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Investigation of density functional theory in spherically symmetric systems

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City University of New York, 1988

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INVESTIGATION OF DENSITY FUNCTIONAL THEORY IN SPHERICALLY SYMMETRIC SYSTEMS

by

Yan Li

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

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ABSTRACT

Investigation of Density Functional Theory in Spherically Symmetric Systems

by

Yan Li

Advisor: Professor J.B.Krieger

In this thesis, we study various density functional approximations (DFT) as applied to atoms and harmonic oscillator systems with complete subshells. First, by confining ourselves to exchange only problems, we show that the exact Kohn-Sham(KS) wavefunctions and the KS exchange potential can be calculated for any system in which the electron states are described by only two different radial wavefunctions. We present the results of the KS solutions for eight(paramagnetic) and four(spin polarized) electrons moving in a harmonic oscillator potential with a variety of spring constants and compare with the corresponding Hartree-Fock(HF) and local spin density approximation(LSD) as well as the Slater exchange results(SLA). We also study the LSD with Self-Interaction-Correction(SIC) applied(LSDSIC). It is shown that the total energy calculations for atoms could be further improved if one takes into consideration the angular dependence of the wavefunctions in the energy functional. By studying the electron-electron interaction within the same subshell, we are able to develop a SIC method which treats the entire intral-shell exchange exactly in the asymptotically large r region. Calculations show that it considerably improves the accuracy of the density functional maximum single particle energy eigenvalue, ε_{max}^{df}, when compared to the exact HF results. In studying the Gradient Expansion Approximation(GEA), we discuss an alternative way of constructing the GEA energy functional which eliminates the singularity in the usual GEA exchange potential as r approaches infinity. With this GEA form, we are able to apply the SIC technique(the GEASIC) and find that this GEASIC can give the atomic total energies that are significantly more accurate than those given by the usual LSDSIC. Finally, by adding the correlation effects, we perform further investigations on the various SIC methods as applied to atoms. By treating exchange exactly, we find that although the total energy calculations are improved, the ε_{max}^{df} for the noble gases become poorer.

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Chapter I

Introduction

1.1 General Survey

The physical world consists of interacting many-particle systems. An accurate description of such systems requires the inclusion of the interparticle potentials in the many-particle Schrodinger equation. In atoms, molecules and solids, such interparticle potentials are the electron-electron, proton-proton and electron-proton Coulomb interactions. Although, in principle, the N-body wavefunction in configuration space contains all the information one needs to know, however, it has been known that a direct solution of the Schrodinger equation forms a formidable problem. Actually, even the simplest multi-electron system, the Helium atom, has so far eluded an exact analytic solution, and for solids, which consist of some 10^{23} electrons, an exact solution of the Schrodinger equation is far from practical if not impossible.

It is therefore necessary to resort to other techniques which usually involve approximations to the exact solutions but otherwise retain the main properties of the system and being exact in certain limits.

Among these, the Thomas-Fermi(TF) [1] [2], Hartree [3], Hartree-Fock(HF) [4], configuration interactions(CI) [5] [6] [7] [8] and the density functional theory [9] [10] stand as the most famous and widely used ones.

The simplest theory in which the electron structure of an atom, molecule or solid is described was given by Thomas and Fermi. In the TF theory, the electrons of a system are treated as essentially a continuous liquid of density n(r). The relation between the number of electrons per unit volume n_0 and the Fermi momentum k_F in a uniform electron gas i.e. $n_0 = [1/(3\pi^2)]k_F^3$ is used for an inhomogenous electron gas such that the n_0 is replaced by n(r) and k_F by $k_F(r)$, and thus the kinetic energy density becomes $k_F^5(r)/(10\pi^2)$, a function of the density n(r) only. Dirac [11] considered the exchange interaction between the electrons and thus the method was further improved to become the Thomas-Fermi-Dirac method(TFD). The TF or TFD is very appealing due to the fact that it uses the density n(r) as the basic function in describing the system instead of a 3N dimensional wavefunction. However, due to the fact that in this method the highly non-local quantity, the kinetic energy, is replaced by a local function of the density, the quantum oscillations of the charge densities (Friedel oscillations) cannot be obtained, and even in those 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.

It is much more reliable to use the Hartree or Hartree-Fock method in studying the electronic structure of the many-body systems. In these methods, the electron is described as moving in the field which is the sum of the external potential and the averaged Coulomb field due to all other electrons. Whereas the Hartree method can be derived from the original Schrodinger equation by assuming a product wavefunction composed of single particle wavefunctions and then employing the variational principle, the HF method is derived by using the same technique but assuming the wavefunction to be a determinant of the single particle wavefunctions. Both methods correctly predicted the shell structures of the atoms. However, only in the HF method has the exchange interaction been included. This so-called exchange interaction is actually a correlation effect due to the Pauli exclusion principle and the antisymmetric property of the wavefunction for the Fermion system, which tends to prevent the electrons from occupying the same spin orbital and tends to reduce the probability of two electrons with the same spin from approaching each other. As a result, the electron Coulomb repulsion energy is reduced and the system total energy is lowered. Being a product of single particle wavefunctions, the Hartree wavefunction can not be antisymmetric although it can still satisfy the Pauli exclusion principle by allowing a spin orbital to be occupied with only one electron. On the other hand, the HF wavefunction, being a determinant of single particle wavefunctions, is antisymmetric and automatically satisfies the Pauli exclusion principle. Thus the exchange energy, which is absent in the Hartree method, occurs in the HF method. Due to its more accurate description of electron systems, the HF method does not only give a good qualitative description of many properties of atoms and molecules, but also provides good quantitative approximation to the exact experimental values. But because the HF equations include the exchange potentials, which involve non-local terms, they are also much more difficult to solve than in the Hartree case. Slater [12] simplified the procedure of solving the HF equations by introducing the so-called Hartree-Fock-Slater method(HFS). In this method, the non-local exchange is approximated by a local function of the electron density which is obtained by taking the average over the exchange energy for the uniform electron gas and thus, only a set of Hartree-like equations need to be solved.

However, all these methods, the Hartree, HF and HFS neglect the effect of electron correlation. The electron correlation arises from the electron-electron Coulomb repulsion which tends to correlate the motions of the electrons in such a way as to reduce the total energy of the system to a minimum. Although this effect is usually very small in atoms, it becomes as important as exchange in the more extended systems like solids, and actually, even in atoms, it plays an important role for the description of the valence electrons.

To include the correlation effect as well as the exchange interaction, one can use the configuration interaction (CI) technique in which the wavefunction is expanded as a sum of determinantal wavefunctions with the constants being determined by employing the variational principle for the energy. Since the determinants of the single particle wavefunctions form a complete set, in principle, the CI method is exact when the number of configurations(determinants) in the expansion approaches infinity. However, in practice, the number of configurations used is generally small. Moreover, this method is so complicated that even for atoms using only a few determinants, the calculations are extremely difficult. So, in practice, the usefulness of the CI method is quite limited. Only systems with few electrons have been treated by the CI method. The results, nevertheless are useful in testing other approximation procedures [13] [14].

The methods discussed so far are evidently not satisfactory for the study of the multi-electron systems, especially, the solid. Whereas the TF, Hartree and HF are inherently flawed in their incomplete description of the many body effects, the CI method is much too difficult to apply in practice.

However, beginning in 1964, Hohenberg and Kohn [9] (HK) and Kohn and Sham [10] (KS) developed a new method of calculating the ground state density and ground state energy which has profoundly changed the way the many electron problem is now treated. This method, like the TF theory, employs the density instead of the N particle wavefunction as the basic variable describing the system, but unlike the TF theory, is in principle exact.

Specifically, HK showed that the ground state energy of a system of interacting electrons in the presence of an external potential $v(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n) = \Sigma_i v(\mathbf{r}_i)$ can be written

$$E[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[n] \qquad (1.1)$$

where F[n] is a universal functional of the density $n(\mathbf{r})$, and that for a given external potential, $v(\mathbf{r})$, the correct ground state density minimizes the expression E[n]. The functional F[n] is, however, not directly given by the theory.

KS subsequently showed that if one writes (using $e=m=\hbar=1$)

$$F[n] = T[n] + (1/2)\int\int d\mathbf{r}d\mathbf{r}'n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + E_{xc}[n] \qquad (1.2)$$

where T[n] is the kinetic energy of a system of non-interacting electrons with the same $n(\mathbf{r})$ as the system of interest, the second term is the classical Hartree electrostatical potential energy and $E_{xc}[n]$ is the exchange correlation energy, then it is possible to find the exact ground state density by solving a system of Hartree-like equations i.e.

$$\{-(1/2)\nabla^2 + v(r) + v_h(r) + v_{xc}[n]\}\psi_i(r) = \varepsilon_i\psi_i(r) \tag{1.3}$$

where

$$n(r) = \Sigma_i|\psi_i(r)|^2, \tag{1.4}$$

$$v_h(r) = \int dr'n(r')/|r-r'| \tag{1.5}$$

and

$$v_{xc}[n] = \delta E_{xc}[n]/\delta n(r) \tag{1.6}$$

The ground state energy is given by

$$E[n] = \Sigma_i\varepsilon_i - (1/2)\int\int drdr'n(r)n(r')/|r-r'|$$

$$+ E_{xc}[n] - \int v_{xc}(r)n(r)dr \tag{1.7}$$

Since in the HK and KS theory, the functional for the exchange and correlation energy, $E_{xc}[n]$, is not known for a general inhomogenous electron system, currently, the central problem in the DFT theory is to provide in certain limits an applicable approximation scheme for this functional and also for its functional derivative, the exchange correlation potential $v_{xc}(r)$, so that the real systems like atoms, molecules and solids could be more accurately described.

It has proved useful to consider E_{xc} as a sum of contributions from exchange-only i.e. E_x, plus a contribution from the correlation effects, E_c. Kohn and Sham showed that in the slowly varying density limit, $E_x[n]$ could be approximated by results obtained from uniform electron gas theory, from which it follows that the exchange potential is two thirds that given by the Slater exchange approximation. Subsequent calculations [15] [16] employing this reduced exchange showed substantial improvement over the SLA method in calculating electron densities of atoms. This local density approximation(LDA) was then further improved and developed by Von Barth and Hedin [17] to include spin effects in a local spin density theory(LSD) and also by Sham [18] who calculated the coefficients of the leading term in a gradient expansion of $E_x[n]$ i.e. through $O(\nabla n)^2$.

Much work has since been done by many investigators seeking to obtain more accurate $E_x[n]$ as well as improving on the Wigner [19] interpolation functional for $E_c[n]$ with the consequent calculation of the total energies and densities of the many electron systems that are in good agreement with experiment or with other detailed calculations such as results obtained from the Hartree-Fock(HF) approximation(as compared to exchange-only density functional calculations) or from configuration interaction calculations.

Although Kohn and Sham initially argued that the single particle energy eigenvalues ε_i in the KS equations were merely Lagrange multipliers having no physical significance i.e. no Koopman's theorem for the ε_i. However, recently, Perdew et al [20] showed that $\varepsilon^{ks}_{max} = E(N) - E(N-1)$ exactly, where E(M) is the exact ground state energy of the M electron system, i.e. the highest occupied orbital energy eigenvalue is equal to the electron removal energy including relaxation. Thus, the accuracy of the ε^{df}_{max} becomes in certain respects a new and more stringent criterion in evaluating the approximations made to the exchange correlation energy functional and its functional derivative the exchange correlation potential $v_{xc}(r)$.

More recently, Laufer and Krieger [21] explicitly tested this theorem and showed it to be true in an exactly solvable two electron model. Furthermore, they found that although various exchange-correlation functionals provide highly accurate estimates of the total ground state energy, these functionals result in approximations for ε^{df}_{max} that are significantly in error.

In another paper, Perdew and Zunger [22] showed that when $E_{xc}[n]$ was modified to correct for the self interaction effects and thus, using their technique, to have orbital dependent terms, the resulting ε^{df}_{max} obtained from the Schrodinger type equations which include both exchange and correlation, are found to be in fairly good agreement with the experimental ionization energies of the atom and are significant improvement over the LSD results. However, a careful analysis of their published results for the Neon atom also showed that in the exchange-only case, the calculated ε^{df}_{max} and the ε^{hf}_{max}, which can be proved to be equal for a finite spherically symmetrical system as found in Appendix B, has a much larger discrepancy than that between the ε^{df}_{max}(including correlation) and the experimental ionization energy.

It is thus appeared that the LSD and other improved versions are still far from satisfactory, at least for systems with few electrons, and that the LSD with self-interaction-correction applied has involved in it a good deal of error cancellations between the exchange and correlation.

1.2 Thesis Outline

In this thesis, we will be principally concerned with the study of the density functional theory as applied to finite systems with spherical symmetry i.e. electron systems with filled sub-shells. In our study, we will be mainly dealing with the atomic problems. But since the HK and KS theories are applicable to electron systems with any external potential, in order to insure that our conclusions are not merely applicable to systems in which the external potential is proportional to -1/r, we will also study the electronic system with the harmonic oscillator potential as the central attractive external potential. To pursue our study, we will separately investigate the exchange and correlation effects and thus see how accurate the separate approximations are in each case.

We begin our investigation by first studying the exchange-only density functional theory.

