows -

$$E_v[n(\vec{r})] = \int n(\vec{r})v(\vec{r})dr + F[n(\vec{r})]$$

where $v(\vec{r})$ is the external potential, $n(\vec{r})$ is the electron density, and $F[n(\vec{r})] = \langle\Psi|T + U|\Psi\rangle$ is a universal functional of the density (i.e., the form of F is independent of $v(\vec{r})$). Furthermore, it is this expression for the energy which is minimized by the correct density. The functional $F[n(\vec{r})]$ is not given directly by the theory.

The major advance is contained in these two theorems in that

(a) The many-body problem has been converted into one concerned only with the density and not the details of the N-particle correlated wave function;

(b) More importantly, we have a method which is in principle exact.

Thus the functional $F[n(\bar{r})]$ which contains both the kinetic energy and the electron-electron interaction now becomes the central item of interest. Should this functional be known we could solve our problem exactly.

$F[n(\bar{r})]$ is commonly rewritten as : $F[n(\bar{r})] = G[n(\bar{r})] + \frac{1}{2}\int\int n(\bar{r})n(\bar{r}')/|\bar{r} - \bar{r}'|d\bar{r}d\bar{r}'$, thus explicitly taking care of the classical electrostatic term. $G[n(\bar{r})]$ is clearly also a functional of $n(\bar{r})$.

$E_{xc}[n]$, the exchange-correlation functional, is then defined as $G[n] - T_s[n]$ where $T_s[n]$ is the kinetic energy of an auxiliary system of N non-interacting particles with the same total density as the interacting system.

Then $E_v[n(\bar{r})] =$

$$\int v(\bar{r})n(\bar{r})d\bar{r} + T_s[n(\bar{r})] + \frac{1}{2}\int\int n(\bar{r})n(\bar{r}')/|\bar{r} - \bar{r}'|\, d\bar{r}\, d\bar{r}' + E_{xc}[n(\bar{r})].$$

At this point the method of calculation resembles the Thomas-Fermi theory in that all quantities entering into a calculation of the total energy are functionals of the density. However, instead of making the usual Thomas-Fermi assumption that the kinetic energy can be written in terms of the local density, Kohn and Sham[9] (KS), expanding on the earlier work by HK, derived a set of self-consistent (non-interacting) single particle equations from whose solutions one can construct the ground state electron density of the original interacting N particle system.

In this formulation the equations to be solved are

$$\{-\tfrac{1}{2}\nabla^2 + \Phi(\vec{r}) + \vartheta_{xc}[n(\vec{r})]\}\phi_i = \varepsilon_i\phi_i \qquad i = 1,..,N \tag{1}$$

where $$\Phi(\vec{r}) = v_{ext}(\vec{r}) + \int n(\vec{r}\,')/|\vec{r}-\vec{r}\,'|d\vec{r}, \tag{2}$$

the sum of the external potential and the Hartree potential, and

$$\vartheta_{xc}[n(\vec{r})] = \delta E_{xc}[n(\vec{r})]/\delta n(\vec{r}). \tag{3}$$

To avoid confusion, we shall denote the external potential by v_{ext}, thus distinguishing it from other potentials that appear.

The density of the interacting system is just the density of the equivalent non-interacting system $n(\vec{r}) = \Sigma_i|\phi_i|^2$, where ϕ_i are the solutions to the Kohn-Sham equation.

The ground state is then given by:

$$E = \Sigma_i\varepsilon_i + E_{xc}[n(\vec{r})] - \int\vartheta_{xc}n(\vec{r})d\vec{r} - \tfrac{1}{2}\int\int n(\vec{r})n(\vec{r}\,')/|\vec{r}-\vec{r}\,'|\; d\vec{r}d\vec{r}\,' \tag{4}$$

Furthermore, Kohn and Sham showed that in the limit of slowly varying density, the functional $E_{xc}[n(\vec{r})]$ is just the total exchange correlation energy of the homogeneous electron gas through $O(\nabla n)$, from which it follows that if we write $\vartheta_{xc} = \vartheta_x + \vartheta_c$ then ϑ_x equals 2/3 of the usual Slater exchange in this local density approximation (LDA). However, unlike other self consistent field calculations, KS caution that the ε_i have no direct physical significance and consequently should not be interpreted as electron removal energies i.e., there is no "Koopman's theorem" for the ε_i.

The early work employing the LDA by Tong and Sham[11] on atomic structure and by Lang and Kohn[12] on jellium surfaces demonstrated the usefulness of these ideas for the study of systems with as few as 2 electrons to the many body problem presented by solids.

In this approach $\vartheta_{xc}[n(\vec{r})]$ is a universal functional of the density (as $F[n(\vec{r})]$ was in HK) and it now becomes the focal point of the problem. If the functional E_{xc} were known, and consequently its functional derivative ϑ_{xc}, the problem would be solved. Thus the main thrust of much contemporary research in density functional theory is geared toward providing more accurate functionals for E_{xc} than given by the LDA, extending the formalism to excited systems, and applying the formalism to calculate properties of molecules and solids.

In light of the above we note that if we could solve a problem for the wave function which included the electron-electron interaction exactly, we could then obtain both the electron density and the ground state energy as well. Furthermore, because of the simple relationship between $n(\vec{r})$ and the single particle wave function (ϕ_i) of the equivalent K-S Schroedinger equation, if we were dealing with a system of only two particles we could then obtain the ϕ_i. This could then be used, by inverting Equation (1), to find the exchange correlation functional ϑ_{xc} as a function of radial distance, r.

$$\vartheta_{xc}(\vec{r}) = \varepsilon_i - \Phi(\vec{r}) + \tfrac{1}{2}\nabla^2\phi_i/\phi_i(\vec{r}) \tag{5}$$

This can then be compared to the values obtained in various local and non-local approximations to $\vartheta_{xc}[n(\vec{r})]$.

In seeking improvements to the LDA the belief that the ε_{ks} were not physically significant led to a relative neglect of the examination of the accuracy of the ϑ_{xc}. The total energy as calculated using E_{xc} was considered to be the test of the accuracy of the functional, while ϑ_{xc} was simply taken as its functional derivative.

However, recently Perdew et. al.[13] have argued that the exact $(\varepsilon_{ks})_{max} = E(N) - E(N-1)$ where E(M) is the exact ground state energy of the M electron system. Thus $(\varepsilon_{ks})_{max}$ is the negative of the ionization energy of a system of N electrons to the totally relaxed state of the remaining N-1 electron system.

Thus the calculated $(\varepsilon_{ks})_{max}$ provided by Langreth and Mehl[14] can be compared to experimental and self consistent calculations of the ionization energy of the atoms they treat. For Helium , we find that their $(\varepsilon_{ks})_{max}$ is more than an electron volt too large in magnitude even though their total energy for the Helium atom is within only ~ 0.1 eV of the exact value. Similar results obtain for the $(\varepsilon_{ks})_{max}$ of other atoms calculated by them, i.e., their calculated $(\varepsilon_{ks})_{max}$ are greater than the exact value by more than the error in the total energy of the atom. Thus, it may be that their very accurate total energies are partly fortuitous i.e., the accuracy of their calculation may in part be due to the cancellation of having too large valence electron binding energies with too small core electron binding energies.

It thus appears that it would be useful to test the validity of the various density functionals that have been proposed for $\vartheta_{xc}[n]$ not merely by seeing whether they produce accurate total energies and good electron densities, but to actually compare the exact values of $\vartheta_{xc}(\vec{r})$ necessary to give the exact density with that given by the functional i.e., in a given case a ϑ_{xc} that is considerably different from the exact one might give good overall agreement for $n(\vec{r})$ and E because the external potential plus the Hartree term is so large as to make the error in ϑ_{xc} unimportant. However, when this same $\vartheta_{xc}[n(\vec{r})]$ is used in another calculation where the v_{ext} plus Hartree term is small these errors in $\vartheta_{xc}[n]$ may lead to substantial errors. Moreover, even for the former calculation the KS eigenvalues must be investigated to see how well they are reproduced.

It would therefore be useful to construct an exactly soluble model so this program of comparison could be implemented.

Such an analysis of ϑ_c has already been performed by Jagannathan[15], who considered the 2 electron atoms H^-, He, and Li^+ and compared his results to the LDA. The densities he employed were obtained from CI wavefunctions that minimized the energy. However, such analysis on 2 electron atoms suffers from certain inherent limitations. Firstly, it is not possible to adjust the nuclear charge Z to make the density arbitrarily slowly varying because H^- is barely bound relative to H + a free electron and any further decrease in Z (if we allow non-integral nuclear charge, while maintaining exactly 2 electrons) leads to a physically unbound state. Secondly, when only integral values of Z are employed, the density varies significantly from one atom to the next which makes it more difficult to understand the trends in the comparison of the exact and approximate ϑ_{xc}. Thirdly when a variational calculation is used to obtain a wavefunction for a two electron atom it is always possible to add an additional term of the form $Ae^{-\alpha(r_1 + r_2)}$ where α is smaller than any other such α in the expansion. Normally, unless this is added to the exact solution, minimizing the energy will result in $A \neq 0$. Thus as $r \to \infty$ the asymptotic density will be determined by this term which can be quite arbitrary unless one knows what the asymptotic density is prior to starting the calculation. Thus the variational solution can lead to the wrong asymptotic density. As we will show below the ε_{ks} are related to the asymptotic density and thus this will lead to incorrect ε_{ks} and $\vartheta_{xc}(\bar{r})$.

Since the validity of the density functional theory is not limited to having v_{ext} given by the coulomb potential due to protons in nuclei, we are free to use any v_{ext} that gives rise to an exactly soluble model. Such a model would be most useful if the v_{ext} contained a parameter which would give rise to a whole family of exactly soluble problems with densities which vary as slowly or rapidly as we wish to study. Such a model is presented in the next section.

Within the framework of the model to be presented we can investigate total energies and their constituents (i.e. exchange, correlation etc.) as well as the exact eigenvalues and eigenfunctions of the Kohn-Sham equation along with the corresponding expectation values of constituents of the potential (i.e. $\langle\phi_{ks}|\vartheta_x|\phi_{ks}\rangle$, $\langle\phi_{ks}|\vartheta_c|\phi_{ks}\rangle$).

The exact values which can be obtained for this problem will then be compared to those obtained by evaluating approximate functionals which are in current use, using the exact electron density.

We will demonstrate that although total energies for the system are in quite good agreement for the entire range of densities considered, the corresponding Kohn-Sham eigenvalues are significantly worse. We attribute this to error in the exchange potential functional and thus conclude that if improvement is to be made in the approximations of density functionals, then the expression for $E_x[n(\vec{r})]$ must be changed in a manner that will not affect the energy much, while making a considerable correction to its functional derivative $\vartheta_x[n(\vec{r})]$.

We will show analytically for our case, without resort to the theorem recently proved by Perdew and co-workers, that the energy of the highest occupied Kohn-Sham orbital is of significance, in that it represents the difference in energy between the ground state of the two electron system and the ground state of the one electron system including all relaxation effects. Thus, in our case where the only ε_{ks} is that of the "highest occupied orbital" it is reasonable to use this energy as a test of the efficacy of various approximate functionals.

3.3 The Model

To this end we consider two electrons attracted to a force center by a harmonic oscillator potential. This model has been employed previously by Kestner and Sinanoglou[16], using the variational principle, to study electron correlation in Helium-like atoms. Thus

$$H = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \tfrac{1}{2}k(r_1^2 + r_2^2) + e^2/|\vec{r}_{12}| \qquad (6)$$

where $\vec{r}_i$ are the coordinates of electron i $\quad$ i = 1, 2.

Note that k is just a measure of the strength of the attractive center and thus can be adjusted to model an entire range of "physical" situations - from dominance of the electron-electron interaction down to the case where the electron-electron interaction is negligible.

It is also worth mentioning that this model will have **no free parameters** - i.e., once we choose a value of k for our Hamiltonian the analysis leads inexorably to a specific energy eigenvalue, density, and exchange-correlationpotential functional as a function of radial distance r.

The problem we wish to solve is $H\Psi = E\Psi$. We start by making the standard transformation to relative and center of mass coordinates as follows:

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \qquad \vec{R} = (\vec{r}_1 + \vec{r}_2)/2$$

$\mu = \frac{1}{2}m$ the reduced mass, $\qquad M_T = 2m$ the total mass.

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{R}, \vec{r})$$

$$H(R, \vec{r}) = -\frac{\hbar^2}{2M_T}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + \frac{1}{4}k\{r^2 + 4R^2\} + e^2/r \qquad (7)$$

Now we separate variables:

$$\psi(\vec{r}, \vec{R}) = f(\vec{r})g(\vec{R})$$

Substituting into the previous equation and dividing both sides by $\psi(\vec{r}, R)$, yields:

$$\frac{\left[-\frac{\hbar^2}{2M_T}\nabla_R^2 + kR^2\right]g(\vec{R})}{g(\vec{R})} + \frac{\left[-\frac{\hbar^2}{2\mu}\nabla_{r}^2 + \frac{1}{4}kr^2 + \frac{e^2}{|\vec{r}|}\right]f(\vec{r})}{f(\vec{r})} = E$$

which leaves us with two equations:

$$[-\frac{\hbar^2}{2M_T}\nabla_R^2 + kR^2]g(\vec{R}) = E_{cm}g(\vec{R}) \quad (8a)$$

$$[-\frac{\hbar^2}{2\mu}\nabla_r^2 + \tfrac{1}{4}kr^2 + e^2/r]f(\bar{r}) = \varepsilon_{rel}f(\bar{r}) \quad (8b)$$

where the total energy E is given by $E_{c.m.} + \varepsilon_{rel} = E$.

At this point we shall convert to atomic units:

$$e^2 = \hbar = m = 1 \qquad a_0 = \hbar^2/me^2 = 1$$

Thus the unit of energy is the Hartree (27.2 eV). Then

$$[-\frac{1}{4}\nabla_R{}^2 + kR^2]g(\vec{R}) = E_{c.m.}g(\vec{R})$$

or

$$[-\nabla_R{}^2 + 4kR^2]g(\vec{R}) = 4E_{c.m.}g(\vec{R}) \quad (9a)$$

and

$$[-\nabla_r{}^2 + \frac{1}{4}kr^2 + 1/r]f(\bar{r}) = \varepsilon_{rel}f(\bar{r}) \quad (9b)$$

We need not concern ourselves with the separate normalization factors in f and g because they will be taken into account through the normalization of the density. We must constrain our solution to those where $\int n(\bar{r})d\bar{r} = 2$, i.e., the integral of the electron density should equal the total number of electrons in the system. Thus $A\int f^2g^2d\tau = 2$ will determine the overall normalization constant.

In the density functional formalism the object of interest is the ground state electron density; thus we need only solve for the ground state wave function and eigenenergy. The equation for g (i.e., Eq. (9a)) is the equation of a spherical harmonic oscillator, so[17]:

$$g(R) = Ce^{-k^{\frac{1}{2}}R^2} \tag{10}$$

$$4E_{c.m.} = 3\{4k\}^{\frac{1}{2}} \Rightarrow E_{c.m.} = 1.5k^{\frac{1}{2}} \tag{11}$$

For the relative coordinate equation, the situation is not that simple. However, with one more transformation we can reduce it to a manageable form. Since the ground state of a one particle Schroedinger equation with a spherically symmetric potential must be an s state[18], we make the following transformation:

Let $f(r) = u(r)/r$. This leads to the one-dimensional differential equation:

$$[-d^2/dr^2 + \tfrac{1}{4}kr^2 + 1/r]u(r) = \varepsilon_{rel}u(r)$$

subject to $u(0) = 0$ and $\lim_{r\to\infty} u(r) \to 0$, and there are no other zeros. No analytic solution of this equation is known and we must employ numerical methods. We will postpone a discussion of this procedure for a later section while we continue to describe the method of solution.

At this stage we have both f(r) and g(R) and proceed to calculate the electron density.

$$n(r_2) = 2 \int_{\text{space}} |\Psi(\vec{r}, \vec{R})|^2 \, d\vec{r}_1$$

$$= 2 \int f^2(|r_1 - r_2|)\, g^2\left(\frac{\vec{r}_1 + \vec{r}_2}{2}\right) d\vec{r}_1 = 2 \int f^2(\vec{r})\, g^2\left(\frac{\vec{r}}{2} + \vec{r}_2\right) d\vec{r}_1$$

$\vec{r} = \vec{r}_1 - \vec{r}_2$ so for fixed $\vec{r}_2$ $d\vec{r} = d\vec{r}_1$

thus

$$n(r_2) = 2 \int f^2(\vec{r})\, g^2\left(\frac{\vec{r}}{2} + \vec{r}_2\right) d\vec{r}$$

$$= C^2 \int f^2(\vec{r})\, e^{-2k^{1/2} \left|\frac{\vec{r}}{2} + \vec{r}_2\right|^2} d\vec{r}$$

$$= C^2 e^{-2k^{1/2} r_2^2} \int e^{-\frac{k^{1/2} r^2}{2}} e^{-k^{1/2} \vec{r} \cdot \vec{r}_2} f^2(\vec{r})\, d\vec{r}$$

or

$$n(r_2) = A^2 \frac{e^{-q r_2^2}}{q r_2} \int_0^{\infty} f^2(r)\, e^{-q r^2/4} \left[e^{q r r_2} - e^{-q r r_2}\right] r\, dr \tag{12}$$

where q = $\{4k\}^{\frac{1}{2}}$ (the coefficient of the harmonic term). We can get the normalization factor by

$\int n(\bar{r})dr = N$, where N = 2 is the number of electrons.

We are now in possession of an exact electron density for a problem with an electron-electron interaction. Because of the simple nature of this problem we can obtain ϑ_{xc}, the exchange and correlation energy density of the system. We recall that the same densities would result if we were to solve a system of non-interacting electrons moving in an effective potential $\Phi(\bar{r}) + \vartheta_{xc}[n(\bar{r})]$, where

$$\Phi(\bar{r}) = v_{ext}(\bar{r}) + \int n(\bar{r}')/|\bar{r}-\bar{r}'|d\bar{r}., \tag{2}$$

Thus we need merely solve the single particle Schroedinger equation

$$\{-\tfrac{1}{2}\nabla^2 + \Phi(\bar{r}) + \vartheta_{xc}[n(\bar{r})]\}\phi_i(\bar{r}) = \varepsilon_i\phi_i(\bar{r})$$

with $n(\bar{r}) = \Sigma_i|\phi_i(\bar{r})|^2$, N the number of electrons.