It has been shown [23] (also refer to Appendix A where we give a simple proof) that when the correlation effect is neglected, the HK and KS theories are still applicable, and in this exchange-only HK and KS version, the KS ground density is just the corresponding HF ground density and that with this density the KS energy functional will assume its minimum value which is just the HF ground state energy. Using these facts and employing the result that for a finite spherically symmetric system the ε^{ks}_{max} is equal to the ε^{hf}_{max}, we show in Chapter 2 that for a system in which electron states are described by only two different radial wavefunctions, the exact exchange-only KS exchange potential and the KS single particle eigenvalues as well as the KS wavefunctions can all be numerically calculated. We present the exact KS results for the harmonic oscillator problems with eight electrons(four spin up and four spin down, corresponding to the paramagnetic case) and four electrons(all having up spins, corresponding to the ferromagnetic case). Comparisons are then made with the exact HF results and with the results obtained by employing the LSD and Slater exchange approximations. Of particular interest of such studies are the results that 1) the exact KS exchange potential nearly coincides with the highest occupied orbital HF effective exchange potential except in the region near the origin, where this potential closely resembles in shape that of the inner HF orbital. 2) although the LSD exchange potential is quite different from that of the exact KS theory near the origin, it is almost parallel to it having nearly a constant difference with the latter when r is greater than r_m, the value of the radial distance at which the radial density has its maximum value. On the other hand, the Slater exchange potential(SLA), even though having approximately the same magnitude as that of the KS at or near r_m, is entirely different in shape. As a result, we find that the KS wavefunctions are not very different from those of the HF and that the LSD wavefunctions are much superior in approximating the HF or KS than those of the SLA. However, the ε_{max} obtained by employing the SLA exchange is closer to ε^{hf}_{max} because the SLA gives an exchange potential which has approximately the correct magnitude.

We continue our exchange-only DFT study in Chapter 3, in which we employ the self-interaction-correction method(SIC) as applied to the LSD which was developed mainly by Perdew and Zunger(PZ) [22] and then propose two new approaches which could in certain cases further improve the results obtained from the original method. The exact equations of LSD with SIC applied are generally not solvable due to the fact that the effective potentials depend non-linearly on the wavefunctions and thus the variables are unseparable. To make it workable, PZ simply replaced all the orbital wavefunctions by their spherical average i.e. by the radial wavefunctions in the exchange energy functional and the exchange potential(LSDSICA). In solving the atomic problems, we find, by keeping the angular dependence of the wavefunction in the exchange energy functional and making approximations only in the exchange potential, that the calculation of the total energy, which involves angular integration only in the exchange energy part, could be much improved over the original treatment as compared with the exact HF results for the atomic problems. Furthermore, when the angular dependence in the exchange potential is also appropriately treated, i.e. one derives the exchange potential directly from the new exchange energy functional which keeps the angular dependences of the wavefunctions, instead of making the approximation as PZ did, the wavefunctions thus obtained are found to be very close to those of PZ(This method will hereafter be refered to as LSDSICE). In addition, the self-consistent total energy calculations for this new energy functional are nearly identical to those obtained by merely substituting the PZ wavefunctions into the LSDSICE energy functional. The latter fact is certainly due to the variational principle for the total energy. Nevertheless, such a complete treatment of the angular dependence results in ε_{max}^{df} that are even farther away from the ε_{max}^{hf} values than those given by PZ. In another approach, by considering the electron interactions in the same subshell and treating the intrashell exchange energy exactly in the asymptotic large r region, we are also able to develop a SIC method which gives the ε_{max}^{df} that is in fair agreement with that of the ε_{max}^{hf} especially for the p and d states(we will give this method a notation LSDSICI). The motivation for this treatment is to try to improve the description for the exchange potential such that the electron density as well as the top eigenvalue, which are all equal to the corresponding HF results in an exact exchange-only KS theory, could be more accurately calculated. Such purposes are in a sense indeed accomplished as we will discuss in detail in the Chapter, with, however, the sacrifice that the total energy becomes too negative because of the overestimation for the E_x value. In order to make further investigation, we also compare the wavefunctions obtained from the various SIC schemes with those of the HF. It is found that the set of the wavefunctions obtained from the LSDSICI method can always yield the expectation value for the HF total energy that is significantly more accurate than those given by the LSDSICA and LSDSICE(although they are actually all very good). In addition, we find another interesting result that in fact one could obtain very good approximations to all the ε_i^{hf} $(i = 1,2,\ldots n)$ by just taking the expectation values of the HF equations using the LSD or LSDSIC type wavefunctions even though those ε_i^{hf} do not satisfy the variational principle. Furthermore, we show that the wavefunctions obtained by employing the Slater exchange approximation are not appropriate for the calculations of the expectation values of either the HF E_{tot} or HF ε_i. The results from both calculations are significantly in error when compared to the results of the LSDSIC type calculations although, surprisingly, it is found that the direct calculations of the ε_{max}^{df} for the noble gases using the SLASICE(compared with LSDSICE) method are very close to the ε_{max}^{hf} values. Naturally, it might be expected that the above conclusions should be also true for systems other than atoms. However, when we employ these different SIC schemes to the harmonic oscillator systems, some distinctive features arises which make the subject more complicated. Unlike in the atomic situation where the LSDSICA method systematically overestimates the exchange energies(except for the Be atom, for which the LSDSICA, LSDSICE and LSDSICI are all the same), the LSDSICA exchange energies for the oscillator systems are fairly close to the HF results(actually, for k=0.01 to k=100 there is a cross over of the LSDSICA exchange energies from being less negative corresponding to small k to too negative for large k compared to the HF values). On the other hand, the LSDSICE method, which gives E_x that are quite close to the HF results in the atomic calculations, now produces E_x which are too small in magnitude. The exchange energies from the LSDSICI, as in the atomic case, are still too negative. As a result, the total energy calculations employing either the LSDSICE or the LSDSICI method are less accurate than those given by the LSDSICA. One additional significant difference between the oscillator systems and the atomic systems is that we find that the wavefunctions obtained from the SLASICE method can give the expectation values of the HF total energy that are significantly more accurate than the same calculations of using the LSDSIC type wavefunctions. In a sense, they form a better set in approximating the HF total wavefunction. This is also quite different from the results we presented in Chapter 2 for the pure SLA(without SIC) case. Although, it appears that the oscillator systems and the atomic systems are quite different when the SIC technique is applied, nevertheless, there are some properties that are in common for both systems. One is that the $\varepsilon_{\max}^{df}$ calculated from the LSDSICI method are still the best one in approximating the $\varepsilon_{\max}^{hf}$. In addition, the expectation values of the HF E_{tot} given by the LSDSICI are still more closer to the exact HF E_{tot} than those given by the LSDSICA and LSDSICE. Finally, the direct calculation of the $\varepsilon_{\max}^{df}$ from the SLASICE, which is ε_{2p}, like those for the noble gases cases, are quite close to the $\varepsilon_{\max}^{hf}$.

In Chapter 4 we study the Gradient Expansion Method(GEA). The development of GEA is of great importance in improving the LSD when one deals with extended systems like solids and surfaces, since in these cases, the uncorrected self-interaction of electrons is no longer a main contribution to the LSD errors as it is for finite systems. On the contrary, the appropriate treatment of the variation of the density which makes the exact exchange interaction different from the uniform electron gas result, the LSD, becomes of major concern. In this Chapter, starting from a different consideration, we first propose a new form of the gradient expansion for the exchange energy functional. When applied to atoms and harmonic oscillator problems, it is found that this new form of GEA gives almost identical results as the one usually implemented. Moreover, such form for the GEA automatically avoids the unphysical singularities of the usual

GEA exchange potential at infinity and it assumes the same expression as that given by Sham when $\xi \equiv |\nabla n|/(2k_F n)$ is very small. In addition, we are now also able to test the GEA with the SIC applied (the GEASIC)which was formerly proposed by Perdew and Zunger but to our knowledge has never before been implemented. This is due perhaps to the fact that the original GEA plus SIC is divergent at the nodes of the single particle wavefunctions which can not be removed even by adding a convergent factor as is the usual practice in treating the GEA without SIC [24]. The total energy calculations using this method for atoms show significant improvement over the GEA and PZ's LSDSICA results. However, the results for the outermost single particle eigenvalues are more complicated: whereas the ε^{df}_{max} of the atoms with the outermost orbital being the s state are in general improved over the PZ results, those with the outermost p orbital are slightly farther away from the ε^{hf}_{max} than those given by PZ. When this GEASIC method is applied to the harmonic oscillator systems, the results are in general poorer than those given by PZ's LSDSICA. In this Chapter, based on the previously mentioned new GEA expression, we also propose several fitted GEA expressions for the exchange energy. The results produced from these fittings are quite encouraging when compared with the corresponding HF values and generally, most of the fitted exchange energy values are even better than those given by Perdew and Wang's Generalized Gradient expansion Approximation(GGA) [25] [26] results. At the end of this Chapter, we go beyond the GEA and study the density matrix method and Harriman orbitals(equal density orbitals) [27]. In studying the integral equations satisfied by the single particle density matrix, we are able to find a solution for a spherically symmetric system of arbitrary density that reduces to the usual uniform electron gas result in the constant density limit. We also show that the same result may be obtained by employing the Harriman orbitals. By analyzing the constructions of the exchange energy expressions for the LSD and that obtained by using the equal density orbitals, we find that the latter is not necessary an improvement of the former, and as a result of this analysis, some new forms for the exchange energy expression are proposed and tested using the HF densities. The results thus produced considerably improved those of the LSD. Most interestingly, the new exchange energy functionals, when expanded for small $\xi \equiv |\nabla n|/(2k_F n)$ are divergent, so there are no gradient expansions for these functionals. Recalling that Kleiman [28] and Geldart et al [29] have proved that the HF exchange is not expandable in terms of the gradient of the density, the agreement here may not be an accident.

Finally, in Chapter 5, we consider the correlation effects on atoms. Although, the correlation energy constitutes only a very small portion of the total energy [30] [31] and has a much smaller influence than does the exchange in solving the atomic problems and the harmonic oscillator systems as we discussed, nevertheless, it is quite vital in correctly describing the behavior of the valence electrons. Actually, as a result of such neglect, the HF method predicts many naturally existing stable ions to be unstable [32],[33]. In studying the correlation effects, we first consider the various LSDSIC methods with correlation included. We calculate the total energies as well as the top eigenvalues which is supposed to be equal to the ionization energy value and then compare with the available experimental results. It is found that the formerly discussed method, which takes account of the angular dependence of the wavefunctions in the energy functional, still gives the total energy values very close to the non-relativistic experimental results. In addition, the ε_{max}^{df} given by this method are also in fair agreement with the experimental results for the ionization energy even though in the exchange-only situation they are off from that of the exact HF. On the other hand, the PZ approach and the method that treats the intra-shell exchange exactly at the large r limit, generate E_{tot} which are too negative, just as they gave too negative E_{tot} values in the exchange-only theory. The $\varepsilon_{\max}^{df}$ values given by the PZ method are very close to the exact experimental ionization energy as previously noted by PZ. However, those given by the method of treating intra-shell exchange exactly are very poor in spite of the fact that in the exchange-only case it gives $\varepsilon_{\max}^{df}$ that are much closer to the $\varepsilon_{\max}^{hf}$ than those of PZ.

KS in their original paper suggested a method which treats the exchange exactly i.e. the HF method plus correlation effect. Baroni and Tuncel [34] have used this method in calculating the total energies and the electron affinities. The results they obtained are quite encouraging. In this Chapter, we make similar calculations and especially we compare the $\varepsilon_{\max}^{df}$ values with those of the experimental ionization energies. It is found, however, that the $\varepsilon_{\max}^{df}$ for the noble gases are much poorer than the LSDSIC type calculations, although, the total energies using these method are superior. For atoms with highest lying s orbitals, these $\varepsilon_{\max}^{df}$ are slightly better(especially for light atoms). Thus, one may conclude that although the currently used LSD exchange and correlation energy functional as a whole accounts quite well for the total energy calculations, there are nontheless a good deal of errors separately. The accuracy of the total energy calculations is due in part to the cancellation of errors in the exchange and correlation energies, and the density dependence of the exchange-correlation energy functional is not very well described yet as shown by the values of the ε_{max}^{df} which intimately depend on the functional derivative of the exchange-correlation functional i.e. the exchange-correlation potential. If we believe that the HF exchange energy expression can well account for the DFT exchange which are slightly different as we will further discuss in the next Chapter, then the effect of correlation, especially the correlation potential, needs considerable improvement in order to simultaneously give accurate results for the total energy, the electron density and the maximum single particle energy eigenvalue.

Chapter II

Exchange Only Kohn-Sham Solutions

Ever since the seminal work of Hohenberg and Kohn and Kohn and Sham, the central problem in the accurate approximation of density functional theory to the calculation of the ground state density and the total energy of many electron systems is the determination of the exchange-correlation functional, $E_{xc}[n]$, and its functional derivative, the exchange correlation potential, $v_{xc}(r)$.

Although finding an exact theoretical expression for this functional with any number of electrons has thus far been unsuccessful, it is nevertheless very interesting to find in some simple cases and in certain limits, the KS exchange energy and the KS exchange potential. For a homogenous electron gas, such a functional has been found in the exchange-only theory, i.e. the LSD results with $n(r)$ being constant. With correlation, however, the $E_{xc}[n]$ is known to be exact only in the high density limit. In the inhomogenous situations, for a quite long time, the LSD method and its modification, the GEA and also LSDSIC, which are exact only in the very slowly varying density limit, were used. Recent investigations have been devoted mainly to the further improvement of the LSD such that it can better be applied to atoms, molecules and solids and few attempts have been made in obtaining the exact E_x or E_{xc} in some simple models. This has created the unfortunate situation that until recently we do not know what the exact KS results, i.e. the KS exchange energy, the KS exchange potential and the KS wavefunctions are and how the LSD exchange is different from the exact KS in extremely inhomogenous systems like atoms except for the trivial two electron system in the exchange-only theory, where the exchange is just equal to the self Coulomb term. The only way to evaluate the accuracy of the various approximations is to compare the calculated values with the experimental results or with the results of CI calculations (and in exchange-only case, to compare with the HF results). However, recently, Laufer and Krieger [21] showed that the exact KS wavefunctions, $\psi_i(r)$ can be obtained if one observes that for a system of two electrons in the ground state, there is only one single particle KS orbital which is proportional to the square root of the electron density. Furthermore, since the density is exactly calculable in a model consisting of two electrons attracted to a fixed center by harmonic oscillator forces, because the Schrodinger equation may be separated once a transformation to center of mass and relative coordinates is employed, by inverting the KS equation for the $\psi_i(r)$, they derived the exact $v_{xc}(r)$. By comparison, they found that although the LSD and gradient expansion method produce quite good results for the total energy and total exchange energy values, the exchange potentials given by those methods were significantly in error when compared to the exact KS v_{xc}. Moreover, the outmost single particle eigenvalue ε_{max}^{df} derived from those approximations are also significantly different from that of HF, even though the exact ε_{max}^{ks} is shown to be equal to ε_{max}^{hf} exactly.