In our case N = 2, and we have 2 equivalent electrons

$$n(\bar{r}) = 2|\phi_i|^2 \quad \Rightarrow \quad \phi_i = [n(\bar{r})/2]^{\frac{1}{2}}.$$

Since we know $n(\bar{r})$, we have ϕ_i as well and can invert the equation to get:

$$\vartheta_{xc}[n(\bar{r})] = \varepsilon_i - \Phi(\bar{r}) + \tfrac{1}{2}\nabla^2\phi_i(\bar{r})/\phi_i(\bar{r}) \tag{5}$$

where $\Phi(\bar{r})$ is as defined above, and $v_{ext}(r) = \frac{1}{2}kr^2$. The second term in $\Phi(\bar{r})$ is easily evaluated using[19]

$$\frac{1}{|\vec{r}-\vec{r}'|} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{r_<^{\ell}}{r_>^{\ell+1}} Y_{\ell m}^{*}(\theta',\varphi') Y_{\ell m}(\theta,\varphi) \tag{13}$$

and

$$\int Y^*_{\ell' m'}(\theta,\varphi)\, Y_{\ell m}(\theta,\varphi)\, d\Omega = \delta_{\ell\ell'}\,\delta_{mm'} \qquad (14)$$

Thus

$$\int \frac{n(\vec r\,')}{|\vec r - \vec r\,'|}\, d\vec r\,' = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \int \frac{n(r')\, r_<^{\ell}}{(2\ell+1)\, r_>^{\ell+1}}\, Y^*_{\ell m}(\theta',\varphi')\, Y_{\ell m}(\theta,\varphi)\, r'^2\, dr'\, d\Omega'$$

Using $Y_{00} = 1/\sqrt{4\pi}$

$$= \sqrt{4\pi}\; 4\pi \sum_{\ell,m} \int \frac{Y_{\ell m}(\theta,\varphi)}{2\ell+1}\, \frac{r_<^{\ell}}{r_>^{\ell+1}}\, n(r')\, r'^2\, dr' \int Y^*_{\ell m}(\theta',\varphi')\, Y_{00}(\theta',\varphi')\, d\Omega$$

$$= (4\pi)^{3/2} \sum_{\ell,m} \int \frac{Y_{\ell m}(\theta,\varphi)}{2\ell+1}\, \frac{r_<^{\ell}}{r_>^{\ell+1}}\, n(r')\, r'^2\, \delta_{\ell 0}\, \delta_{m0}\, dr'$$

$$= (4\pi)\sqrt{4\pi} \int \frac{Y_{00}(\theta,\varphi)}{1}\, \frac{n(r')\, r'^2}{r_>} = 4\pi \int_0^{\infty} \frac{n(r')\, r'^2}{r_>}\, dr'$$

Thus

$$\int \frac{n(\vec r\,')}{|\vec r - \vec r\,'|}\, d\vec r\,' =$$

$$\frac{4\pi}{r} \int_0^{r} n(r')\, r'^2\, dr' + 4\pi \int_r^{\infty} n(r')\, r'\, dr' \qquad (15)$$

We now return to the method of obtaining the solution of the relative coordinate equation.

3.3.1 The Relative Coordinate Problem

Recall that we had reduced our problem to a solution of the following equation: $[d^2/dr^2 + \frac{1}{4}kr^2 + 1/r]u(r) = \varepsilon_{rel}u(r)$, subject to conditions $u(0) = 0$, $\lim_{r\to\infty} u(r) \to 0$, and there are no additional zeros.

The system under consideration must have a solution which is totally antisymmetric with respect to interchange of the co-ordinates (both space and spin) of the two electrons. Referring to the Hamiltonian we observe S^2 and s_z to be good quantum numbers, then the wavefunction can be written as either $\Psi_S\chi^0$ or $\Psi_A\chi^1$(where S means symmetric and A means antisymmetric space part).

Then $E_{gs} = \langle\Psi_{gs}|H|\Psi_{gs}\rangle = \langle\psi_{space}|H|\psi_{space}\rangle$, and thus proceeding to obtain the ground state energy leads us to a symmetric space part of the wavefunction, necessitating the use of χ^0 - the antisymmetric singlet state. This means that the ground state consists of 2 electrons of opposite spin - a point which will be exploited in our analysis.

A numerical approach [variable Gear method[20]] is employed to integrate the differential equation out from r = 0. However, the boundary condition at ∞ does not lend itself to this procedure, so we make a convenient replacement - we let $u(0) = 0$ and $u'(0) = C$, $C \neq 0$.

The constant C is totally arbitrary at this stage and (because of the linearity of the o. d. e.) only affects the normalization. After the correct ε_{rel} has been found, a scale factor is introduced to achieve normalization. This is equivalent to choosing C equal to the correct value of $u'(0)$ for the properly normalized wave function. We then carry out the integration with a specific ε_{trial} for ε. Then if we find an ε which satisfies the boundary conditions, the only question is one of normalization which has already been anticipated.

For $\varepsilon_{trial} \neq \varepsilon_{rel}$ the numerically integrated solution will diverge[21].

If $\varepsilon_{trial} > \varepsilon_{rel}$ $u(r) \to -\infty$

$\varepsilon_{trial} < \varepsilon_{rel}$ $u(r) \to +\infty$

provided that ε_{trial} is less than ε_2, the energy of the second energy state. We can use this to home in on the correct energy eigenvalue.

However, as r grows, the numerical error inherent in the procedure starts piling up. Since the value of u(r) is falling off the error may become a significant fraction of the total value, thus affecting our calculated values of u(r) dramatically.

A serious problem arises out of this difficulty. From the equation (5) for ϑ_{xc} it is clear that the Kohn-Sham single particle eigenvalue ε_{ks} enters into $\vartheta_{xc}(r)$ as an additive constant at all values of r. However, the condition that $v_{xc} \to 0$ as $r \to \infty$ is sufficient to determine the ε_{ks} without actually solving the KS equation,

i.e., $$\varepsilon_{ks} = \lim \{\vartheta_{xc}[n(r)] + \Phi(r) - \tfrac{1}{2}\nabla^2\phi_{ks}(r)/\phi_{ks}(r)\} \quad (16)$$

A first attempt to establish ε_{ks} by looking at ϑ_{xc} vs. 1/r and extrapolating to 1/r = 0 was unsatisfactory because of the incremental relative error in the f(r), and hence the wave function at very large r. If we are to know ϑ_{xc} exactly, not just to within an additive constant, it becomes necessary to find f(r) accurately for very large r. To achieve this we would like an analytic form for u(r) at large r. In the next section we show how to derive, within the WKB approximation, an analytic expression for u(r)/r at large r. We then compare our calculated values to the analytic form - when we find agreement over a considerable range of values for u(r) [in actual practice as much as 3 - 4 orders of magnitude], we feel justified in using the analytic form of f(r) for all larger values of r. This WKB form will also be used in Equation (16) to determine the value of ε_{ks}.

3.3.2 WKB Form for u(r)

One of the earliest and simplest methods of obtaining approximate eigenvalues of the one-dimensional Schroedinger equation was originally proposed by Wentzel, Kramers, and Brillouin[22-24]. The method was further developed by Dunham[25,26], who obtained the higher-order correction terms to the WKB quantization condition. The evaluation of these correction terms is very useful in improving the precision of the WKB calculated eigenvalues[27,28] and wavefunctions.

The ordinary differential equation for u(r), although one-dimensional, arises out of a radial portion of a spherical problem. In this circumstance the potential V(r) must be replaced by $V(r) + \hbar^2(\ell + 1/2)^2/2mr^2$ in doing a WKB expansion.

That this is the correct form for $V_{eff}(r)$, in a spherical case - and not $V(r) + \hbar^2\ell(\ell + 1)/2mr^2$ - was first proved by Langer[29], although it was recognized much earlier that this was necessary to obtain correct results.

Krieger and Rosenzweig[30] extended Langer's work to obtain the higher-order terms for the radial problem -

$$f(r) = \frac{u(r)}{r}$$

$$= \frac{A}{r} \frac{1}{\sqrt{p_r}} \exp \left\{ \frac{i(2m)^{1/2}}{\hbar} \oint \left[E - V(r) - \frac{\hbar^2(\ell + 1/2)^2}{2mr^2} \right]^{1/2} dr \right.$$

$$\left. - \frac{i(2m)^{1/2}}{\hbar} \cdot \frac{\hbar^2}{64m} \oint \frac{\left\{ \frac{d}{dr} \left[r^2 (V(r) - E) \right] \right\}^2}{\left\{ E - V(r) - \frac{\hbar^2 (\ell + 1/2)^2}{2mr^2} \right\}^{5/2}} \frac{dr}{r^4} \right\}$$

where

$$p_r = \left[E - V(r) - \frac{\hbar^2(\ell + \frac{1}{2})^2}{2mr^2} \right]^{1/2}$$

It is important to note that this expression is **not** equivalent to letting $V_{eff}(r) = V(r) + \hbar^2(\ell + \frac{1}{2})^2 / 2mr^2$ in Dunham's expression for the higher-order one-dimensional WKB expansion.

If we only consider the first integral in the exponential, i.e., $u(r) = Ae^{(i/\hbar)\int p_r dr}/\sqrt{p_r}$, which is just standard second order WKB, we get the correct energy for the harmonic oscillator[30] from the WKB quantization condition for the energy. However, the replacement of $\ell(\ell+1)$ by $(\ell+\frac{1}{2})^2$ is no longer valid if higher order integrals are to be included. It is the formula derived in Krieger and Rosenzweig which is the correct form and must be used for a general potential.

Our potential, $V(r) = \frac{1}{4}kr^2 + 1/r$ is rapidly varying for large r; however, the third order WKB gives the exact wavefunction asymptotically for the harmonic oscillator $V = \frac{1}{2}kr^2$. In addition, all higher-order terms in the expansion for the energy are identically zero[30]. Thus, we can look on 1/r as a small perturbation (at large r) on this, and thus expect the WKB to give a good approximation to the wave function.

Thus we include the integral I_2 below as well and consider the fact that we are only concerned with the region of large r. Therefore we can expand the terms in orders of 1/r and then collect terms of leading order to get the results as r --> ∞ .

$$I_1 = \oint \left[E - V(r) - \frac{(\ell+\frac{1}{2})^2 \hbar^2}{2mr^2} \right]^{1/2} dr$$

$$I_2 = -\frac{\hbar^2}{64m} \int \frac{\left\{ \frac{d}{dr} \left[r^2 \left(V(r) - E \right) \right] \right\}^2}{r^4 \left\{ E - V(r) - \frac{\hbar^2 (\ell+1/2)^2}{2mr^2} \right\}^{5/2}} \, dr \tag{17}$$

In the following calculation we will retain both ħ and e in order to make the analysis more transparent. This will allow one to see immediately that in the limiting case of no e-e interaction our result reduces to the simple harmonic oscillator. Furthermore, it will demonstrate an interesting feature of our WKB expansion (which is an expansion in orders of ħ) - that it is necessary to collect terms from different terms in the expansion if we are to go to the same order in ħ consistently. This is because of the form of the centripetal potential. We are treating the ground state of a spherically symmetric potential which must be an s state, so $\ell = 0$.

Since we have a bound state $V_{eff} > E$

$$J_1 = i|I_i|, \qquad J_2 = i|I_2|,$$

$$u(r)/r = A/(r\sqrt{p_r})\times\exp[-(2m)^{\frac{1}{2}}(J_1 + J_2)/\hbar]$$

$$J_1 = \int [V(r) + \hbar^2(\ell+\tfrac{1}{2})^2/(2mr^2) - E]^{\frac{1}{2}}dr$$

$$V(r) = \tfrac{1}{4}kr^2 + e^2/r$$

$$J_1 = \int [\tfrac{1}{4}kr^2 + e^2/r + \hbar^2(\ell+\tfrac{1}{2})^2/(2mr^2) - E]^{\frac{1}{2}}dr$$

$$= \left(\frac{K}{4}\right)^{1/2} \int r \left[1 + \frac{4e^2}{Kr^3} + \frac{4\hbar^2(\ell+\frac{1}{2})^2}{2mKr^4} - \frac{4E}{Kr^2}\right]^{1/2} dr$$

$$\approx \left(\frac{K}{4}\right)^{1/2} \int r \left[1 + \frac{1}{2}\left\{\frac{4e^2}{Kr^3} + \frac{\hbar^2}{2mKr^4} - \frac{4E}{Kr^2}\right\} - \frac{1}{8}\left\{\frac{4e^2}{Kr^3} + \frac{\hbar^2}{2mKr^4} - \frac{4E}{Kr^2}\right\}^2 + \ldots\right] dr$$

$$= \left(\frac{K}{4}\right)^{1/2} \int \left[r - \frac{2E}{Kr} + \frac{2e^2}{Kr^2} + \frac{1}{Kr^3}\left\{\frac{\hbar^2}{4m} - \frac{2E^2}{K}\right\} + O\left(\frac{1}{r^4}\right)\right] dr$$

$$J_1 = \left(\frac{K}{4}\right)^{1/2}\left[\frac{r^2}{2} - \frac{2E}{K}\ln r - \frac{2e^2}{Kr} - \frac{1}{2Kr^2}\left\{\frac{\hbar^2}{4m} - \frac{2E^2}{K}\right\}\right] \tag{18}$$

$$J_2 = \frac{-\hbar^2}{64m}\int \frac{\left\{\frac{d}{dr}\left[r^2(V-E)\right]\right\}^2}{r^4\left\{V(r) - E - \frac{\hbar^2(\ell+1/2)^2}{2mr^2}\right\}^{5/2}}\,dr$$

$$= \frac{-\hbar^2}{64m}\int \frac{\left\{\frac{d}{dr}\left[r^2\left(\frac{1}{4}Kr^2 + \frac{e^2}{r} - E\right)\right]\right\}^2}{r^4\left\{\frac{1}{4}Kr^2 + \frac{e^2}{r} - \frac{\hbar^2}{8mr^2} - E\right\}^{5/2}}\,dr$$

$$\approx -\frac{\hbar^2}{64m}\int \frac{(Kr^3)^2}{r^4\left(\frac{1}{4}Kr^2\right)^{5/2}}\,dr = -\frac{\hbar^2}{64m}\cdot\frac{4^{5/2}}{K^{1/2}}\int r^{-3}\,dr$$

$$J_2 = \frac{\hbar^2}{4m}\,\frac{1}{K^{1/2}r^2} = \left(\frac{K}{4}\right)^{1/2}\frac{\hbar^2}{2mKr^2} \tag{19}$$

So

$$J_1 + J_2 = \left(\frac{K}{4}\right)^{1/2}\left[\frac{r^2}{2} - \frac{2E}{K}\ln r - \frac{2e^2}{Kr} + \frac{1}{2Kr^2}\left\{\frac{3\hbar^2}{4m} + \frac{2E^2}{K}\right\}\right] \tag{20}$$

and

$$p_r^{1/2} \propto (mK)^{1/4}\, r^{1/2}\left[1 - E/Kr^2\right] \tag{21}$$

Now let us convert to the specific case at hand:

$V = \frac{1}{2}qr^2 + 1/r$ where $q = \frac{1}{2}k$,

$m = \frac{1}{2}m_e = \frac{1}{2}$ in atomic units so $mk = \frac{1}{2}k$,

$q/m = k$, and now setting $\hbar = 1$,

$$f(r) = \frac{u(r)}{r} = A\,\frac{e^{-k^{1/2}r^2/4}\; r^{E/k^{1/2}}\; e^{e^2/k^{1/2}r}\; e^{-\frac{1}{16k^{1/2}r^2}\left\{\frac{3}{m} + \frac{8E^2}{k}\right\}}}{r^{3/2}\left(1 - E/kr^2\right)} \tag{22}$$

Now since this is an harmonic oscillation with a perturbation we can write E as $E_{H.O.}$ + additional terms.

i.e.,

$$E = (q/m)^{\frac{1}{2}}[3/2 + \delta] = k^{\frac{1}{2}}(3/2 + \delta) \tag{23}$$

$$f(r) \sim r^{\delta}[1 - \delta(\delta+1)/(2k^{\frac{1}{2}}r^2)]\; e^{-\frac{1}{4}k^{\frac{1}{2}}r^2} \exp[e^2/(k^{\frac{1}{2}}r)] \tag{24}$$

where we expanded the rightmost exponential. A comparison of the numerically calculated f and the WKB form (after including a constant multiplicative factor) shows very good agreement for large r (Table 2). In fact for very large r we believe that because of round off error the WKB form is more accurate than that obtained from integration of the Schroedinger equation.

We can now proceed to use this WKB wave function to find the behavior of the density at large r, and hence the value of ε_{ks} through

$$\varepsilon_{ks} = \lim\; [\vartheta_{xc}[n(r)] + \Phi(r) - \tfrac{1}{2}\nabla^2\phi_{ks}(r)/\phi_{ks}(r)] \tag{16}$$

and using $\lim r \rightarrow \infty$ $\vartheta_{xc}[n(r)] \rightarrow 0$, we get

$$\epsilon_{KS} = \lim_{r\to\infty}\left[\frac{1}{2}kr^2 + \frac{2}{r} - \frac{\nabla^2[n^{1/2}(r)]}{2n^{1/2}(r)}\right] = \lim_{r\to\infty}\left[\frac{1}{2}kr^2 - \frac{\nabla^2[n^{1/2}(r)]}{2n^{1/2}(r)}\right] \tag{25}$$

r	f	WKB	DIV
0.18000D 01	0.12662386D 00	0.11819712D 00	0.11040167D 01
0.19000D 01	0.96052897D-01	0.89445185D-01	0.11032221D 01
0.20000D 01	0.71677787D-01	0.66608350D-01	0.11025790D 01
0.21000D 01	0.52620554D-01	0.48810667D-01	0.11020528D 01
0.22000D 01	0.38004823D-01	0.35197462D-01	0.11016180D 01
0.23000D 01	0.27005284D-01	0.24975664D-01	0.11012557D 01
0.24000D 01	0.18879846D-01	0.17439423D-01	0.11009512D 01
0.25000D 01	0.12986724D-01	0.11982791D-01	0.11006936D 01
0.26000D 01	0.87894743D-02	0.81020873D-02	0.11004741D 01
0.27000D 01	0.58532651D-02	0.53907813D-02	0.11002859D 01
0.28000D 01	0.38354337D-02	0.35296003D-02	0.11001236D 01
0.29000D 01	0.24729767D-02	0.22741638D-02	0.10999830D 01
0.30000D 01	0.15689984D-02	0.14419288D-02	0.10998606D 01
0.31000D 01	0.97955532D-03	0.89969494D-03	0.10997537D 01
0.32000D 01	0.60179151D-03	0.55243305D-03	0.10996602D 01
0.33000D 01	0.36381459D-03	0.33381081D-03	0.10995791D 01
0.34000D 01	0.21644003D-03	0.19850018D-03	0.10995110D 01
0.35000D 01	0.12671444D-03	0.11616210D-03	0.10994606D 01
0.36000D 01	0.73005831D-04	0.66898176D-04	0.10994446D 01
0.37000D 01	0.41395924D-04	0.37915206D-04	0.10995156D 01
0.38000D 01	0.23104473D-04	0.21147783D-04	0.10998390D 01
0.39000D 01	0.12699517D-04	0.11608375D-04	0.11009473D 01

Table 2

The relative coordinate wavefunction, f, and the WKB form used to approximate it for large r. Div is the ratio of f to the WKB form. The table is for k=10.

Ordinarily the normalization of n(r) would require us to find an appropriate method of matching the WKB form of the wave function to the wave function computed at small r. However, since we only encounter n(r) in the ratio $\nabla^2(n^{\frac{1}{2}})/n^{\frac{1}{2}}$, the normalization constant will cancel and we need not concern ourselves with it.

Recall

$$n(r) \propto \frac{e^{-2K^{1/2}r^2}}{K^{1/2}\,r}\int_0^\infty f^2(r)\,e^{-\frac{K^{1/2}r'^2}{2}}\left[e^{2K^{1/2}rr'}-e^{-2K^{1/2}rr'}\right]r'\,dr'$$

Further analysis leads to the result :

$$n(r) \sim r^{2\delta}e^{-\alpha r^2} \qquad (26)$$

[The details of the calculation can be found in the Appendix.]

A numerical calculation of n(r) using the WKB form for the relative coordinate wavefunction at large values of r is in good agreement with the WKB form of the density, n(r), as can be seen by referring to Table 3. The WKB form is used from the point where the ratio of f(r) to the WKB is stable and on out. We reason that from that point on the WKB is improving (since we are going to ever increasing r) while the numerically integrated f is deteriorating.

The column labeled DIV in Table 3 is just for convenience in making comparisons. There is no significance in DIV being equal to 1.0, or in that corresponding value of r.

r	n	WKB	DIV
0.30000D 01	0.17819613D-11	0.17819613D-11	0.10000000D 01
0.31000D 01	0.26459797D-12	0.26622702D-12	0.99388098D 00
0.31500D 01	0.99551443D-13	0.10046084D-12	0.99094778D 00
0.32000D 01	0.36862754D-13	0.37306236D-13	0.98811239D 00
0.32500D 01	0.13434082D-13	0.13633550D-13	0.98536933D 00
0.33000D 01	0.48184677D-14	0.49032278D-14	0.98271339D 00
0.33500D 01	0.17009495D-14	0.17354155D-14	0.98013965D 00
0.34000D 01	0.59095739D-15	0.60447123D-15	0.97764354D 00
0.34500D 01	0.20207098D-15	0.20720536D-15	0.97522083D 00
0.35000D 01	0.68004178D-16	0.69900747D-16	0.97286768D 00
0.35500D 01	0.22524335D-16	0.23207072D-16	0.97058067D 00
0.36000D 01	0.73426707D-17	0.75826092D-17	0.96835674D 00
0.36500D 01	0.23558238D-17	0.24382534D-17	0.96619321D 00
0.37000D 01	0.74390817D-18	0.77161872D-18	0.96408777D 00
0.37500D 01	0.23119834D-18	0.24032133D-18	0.96203837D 00
0.38000D 01	0.70719647D-19	0.73662983D-19	0.96004322D 00
0.38500D 01	0.21290536D-19	0.22221605D-19	0.95810071D 00
0.39000D 01	0.63084888D-20	0.65973929D-20	0.95620936D 00
0.39500D 01	0.18397441D-20	0.19277098D-20	0.95436775D 00
0.39900D 01	0.67865799D-21	0.71218079D-21	0.95292936D 00

Table 3

The electron density, n(r), and a numerical tabulation of the WKB expression employed for large r. Div is the ratio of n(r) to the WKB form. The table is for k=10.

Now that we have the form of n(r) for large r we are ready to proceed in our calculation of ε_{ks}. To find ε_{ks} we need to calculate $\nabla^2(n^{\frac{1}{2}})/2n^{\frac{1}{2}}$

$$\nabla^2(n^{\frac{1}{2}}) = \frac{1}{r}(d^2/dr^2)[rn^{\frac{1}{2}}] = (1/r)(d^2/dr^2)\ [r^{\delta+1}e^{-\frac{1}{2}\alpha r^2}]$$

$$= [\delta(\delta+1)r^{\delta-2} - \alpha(2\delta+3)r^{\delta} + \alpha^2 r^{\delta+2}]e^{-\frac{1}{2}\alpha r^2} \qquad (27)$$

and

$$\tfrac{1}{2}\nabla^2(n^{\frac{1}{2}})/n^{\frac{1}{2}} = \tfrac{1}{2}\{\delta(\delta+1)/r^2 - \alpha(2\delta+3) + \alpha^2 r^2\} \qquad (28)$$

Using equation (25):

$$\varepsilon_{ks} = \lim_{r\to\infty}\{\tfrac{1}{2}kr^2 - \tfrac{1}{2}[\alpha^2 r^2 - \alpha(2\delta+3)]\} \qquad (29)$$

But $\alpha = k^{\frac{1}{2}}$ and $E_{rel} = k^{\frac{1}{2}}(1.5 + \delta)$

Thus:

$$\varepsilon_{ks} = k^{\frac{1}{2}}(1.5 + \delta) = E_{rel} \qquad (30)$$

Thus the ε_{ks} is just equal to the energy eigenvalue of the relative coordinate equation, i.e., $\varepsilon_{ks} = \varepsilon_{rel}$. In a two particle problem we have an additional simplification which allows us to investigate correlation and exchange independently.

3.4 Analytic Demonstration Of Significance Of $(\epsilon_{ks})_{max}$

In this section we shall show analytically that the theorem of Perdew et. al.[13] regarding the relationship between the separation energy of the system and the maximum Kohn-Sham eigenvalue (in the g.s.) is satisfied for our model.

For the two particle problem we have written the energy:

$$\begin{aligned} E(N{=}2) &= E_{c.m.} + \varepsilon_{rel} \\ &= 1.5k^{\frac{1}{2}} + \varepsilon_{rel} \end{aligned} \tag{31}$$

For the case of one particle in an harmonic oscillator potential:

$$E(N{=}1) = 1.5k^{\frac{1}{2}}, \qquad \text{for the lowest state.}$$

thus

$$E(N{=}2) - E(N{=}1) = \varepsilon_{rel} \tag{32}$$

However, we have shown (eqn. 30) that $\varepsilon_{rel} = \varepsilon_{ks}$ exactly for this two particle problem, and thus

$$E(N{=}2) - E(N{=}1) = \varepsilon_{ks} \tag{33}$$

In this case there is only one ε_{ks}, so $\varepsilon_{ks} = (\varepsilon_{ks})_{max.}$, which is a direct confirmation of the theorem.

3.5 Exact Densities, Exchange and Correlation Functionals

Figures 4-7 are densities generated by our program to evaluate equation (11). We shall present figures and tables for k = .01, 1, and 100 to show the evolution of certain features as k varies. We include k

= 10 since it is a density which corresponds to the "physical range" if we gauge that by an average r_s

$$(r_s)_{avg} = \int n(r) r_s(n) d\bar{r} \tag{34}$$

where $(r_s)_{avg}$ is ~ 1 a.u.. (Using this measure $(r_s)_{avg}$ varies from .517 at k= 100 to 5.87 at k=.01.)

Figure 8 shows $n(r)/n_k(r)$ vs. $k^{\frac{1}{4}}r$ for three values of k, where $n_k(r)$ is the electron density of two particles in a harmonic oscillator potential with no e-e interaction. From these figures we see the effect of the e-e interaction on the density profile. We observe that as k decreases, i.e. the relative strength of the e-e interaction increases, the electron repulsion causes a spreading out of the electrons increasing the density at large distances, while dropping the value of the central density in order to conserve the number of particles. This is evident in Figure 8 as well, since as was to be expected the smaller k values show a larger deviation from the h.o. density since it is for this region that the e-e interaction is important . In fact in the limit k => ∞ we would expect no deviation at all.

For $k^{\frac{1}{4}}r$ = 2.6, the endpoint of the plot, the ratio of n(r) to n(0) for k = 100, 1, .01 is .0015, .0024, and .0081 respectively.