The two electron problem is, however, a very stringent test of any approximate v_{xc} due to the statistical assumptions employed in deriving an approximate $E_x[n]$ from which it is obtained. In fact, in any two electron problem with spin degeneracy the entire exchange interaction is merely the self interaction term, which is not exactly included in any calculation that treats $E_x[n]$ as a functional only of n i.e. the method of Perdew and Zunger requires additional orbital dependent terms which exactly cancel the self interaction terms in the Hartree potential.

It would be interesting to extend the work of Laufer and Krieger to systems containing more than two electrons in order to generate the exact v_{xc}, which could then serve as a basis to test the accuracy of any approximate exchange-correlation functional. Unfortunately, we are not aware of any exactly soluble models in which more than two electrons are in a common potential with mutual Coulomb repulsion. However, it is possible to numerically solve the Hartree-Fock(HF) equations and thus it may be possible to construct the exact exchange-only potential v_x and KS single particle wavefunctions and energy eigenvalues which could be used to test the accuracy of the usual analytic approximations.

Indeed Payne [23] has argued that the HK an KS theorem can be derived for exchange-only systems with the resulting KS equations for the single particle orbitals having the usual form with v_{xc} replaced by v_x. In Appendix A, we show using exactly the same argument employed by HK that

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

where E_{hf} is the total HF energy, v is the external potential, n(r) is the exact HF density and F[n] is a universal functional of n(r). It thus follows from taking

$$F[n] = T_s[n] + U_h[n] + E_x^{ks}[n]$$

where $T_s[n]$ is the kinetic energy of a non-interacting electron gas having the same density and $U_h[n]$ is the Hartree energy, that the exchange-only KS orbitals satisfy the KS single particle equations with $v_x^{ks}(r)$ given by the functional derivative of the exchange energy functional $E_x^{ks}[n]$. It thus follows from the fact that n(r) is the sum of the single particle KS orbital densities and the fact that as $r \to \infty$ for a system of a finite number of electrons the leading term in the density arises from the orbital with the highest single particle energy, that $\varepsilon_{max}^{hf} = \varepsilon_{max}^{ks}$ exactly. We therefore observe that in an exchange-only KS theory, it follows from Koopman's theorem that ε_{max}^{ks} equals the removal energy of an electron without relaxation whereas it follows from the theorem of Perdew et al that in a KS theory for the full hamiltonian, ε_{max}^{ks} is the removal energy including relaxation.

It should be noted that the KS exchange-only theory discussed above and in the appendix is not exactly equivalent to the calculations of Talman et al [35] [36]. They obtained the optimum orbital independent single particle potential which is the potential whose eigenfunctions yield the lowest HF total energy expectation value which is an upper bound to the exact HF total energy. In addition, their calculated total density is different from the exact HF results as can be seen by comparing their results for the expectation value of r^2 with the HF results and their highest single particle energy eigenvalues are close to, but generally slightly different from ε_{max}^{hf}. On the other hand, in the exact exchange-only KS theory, the total energy, total density and the highest single particle energy eigenvalue are all identical to the corresponding HF results.

In section 2.1, we show that for any spherically symmetric external potential, it is possible to derive an eigenvalue equation for the single particle KS orbitals provided there are only two with different r dependence. If the exact HF density is known, it is then possible to solve those equations for the orbitals and single particle eigenvalues ε_i^{ks} and construct $v_x^{ks}(r)$, the exact exchange potential as a function of r as well as calculate the exact numerical value of the density functional expression for the total exchange energy E_x^{ks}. We apply this technique to two problems with spherically symmetrical densities. In each case the central external potential is given by a harmonic oscillator potential. In the first problem we consider four spin up and four spin down, the ground state of eight electrons, which completely fill two subshells. In the second problem we consider the ground state of four totally spin polarized electrons which also fill the same two subshells. We compare the results of the exact exchange-only calculations with those obtained assuming LSD and the Slater exchange approximation(SLA) as well as compare the calculated wavefunctions and potentials with the HF wavefunctions and effective HF exchange potential in section 2.2.

2.1 Calculation of Exact Exchange-Only KS Single Particle Orbitals and Exact Exchange Potential

The KS equations for any spherically symmetric system may be written(using atomic units e=m=ħ)

$$[- (1/2)\nabla^2 + v_{eff}(r)]\psi_i(r) = \varepsilon_i\psi_i(r). \tag{2.1}$$

Then taking

$$\psi_i(r) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{2.2}$$

Eq.(2.1) may be written

$$[-(1/2)d^2/dr^2 + v_{eff}(r) + l(l+1)/(2r^2)]u_{nl} = \varepsilon_{nl}u_{nl} \tag{2.3}$$

where

$$u_{nl}(r) = rR_{nl}(r). \tag{2.4}$$

Now consider the case where there are only two different u_{nl} i.e. u_1 and u_2 corresponding to two subshells. Then since the ground state of a spherically symmetric potential must have $l = 0$, we have from (2.3)

$$[-(1/2)d^2/dr^2 + v_{eff}(r)]u_1 = \varepsilon_1u_1 \tag{2.5}$$

so

$$v_{eff}(r) = (\varepsilon_1 + 1/(2u_1)d^2u_1/dr^2) \tag{2.6}$$

But the total density for two filled subshells is given by

$$n(r) = \Sigma_i |\psi_i(r)|^2 = n_1 R_1{}^2 + n_2 R_2{}^2 = n^{hf}(r) \tag{2.7}$$

where n_i is the number of electrons in each subshells, the R_i are separately normalized to unity, and we have made use of the fact that in an exchange-only KS theory, the exact density is the HF density. Eq.(2.7) may be solved for u_1 in terms of n^{hf} and u_2, so that v_{eff} as given by the right hand side of Eq.(2.6), may be written in terms of n^{hf} and u_2. Substituting Eq.(2.6) into the equation satisfied by u_2 we obtain

$$[-(1/2)d^2u_2/dr^2 + l(l+1)/(2r^2) + 1/(2u_1)d^2u_1/dr^2]u_2 = (\varepsilon_2 - \varepsilon_1)u_2 \tag{2.8}$$

where l is the angular momentum quantum number corresponding to the state ψ_2.

Eq.(2.8) is an eigenvalue equation for the eigenvalue $\varepsilon = \varepsilon_2 - \varepsilon_1$. It may be solved self-consistently by substituting u_1 obtained from Eq.(2.7) in terms of the known $n^{hf}(r)$, which is obtained from a separate calculation, and a trial function for u_2. The resulting eigenvalue equation is then solved and the new value of u_2 may be replaced to calculate u_1 until self-consistency is achieved. Since $\varepsilon^{hf}_{max} = \varepsilon^{ks}_{max}$, $\varepsilon_2 = \varepsilon^{hf}_2$, we obtain ε_1 from

$$\varepsilon_1 = \varepsilon - \varepsilon^{hf}_2 \tag{2.9}$$

Finally, the exact KS exchange potential is then obtained from

$$v_x^{ks}(r) = v_{eff}(r) - v_h(r) - v(r) \qquad (2.10)$$

where $v_h(r)$ is the Hartree potential, $v(r)$ is the external potential and $v_{eff}(r)$ is obtained from Eq.(2.6) or equivalently from

$$v_{eff}(r) = (\varepsilon_2 - l(l+1)/(2r^2) + 1/(2u_2)d^2u_2/dr^2) \qquad (2.11)$$

We note that by considering only systems with filled subshells any problems related to the existence of degenerate ground states are removed. Thus, not only must v_{eff} be a function of r only, but in addition there is no ambiguity in determining the HF density i.e. we do not have to make a statistical average of various possible configurations to obtain a spherically symmetric HF density for an open shell system.

We may also obtain the exact value of the exchange energy in density functional theory by observing that since

$$E_{hf} = E_{tot} = T_s + V + U_h + E_x^{ks} \qquad (2.12)$$

where

$$V = \int v(r)n(r)dr \qquad (2.13)$$

then

$$E_x^{ks} = E_{hf} - (T_s + V + U_h) \qquad (2.14)$$

where all the terms on the right hand side of Eq.(2.14) can be directly calculated. We note that since V and U_h have the same numerical value in either the HF or exact density functional exchange-only theory, since the densities in both calculations are the same, it follows from Eq.(2.14) and the analogous equation for the exchange energy in the HF approximation, E_x^{hf}, that

$$E_x^{ks} - E_x^{hf} = T_{hf} - T_s \tag{2.15}$$

where T_{hf} is the total kinetic energy in the HF approximation. The right hand side of Eq.(2.15) is not in general equal to zero because the kinetic energy depends on the separate wavefunctions, which are not identical in the two methods of calculations.

Finally we note that the exact value for E_x obtained by employing Eq.(2.14) is not in general identical to the approximation obtained by substituting the single particle density functional wavefunctions $\psi_i(r)$ into the usual expression for the exchange energy given in the HF approximation. This follows from the fact that if such a functional for E_x^{ks} were substituted into Eq.(2.12), then minimizing E_{tot} with respect to the single particle wavefunctions would lead to precisely the HF equations for the density functional orbital. However, it is known from the work of Talman et al, that there exist no orbital independent potential whose eigenfunctions will be the HF single particle wavefunctions(except in the trivial case when there is only one orbital). Thus the density functional orbitals, which are derived from an orbital independent single particle potential, cannot be identical to the HF orbitals and consequently the assumption that the density functional expression for E_x can be so written must be incorrect.

Since density functional theory is valid for an arbitrary external potential, the above analysis is applicable to any spherically symmetric system of electrons whose single particle orbitals fill two subshells. In the present work we employ a model in which electrons are attracted by a central harmonic oscillator potential with arbitrary spring constant k. This model has previously been employed by Laufer and Krieger to consider the effects of both exchange and correlation in the two electron system when only the lowest KS orbital is occupied. In an exchange-only theory the two electron problem is trivial since the lowest KS orbital is then identical to the lowest HF orbital in order that the densities be identical.

In the absence of electron-electron interaction, the lowest energy orbitals of electrons in a spherically symmetric harmonic oscillator potential are 1s and 2p states corresponding to an m_l degeneracy of 1 and 3 respectively and a spin degeneracy of 2 for each orbital. The inclusion of e-e interactions does not lift these degeneracies. Thus the simplest situations in which the density is spherically symmetric and there are only two radial wavefunctions u_1 and u_2 are 1) eight electrons, with 2 electrons in the 1s state and 6 electrons in the 2p state corresponding to a paramagnetic system with zero net spin, and 2) four electrons, one in the 1s and three in the 2p with all electrons having spin up corresponding to a ferromagnetic system. Although the second case is not an absolute ground state, the HK theorem and the KS analysis still apply because it is the ground state of the system with total spin S=2.

Using the method described above, we have numerically solved the HF equations for both the eight and four electron cases for a variety of spring constants from k = 0.01 to k = 100. Using these results, we have been able to obtain numerically the KS 1s and 2p wavefunctions, the single particle eigenvalues as well as the KS exchange potentials. In addition, in order to compare these results to those obtained by employing approximate exchange potentials, we have also solved the KS equations in the LSD approximation and also using the Slater exchange approximation.

In each case the figures and those tables for which our results are displayed for only one value of k, the value of k is k=10, for which the average value of r_s is close to the usual atomic values [21].

2.2 Discussion of Results.

2.2.1 Comparison of Exact KS Theory with LSD and SLA

Figure 1(a) shows the exact exchange KS potential v_x^{ks} as well as that given by the LSD and the SLA for eight particles with k=10. Figure 1(b) illustrates the corresponding results for the ferromagnetic case with four particles. Results for other values of k are similar. From each of those figures we see that although the KS exchange potential is significantly different from the LSD results in magnitude and in shape from the origin to r_m, the point at which the density has its maximum value, they are nearly parallel, different by almost a constant from r_m to the region in which the density has fallen two orders of magnitude. On the other hand, the exchange potential in the SLA , though having almost the same magnitude as v_x^{ks} in the region near r_m, is very different in shape from v_x^{ks} almost everywhere.