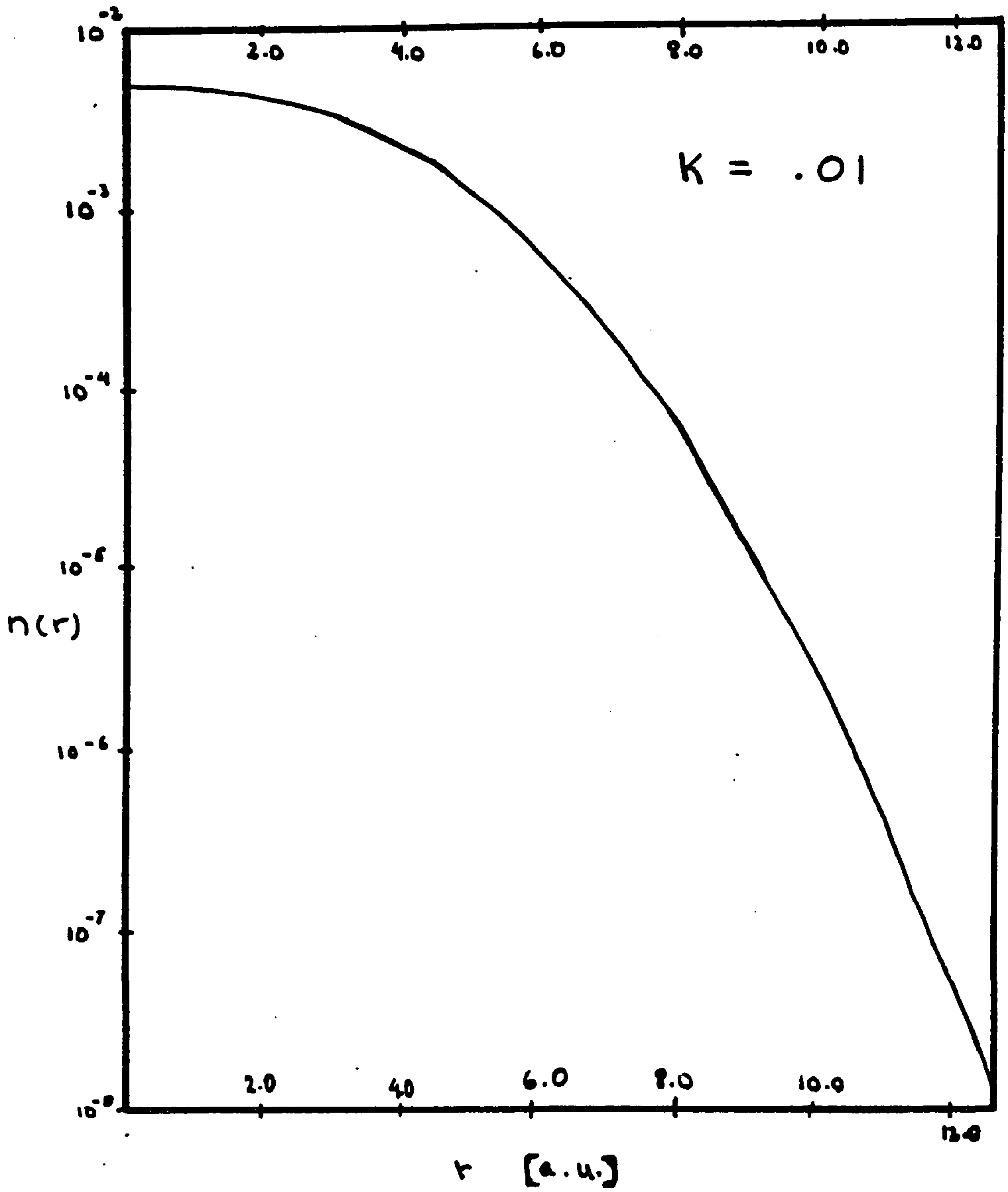


Figure 4: n(r) vs. r for k = .01

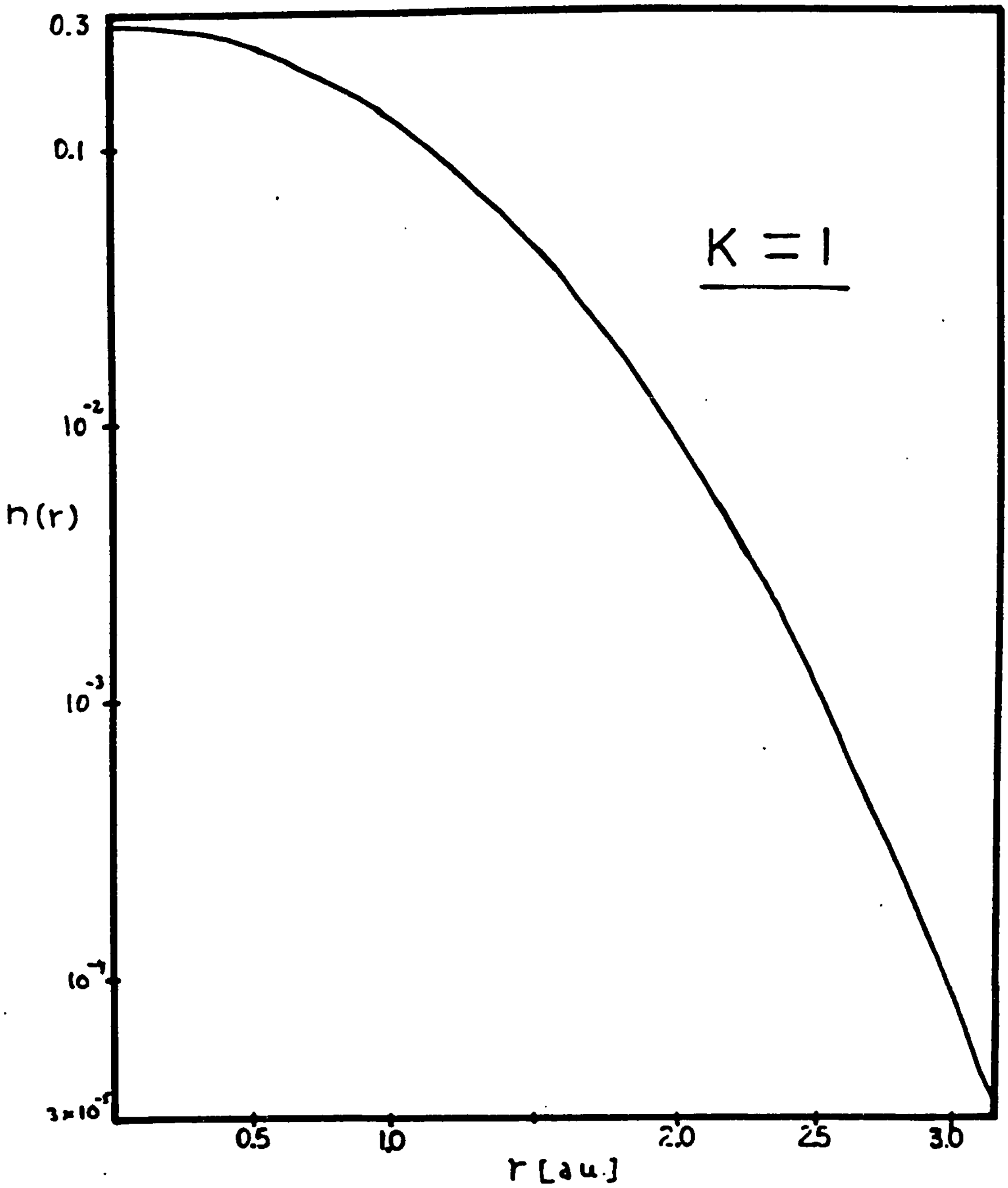


Figure 5: n(r) vs. r for k = 1

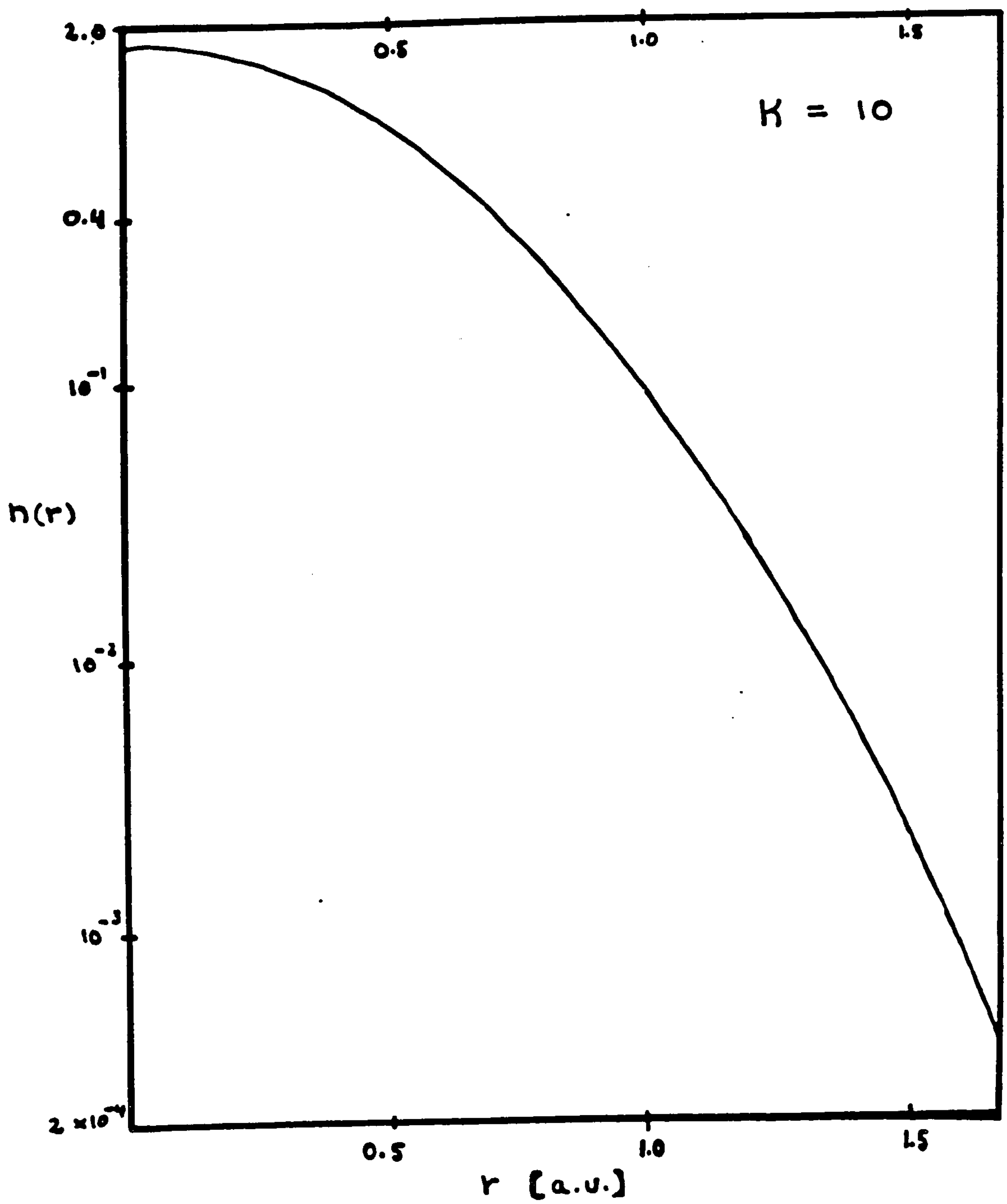


Figure 6: n(r) vs. r for k = 10

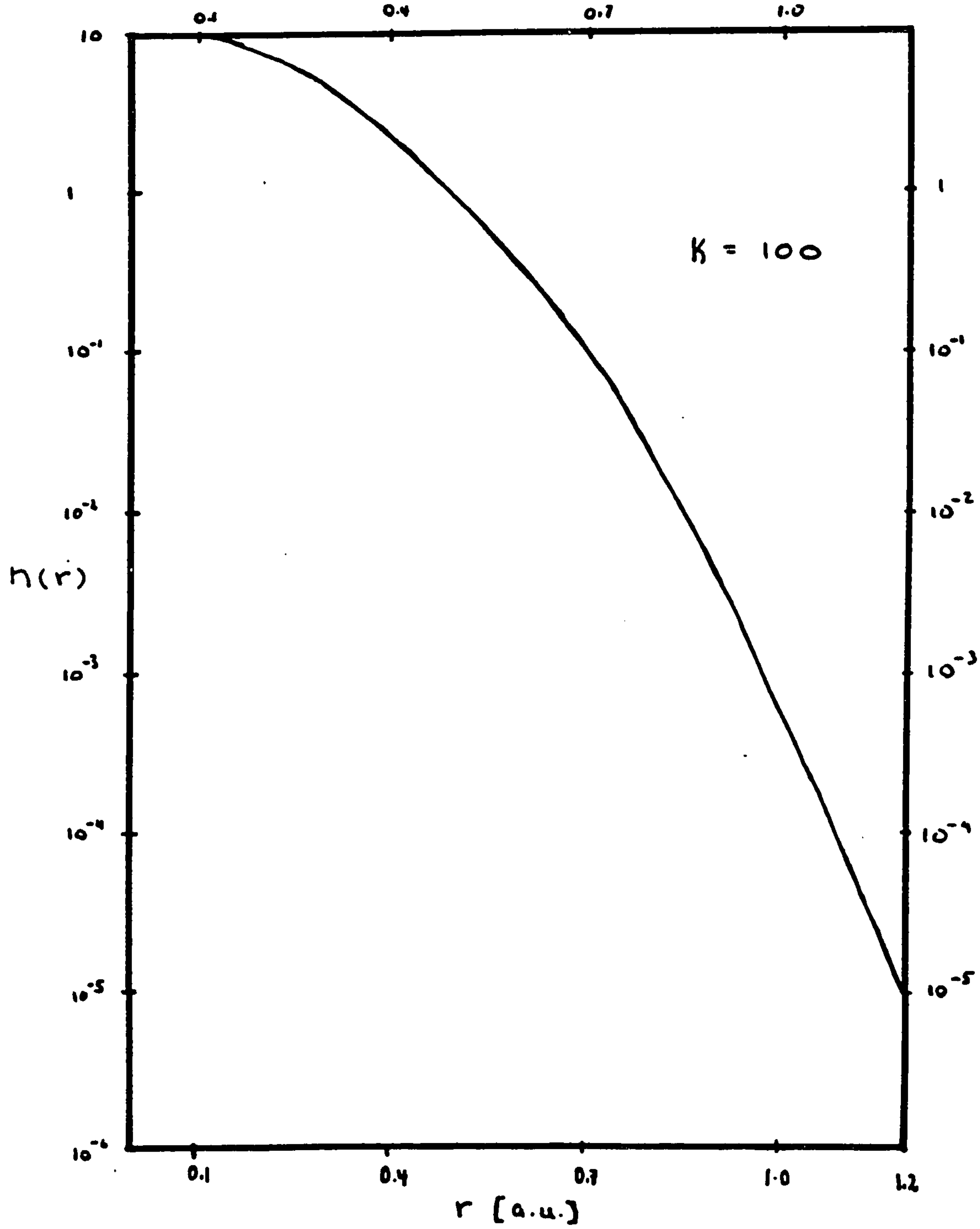


Figure 7: n(r) vs. r for k = 100

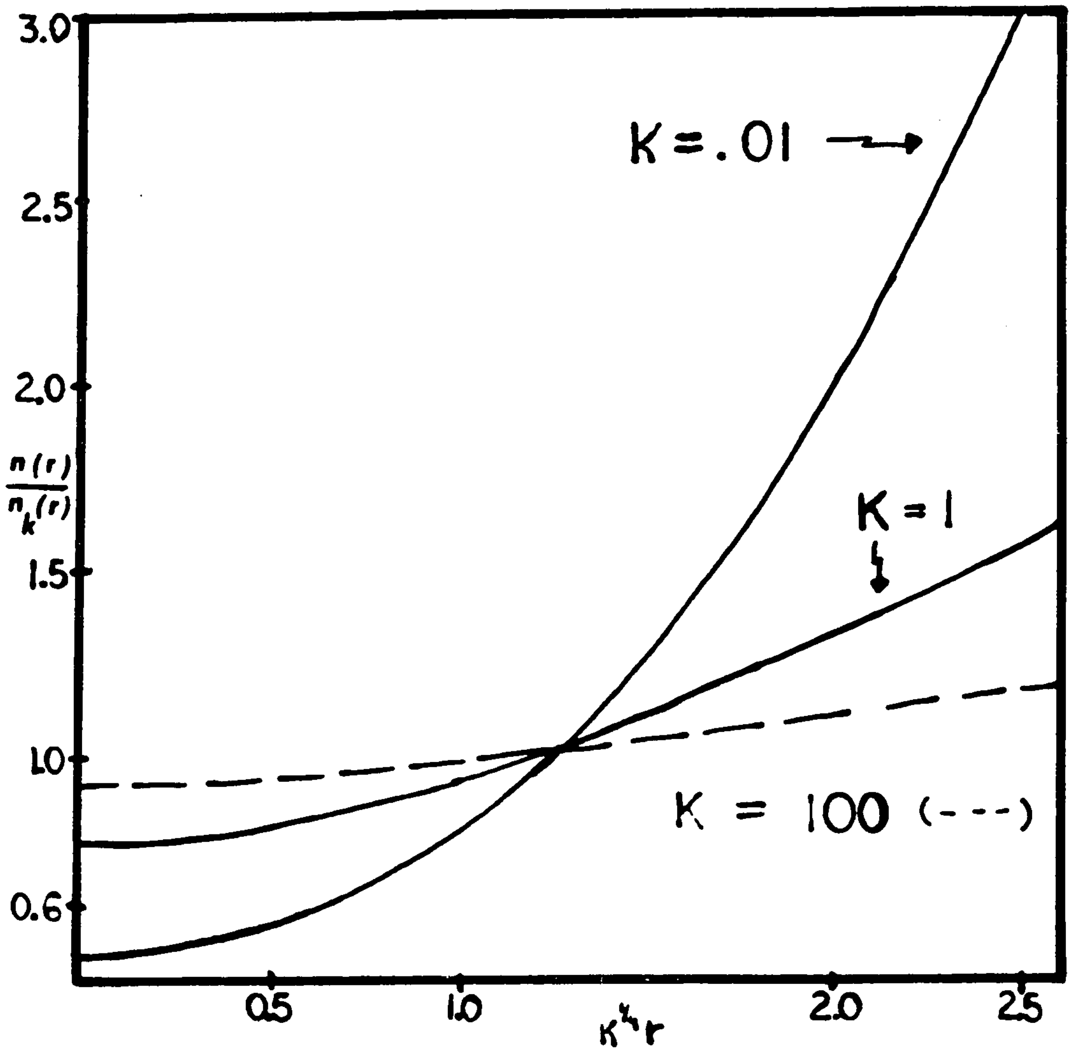


Figure 8: Scaled Density vs. $k^{1/4}r$ for k = .01, 1, 100

For two particles

$$\vartheta_x = -\tfrac{1}{2}\int n(\vec{r}')/|\vec{r} - \vec{r}'|\, d\vec{r}' \tag{35}$$

and thus

$$\vartheta_c = \varepsilon_i + \nabla^2\phi_i/2\phi_i - v(r_i) - \tfrac{1}{2}\int n(\vec{r}')/|\vec{r} - \vec{r}'|\, d\vec{r}'. \tag{36}$$

In Figure 9 we present ϑ_x^{LDA} and ϑ_x^{exact} vs. r_s. Note that the exchange potential functional is non-local and always of greater magnitude than ϑ_x^{LDA}. As k decreases and we approach the free electron gas ϑ_x appears to approach the free electron gas results. However, this way of representing it is deceptive - we know that for large distances the LDA exchange falls as an exponential, while the exact exchange falls as 1/r. Furthermore, for our case we shall see that for the entire range of k values treated the exchange in the LDA will not approach the exact value.

In Figure 10 we present ϑ_c^{exact} vs. r_s for k = .01, 1, 100 and in Figure 11 ϑ_c^{exact} vs. r_s for k = 10, .01 along with the Ceperley-Alder and Wigner local forms of ϑ_c. It appears from Figure 11 that for k = .01 the correlation functional does quite well - which is what we would like to believe as these should be accurate for the uniform electron gas.

Figures 12-15 show $\vartheta_x^{LDA}/\vartheta_x^{exact}$ and $4\pi r^2 n(r)$ vs. r for 4 k values. This demonstrates that in the region of interest, i.e. when the weighted density is substantial, the ratio is ~ 0.6 for all values of k.