The fact that v_x^{sla} has nearly the same magnitude as v_x^{ks} leads to the result that the single particle energy eigenvalues for 1s and 2p states obtained using the SLA are much closer to the exact KS results than those given by employing the LSD approximation as shown in Tables 1 and 2 for both the unpolarized(8 electrons) case and the totally spin polarized(4 electrons) case. Nevertheless, as can be seen from Figure 1, the fact that the v_x^{lsd} is similar in shape to

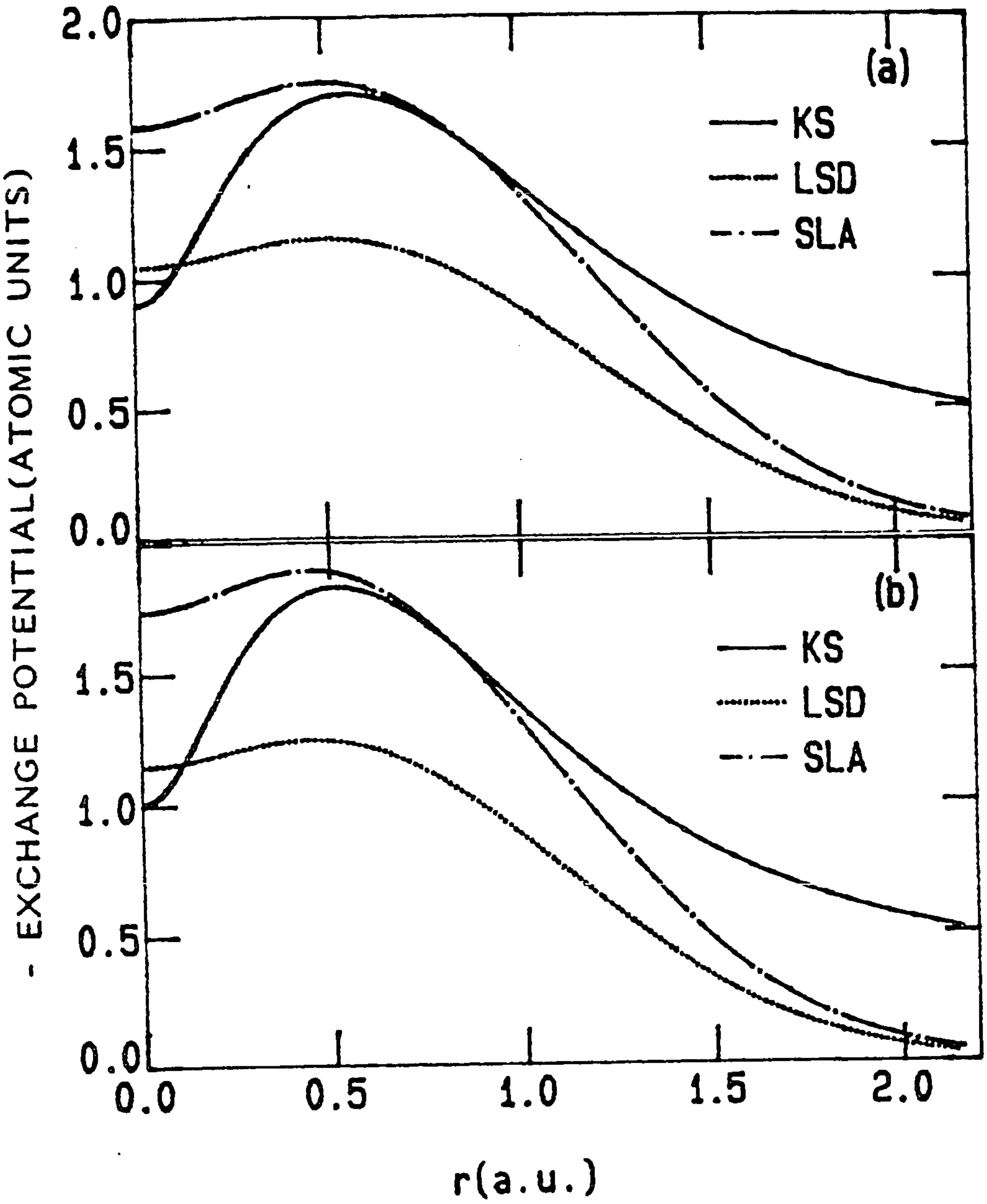

Figure 1: The KS, LSD and SLA exchange potentials for harmonic oscillator systems with k=10. The top graph shows these potentials for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

Table 1: Single particle energy eigenvalues for harmonic oscillator systems with 8 electrons.

Paramagnetic case. The two fully occupied orbitals with lowest energies are the 1s and 2p states. Listed are the single particle eigenvalues of these two orbitals obtained from the HF, KS, LSD and SLA schemes(all in atomic units).

k	HF	KS	LDA	SLA
1s state				
.01	1.097	1.137	1.201	1.152
.1	2.377	2.464	2.593	2.487
1	5.213	5.395	5.647	5.422
10	11.788	12.150	12.630	12.172
100	28.062	28.753	29.646	28.750
2p state				
.01	1.171	1.171	1.235	1.186
.1	2.614	2.614	2.743	2.642
1	6.016	6.016	6.270	6.063
10	14.516	14.516	15.002	14.508
100	37.183	37.183	38.086	37.298

the exact v_x^{ks} leads to the result that the single particle orbitals derived from employing the LSD approximation more closely approximate the exact KS orbitals than those obtained by employing the SLA. Similar results are obtained for the totally spin polarized(4 electrons) case. Moreover, the more rapid variation of the v_x^{sla} compared to v_x^{ks} or v_x^{lsd} for $r > r_m$ leads to the result that the attractive exchange force on the electron in the large r region is too

Table 2: Single particle energy eigenvalues for harmonic oscillator systems with 4 electrons.

Ferromagnetic case. The 1s and 2p orbitals are still the only two occupied states. Listed are the single particle eigenvalues for these two orbitals obtained from the HF, KS, LSD and SLA schemes(all in atomic units).

k	HF	KS	LDA	SLA
1s state				
.01	0.566	0.617	0.696	0.631
.1	1.271	1.377	1.528	1.391
1	2.986	3.195	3.476	3.203
10	7.466	7.861	8.375	7.853
100	19.928	20.655	21.588	20.616
2p state				
.01	0.6715	0.6715	0.7505	0.6891
.1	1.593	1.593	1.745	1.628
1	3.993	3.993	4.276	4.035
10	10.635	10.635	11.156	10.700
100	29.935	29.935	30.878	30.038

large which has the effect of making both 1s and 2p SLA orbitals too small in the large r region which leads to the SLA density being too low for large r as shown in Figure 2. On the other hand, in addition to the fact that the LSD orbitals separately more closely approximate the KS orbitals, the separate errors in the orbital densities in the LSD approximation tend to cancel out least in small r, so the resulting LSD density closely approximates the exact density. An

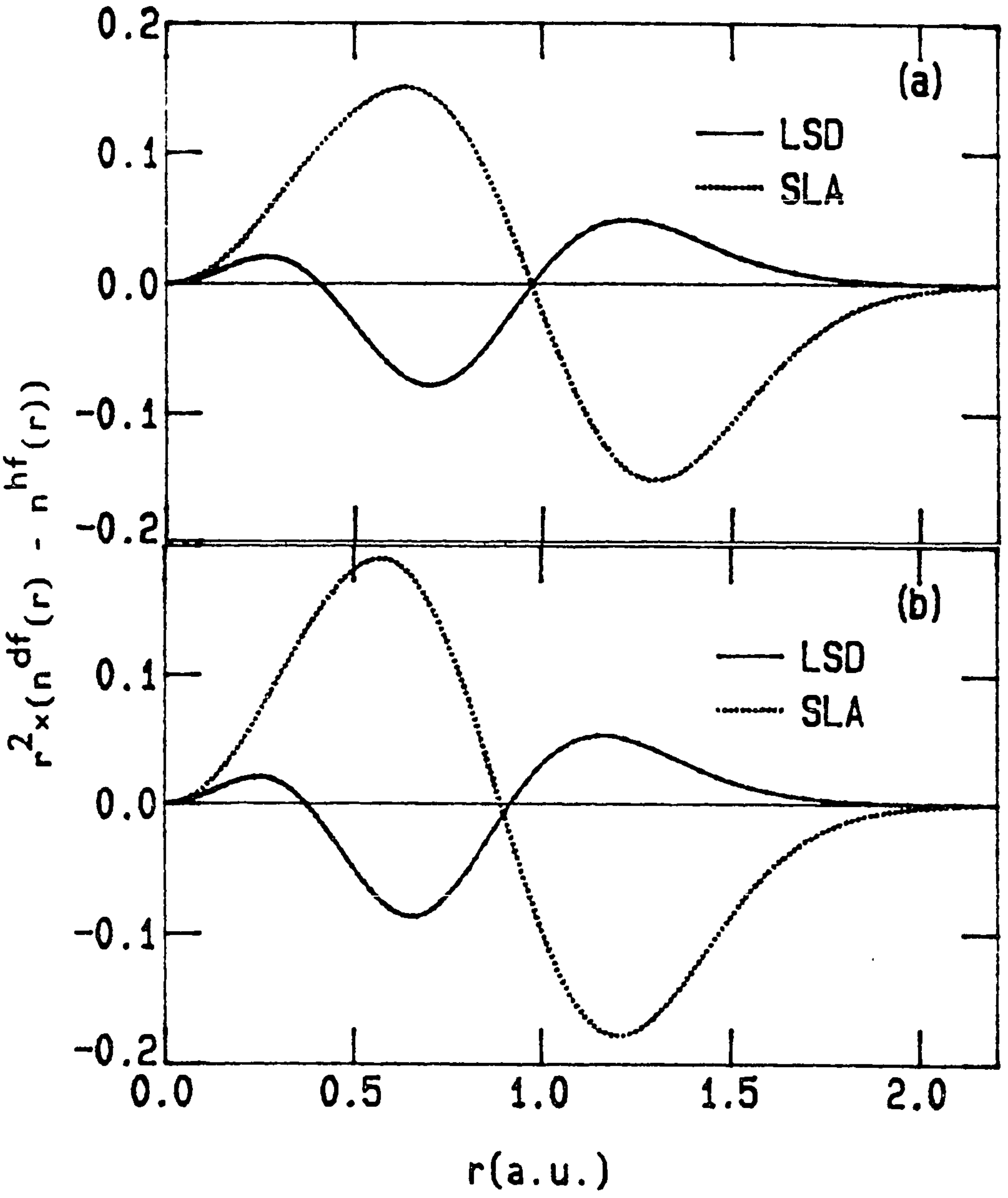

Figure 2: Deviations of the electron density of the LSD and SLA from the HF or KS for harmonic oscillator systems with k=10. The top graph shows the deviations for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

Table 3: Overlap integrals for the harmonic oscillator systems with oscillator strength k=10.

The overlap integrals between the HF wavefunctions and those obtained from the KS, LSD and SLA <hf,df> and between the KS wavefunctions and those of the HF, LSD and SLA <ks,df> for both the 1s and 2p states are given.

(paramagnetic)

<hf,df>	KS	LDA	SLA
1s	0.999962	0.999946	0.999751
2p	0.999994	0.999976	0.999926

<ks,df>	HF	LDA	SLA
1s	0.999962	0.999989	0.999900
2p	0.999994	0.999991	0.999900

(ferromagnetic)

<hf,df>	KS	LDA	SLA
1s	0.999965	0.999951	0.999707
2p	0.999995	0.999974	0.999902

<ks,df>	HF	LDA	SLA
1s	0.999965	0.999990	0.999868
2p	0.999995	0.999989	0.999873

additional measure of the accuracy of these orbital wavefunctions is their overlap integral with the exact KS orbitals, i.e.

$$<\psi_i^{df}|\psi_i^{ks}> = \int[\psi_i^{df}(r)]^{*}\psi_i^{ks}(r)dr \qquad (2.16)$$

which are tabulated in Table 3. Although the overlap integral $<\psi_i^{ks}|\psi_i^{sla}>$ is close to unity, the overlap integral $<\psi_i^{ks}|\psi_i^{lsd}>$ is even better. In fact, since the sum of the squares of the amplitudes in all other states equals 1 - $<\psi_i^{ks}|\psi_i^{app}>^2$ where ψ_i^{app} is an approximate orbital, we see that the LSD results are an order of magnitude more accurate than those given by the SLA if we compare the sums of the squares of the overlap integrals with other than the corresponding states.

2.2.2 Comparison of Exact KS Exchange-Only Theory with the HF Approximation

As already noted, the exact KS theory yields the same total energy, electron density and highest single particle energy eigenvalues as in the HF approximation. However, due to the fact that the KS theory employ a single orbital independent local exchange potential while the HF equations involve a non-local orbital dependent exchange interaction, the corresponding orbitals will not in general be identical. Figs. 3 and 4 show the difference $r\times(R_i^{ks}(r) - R_i^{hf}(r))$ for i=1s and i=2p respectively, as a function of radial distance. Table 3 gives the respective overlap integrals which are incredibly close to unity, especially for the 2p state. The corresponding figures for the spin polarized case show similar behavior to the overlap integrals given in the same table. These results may be understood by com-

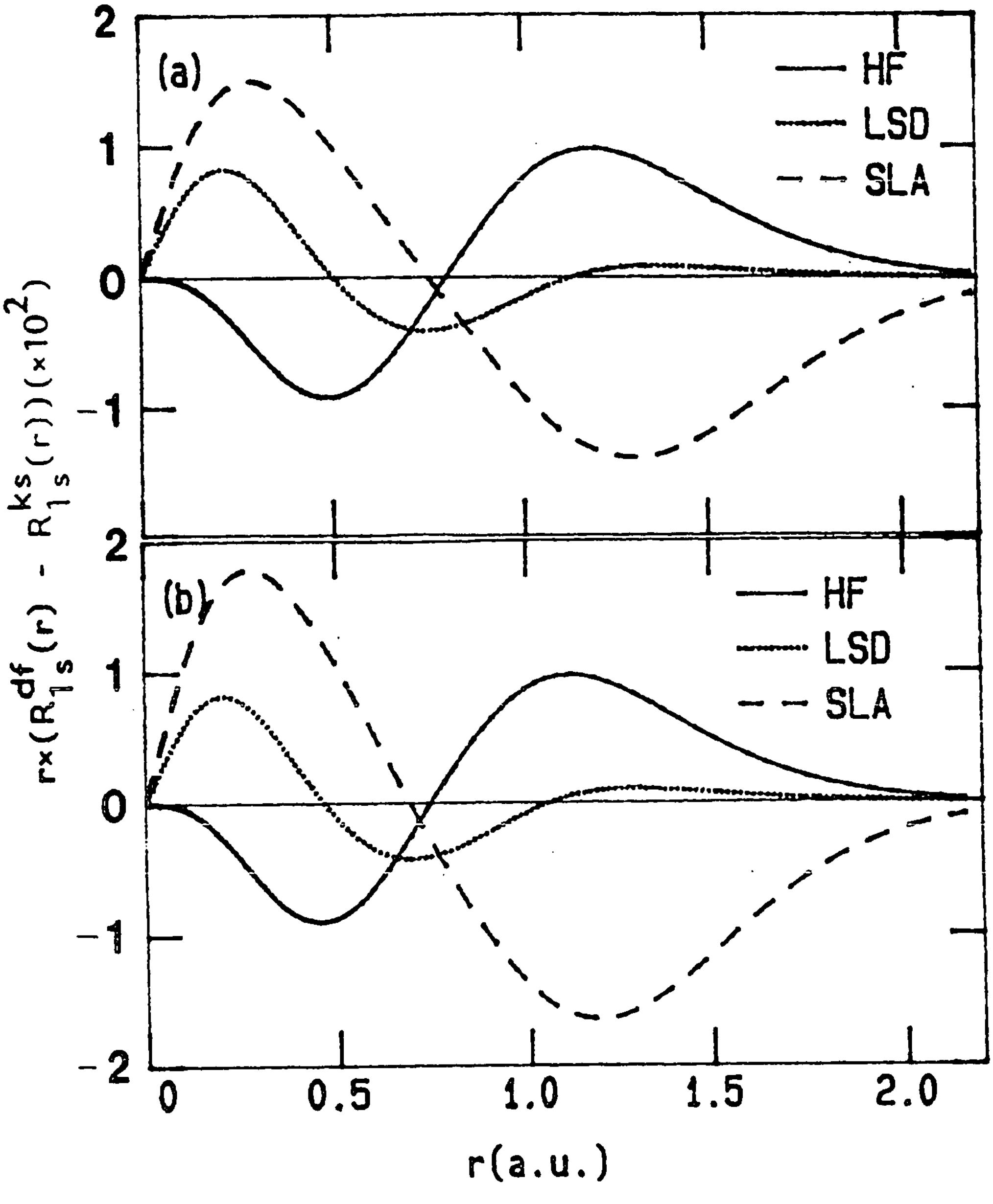

Figure 3: Deviations of the 1s wavefunctions of the HF, LSD and SLA from the KS for harmonic oscillator systems with k=10. The top graph shows the deviations for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

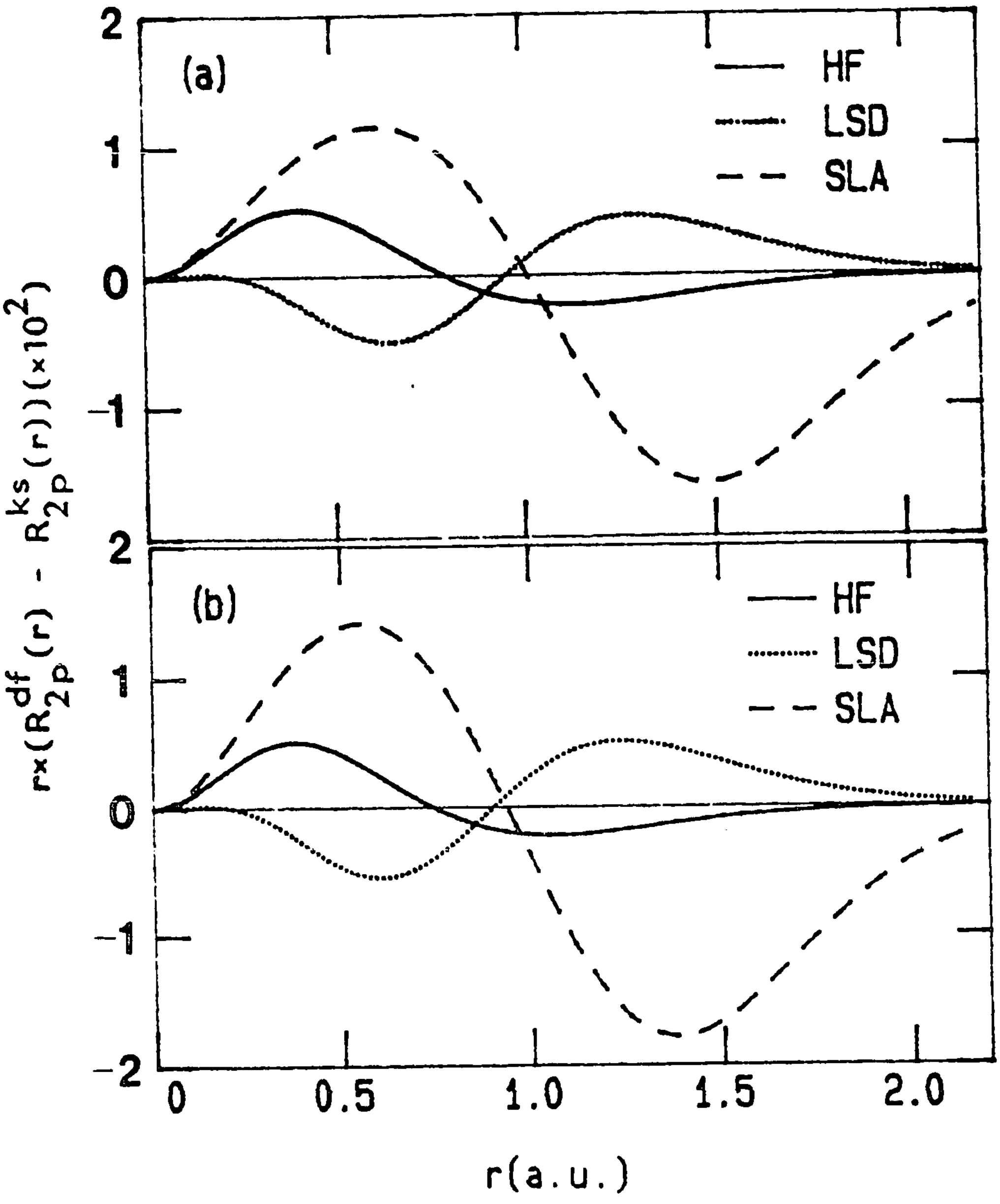

Figure 4: Deviations of the 2p wavefunctions of the HF, LSD and SLA from the KS for harmonic oscillator systems with k=10. The top graph shows the deviations for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

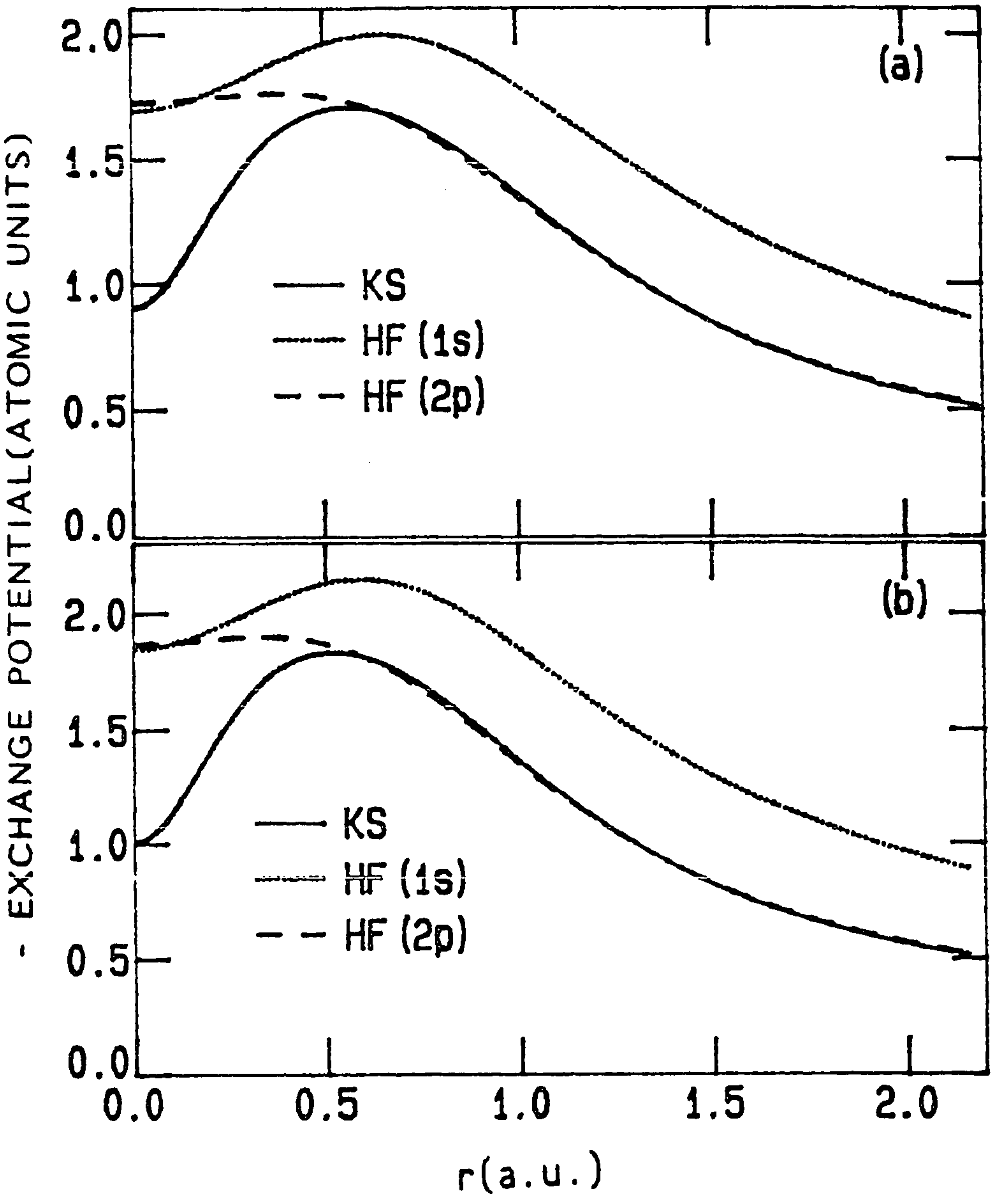

Figure 5: The KS and HF 1s and 2p exchange potentials for harmonic systems with k=10. The top graph shows these potentials for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

Table 4: Exchange energies for harmonic oscillator systems.

The negative of the HF exchange energies and the KS exchange energies calculated from Eq.(2.14) are given for both the paramagnetic (8 electrons) and ferromagnetic(4 electrons) cases. Also listed are the exchange energies calculated from the expectations of the HF exchange expression using the KS wavefunctions(HFKS).

k	HF	KS	HFKS
Paramagnetic			
.01	0.7958	0.7964	0.7942
.1	1.6068	1.6079	1.6044
1	3.1554	3.1569	3.1522
10	6.0199	6.0216	6.0163
100	11.2069	11.2087	11.2031
Ferromagnetic			
.01	0.4865	0.4869	0.4586
.1	0.9350	0.9356	0.9336
1	1.7515	1.7523	1.7498
10	3.2180	3.2189	3.2162
100	5.8356	5.8365	5.8336

paring the v_x^{ks} with the effective HF potential i.e the orbital dependent local potentials which would give the same HF single particle wavefunctions and eigenvalues as given by the non-local orbital dependent HF exchange term. It follows from the Schrodinger equation that these potentials are

$$v_{x,i}^{hf}(r) = \varepsilon_i + (1/2)\nabla^2\psi_i(r)/\psi_i(r) - v_h(r) - v(r) \qquad (2.17)$$

Table 5: HF Total energy expectation values for harmonic oscillator systems with 8 electrons.

The HF total energy expectation values using the wavefunctions obtained from the KS, LSD and SLA methods are listed for both the paramagnetic (8 electrons) and ferromagnetic (4 electrons) cases.

k	HF	KS	LDA	SLA
(paramagnetic)				
.01	5.8624	5.8633	5.8641	5.8680
.1	13.5752	13.5765	13.5776	13.5828
1	32.9240	32.9257	32.9271	32.9343
10	84.5846	84.5864	84.5880	84.5973
100	230.4828	230.4847	230.4865	230.4973
(ferromagnetic)				
.01	1.7877	1.7882	1.7887	1.7924
.1	4.5062	4.5069	4.5076	4.5121
1	12.0483	12.0491	12.0500	12.0553
10	33.9873	33.9883	33.9892	33.9950
100	99.9408	99.9417	99.9427	99.9489

Those exchange potentials are shown in Figure 5 for the 1s and 2p states along with the exact v_x^{ks}. We see that for $r > r_m$, the $v_{x,2p}^{hf}$ and the v_x^{ks} are almost identical which ensures that $\varepsilon_{2p}^{hf} = \varepsilon_{2p}^{ks}$. Moreover, since the behavior of the potential near the origin has only a small effect on the 2p state because $u_{2p} \rightarrow 0$ as $r \rightarrow 0$, the similarity of $v_{x,2p}^{hf}$ and v_x^{ks} assures not only that the asymptotic density as $r \rightarrow \infty$ in both calculations will be equal, but also leads to the result that both 2p wavefunctions are nearly the same everywhere. In addition, we observe that v_x^{ks} is nearly parallel to $v_{x,1s}^{hf}$ except for a small region in configuration space near the origin, from which it follows that the u_{1s} will be similar in both calculations, but the single particle eigenvalues, ε_{1s}, will be significantly different, being lower in the HF approximation because the $v_{x,1s}^{hf}$ is more negative than v_x^{ks}. This is precisely the case as shown in Table 1 for the unpolarized case(8 electrons) and in Table 2 for the spin polarized case(4 electrons). In addition, Table 4 gives a comparison of the exchange energies given by the HF approximation, the KS theory calculated from Eq.(2.14), and that obtained by substituting the KS orbitals in the usual HF exchange energy expression. We see that as discussed in 2.1, $E_x^{hf} \neq E_x^{ks}$ and furthermore the HF exchange energy calculated with KS orbitals is not exactly equal to either although all three calculations do give similar results, with differences of less than 0.2%. Finally, since the overlap integral between corresponding KS and HF orbitals is so close to unity, one anticipates that employing the KS orbitals in the HF total energy functional should give results only slightly higher than the exact HF values. Table 5 demonstrates that this is in fact correct with the error in E_{tot} only $\simeq$ 0.02% which is similar to results obtained by Talman et al for atoms when they employed orbitals obtained from an optimized potential. In addition we see from Table 7 that if the KS wavefunctions are used to calculate the expectation values of the HF single particle eigenvalues, the results for both ε_{1s}, and ε_{2p} for all k are within 0.1% of the exact HF results even though the ε^{ks}_{1s} are 3 to 4% higher than the ε^{hf}_{1s} values.