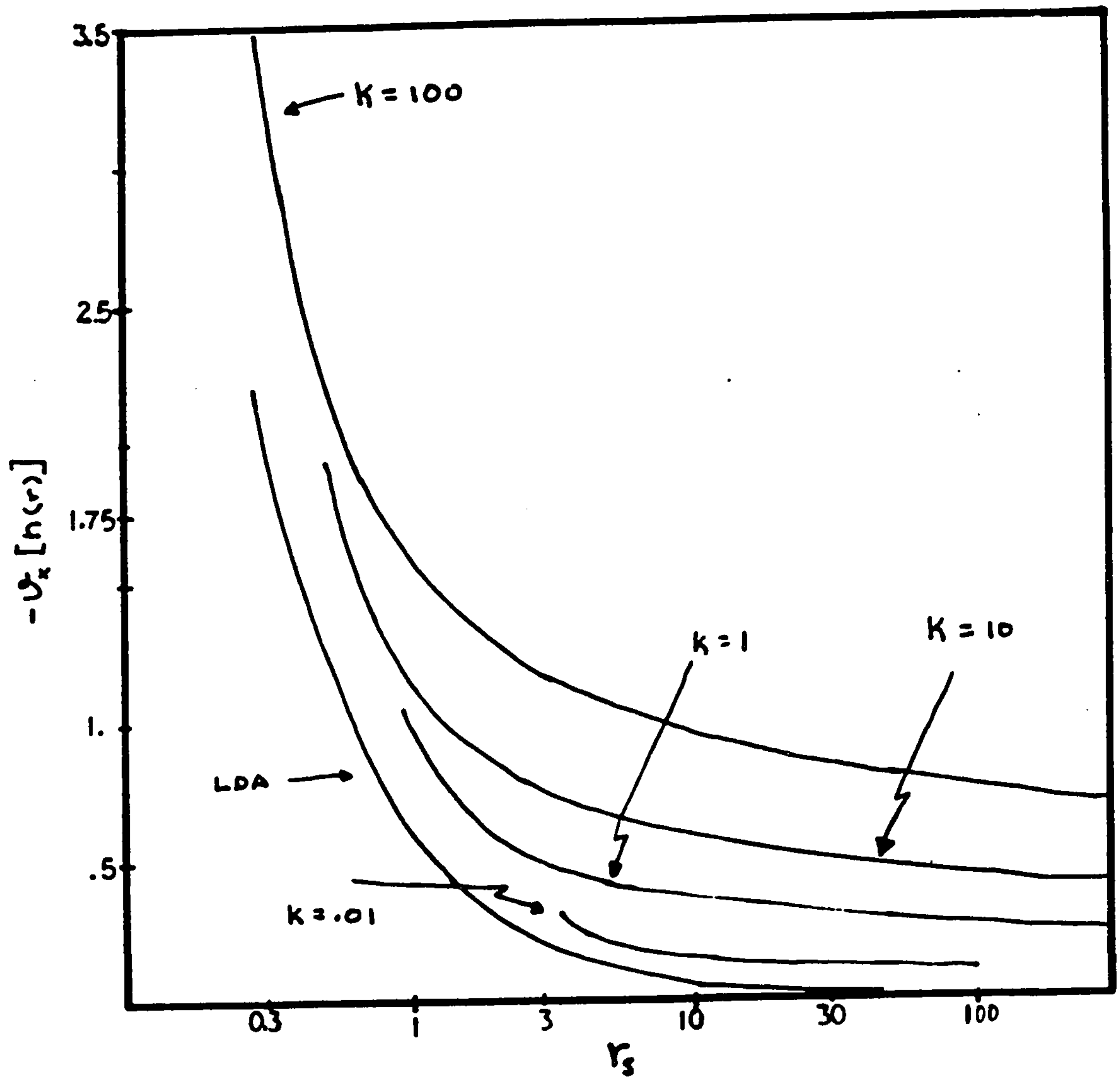


Figure 9: Exchange Potential for Various k

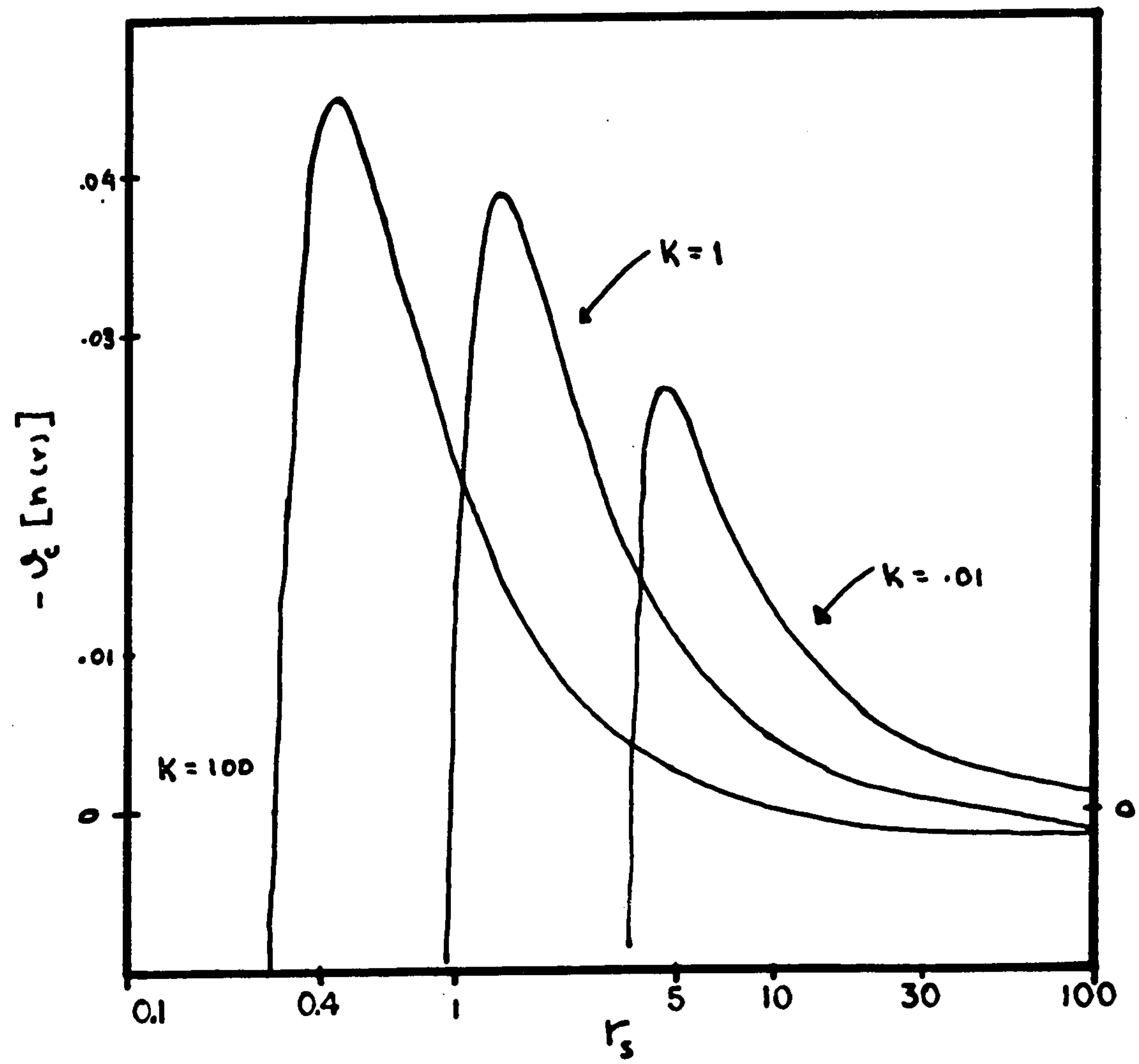


Figure 10: Correlation Potential for k = 100, 1 and .01

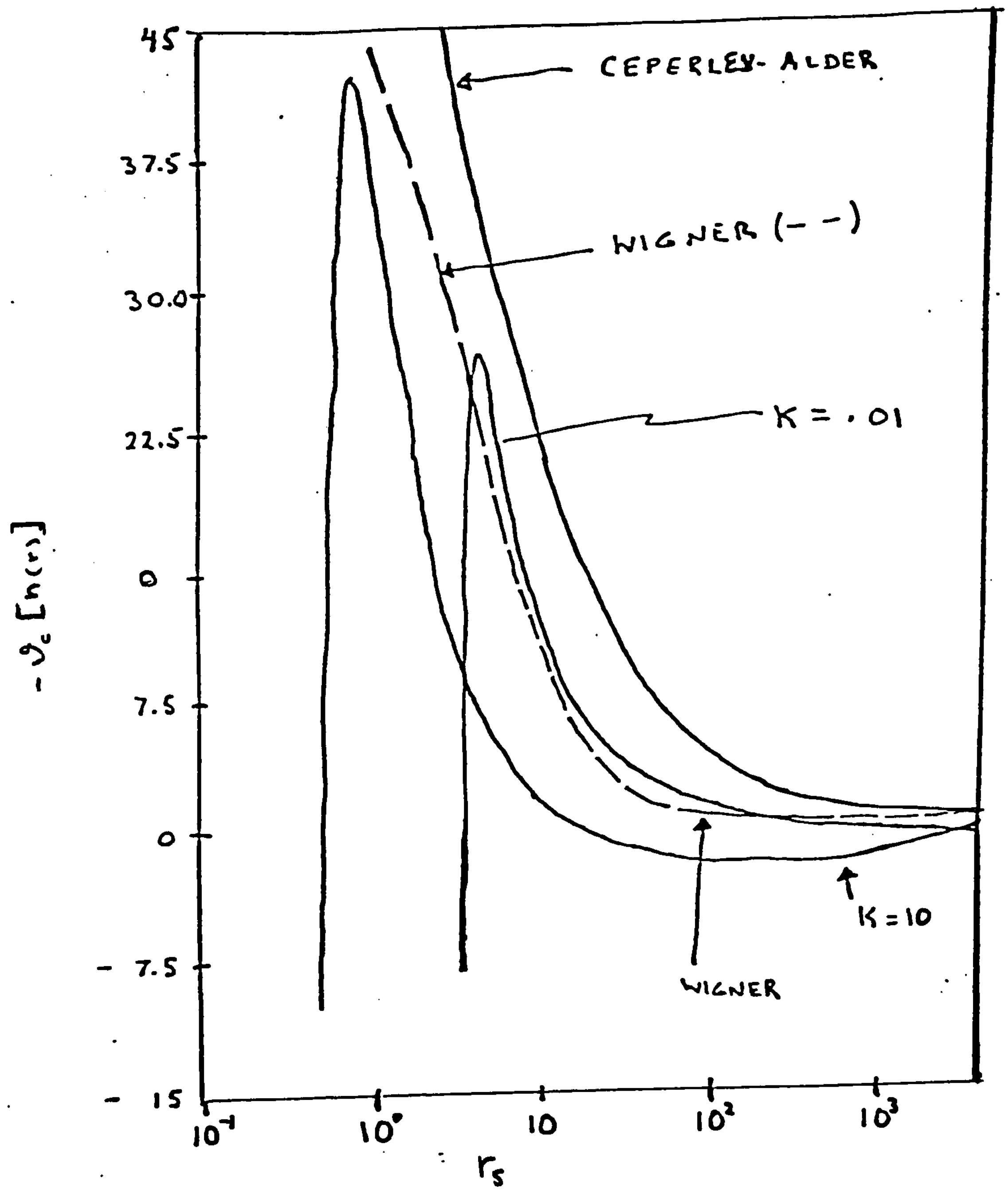


Figure 11: Correlation Potential for k = 10, .01 and local forms

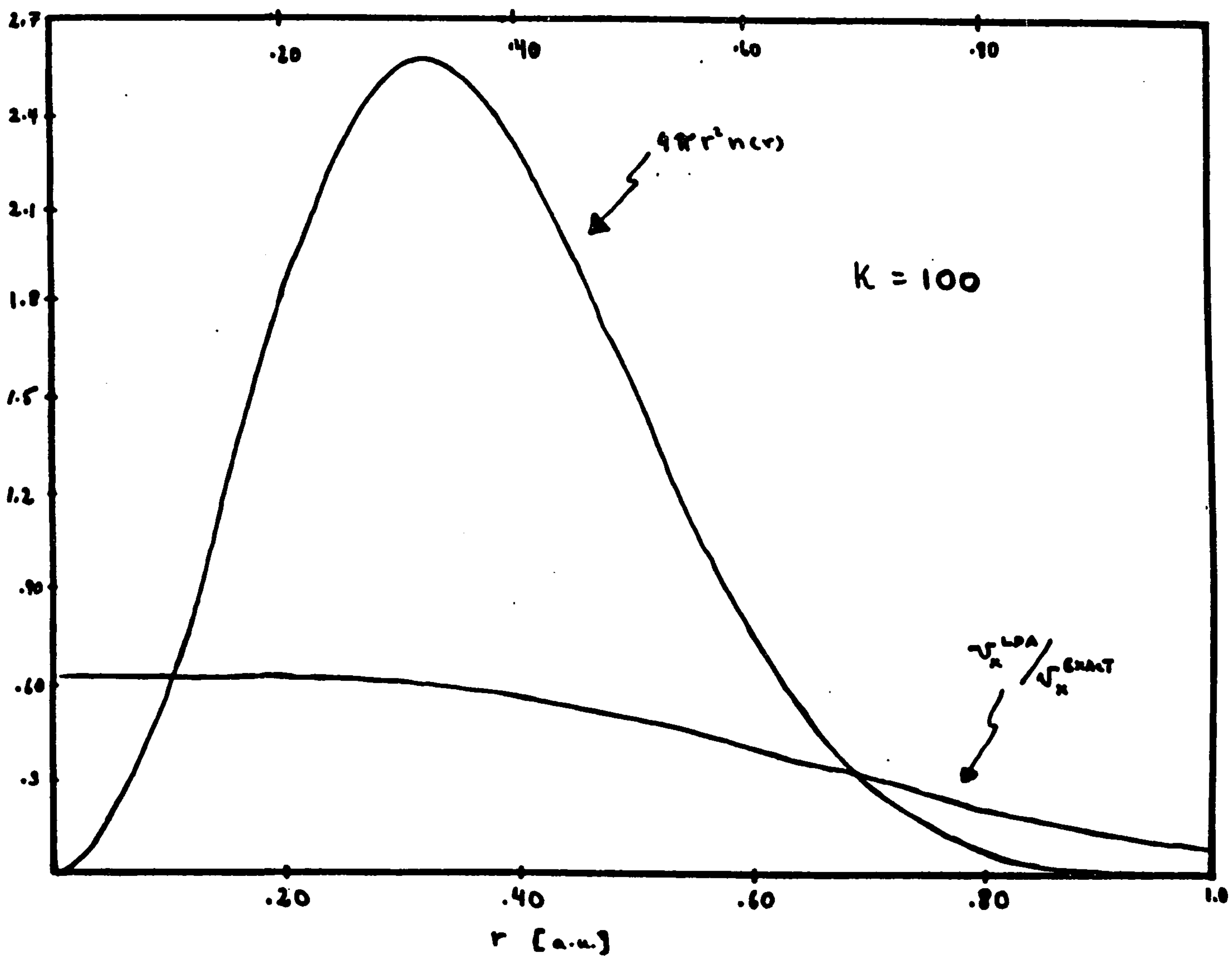


Fig. 12 Ratio of LDA to Exact Exchange Potential for k = 100

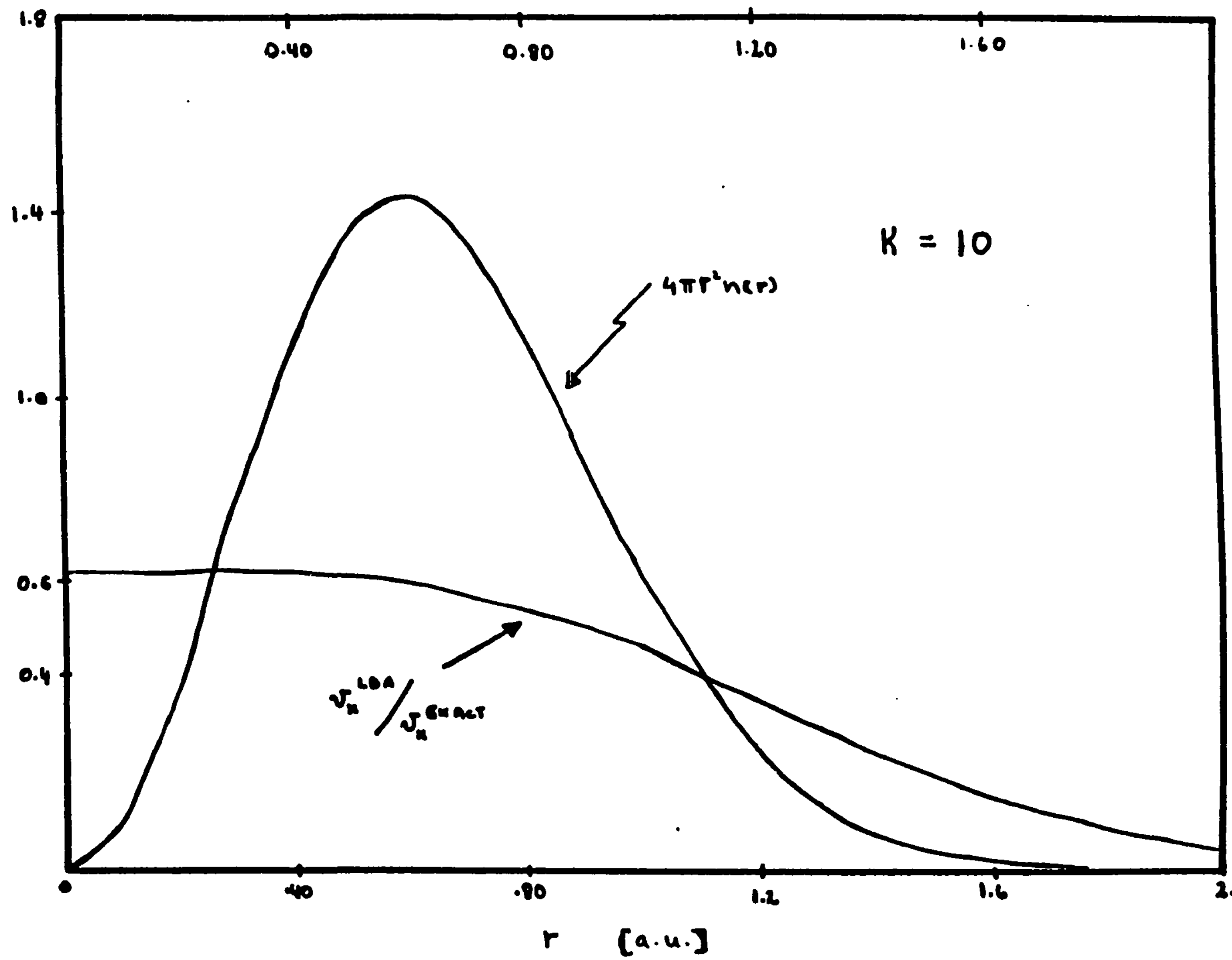


Fig. 13 Ratio of LDA to Exact Exchange Potential for k = 10

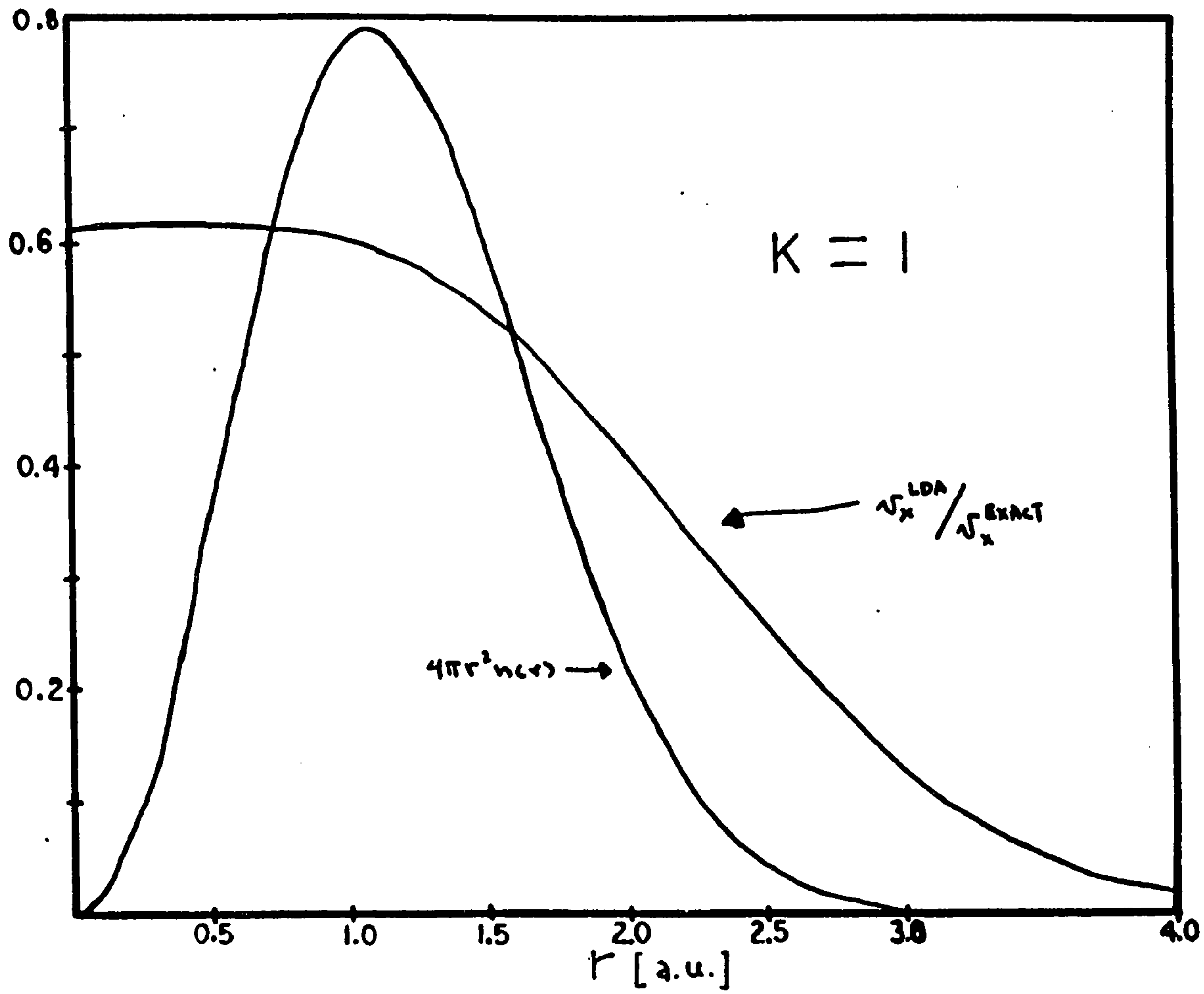


Fig. 14 Ratio of LDA to Exact Exchange Potential for k = 1

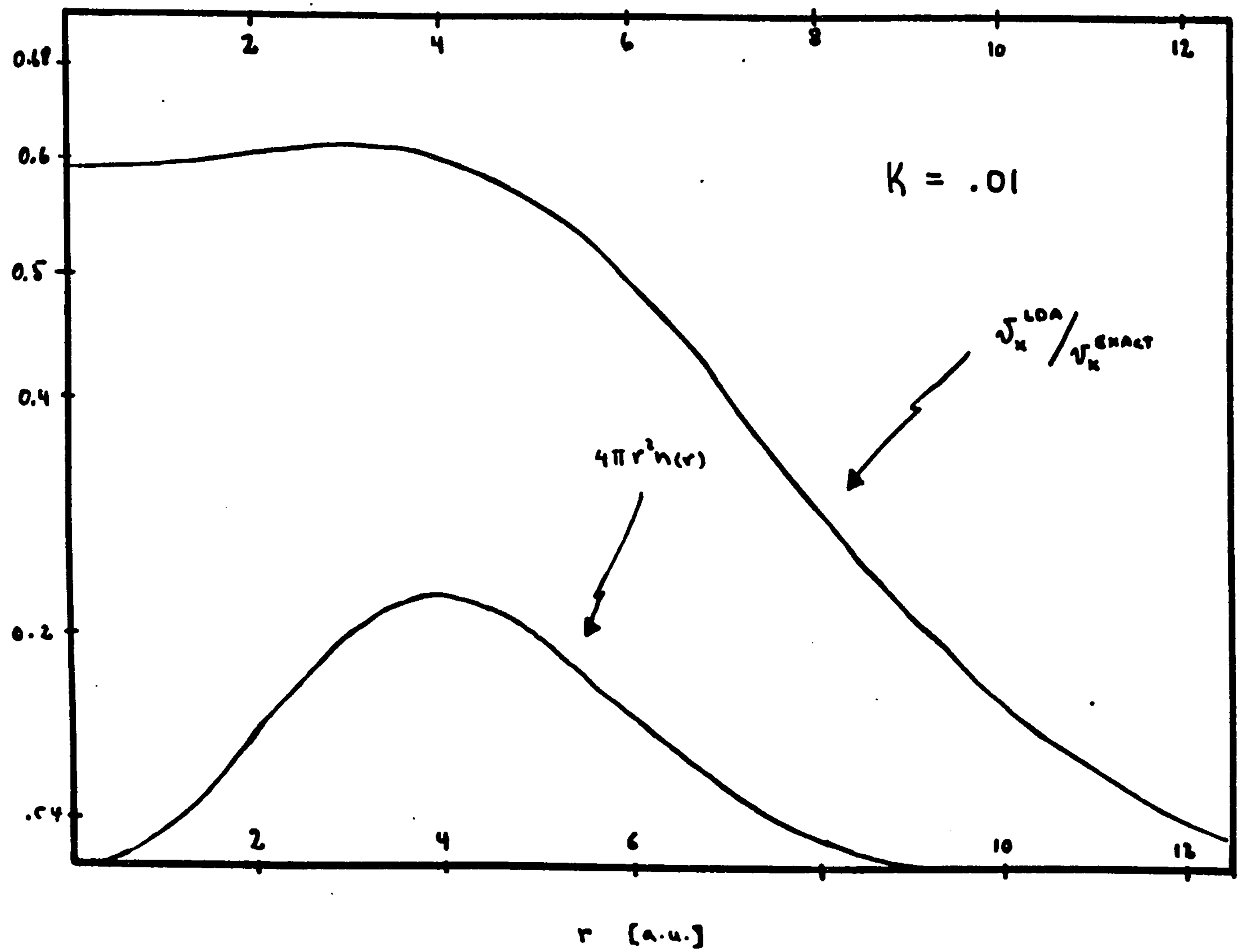


Fig. 15 Ratio of LDA to Exact Exchange Potential for k = .01

3.6 Energies and Expectation Values of Potentials

We have within the Kohn-Sham theory the expression :

$$E = \Sigma_i \varepsilon_i + E_{xc}[n(\bar{r})] - \int \vartheta_{xc} n(\bar{r}) d\bar{r} - \tfrac{1}{2}\int\int n(\bar{r})n(\bar{r}')/|\bar{r}-\bar{r}'|\, d\bar{r}d\bar{r}'$$

which gives the total energy of the interacting N electron system in terms of the single particle eigenvalues and various functionals of the derived density.

For our model system $E_{tot}[n]$ is known exactly, as is ε_{ks}, $n(r)$, $\vartheta_x[n(r)]$, and $\vartheta_c[n(r)]$. In fact we can invert the previous equation to write:

$$E_{xc}[n(\bar{r})] = E - \Sigma_i \varepsilon_i + \int \vartheta_{xc} n(\bar{r}) d\bar{r} + \tfrac{1}{2}\int\int n(\bar{r})n(\bar{r}')/|\bar{r}-\bar{r}'|\, d\bar{r}d\bar{r}' \qquad (37)$$

and obtain E_{xc} exactly.

Moreover, for the 2-particle case it is clear that

$$\vartheta_x = -\tfrac{1}{2}\int n(\bar{r}')/|\bar{r} - \bar{r}'|\, d\bar{r}' \qquad (35)$$

and thus,

$$E_x[n] = -\tfrac{1}{4}\int\int n(\bar{r})n(\bar{r}')/|\bar{r}-\bar{r}'| d\bar{r}d\bar{r}' \qquad (38)$$

enabling us to obtain $E_x[n]$ and $E_c[n] = E_{xc}[n] - E_x[n]$ exactly.

We wish to investigate the accuracy of various approximate functionals in predicting energies and related potentials. One approach would be to use these functionals for the potential, ϑ_{xc}, in the Kohn-

Sham equations and solve for the density n(r) and the corresponding ε_{ks}^{app}. These could then be used to obtain total energies as well.

An alternative approach - the one which we employ - is to evaluate the approximate functionals using the exact density, $n(\vec{r})^{ex}$, generated by the solution of the Schrodinger equation, to obtain potentials (as projected on r space), energies, and potential expectation values to be compared to the correct ones. It is worth noting that if we use this second method the only terms in which error can be introduced (in considering energies) are E_x, E_c, $\langle\Psi_{ks}|\vartheta_x|\Psi_{ks}\rangle$ and $\langle\Psi_{ks}|\vartheta_c|\Psi_{ks}\rangle$, since the other terms are exact. Thus we are actually testing the functional forms of exchange correlation energies and potentials.

It is also to be expected that if there is a significant error in the terms under investigation evaluated in the second manner, a calculation of the first type would not rectify matters. This is because in order to offset a change of order δ in the energies calculated the density would need to be changed even more drastically, i.e. of $O(\delta^{\frac{1}{2}})$ thus giving rise to a poor density profile.

We now proceed to set forth the various approximations employed.

3.6.1 Functionals and Expectation Values

(1) Exchange Only - Because correlation makes a contribution to the total energy which is never more than ~5% for our model, a first approximation of interest is to consider exchange only.

(a) LDA: The LDA[8] treats exchange by taking the energy density at each point in space as if there were a uniform electron gas of the local electron density.

i.e., the exchange energy density, $\varepsilon_x = -(3/4)(3n/\pi)^{1/3}$

$$E_x[n] = \int \varepsilon_x n(\vec{r})d\vec{r} = -(3/4)(3/\pi)^{1/3}\int n^{1/3}(\vec{r})n(\vec{r})\, d\vec{r}$$

and

$$\vartheta_x = \delta E_x/\delta n(\vec{r}) = \frac{d}{dn}[n\varepsilon_x]$$

in the local approximation

$$\vartheta_x(r) = -(3n(r)/\pi)^{1/3}$$

(b) Non-Local: LDA with Gradient Energy Expansion (GEA)[8,31-33]

$$E_x[n] = E_x^{LDA} - C_x\int|\nabla n|^2 n^{-4/3}d\vec{r} + \ldots$$

$$C_x = 7\pi(3\pi^2)^{-4/3}/144 = 0.001667 \text{ a.u.}$$

and the corresponding potential term is:

$$\vartheta_x = \vartheta_x^{LDA} - C_x\left[\frac{4}{3}\frac{|\nabla n|^2}{n^{7/3}} - 2\frac{\nabla^2 n}{n^{4/3}}\right]$$

(c) Non-Local: LDA + Langreth-Mehl[34,14] (LM)

$$E_x^{LM} = E_x^{LDA} - a(7/9 + 18f^2)\int|\nabla n(\vec{r})|^2 n^{-4/3}d\vec{r}$$

where $a = \pi/[16(3\pi^2)^{4/3}] = 2.144 \times 10^{-3}$ a.u. and we used $f = 0.15$ as suggested by LM.

(2) Exchange and Correlation

A. Local: $E_{xc}[n] = E_x[n] + E_c[n]$, where exchange is given by LDA (as in 1A) and E_c has a local form as well. i.e.,

	RPA		Ceperley-Alder	
Parameter	U	P	U	P
A	0.0311	0.01555	0.0311	0.01555
B	-0.071	-0.0499	-0.048	-0.0269
C	0.0021	0.0005	0.0020	0.0007
D	-0.0078	-0.0020	-0.0116	-0.0048
γ	-0.2044	-0.1104	-0.1423	-0.0843
β_1	1.5023	1.1102	1.0529	1.3981
β_2	0.0916	0.0170	0.3334	0.2611

Table 4

Parameters used in the Ceperley-Alder form of the correlation energy density as given by Perdew and Zunger[35], and Cole and Perdew[37]. (U denotes unpolarized, while P denotes completely polarized.)

$$\varepsilon_c = \int n(\vec{r})\varepsilon_c(n)\, d\vec{r}$$

where ε_c, the correlation energy density per electron, is given by the parametrization of Perdew and Zunger[35] of a form due to Ceperley and Alder[36]:

$$\varepsilon_c = A\, \ell n(r_s) + B + C\, r_s \ell n(r_s) + D\, r_s \qquad r_s \le 1$$

$$\varepsilon_c = \gamma/(1 + \beta_1\sqrt{r_s} + \beta_2 r_s) \qquad r_s \ge 1$$

where $4(\pi r_s^3)/3 = n^{-1}$

B. Non-Local:

$$E_{xc}[n] = E_x^{LDA} + E_c^{RPA} + \Delta E_x^{LM} + \Delta E_c^{LM}$$

In this case it is necessary to use the RPA parametrization of the Ceperley-Alder parametrization as given by Cole and Perdew[37]. This is because LM has been derived within the RPA scheme.

$$E_c^{LM} = E_c^{LDA} + a\int n^{-4/3}\,(2e^{-F} + 18f^2)\,|\nabla n(\vec{r})|^2 d\vec{r}$$

a and f are as noted previously (1c) and $F = b|\nabla n(\vec{r})|/n(\vec{r})^{7/6}$, where $b = (9\pi)^{1/6} f = 0.2618$

(3) Self-Interaction Correction

We employ a Local Spin Density (LSD) formalism in this instance. This is designed such that for a two fermion system the exchange cancels half the Hartree term thus ensuring that at least in this simple case there is no electrostatic self interaction remaining.

In this formalism, we define $\zeta = (n_u - n_d)/n$, as the degree of polarization (where u and d denote spin up and down respectively). Then $\zeta = 0$ corresponds to an unpolarized system, while $\zeta = 1$ corresponds to a completely polarized configuration. For intermediate polarizations ($0 < \zeta < 1$), the interpolation formula of Von Barth and Hedin[38] is employed.

$$\varepsilon_c(r_s,\zeta) = \varepsilon_c^u(r_s) + f(\zeta)\,[\varepsilon_c^p(r_s) - \varepsilon_c^u(r_s)] \tag{39}$$

where $f(\zeta) = [(1+\zeta)^{4/3} + (1-\zeta)^{4/3}]/[2^{4/3}-2]$

We implement this using the Ceperley-Alder form for ε_c.
The expression for self-interaction corrected correlation is[35,39,40]:

$$E_c^{SIC} = \int [\varepsilon_c(n_u,n_d)n(\bar{r}) - \Sigma_{\alpha\sigma}\varepsilon_c(n_{\alpha\sigma},0)n_{\alpha\sigma}(\bar{r})]d\bar{r} \tag{40}$$

The parameters used can be found in Table 4. In this case, because there is only one particle with spin up and one with spin down, exchange is given exactly and thus the only source of error is in the approximation for correlation. In our case of two identical particles this reduces to:

$$E_c^{SIC} = \int \varepsilon_c(\tfrac{1}{2}n,\tfrac{1}{2}n)n(\vec{r})d\vec{r} - \int [\varepsilon_c(\tfrac{1}{2}n,0)-\varepsilon_c(0,\tfrac{1}{2}n)]\tfrac{1}{2}n(\vec{r})d\vec{r}$$

$$= \int n(\vec{r})\varepsilon_c^u(n)d\vec{r} - 2\int \tfrac{1}{2}n(\vec{r})\varepsilon_c^p(\tfrac{1}{2}n)d\vec{r}$$

$$= \int [\varepsilon_c^u(n) - \varepsilon_c^p(n)]n(\vec{r})d\vec{r} \qquad (41)$$

In the next section we consider the following quantities to ascertain the efficacy of the various approximations.

1. $E_x = \int n(\vec{r})\varepsilon_x[n]\, d\vec{r}$

2. $E_c = \int n(\vec{r})\varepsilon_c[n]\, d\vec{r}$

3. $V_x = \langle\psi_{ks}|\vartheta_x|\psi_{ks}\rangle$

4. $V_c = \langle\psi_{ks}|\vartheta_c|\psi_{ks}\rangle$

5. $E_{total} = (E_{total} - E_{xc})^{exact} + E_{xc}^{app.}$

6. $\varepsilon_{ks} = (\varepsilon_{ks} - V_{xc})^{exact} + V_{xc}^{app.}$

3.7 Results and Conclusions

Recall that over the range of k values under consideration, the central density varies by a factor of almost 2,000. While in $\vec{r}$ space the densities evolve with increasing k, from slowly to rapidly varying, the criterion for applicability of the LDA or the GEA expansion based on the local fermi wavevector, $|\nabla n|/(k_F n) \ll 1$, is never satisfied for our model. However, since this is the case for other systems as well, in which LDA has achieved some success we will apply it here as well. Various arguments have been proposed to explain the success of LDA and GEA in such systems where the aforementioned criterion is not satisfied[41-43].

3.7.1 Total Energy and Kohn Sham Single Particle Eigenvalues

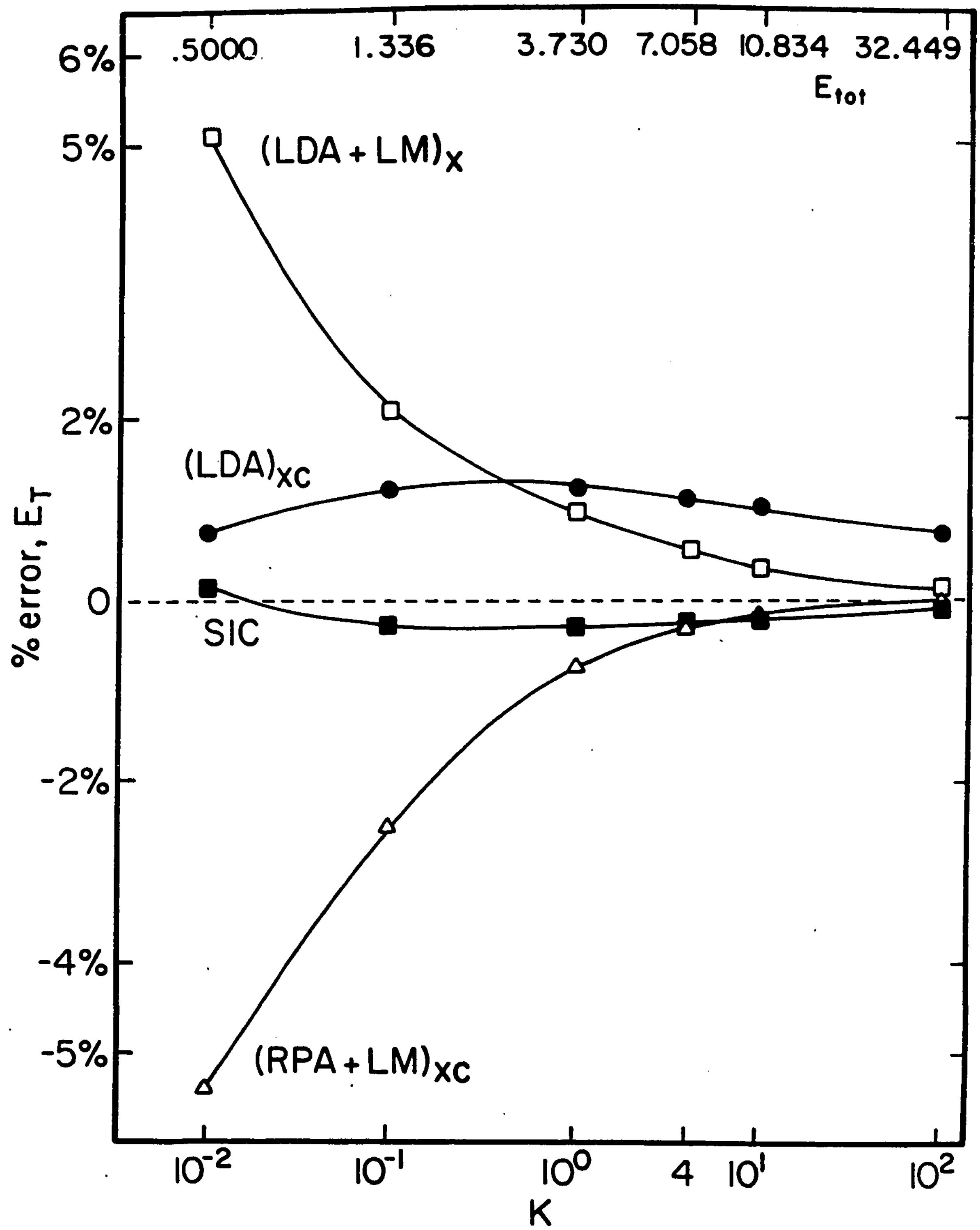
Table 5 lists the total energy of our model system, for a series of k values, calculated exactly and within various approximations. Figure 16 is the % error in the calculations of E_{total} using the same approximations. As can be seen by reference to both table and graph, the discrepancies in the total energy are quite small - on the order of hundredths of a.u. (i.e. ~ 5%) in the worst case (k = .01) and in the range of 1% or better over the remainder of the range.

That is, for the entire range, any approximation we use for exchange-correlation is quite good for the calculation of the total energy. Referring to the tables and figures on exchange and correlation energies (Tables 7 and 10; Figures 18 and 20) we see that exchange-correlation ranges from 8% to 48% of the magnitude of the total energy. Thus the good agreement of E_{total}, irrespective of the approximation for E_{xc}, cannot be attributed to exchange-correlation being a small component of the energy in this problem.

K	.01	0.1	1.0	4.0	10	100
EXACT	.50000	1.33605	3.73012	7.05788	10.83377	32.44869
$(LDA+GEA)_x$	.5371	1.3893	3.8052	7.1510	10.9420	32.6121
$(LDA+LM)_x$	.5256	1.3682	3.7666	7.1108	10.8761	32.4864
LDA_{xc}	.5038	1.3526	3.7777	7.1401	10.9485	32.6968
$(RPA+LM)_{xc}$	.4728	1.3074	3.7037	7.0516	10.8222	32.4619
SIC	.5007	1.3323	3.7191	7.0415	10.8133	32.4158

Table 5

Total energy of the two particle system, for a range of k values, exact and within various approximations. (See the text for legend.)



<u>Figure 16</u>: % Error in the Total Energies

Note that using a strictly local (LDA_{xc}) approximation the error is always on the order of 1%. Of course SIC yields even better results since it eliminates the error in exchange and thus limits the introduction of error to the correlation term alone which only varies from 0.2% to 5.8% of the total energy.

We next consider the Kohn-Sham eigenvalue ε_{ks} (Table 6 and Figure 17). Table 6 shows that the discrepancy in ε_{ks} can be comparatively large - on the order of 1 a.u. . Figure 17 shows the percentage error in the calculation of the eigenvalue within the given approximations.

We observe that although the SIC gives remarkable agreement (~ 0.2% or better, ~.01 a.u. or better), all the other approximations, both local and non-local, are quite poor. That is, for high k, where the error in the total energy is ~ 1% the error in the corresponding ε_{ks} is > 5% while for low k, where E_{total} is in error from 1% - 5% depending on the approximation employed, ε_{ks} is in error by approximately 20 to 30 percent.

Thus we may draw the following significant conclusion: Although a given approach may yield highly accurate total energies, this does not ensure the accuracy of the corresponding Kohn-Sham eigenvalues.

We now endeavor to obtain an understanding of this phenomenom by investigating the exchange and correlation terms (the only terms which are being approximated) individually.

K	.01	0.1	1.0	4.0	10	100
EXACT	.3500	0.8617	2.23012	4.05788	6.09035	17.44869
$(LDA+GEA)_x$	.4530	1.0455	2.5552	4.5156	6.6642	18.4630
$(LDA+LM)_x$	.4493	1.0385	2.5424	4.4972	6.6409	18.4212
LDA_{xc}	.4275	1.0141	2.5222	4.4851	6.6373	18.4565
$(RPA+LM)_{xc}$	.4130	0.9952	2.4942	4.4478	6.5918	18.3779
SIC	.3531	0.8636	2.2295	4.0549	6.0855	17.4378

Table 6

The Kohn-Sham eigenvalues - both exact and in various approximations

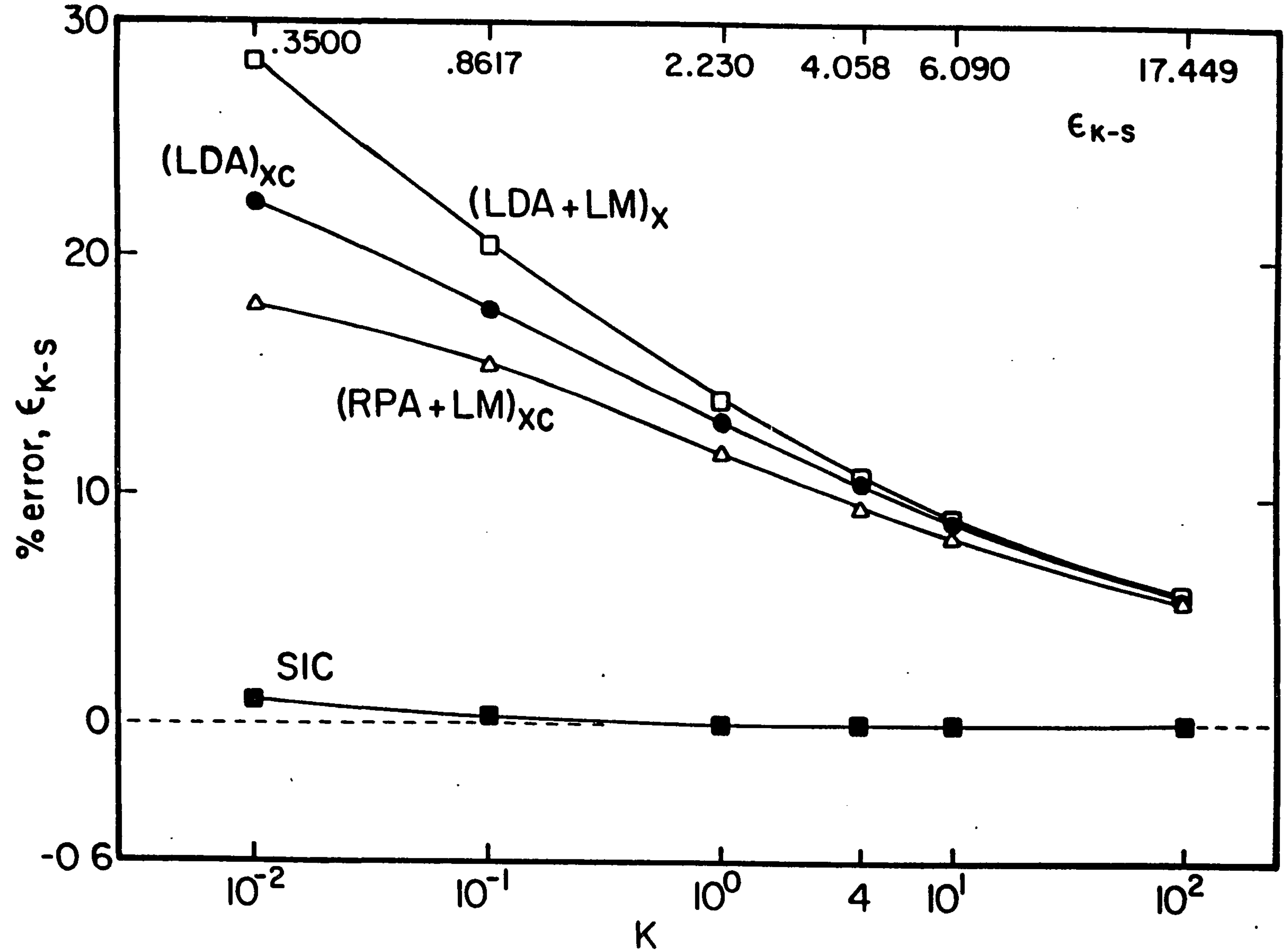


Fig. 17 % Error in the Kohn-Sham Eigenvalues

3.7.2 Exchange

Table 7 contains the negative of the exchange energy for each case and approximation; Figure 18 shows the percent error in the calculated values.