2.3 Comparison of HF with Exchange-Only LSD and SLA Calculation

Whereas the comparison between the results obtained from the exact KS exchange-only theory and those obtained from LSD and SLA as presented in Sec. 2.2.1 and the comparison between the exact KS theory and the HF approximation as presented in Sec. 2.2.2 have not been previously discussed due to the lack of the exact KS potential, comparisons have been made between HF with exchange-only LSD and SLA calculations for atoms [15] [16]. The discussion below supplements those previous comparisons.

Comparing the v^{lsd}_x and v^{sla}_x potentials in Figure 1 with the HF effective exchange potential $v^{hf}_{x,1s}$ and $v^{hf}_{x,2p}$ in Figure 5(in both Figures, the same v^{ks}_x is plotted), we see that v^{sla}_x is approximately the same magnitude as $v^{hf}_{x,2p}$ whereas v^{lsd}_x is much smaller in magnitude but is essentially parallel to $v^{hf}_{x,2p}$ for $r > r_m$ and parallel to $v^{hf}_{x,1s}$ except for a small region of configuration space

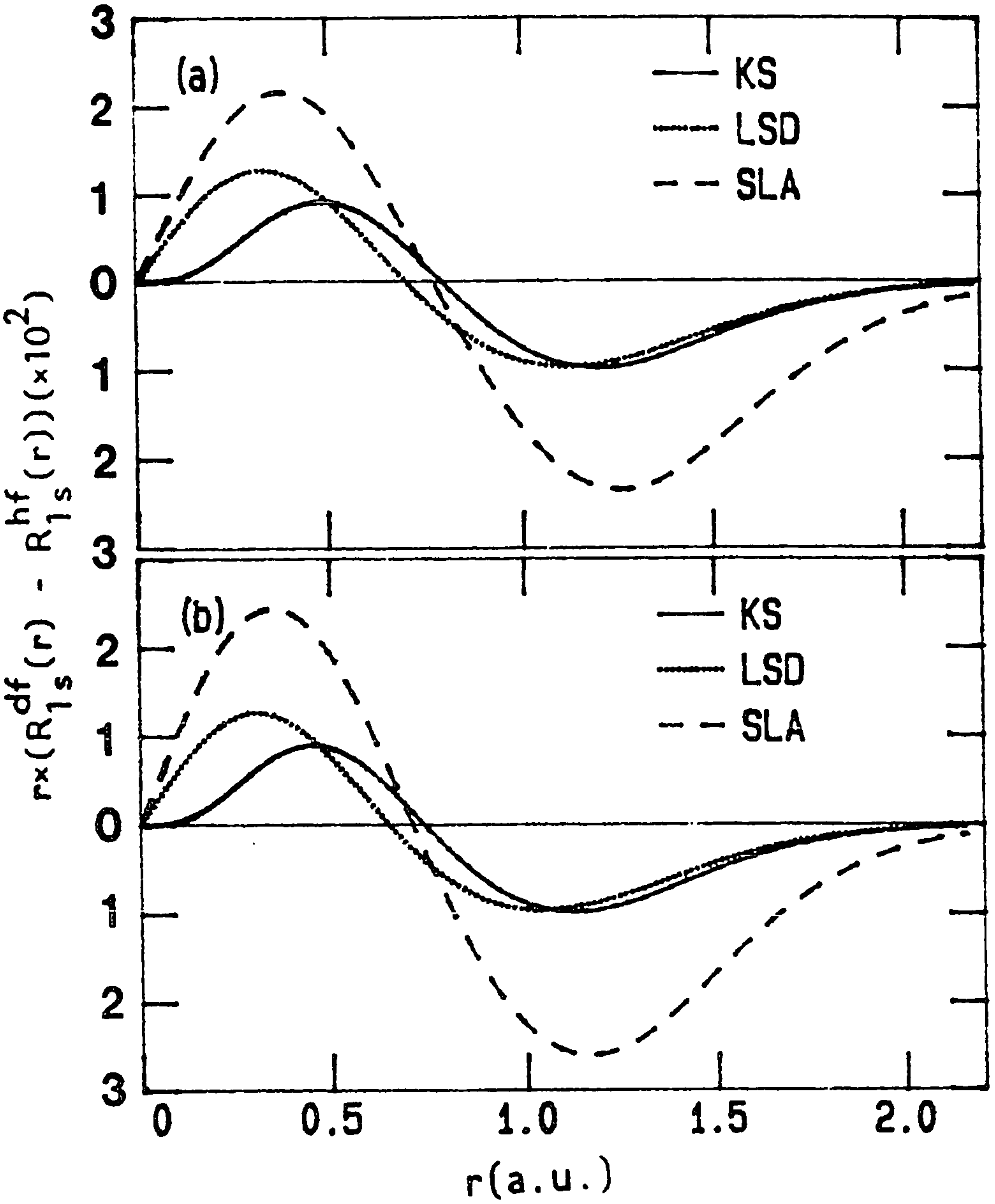

Figure 6: Deviations of the 1s wavefunctions of the KS, LSD and SLA from the HF for harmonic oscillator systems with k=10. The top graph shows the deviations for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

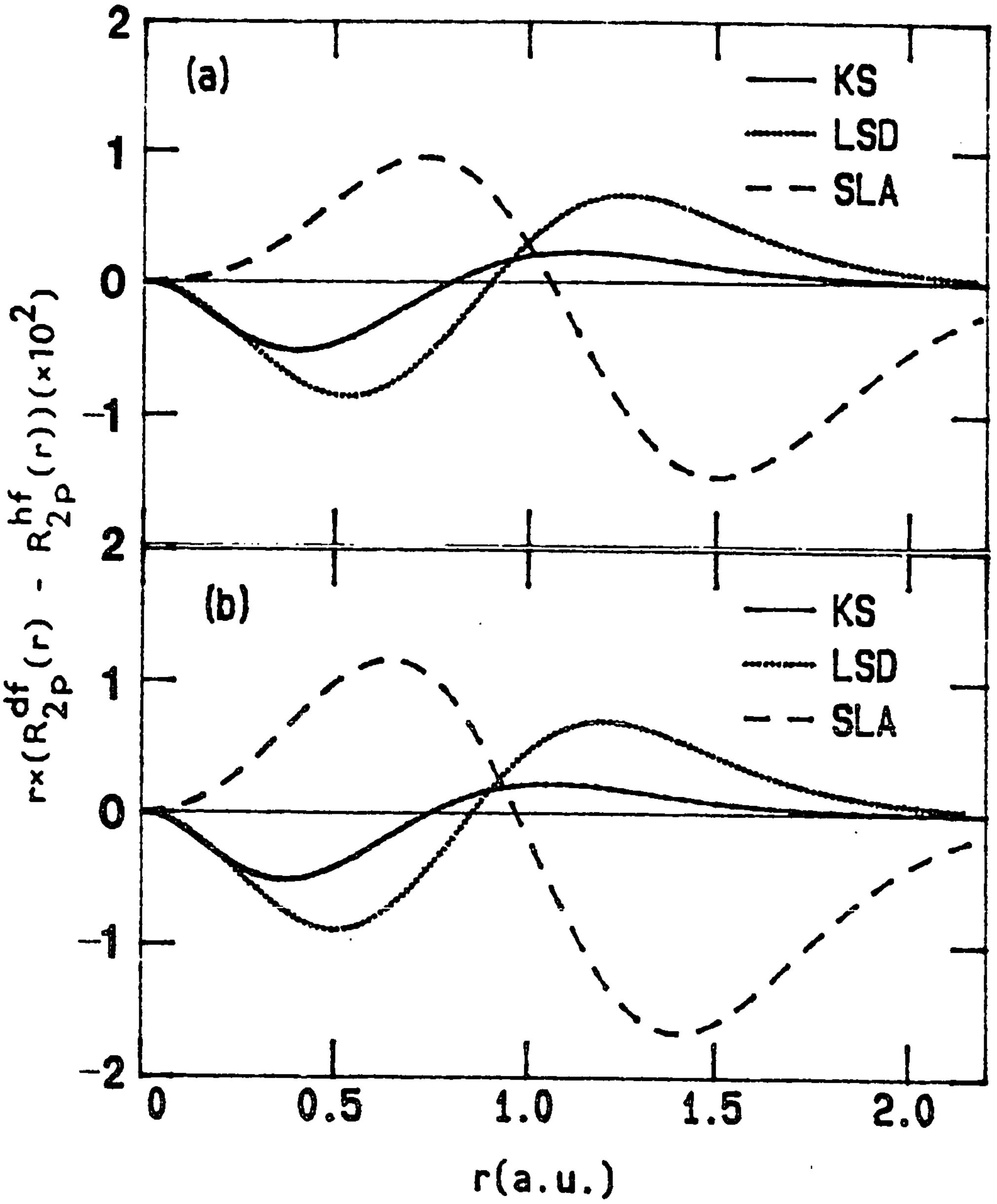

Figure 7: Deviations of the 2p wavefunctions of the KS, LSD and SLA from the HF for harmonic oscillator systems with k=10. The top graph shows the deviations for the paramagnetic case with eight electrons, the lower one is for the ferromagnetic case with four electrons.

Table 6: HF single particle expectation energy eigenvalues for harmonic oscillator systems with 8 electrons.

Paramagnetic case. The ε_i^{hf} are calculated from the expectations of the HF single particle hamiltonian using the wavefunctions obtained from the KS, LSD and SLA schemes. Also listed in the table are the exact ε_i^{hf} (all in atomic units).

k	HF	KS	LDA	SLA
1s state				
.01	1.0973	1.0965	1.0937	1.1068
.1	2.3767	2.3755	2.3712	2.3940
1	5.2129	5.2114	5.2055	5.2400
10	11.7883	11.7866	11.7792	11.8246
100	28.0620	28.0602	28.0516	28.1052
2p state				
.01	1.1708	1.1715	1.1696	1.1807
.1	2.6138	2.6148	2.6121	2.6302
1	6.0157	6.0170	6.0134	6.0395
10	14.5164	14.5179	14.5134	14.5467
100	37.1829	37.1844	37.1793	37.2179

near the origin. Consequently, as in Sec. 2.2.1, the SLA single particle eigenvalues are closer to the corresponding ε_{1s}^{hf} and ε_{2p}^{hf} than are the LSD eigenvalues as shown in Tables 1-2 which are similar to results for atoms, and the LSD wavefunctions closely approximate the HF wavefunctions as shown in Figs. 6-7 with overlap integrals

$$\langle\psi_i^{df}|\psi_i^{hf}\rangle = \int[\psi_i^{df}(r)]^*\psi_i^{hf}(r)dr \qquad (2.18)$$

Table 7: HF single particle expectation energy eigenvalues for harmonic oscillator systems with 4 electrons.

Ferromagnetic case. The ε_i^{hf} are calculated in the same way as those in Table 6.

k	HF	KS	LDA	SLA
1s state				
.01	0.5662	0.5652	0.5632	0.5737
.1	1.2709	1.2696	1.2669	1.2814
1	2.9864	2.9848	2.9815	2.9993
10	7.4662	7.4645	7.4608	7.4808
100	19.9280	19.9262	19.9223	19.9437
2p state				
.01	0.6715	0.6723	0.6711	0.6812
.1	1.5931	1.5943	1.5930	1.6065
1	3.9929	3.9942	3.9929	4.0090
10	10.6355	10.6370	10.6355	10.6533
100	29.9353	29.9369	29.9353	29.9542

given in Table 3. Again, as in Sec. 2.2.1, the SLA potential is too rapidly varying for $r > r_m$ which leads to the results that the exchange forces on the electrons for large r are too attractive. This results in SLA wavefunctions which systematically underestimate the HF results in this region. However, the LSD wavefunctions tend to have differences of opposite sign when compared to HF wavefunctions which leads to the LSD density being much closer to the exact HF results than is the density derived using the SLA as shown in Figure 2. The fact that the LSD density is much closer to the exact results yields an LSD Hartree potential which is much more accurate than that given by the SLA. As a result of this, when the density functional wavefunctions are employed to calculate the average value of the HF single particle energy eigenvalues, we see from Tables 6-7 that the LSD results are highly accurate and are in error by only approximately one tenth of the error in the SLA results for the 2p state and approximately one quarter of the error in the SLA results for the 1s state. In addition we see from Table 6 that the LSD calculated expectation values of the total HF energy has an error of approximately 1/3 to 1/4 that obtained from the SLA calculated values. Our results for both single particle eigenvalues and total energy are similar to those obtained for atoms [15] [16]. Finally we observe from Tables 3,5-7 that the single particle wavefunctions, the average value of the total HF energy and HF single particle eigenvalues are more accurately calculated by using the exact KS orbitals than those of employing the LSD or SLA orbitals. Consequently, we anticipate that further improvement of the LSD approximation for the exchange potential can lead to the calculation of orbitals that more closely approximate those of HF with the consequent improvement in the calculation of HF averages without the necessity of first calculating HF orbitals. As we have seen above, the calculation of the average

ε^{hf}_{max} is very close to the exact HF result and is generally more accurate than ε^{df}_{max} calculated using some approximate density functional for the exchange potential. The same is true for calculations of the total HF energy. In addition the calculation of the other average ε^{hf}_{i} using density functional orbitals is also close to the exact HF results whereas the corresponding ε^{df}_{i}, having been derived from the same orbital independent density functional exchange potential, do not closely approximate the HF results. Thus, although the ε^{ks}_{i} do not in principle equal the ε^{hf}_{i} except for i = highest occupied orbital(as can exactly be seen even for the free electron gas problem), the orbitals derived from density functional calculations may be employed to calculate the expectation values of the single particle HF eigenvalues which are very close to the exact result.

Chapter III

Study of the Self-Interaction-Correction Method in DFT

3.1 Perdew and Zunger's LSDSICA

Ever since HK and KS laid down the rigorous basis for the Density Functional Theory, the Local density approximation(LDA) and later on the Local spin density(LSD) approximation [17] has been the most commonly used method in calculating the properties of atoms, molecules and solids. Although the LSD method is quite successful in many respects, some worrisome failures remain unsolved. In the past, much of the criticism of the LSD approximation has been directed toward its incomplete description of many-body correlation effects. But recently, Perdew and Zunger(PZ) in a paper entitled 'Self-interaction correction to density functional approximation for many-electron systems', claimed that most of the discrepancies of the LSD approximation are interrelated to the fact that the LSD involves unphysical self-interaction parts whereas the exact DFT for the ground state energy should be strictly self-interaction-free(SIF).

Using this fact they showed formally that the exchange-correlation energy of a single, fully occupied orbital must exactly cancel its self-direct Coulomb energy, i.e.

$$U[n_{\alpha\sigma}] + E_{xc}[n_{\alpha\sigma},0] = 0 \tag{3.1}$$

where $U[n_{\alpha\sigma}]$ is the Hartree energy defined as

$$U[n] = (1/2)\int\int dr dr' n(r)n(r')/|r-r'|$$

with $n(r)$ replaced by $n_{\alpha\sigma}(r)$, and $E_{xc}[n_{\alpha\sigma},0]$ is the exact exchange-correlation energy functional with $n_{\alpha\sigma},0$ replacing $n_\uparrow$ and $n_\downarrow$ respectively.

In the exchange-only case, Eq.(3.1) becomes.

$$U[n_{\alpha\sigma}] + E_{x}[n_{\alpha\sigma},0] = 0 \tag{3.1'}$$

In the Hartree-Fock approximation, where one neglects the correlation effect, expression (3.1') is satisfied exactly as can be seen from the definition of the HF exchange energy for a single orbital, which just cancels the corresponding $U[n_{\alpha\sigma}]$. But in the LSD and many other DFT approximations, (3.1) or (3.1') is not exactly satisfied. A spurious residue remains which usually has non-negligible effects.

Perdew and Zunger then introduced the E_{xc}^{sic}

$$E_{xc}^{sic}[n_\uparrow,n_\downarrow] = E_{xc}^{app}[n_\uparrow,n_\downarrow] - \Sigma_{\alpha\sigma}\delta_{\alpha\sigma} \tag{3.2}$$

where

$$\delta_{\alpha\sigma} = U[n_{\alpha\sigma}] + E_{xc}[n_{\alpha\sigma},0]$$

is the self-interaction of orbital $\alpha\sigma$ and is zero when E_{xc}^{app} happens to be the exact $E_{xc}[n_\uparrow,n_\downarrow]$

The total energy functional becomes:

$$E_{tot}^{sic} = T_s + V + U_h + E_{xc}^{sic} \tag{3.3}$$

where T_s, V and U_h are defined as before. Expression (3.3) thus physically guarantees the SIF requirement for the ground state energy functional which was lost in the original approximation.

Taking the functional derivative with respect to the normalized orbitals, a set of Schrodinger type equations are then derived:

$$[- (1/2)\nabla^2 + v_{\alpha\sigma}^{sic}(r)]\psi_{\alpha\sigma}(r) = \varepsilon_{\alpha\sigma}^{sic}\psi_{\alpha\sigma}(r) \tag{3.4}$$

with

$$v_{\alpha\sigma}^{sic}(r) = v(r) + v_h([n],r) + v_{xc,\alpha\sigma}^{sic} \tag{3.5}$$

where

$$v_{xc,\alpha\sigma}^{sic} = v_{xc}^{app}([n_\uparrow,n_\downarrow],r) - \{v_h([n_{\alpha\sigma}],r) + v_{xc}^{app}([n_{\alpha\sigma},0],r)\}$$

$$v_h([n],r) = \int dr'n(r')/|r-r'|$$

$$v_{xc}^{app}([n_\uparrow,n_\downarrow],r) = \delta E_{xc}^{app}([n_\uparrow,n_\downarrow],r)/\delta n_{\alpha\sigma}$$

In principle, these equations can be solved and the wavefunctions thus obtained are SIF. Especially with E_{xc}^{app} being E_{xc}^{lsd} we have the so-called LSDSIC approximation. However, even in this case, because of the fact that the effective potential is orbital dependent, the solution of Eq.(3.4) is not without difficulties.

In solving the atomic problems, PZ simply replaced all the $n_{\alpha\sigma}(r)$ by its spherical average $n_{nl}(r)$ in the exchange energy and potential, a method we thereafter refered to as LSDSICA, and solved a set of Schrodinger type equations with spherically symmetric effective potentials:

$$v_{\alpha\sigma}^{sic}(r) = v(r) + v_h([n],r) + v_{xc}^{lsdsica}$$

where

$$v_{xc}^{lsdsica} = v_{xc}^{lsd}([n_\uparrow,n_\downarrow],r) - \{v_h([n_{\alpha\sigma}],r)+v_{xc}^{lsd}([n_{\alpha\sigma},0],r)\} \quad (3.6)$$

The results thus obtained are indeed very impressive in spite of the approximation they made. When compared to the LSD, it is found that many of the significant failures of the latter have disappeared, an indication of the importance of the SIF requirement.

3.2 Alternative Method

As described by PZ, the LSDSICA remedies many systematic errors produced by the uncorrected LSD. However, by a detailed study of the results they published, one can see that although the LSDSICA significantly improves the LSD, substantial errors still remain in the calculation of the total energy when compared with experimental results. And in the exchange-only case, both the total energy and the top eigenvalues are in error when compared to the exact, i.e the HF, values.

Since PZ made the approximation $\psi_{\alpha\sigma}(r) \rightarrow R_{nl}(r)$ (and $n_{\alpha\sigma}(r) \rightarrow n_{nl}(r)$, where $n_{nl}(r) = |R_{nl}(r)|^2$) in the exchange energy and potential in solving the Schrodinger type equations, the solutions they obtained are thus not the optimized ones for the SIC equations.

If one analyzes the SIC energy functional in detail, it is not difficult to see that there is actually an alternative approach which, although, still not an exact solution to the single particle equations, can be more accurate than the LSDSICA. We will discuss this method in detail in the following and refer it hereafter as LSDSICE.

We make the usual assumption that the effective potential is spherically symmetric, a condition that is of course exactly satisfied for closed shell systems with a spherically symmetric external potential. The procedure is then actually quite simple. As in the usual derivation of the HF equations for the radial functions, we can assume the wavefunctions to be of the form of a product of a radial function and an angular function, $\psi_{\alpha\sigma}(r) = R_{nl}(r)f_{lm}(\theta,\phi)$. Then, we have two choices for the forms of the angular function. One is that we can chose it to be a spherical harmonic. The other is that we can assume it to be a Cartesian orbital. Our calculations show that the latter gives much lower total energy than the former. (The reason these two different types of orbitals yield different results arises from the fact that the LSDSIC exchange energy functional depends not only on the electron density, but on the separate orbitals.) Thus in what follows we will only present and discuss the results using the Cartesian orbitals and only angular momentum number l values up to 2, or s,p and d states are considered.

In the Cartesian orbital expression, we have

1 s state : $\{1\}$,

3 p states: $\{x,y,z\}/r$ and

5 d states: $\{xy,yz,zx,x^2-y^2,3x^2-1\}/r^2$.

We can now insert these orbitals into the energy functional, perform the angular integration and finally, take the functional derivative with respect to the radial function. We then obtain the following expression for the exchange potential(the other constituents of the effective potential are the same as those in Eq.(3.5).

$$v_x^{l\,sdsice} = v_x^{l\,sd}([n_\uparrow, n_\downarrow], r) - \{v_h([n_{\alpha\sigma}], r) + \beta_l v_x^{l\,sd}([n_{nl}, 0], r)\} \quad (3.7)$$

with

$$v_h([n_{\alpha\sigma}], r) = v_h([n_{nl}], r) + \int n_{nl}\{\gamma_{l0}(r_<^2/r_>^3) + \gamma_{l1}(r_<^4/r_>^5)\}4\pi r'^2 dr'$$

where, the β_l and $\gamma_{ll'}$ are l dependent, being derived from first principle and are non-adjustable. The derivation is given in Appendix C. Table 8 shows their values for l = 0, 1, 2.

Table 8: Non-adjustable constants in the LSDSICE exchange potential.

l	β_l	γ_{l0}	γ_{l1}
0	1	0	0
1	1.18	4/25	0
2	1.24	4/49	4/49

We see, that when l=0, $v_x^{l\,sdsice} = v_x^{l\,sdsica}$ as should be the case since the s state is already spherically symmetric. But for l = 1 and l = 2 the two expressions are different.

Table 9: Total energies and exchange energies of atoms from exchange-only DFT calculations compared with the HF values

Listed are the negative values of the energies(atomic units are used).

Total Energy($-E_{tot}$)

Atom	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Be	14.5730	14.5799	14.5799	14.5799	14.5773
Ne	128.547	128.862	128.617	128.925	128.602
Mg	199.615	200.031	199.701	200.142	199.680
Ar	526.818	527.607	526.896	527.910	526.854
Ca	676.758	677.684	676.851	678.053	676.803
Zn	1777.85	1780.19	1778.05	1780.85	1777.95
Kr	2752.06	2754.96	2751.96	2756.00	2751.84
Sr	3131.55	3134.67	3131.40	3135.82	3131.27
Cd	5465.13	5469.59	5464.55	5471.34	5464.35
Xe	7232.14	7237.27	7231.14	7239.46	7230.93

Exchange Energy($-E_x$)

Atom	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Be	2.667	2.664	2.664	2.664	2.680
Ne	12.108	12.408	12.135	12.505	12.270
Mg	15.994	16.401	16.044	16.539	16.196
Ar	30.185	30.929	30.178	31.259	30.457
Ca	35.211	36.100	35.229	36.485	35.532
Zn	69.641	71.880	69.616	72.607	70.263
Kr	93.856	96.685	93.576	97.775	94.308
Sr	101.95	105.01	101.64	106.21	102.40
Cd	148.91	153.23	148.04	155.01	149.12
Xe	179.10	184.12	177.86	186.31	179.04

Using this method, we have solved the corresponding Schrodinger

Table 10: Total energies and exchange energies of harmonic oscillator systems from exchange-only DFT calculations(in a.u.).

Total Energy(E_{tot})

k	0.01	0.1	1	10	100
HF	5.86236	13.57516	32.92404	84.58462	230.48278
KS	5.86236	13.57516	32.92404	84.58462	230.48278
LSDSICA	5.86781	13.57799	32.91665	84.55383	230.40651
LSDSICE	5.89336	13.63002	33.01952	84.75095	230.77443
LSDSICI	5.84020	13.52468	32.81554	84.36545	230.06094
SLASICE	5.89422	13.63140	33.02141	84.75325	230.77701

Exchange Energy($-E_x$)

k	0.01	0.1	1	10	100
HF	0.7958	1.6068	3.1554	6.0199	11.2069
KS	0.7964	1.6079	3.1569	6.0216	11.2087
LSDSICA	0.7873	1.6006	3.1596	6.0479	11.2809
LSDSICE	0.7602	1.5459	3.0530	5.8460	10.9074
LSDISIC	0.8166	1.6562	3.2637	6.2400	11.6307
SLASICE	0.7666	1.5559	3.0668	5.8634	10.9274

type equations self-consistently for both atoms and harmonic oscillators. Our results show that in the atomic case, the total energies and exchange energies thus calculated are much closer to the HF values than the corresponding LSDSICA (as can be seen in Table 9. For the harmonic oscillator systems, however, the E_x values are too small in magnitude and are less accurate than those given by the

LSDSICA method. As a result, the total energies calculated from the LSDSICE scheme are poorer than those given by the LSDSICA method(refer to Table 10). Nevertheless, this might not be conclusive, since the oscillator systems we are considering contain only two orbitals. As can be seen from the LSDSICA exchange energy values for atoms in Table 9, the E_x for the Be atom which has only two orbitals is smaller than the HF value whereas the opposite is true for atoms requiring more than two orbitals to describe the electron states. One common feature for the LSDSICE calculations for both systems is the result that the maximum single particle eigenvalues thus obtained are slightly farther away from the HF results in both cases(see Table 11).

Finally, we observe here that actually, in order to get improved total energy calculations for atoms, a much simplified procedure is applicable when one realizes that the total energy of the ground state satisfies the variational principle and that the single particle atomic wavefunctions calculated from the LSDSICA are not very different from those obtained by solving the self-consistent LSDSICE equations. Thus one can simply use the LSDSICA wavefunctions and calculate the atomic E_{tot} by taking the expectation value of the exact LSDSICE energy functional. In Table 12, we show the total energy calculations using this method as compared with the exact LSDSICE values. It is seen that the differences are in the 7th digit.

Table 11: Comparison of the outermost orbital energy eigenvalues of DFT and HF(in Ry.).

Atoms($-\varepsilon_{max}$)

Atom	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Be(2s)	0.6185	0.6157	0.6157	0.6157	0.6334
Ne(2p)	1.7008	1.6144	1.5800	1.7233	1.7116
Mg(3s)	0.5061	0.5118	0.5127	0.5104	0.5386
Ar(3p)	1.1820	1.0982	1.0820	1.1817	1.1833
Ca(4s)	0.3911	0.4009	0.4018	0.3998	0.4264
Zn(3d)	1.5651	1.4684	1.3809	1.5689	1.5739
(4s)	0.5850	0.6238	0.6316	0.6159	0.6837
Kr(4p)	1.0484	0.9682	0.9569	1.0444	1.0527
Sr(5s)	0.3569	0.3689	0.3698	0.3676	0.3950
Cd(4d)	1.5273	1.4019	1.3349	1.5062	1.5060
(5s)	0.5297	0.5711	0.5778	0.5641	0.6343
Xe(5p)	0.9146	0.8413	0.8327	0.9098	0.9189

Harmonic Oscillators(ε_{max})

k	0.01	0.1	1	10	100
HF	1.17080	2.61379	6.01575	14.51644	37.18287
LSDSICA	1.18737	2.64508	6.07291	14.61924	37.36665
LSDSICE	1.18839	2.64763	6.07889	14.63221	37.39290
LSDSICI	1.17198	2.61460	6.01389	14.50753	37.15952
SLASICE	1.17570	2.62107	6.02469	14.52519	37.18845

Table 12: The LSDSICE total energies.