Before examining these displays we digress to make an observation with regard to the LM and GEA approximations. If we refer to section 3.6 in which we define the different approximations we find that both LM and the second order gradient energy expansion for exchange can be written as:

$$E_x^i = E_x^{LDA} + C^i \int |\nabla n|^2 n^{-4/3} d\bar{r}$$

where i = GEA, LM. Thus the correction to LDA afforded by each of these differs only through the multiplicative constant C^i.

i.e.

$$\frac{\Delta E_x^{LM}}{\Delta E_x^{GEA}} = \frac{C_x^{LM}}{C_x^{GEA}} = \frac{a(7/9 + 18f^2)}{7\pi/[144(3\pi^2)^{4/3}]}$$

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

$$\frac{\Delta E_x^{LM}}{\Delta E_x^{GEA}} = \frac{9}{7}\left(\frac{7}{9} + 18f^2\right) = 1 + \frac{162}{7} f^2 = 1.521 \qquad (43)$$

for f = 0.15, the value given by LM.

K	.01	0.1	1.0	4.0	10	100
EXACT	.2110	.4014	.7467	1.0757	1.3654	2.4684
LDA	.1811	.3438	.6389	0.9201	1.1677	2.1104
GEA	.2031	.3844	.7130	1.0262	1.3020	2.3519
LM	.2146	.4055	.7516	1.0814	1.3718	2.4775

Table 7

Exchange energy expectation value, $-E_x$, exact, LDA, and corrections to LDA, for a range of k values

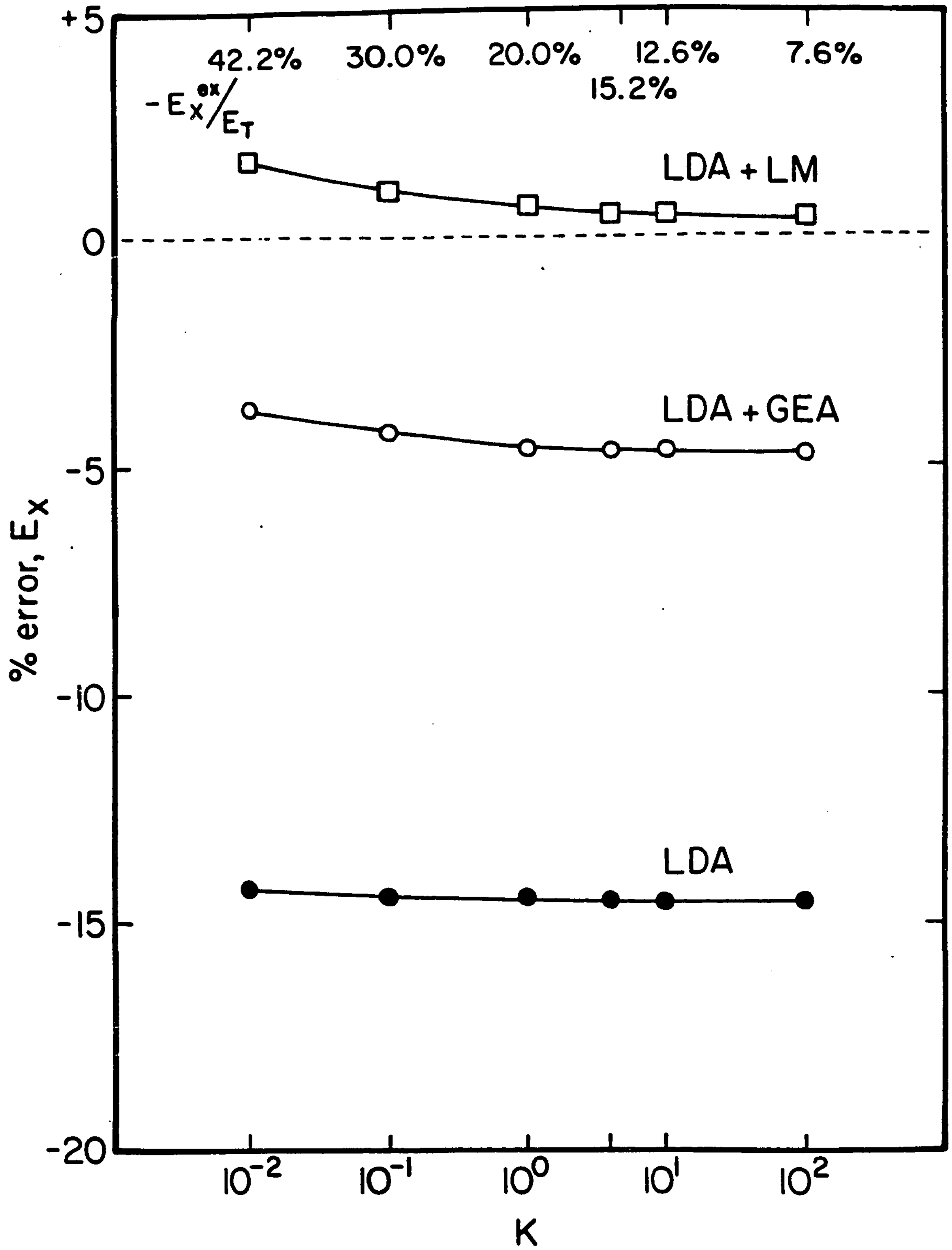


Figure 18: % Error in the Exchange Energies

Figure 18 shows the % error for $(-E_x)$. Along the upper border is the percentage of E_{total}, in magnitude that E_x represents. This is not an alternate scale (x - axis) for the plot, but only shows the values we have calculated and can be used at most as a guide to determine the relative importance of exchange for the given k region. We observe that in the LDA the exchange energy is ~ 14% less than the exact value throughout . The GEA correction reduces the error to ~ 5% and the LM form overcompensates slightly yielding values between 0.2% and 2% too large.

When considering the companion quantity $-V_x$, the negative of the expectation value of $\vartheta_x[n]$, we see a very different picture. Table 8 and Figure 19 make it evident that the exchange potential is not being modelled well at all. We find that for the LDA the % error is ~ 43% throughout (as compared to 14% for E_x) and although both the GEA and the LM improve E_x considerably they have a much smaller effect on the expectation value V_x. In fact the % error even after the corrections is never less than 37% as compared to roughly 1% error in the total energy for the corresponding k value within the same approximation (LM).

Some of the points which have been touched upon in the discussion of results for exchange can be understood with a little analysis:

(a) E_x^{LDA} = ~85% of E_x^{exact} for the entire range of k values.

(b) V_x^{LDA} = ~57% of V_x^{exact} for the entire range of k values.

K	.01	0.1	1.0	4.0	10	100
EXACT	.2110	.4014	.7467	1.0757	1.3654	2.4684
LDA	.1207	.2292	.4259	0.6134	0.7785	1.4070
GEA	.1280	.2427	.4506	0.6487	0.8232	1.4874
LM	.1318	.2497	.4634	0.6671	0.8465	1.5292

Table 8

Exchange potential expectation value exact, $-V_x$, LDA and corrections to LDA, for a range of k values

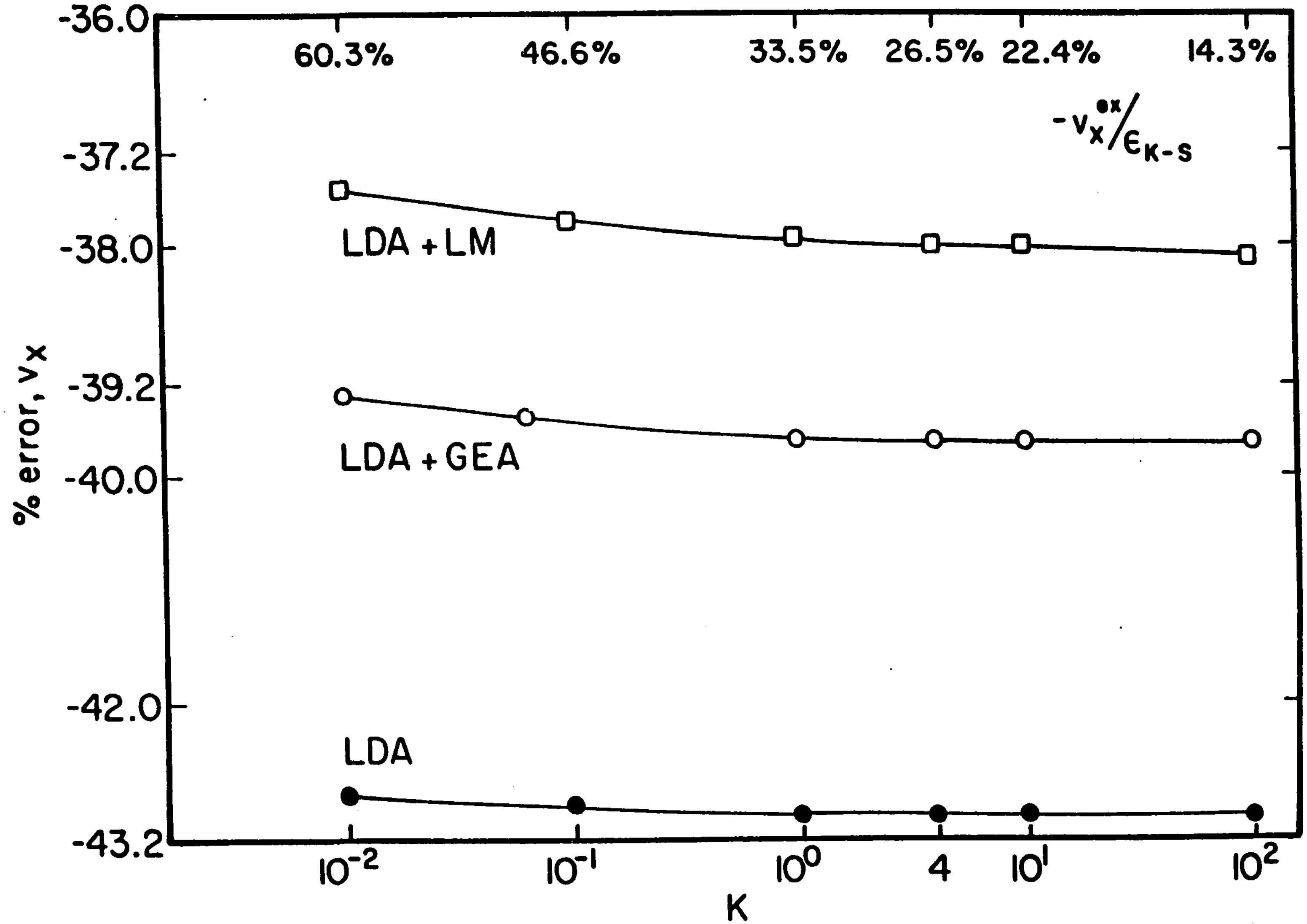


Figure 19: % Error in the Fxchange Potential Fxpectation Values

Two questions present themselves here: (1) Why does LDA (and its corrections) work so well for the energy, E_x, but not for V_x? (2) Why does LDA give approximately the same value- i.e., the same percentage of the exact answer - over the entire spectrum of densities we have investigated?

The second question can be answered by reference to Figures 12-15, which show that for the region of space where the quantity $4\pi r^2 n(r)$ is substantial, the ratio ϑ_x^{LDA} to ϑ_x^{exact} is ~ 0.6. In addition, we shall present a calculation which should make this plausible on analytic grounds as well.

To address the first question: Recall that for any 2 electron system

$$E_x[n] = -\tfrac{1}{4}\int\int n(\vec{r})n(\vec{r}')/|\vec{r}-\vec{r}'|d\vec{r}d\vec{r}' \quad (34)$$

and,

$$\vartheta_x = -\tfrac{1}{2}\int n(\vec{r}')/|\vec{r} - \vec{r}'|\, d\vec{r}' \quad (35)$$

so

$$V_x = \langle\psi_{ks}|\vartheta_x|\psi_{ks}\rangle = -\frac{1}{2}\int \frac{n(\vec{r})}{2}\int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}'$$

$$= -\frac{1}{4}\int \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' = E_x$$

Thus

$$V_x^{exact} = E_x^{exact} \quad (44)$$

However, in the LDA:

$$E_x^{LDA} = -(3/4)(3/\pi)^{1/3} \int n^{4/3}(\bar{r})d\bar{r}$$

$$\vartheta_x^{LDA} = -(3/\pi)^{1/3} n^{1/3}(\bar{r})$$

$$V_x = \langle\psi_{ks}|\vartheta_x|\psi_{ks}\rangle = \tfrac{1}{2}\,(3/\pi)^{1/3} \int n^{4/3}(\bar{r})d\bar{r}$$

Therefore: $$V_x^{LDA} = (2/3)E_x^{LDA} \qquad (45)$$

Thus comparing equations (44) and (45) , it is evident that if the LDA is a good first approximation for E_x, as it is in Helium-like atoms[14], it is necessarily poor for the exchange potential V_x. [It is interesting to note that Slater Exchange, i.e. (3/2)LDA, will give very good results for the exchange potential in the case of 2-electron atoms, when LDA is a good approximation for the exchange energy.] This points up the inadequacy in attempts to improve LDA by addressing the issue of the energy alone. It is clear that merely seeking a correction to E_x^{LDA} which is assumed small without reference to ϑ_x will not necessarily lead to improvement in the V_x, thus leaving a major source of error in the calculation of ε_{ks}.

In fact it may be argued that a more meaningful approach would be to begin by attempting to improve the potential functional ϑ_x. Then an appropriate energy functional from which this ϑ_x can be derived may be constructed. Since $E_x[n]$ is a far smoother object than its functional derivative ϑ_x, the matching of E_x should be a far less difficult task (given a reasonable potential) than that of matching the potential.

Some light may be shed on the second question through consideration of limiting cases. First let us consider two electrons in a spherical harmonic oscillator potential with no e-e interaction. This can be thought of as the k ==> ∞ limit or alternatively we can think of it as a first approximation to our model where the e-e term, $1/|\vec{r}|$ is treated as a perturbation.

Then $\Psi(\vec{r}_1,\vec{r}_2) = (\alpha/\pi)^{3/4}\exp[-\frac{1}{2}\alpha(r_1^2 + r_2^2)]$ where $\alpha = k^{\frac{1}{2}}$.

and $n(r) = 2(\alpha/\pi)^{3/2}e^{-\alpha r^2}$

Then a calculation of the exchange energies and potentials yields:

$$E_x^{exact} = -(2\alpha/\pi)^{\frac{1}{2}} = V_x^{exact}$$

$$E_x^{LDA} = -(9/16)(6/\pi)^{1/3}(3\alpha/\pi)^{\frac{1}{2}}$$

$$\implies \quad V_x^{LDA} = -(3/8)(6/\pi)^{1/3}(3\alpha/\pi)^{\frac{1}{2}}$$

Thus

$$E_x^{LDA}/E_x^{ex} = \frac{9}{16}\left(\frac{6}{\pi}\right)^{1/3}\left(\frac{3}{2}\right)^{1/2} = .855$$

and

$$V_x^{LDA}/V_x^{ex} = .570$$

In addition:

$$\Delta E_x^i = -[27(3\pi\alpha/2)^{\frac{1}{2}}/2^{1/3}]C_x^i$$

where i = LM or GEA.

then the correction term due to LM or GEA is:

$$\Delta E_x^{GEA}/E_x^{ex} = .0972 \qquad \text{while} \qquad \Delta E_x^{LM}/E_x^{ex} = .1478$$

$$\Delta V_x^i = -[9(3\pi\alpha/2)^{\frac{1}{2}}\times 2^{1/6}]C_x^i$$

$$\Delta V_x^{GEA}/V_x^{ex} = .0648 \qquad \text{while} \qquad \Delta V_x^{LM}/V_x^{ex} = .0985$$

The analysis above shows that for large k, (or to first order for all k) the LDA will give 85.5% of the correct exchange energy. This explains why we find a %error of approximately 14+% throughout regardless of k. In addition, it shows that when GEA is taken for the correction, the energy is then ~ 95% of the correct value, while LM yields approximately 100.3%, which is consistent with our findings. We do not expect to get these values exactly as that would only be in the limit of 1/r being a negligible perturbation, however, we do get an idea of where our answers should lie and this is borne out by the calculations.

In a similar vein, we find that for the expectation value of the exchange potential the LDA is 57.0% of the exact value - corresponding to the -43% error we found in our calculations. For the V_x we see that the GEA only brings us to 63.5% and the LM to 66.9%. Thus we see that the exchange potential is not as well given as the exchange energy. It is interesting to note that the correction to the expectation value of the potential as calculated deviates from the limiting value to a far greater extent than is the case for the energy. Thus we see that the exchange potential is not as well given as the exchange energy.

We can also consider another 2 electron model in which the e-e interaction is negligible compared to the strength of the central potential; i.e., a Helium-like ion in the limit of large Z.

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z(1/r_1 + 1/r_2)$$

Then $\Psi(\vec{r}_1,\vec{r}_2) = (Z^3/\pi)\exp[-Z(r_1 + r_2)]$

and $n(r) = 2(Z^3/\pi)e^{-2Zr}$

Then a calculation of the exchange energies and potentials yields:

$$E_x^{exact} = -(5/8)Z = V_x^{exact}$$

$$E_x^{LDA} = -(81/64)\times(3^{1/3}/2^{2/3})\times\pi^{-2/3}Z$$

$$\Longrightarrow \quad V_x^{LDA} = -27(3^{1/3}/2^{17/3})\times\pi^{-2/3}Z$$

Thus

$$E_x^{LDA}/E_x^{ex} = \frac{81}{40}\cdot\frac{3^{1/3}}{2^{2/3}\pi^{2/3}} = .8577$$

and $V_x^{LDA}/V_x^{ex} = .5718$

In addition:

$$\Delta E_x^i = -[27(\pi/2)^{1/3}]C_x^i Z$$

$$\Delta E_x^i = -9[\pi^{1/3}2^{1/6}]C_x^i Z$$

where i = LM or GEA. then the correction term due to LM or GEA is:

$$\Delta E_x^{GEA}/E_x^{ex} = .0837 \quad \text{while} \quad \Delta E_x^{LM}/E_x^{ex} = .1274$$

$$\Delta V_x^{GEA}/V_x^{ex} = .0333 \quad \text{while} \quad \Delta V_x^{LM}/V_x^{ex} = .0507$$

In this case as well, the LDA exchange energy is ~ 85.8% of the exact exchange energy, and GEA and LM bring that value to 94.4% and 98.5% respectively. For the exchange potential the percentages of the exact expectation value for LDA, GEA, and LM are 57.2%, 60.5%,and 62.3% respectively. These values are similar to those obtained in the exact calculations and our other model calculation as well. The LM value of 62.3% is indeed what we see in the exact calculation over almost all of the range. The results of these two limiting cases substantiate the reliability of the numerical calculations. It also shows that for a totally different central potential we get similar results. Thus, our results can not be brushed aside as merely an artifact of the harmonic oscillator potential, as we see it persists for the physical coulomb attractive center as well.

We observed earlier that second order GEA and LM differ only in the constant used in the correction term. For all our 2-particle model systems the LM coefficient yields far more accurate results. We investigate this further by looking at results for real systems as well.Table 9 is a display from reference 32 of the "exact" Kohn-Sham and Hartree-Fock exchange energies and the % errors obtained when calculating the E_x in the LDA or GEA. (The values were gleaned from various sources as noted in reference 25.) "Exact" in this context means exchange only Kohn-Sham. Expanding the table we have added a column labeled "LM". This is the % error an LM calculation would have resulted in for these noble atoms. The method of obtaining these value was:

$$LM = LDA + (GEA - LDA) \times C_x^{LM}/C_x^{GEA} \quad (46)$$

Once again we see LM yielding results superior to GEA.

	Exact values (a.u.)		% Error		
Atom	HF	KS	LDA	GEA	LM
H	0.3125	0.3125	-14.2	-5.9	-1.6
He	1.03	1.03	-13.6	-5.3	-1.0
Ne	12.13	12.10	- 8.8	-4.6	-2.4
Ar	30.30	30.16	- 7.5	-4.2	-2.5
Kr	94.63	93.78	- 5.4	-3.2	-2.1

Table 9

Hartree-Fock and Kohn Sham exchange energies for a series of atoms and the % errors (relative to Kohn-Sham) of the local density (LDA), second order gradient expansion (GEA), and Langreth-Mehl (LM), approximations for the exchange energy ($-E_x$). All entries except LM obtained from Ref. 32.

3.7.3 Correlation

The contribution to the total energy due to correlation is shown in Table 10 and Figure 20. The correlation as a percentage of the total energy is given inside the upper border for each of the points actually calculated. We see that correlation varies from 0.2% to 5.8% of the total energy and thus it is a significantly smaller percentage of the total energy than is exchange. However, it is worth noting that with the exception of the SIC none of the approximations for correlation give reasonable results - the errors varying from 50% to more than 300%. Among these the RPA+LM is best in that its error ranges between -50% and +80%. This is because the sign on the LM correction for correlation is opposite that of all other terms, and for large k the correction term is even greater in magnitude than the RPA value. Furthermore, the error in correlation is 2 orders of magnitude worse than that in exchange for the LM, therefore the relative success of LM does not indicate that it is a satisfactory approximation.

Even the SIC which does give better results is not very promising. For low k the error is on the order of 6% but this grows with k until at k = 100 it is on the order of 70%. However as we have noted previously this will not affect the very fine results for total energy because SIC gets exchange exactly for the two particle problem and the correlation energy for k = 100 is only 0.2% of the total energy. Table 11 and Figure 21 give the results for $-V_c$. The upper border of the

K	.01	0.1	1.0	4.0	10	100
EXACT	.0292	.036	.041	.044	.045	.047
RPA	.0830	.109	.137	.155	.167	.198
CEP-ALD	.055	.077	.101	.117	.128	.157
RPA+LM	.053	.061	.063	.059	.054	.024
SIC	.0285	.040	.052	.060	.065	.080

Table 10

Correlation energy expectation, $-E_c$, values exact and in various approximation schemes

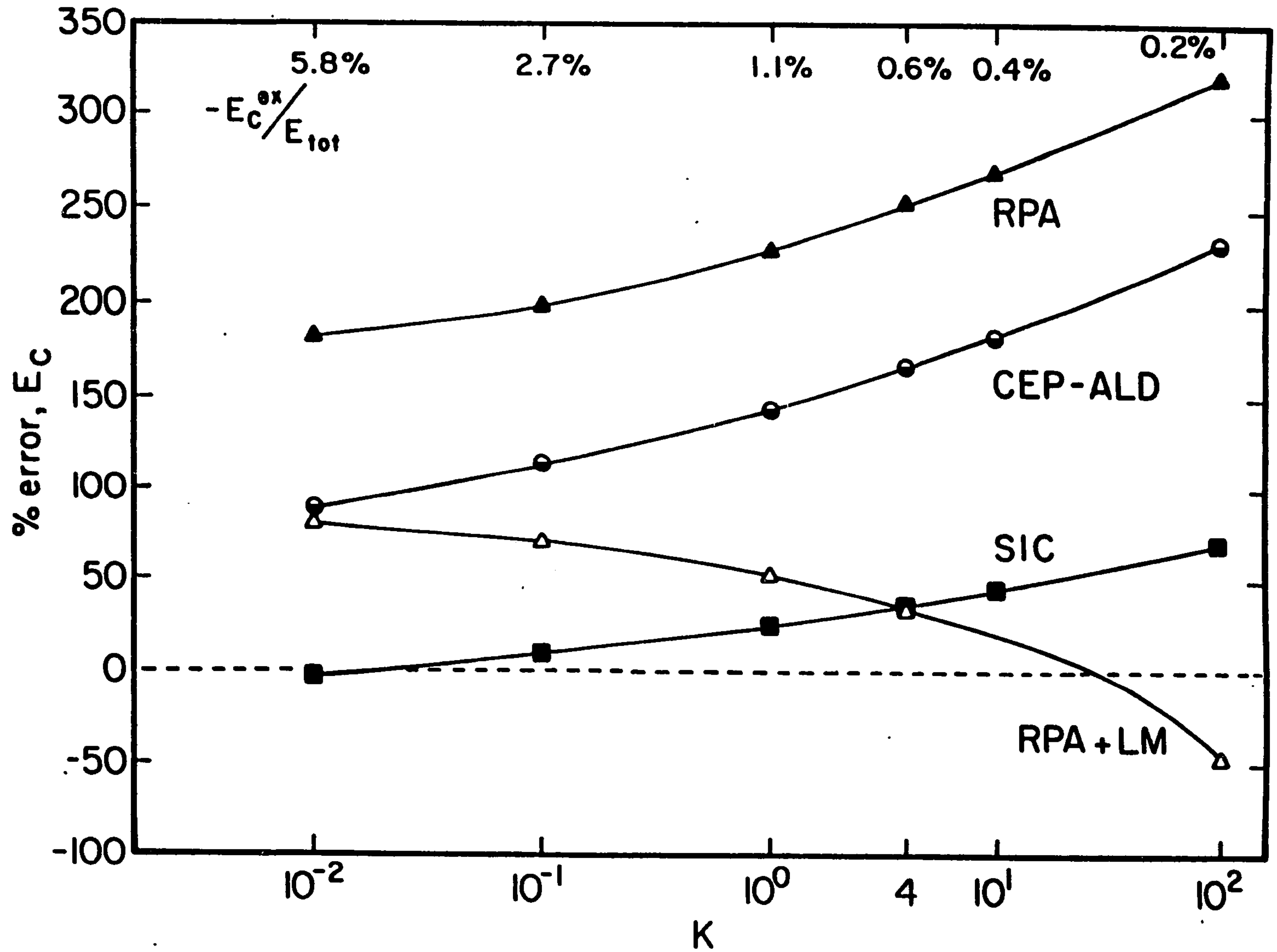


Fig. 20 % Error in the Correlation Energies figure contains $-V_c$ as a percentage of the Kohn-Sham eigenvalue. Unlike exchange ,the expectation value of the correlation potential is more accurate than the correlation energy,though when dealing with such large errors it is doubtful whether there is any significance to this at all. It is evident from these results that neither E_c nor V_c is modelled satisfactorily by any of the functionals.

However, we do now have an explanation for the excellent agreement for the values of total energy. Referring to the figures (and tables) we see that the correlation energy is overestimated by large relative amounts(which are not large in absolute terms since correlation is only a small part of the total energy). For exchange exactly the opposite is the case - the energy was consistently underestimated. Thus the errors in exchange and correlation being of opposite sign cooperate to give very good results for total energy through large cancellation. It also becomes clear that if correlation, although small,was given accurately , then the error in total energy as given by LDA would increase appreciably, while the (LDA + LM) result would improve.

3.7.4 Summary

In this concluding section we collect the results in a concise manner.

1. Total energies are obtained to good accuracy in the LDA along with standard corrections.
2. Exchange energies are obtained to good accuracy in the LDA along with standard corrections.

3. Kohn-Sham (maximal) energy eigenvalues are given very poorly within these same approximations.
4. Expectation values of the exchange potential are given very poorly in these same approximations.
5. Correlation energies are given very poorly in the LDA along with standard corrections.
6. Expectation values of the correlation potential are given very poorly in these same approximations.
7. The SIC gives good results for the exchange-correlation potential and thus for the Kohn-Sham eigenvalues as well.

The results quoted above lead us to conclude that:

(A) Total energies are not an adequate measure of the efficacy of an energy functional. The functional derivative, i.e. the potential functional, must be considered as well.

(B) From the large errors in exchange potential expectation values we infer that improving correlation alone will not cure the difficulties of density functional theory but rather improvement of exchange potentials is still the first priority.

K	.01	0.1	1.0	4.0	10	100
EXACT	.0201	.0251	.0290	.0307	.0316	.0333
RPA	.0477	.0615	.0765	.0859	.0922	.1086
CEP-ALD	.0329	.0449	.0577	.0658	.0716	.0869
RPA+LM	.0363	.0433	.0482	.0494	.0491	.0434
SIC	.0170	.0232	.0296	.0337	.0365	.0442

Table 11

Correlation potential expectation values, $-V_c$, exact and in various approximation schemes

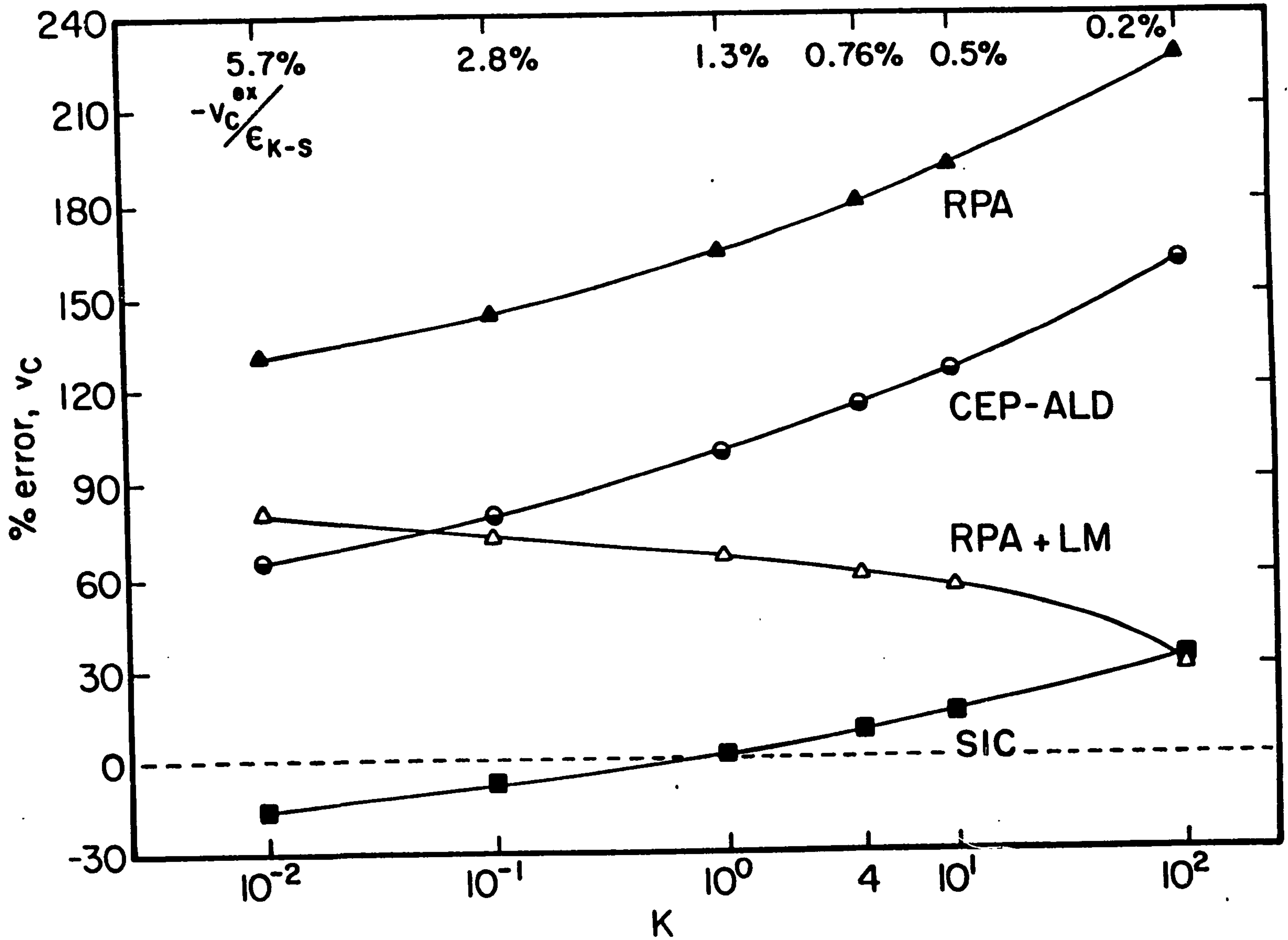


Fig. 21 % Error in the Correlation Potential Expectation Values

Appendix C

WKB Approximation - Expression For Density

In this section we will show two things in the limit of large r:

(1) The integrand has a maximum value at $r' \approx r$

(2) $n(r) \sim r^{2\delta} e^{-k^{\frac{1}{2}} r^2}$.

The physical significance of $r' \sim r$ governing the behavior of n(r) can be explained in the following manner. In the case of two non-interacting particles, it is clear that the probability of finding a particle at a distance r from the origin depends very heavily on the separation between the two particles being approximately that same distance. This is because the wavefunction of each particle falls off exponentially as we move away from the origin, and thus one particle in the vicinity of the origin with the other at a distance r away will be far more probable than any other configuration. (For example, the second particle at r/2, so the distance between them would only be r/2.) Thus the probability (when cast in our formulation, which gives the probability of a particle being at r_1 as an integral over the relative co-ordinate) will depend almost entirely on the region where $r' \sim r$. Then the addition of the coulomb term merely acts as a small perturbation thus shifting the most important region slightly from r' = r to r' = r + Δ.

Since we are only interested in obtaining an expression for the density at asymptoticaly large r, the preceding argument indicates that it is adequate to employ a form of f(r') which is in itself valid only for large r' in the calculation of the density.

i.e.,

$$f(r') = r'^{\delta} e^{-\frac{1}{4}\alpha r'^2}$$

[Where we have replaced $k^{\frac{1}{2}}$ by α]. Recall

$$n(r) \propto \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty f^2(r')\, e^{-\alpha r'^2/2} \left[e^{2\alpha r r'} - e^{-2\alpha r r'} \right] r'\, dr'$$

For large r, $e^{2\alpha r r'} >> e^{-2\alpha r r'}$, r' non-negligible. Thus as r--> ∞

$$n(r) \propto \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty f^2(r')\, e^{-\frac{\alpha r'^2}{2}}\, e^{2\alpha r r'}\, r'\, dr'$$

Then

$$n(r) \propto \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty r'^{2\delta}\, e^{-\alpha r'^2/2}\, e^{-\alpha r'^2/2}\, e^{2\alpha r r'}\, r'\, dr'$$

$$= \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty r'^{(2\delta+1)}\, e^{(2\alpha r r' - \alpha r'^2)}\, dr'$$

$$= \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty e^{(2\delta+1)\ln r'}\, e^{(2\alpha r r' - \alpha r'^2)}\, dr'$$

Thus $n(r) = Ce^{-2\alpha r^2}/(\alpha r) \times M$, where $M = \int e^{h(r',r)} dr'$.

We would like to investigate the behavior of M by expanding the integrand about a maximum. Note that the integrand has an extremum where $h(r',r)$ is extremized. Since we are dealing with fixed r we treat h as a function of r' alone.

Thus

$$h(r') = h(r_o') + h'(r')|_{r_o'}(r'-r_o') + \tfrac{1}{2}h''(r')|_{r_o'}(r'-r_o')^2 + \ldots$$

where the primes on h denote derivatives with respect to r'.

$$h(r') = (2\delta+1)\ln(r') + 2\alpha r r' - \alpha r'^2$$

$$h'(r') = (2\delta+1)/r' + 2\alpha r - 2\alpha r'$$

$$h''(r') = -(2\delta+1)/r'^2 - 2\alpha = -\{(2\delta+1)/r'^2 + 2\alpha\}$$

Thus we have a maximum at $h'(r') = 0$

$$r'^2 - rr' - \tfrac{1}{2}(2\delta+1)/\alpha = 0$$

$$r_o' = \tfrac{1}{2}r \pm \tfrac{1}{2}\{r^2 + 2(2\delta+1)/\alpha\}^{\frac{1}{2}}$$

or expanding the square root for large r:

$$r_o' = r + (2\delta+1)/(2\alpha r)$$

So

$$h(r') = h(r_o') + \tfrac{1}{2}h''(r')|_{r_o'}(r'-r_o')^2 + \ldots$$

$$= (2\delta+1)\{\ln[r + (2\delta+1)/(2\alpha r)] - 1\} - \tfrac{1}{2}\{2\alpha + (2\delta+1)/r_o'^2\}(r'-r_o')^2$$

$M = \int e^{h(r',r)} dr'$. and $r \rightarrow \infty$, thus we only keep terms of order $\ln(r)$ or higher in $h(r,r')$.

$$h(r',r) \approx (2\delta+1)\ln(r) - (2\delta+1) - \alpha(r' - r_o')^2$$

$$\approx (2\delta+1)\ln(r) - (2\delta+1) - \alpha\{r' - [r + (2\delta+1)/(2\alpha r)]\}^2$$

$$\approx (2\delta+1)\ln(r) - (2\delta+1) - \alpha\{r'^2 - r^2 - (2\delta+1)/\alpha - (2\delta+1)^2/(2\alpha r)^2\}$$

thus to leading order:

$$\int e^{h(r',r)} dr' = r^{2\delta+1} e^{-(2\delta+1)} e^{\alpha r^2} = \text{const} \times r^{2\delta+1} e^{\alpha r^2}$$

Thus as $r \Longrightarrow \infty$

$$n(r) \propto \frac{e^{-2\alpha r^2}}{\alpha r} \int_0^\infty r^{2\delta+1} e^{\alpha r^2} S(r')\, dr'$$

or

$$n(r) \sim r^{2\delta} e^{-\alpha r^2}$$

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