Here is a comparison of the self-consistent LSDSICE total energies(LSDSICE) and the expectation values of the LSDSICE Hamiltonian using the wavefunctions from the LSDSICA scheme(SICAE). The HF values are also appended for reference. Energies are in units of a.u. and are listed as $-E_{tot}$.

Atom	HF	LSDSICE	SICAE
Be	14.5730	14.5799	14.5799
Ne	128.5471	128.6174	128.6165
Mg	199.6146	199.7007	199.6999
Ar	526.8175	526.8961	526.8959
Ca	676.7582	676.8514	676.8514
Zn	1777.848	1778.046	1778.044
Kr	2752.055	2751.964	2751.962
Sr	3131.546	3131.403	3131.401
Cd	5465.133	5464.546	5464.545
Xe	7232.138	7231.144	7231.144

3.3 Treating Intra-shell Exchange Exactly

One drawback of the LSD exchange is that it does not have the right asymptotic behavior for large r. Instead of approaching -1/r for large r, the LSD exchange potential goes to zero exponentially. The SIC method has the virtue that it restores this property, and as a result, correctly describes the large r behavior of the exchange potential. If, however, we consider the region in space in which the density is essentially given by the density of electrons of a given subshell, we find there are still significant differences between the LSDSIC potential and effective HF potential.

Consider the single particle equations:

$$[-(1/2)\nabla^2 + v_h + v + v^{sic}_{x,max}]\psi^{sic}_{max} = \varepsilon^{sic}_{max}\,\psi^{sic}_{max} \tag{3.8}$$

$$[-(1/2)\nabla^2 + v_h + v + v^{hf}_{x,max}]\psi^{hf}_{max} = \varepsilon^{hf}_{max}\,\psi^{hf}_{max} \tag{3.9}$$

Here

$$v^{hf}_{x,max} = \Sigma_{\alpha\sigma}\{\int\psi_{max}(r')\psi_{\alpha\sigma}(r')/|r-r'|dr'\}\psi_{\alpha\sigma}(r)/\psi_{max}(r) \tag{3.10}$$

The sum on σ will actually only include those states with σ having the same spin projection as ψ_{max}.

Since in an exact PZ theory,

$$n^{sic}(r) = n^{hf}(r),$$

$$\varepsilon^{sic}_{max} = \varepsilon^{hf}_{max}$$

and

$$n(r) = \Sigma_i f_i|\psi_i(r)|^2$$ (f_i is the occupancy number.)

so for large r,

$$n(r) \rightarrow f_{max}|\psi_{max}|^2,$$

thus, we must have

$$v^{sic}_{x,max}(r) \rightarrow v^{hf}_{x,max}(r).$$

This suggests that we should make $v^{sic}_{x,max}$ look as close as possible to $v^{hf}_{x,max}$ when r is large.

For atoms with complete subshells, the $v^{hf}_{x,max}$ has the asymptotic form

$$v^{hf}_{x,max}(r) = \int n_{max}\{(1/r_>) + \gamma_{10}(r_<^2/r_>^3) + \gamma_{11}(r_<^4/r_>^5)\}4\pi r'^2 dr' \quad (3.11)$$

where n_{max} is the spherically averaged single particle orbital density. This arises from the fact that in deriving the HF equations, one assumes the same radial function for all states in the same subshell, and this term represents the contribution to the exchange potential by intra-shell interaction. We find we may obtain the same term by modifying the Hartree-like term in the SIC expression such that it includes the entire intra-shell exchange energy i.e. we subtract from the LSD exchange not only the self-coulomb term but also the coulomb interaction with the other electrons of the same spin in the same subshell.

$$E_x^{sic} = E_x^{lsd}[n_\uparrow, n_\downarrow] - \{\Sigma_{\alpha\sigma} E_x^{lsd}[n_{\alpha\sigma}, 0] + \Sigma_{\alpha\sigma,\alpha'\sigma'} h_{\alpha\sigma,\alpha'\sigma'}\} \quad (3.12)$$

with

$$h_{\alpha\sigma,\alpha'\sigma'} = (1/2)\int\int dr dr' \psi^*_{\alpha\sigma}(r)\psi_{\alpha\sigma}(r')\psi^*_{\alpha'\sigma'}(r')\psi_{\alpha'\sigma'}(r)/|r-r'|$$

where the sum on α' are those which have the same nl as the state α but different m. If we then use the same procedure as in dealing with LSDSICE. we have in this LSDSICI approximation:

$$v_x^{l\,sdsici} = v_x^{l\,sd}([n_\uparrow, n_\downarrow], r) - \{v_h([n_{nl}], r) + \beta_l v_x^{l\,sd}([n_{nl}, 0], r)\} \quad (3.13)$$

with

$$v_h([n_{nl}], r) = v_h([n_{nl}], r) + \int n_{nl}\{\gamma_{l0}(r_<^2/r_>^3) + \gamma_{l1}(r_<^4/r_>^5)\}4\pi r'^2 dr'$$

Compared with (3.7) the only change is in the values of γ_{l0}, and γ_{l1}. Now they have exactly the values as obtained in HF theory(see Table 13)

Table 13: Non-adjustable constants in the LSDSICI exchange potential

l	β_l	γ_{l0}	γ_{l1}
0	1	0	0
1	1.18	2/5	0
2	1.24	2/7	2/7

We notice here that by using expression(3.13), not only do we correctly mimic the exchange potential for the outermost orbital, the description of the inner orbital's exchange is improved as well i.e. for large r, the HF exchange potential has the same asymptotic behavior. Although in the DFT theory, there is no theorem regarding the physical meaning of the inner orbital energy eigenvalues, in the

Table 14: Comparison of the exchange-only single particle energy eigenvalues of DFT and HF for the Kr and Zn atoms.

Listed are the negative values of ε_i(in Ry.)

nl	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom					
1s	1040.33	1038.47	1038.73	1038.42	1038.33
2s	139.806	136.085	136.279	136.015	137.412
2p	126.020	124.563	124.464	125.486	125.019
3s	21.699	19.736	19.823	19.674	20.484
3p	16.663	15.293	15.287	15.539	15.762
3d	7.650	7.372	7.216	7.609	7.564
4s	2.306	1.982	2.000	1.960	2.166
4p	1.048	0.968	0.957	1.044	1.053
Zn Atom					
1s	706.609	705.182	705.443	705.119	704.971
2s	88.7235	85.828	86.031	85.749	86.779
2p	77.850	76.857	76.819	77.579	77.104
3s	11.276	9.913	10.014	9.839	10.434
3p	7.679	6.798	6.824	6.958	7.098
3d	1.565	1.468	1.381	1.569	1.574
4s	0.585	0.624	0.632	0.616	0.684

LSDSIC, with the effective potential being orbital dependent, we naturally hope to get these ε_i which are close to the HF values.

Using this LSDSICI method, we find significant improvement over the LSDSICA for the energy eigenvalue calculation of the highest lying p and d orbitals for both the atoms and harmonic oscillators.

Table 15: Comparison of the 1s orbital energy eigenvalues of DFT and HF for harmonic oscillator systems(in Ry.)

k	0.01	0.1	1	10	100
HF	1.09730	2.37667	5.21288	11.78827	28.06201
KS	1.13728	2.46375	5.39481	12.15007	28.75263
LSDSICA	1.14408	2.46847	5.38867	12.11723	28.66651
LSDSICE	1.14268	2.46621	5.38543	12.11311	28.66172
LSDSICI	1.14459	2.46938	5.39008	12.11913	28.66880
SLASICE	1.12565	2.43070	5.31255	11.96817	28.38323

For the highest lying s orbitals, however, the improvement is minor(because the form of $v^{sic}_{x,\alpha\sigma}$ is unchanged by this procedure), but in all cases, this method gives the most accurate ε_{max}. Table 11 show the eigenvalues of the highest lying orbitals for both the atoms and harmonic oscillators. In Table 14 we list all the eigenvalues calculated in different schemes for the Kr and Zn atoms. For harmonic oscillator systems, we show the the direct calculations of the ε_{1s} in all the schemes in Table 15. Most ε_i of p and d orbitals get improved in the LSDSICI over the LSDSICA and LSDSICE. One drawback to this method, however, is the result that the total energy calculation becomes even more negative than those obtained from the LSDSICA due to the fact that the exchange energy produced from this method becomes even larger in magnitude than those of LSDSICA which already overestimates the exchange energy compared with HF(refer to Tables 9-10). and Table 10)

3.4 Results and Discussion

In the previous two sections, we have described briefly the results of LSDSICE and LSDSICI in comparing with the HF and the LSDSICA. We know that whereas LSDSICE gives better total energies for atoms, its highest lying single particle eigenvalues are poorer than those given by LSDSICA(for oscillator systems with eight electrons occupying two orbitals, they are both poorer than the LSDSICA results). On the other hand, the LSDSICI method, which produces very good results for the top eigenvalues, but not so for its total energy calculations(for both the atomic and oscillator systems). In order to further evaluate these approximations, we shall make more detailed comparisons in this section. We will compare the $<r^n>_i$ ($n = -1, 1, 2$) average values for all the orbitals and also for the total density. We will also calculate the overlap integrals between the DFT wavefunctions and the HF wavefunctions which is defined as in Chapter 2, Eq.(2.18), to see how good the SIC method is in approximating the HF, which is of interest because of the well known usefulness of the HF solutions and the fact that the SIC equations are much more easy to solve than the HF equations when dealing with systems with large number of electrons like molecules and solids. We will also plot graphs for comparison. Finally, we will employ these wavefunctions to calculate the expectation values of the HF total energy and the HF single particle eigenvalues, the importance of the latter is implied by Koopman's theorem.

3.4.1 Atoms

Tables 16-18 compare the $<r>_i$, $<r^2>_i$ and $<1/r>_i$ (i = 1s,..,4p and density n)for the Kr and Zn atoms calculated self-consistently in the schemes of HF,LSDSICA, LSDSICE and LSDSICI(We have also include the SLASICE results which will be discussed in the next section). It is evident from these tables that the LSDSICI results are always closer to the HF than the others for the outer orbitals. For the Kr atom(and also true in general for most of the other atoms considered)the average $<r^n>$ values over the density are also pretty closer to the HF results. However, for the Zn atom, due to the fact that the inner orbitals produce errors that are larger than the LSDSICA or LSDSICE, the $<r>_n$ and $<r^2>_n$ values are poorer than those given by the other two schemes(the $<1/r>_n$ is, nevertheless, still the best one).

Another comparison is the orbital overlap integral values. We still use the Kr and Zn atoms as examples. In Table 19, we present their overlap integral values from the different calculation schemes.

Table 16: Orbital expectation values <r> for the Kr and Zn atoms(in a.u.).

nl	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom					
1s	0.04244	0.04243	0.04243	0.04243	0.04247
2s	0.18726	0.18816	0.18812	0.18815	0.18760
2p	0.16188	0.16166	0.16180	0.16145	0.16166
3s	0.53780	0.54366	0.54305	0.54391	0.53771
3p	0.54263	0.54717	0.54757	0.54701	0.54197
3d	0.55088	0.55148	0.55401	0.54911	0.54767
4s	1.62939	1.60640	1.60177	1.61010	1.56499
4p	1.95161	1.96504	1.97197	1.95258	1.89341
n	0.72887	0.73109	0.73275	0.72852	0.71457
Zn Atom					
1s	0.05109	0.05107	0.05107	0.05107	0.05113
2s	0.22877	0.23033	0.23028	0.23032	0.22942
2p	0.19951	0.19937	0.19959	0.19905	0.19930
3s	0.69059	0.69524	0.69361	0.69598	0.68690
3p	0.71979	0.72151	0.72144	0.72109	0.71406
4s	2.89773	2.75575	2.73372	2.77806	2.57622
3d	0.87487	0.88891	0.89878	0.88016	0.87127
n	0.73336	0.72931	0.73104	0.72778	0.70934

It appears that all the wavefunctions are not much different from the HF. The values are very close to one especially for the core orbitals. But again, the LSDSICI wavefunctions have slightly larger overlap integral values especially for the outer orbitals.

Table 17: Orbital expectation values $\langle r^2 \rangle$ for the Kr and Zn atoms(in a.u.).

nl	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom					
1s	0.00241	0.00241	0.00241	0.00241	0.00241
2s	0.04128	0.04164	0.04163	0.04164	0.04143
2p	0.03200	0.03191	0.03196	0.03181	0.03193
3s	0.33173	0.33972	0.33894	0.34006	0.33254
3p	0.34354	0.35016	0.35065	0.34949	0.34394
3d	0.37148	0.37386	0.37763	0.36966	0.36907
4s	3.04035	2.96626	2.94859	2.98070	2.81745
4p	4.45507	4.55569	4.59030	4.47269	4.22833
n	1.09806	1.11292	1.11880	1.09861	1.04732
Zn Atom					
1s	0.00350	0.00349	0.00349	0.00349	0.00350
2s	0.06167	0.06248	0.06245	0.06248	0.06205
2p	0.04873	0.04866	0.04876	0.04847	0.04866
3s	0.55022	0.55923	0.55648	0.56056	0.54613
3p	0.61117	0.61571	0.61543	0.61385	0.60365
4s	9.86938	8.94526	8.80120	9.09311	7.83330
3d	1.00501	1.05512	1.08346	1.02601	1.01120
n	1.16597	1.12261	1.12223	1.12244	1.03053

A more appropriate way to demonstrate the difference of the orbitals and density from those of the HF is perhaps to draw the graphs of the deviations of various DFT radial wavefunctions and densities from the HF as functions of r.

Table 18: Orbital expectation values <1/r> for the Kr and Zn atoms(in a.u.).

nl	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom					
1s	35.498	35.497	35.496	35.497	35.472
2s	7.9188	7.8551	7.8565	7.8553	7.9056
2p	7.8684	7.8805	7.8735	7.8856	7.8858
3s	2.6376	2.6120	2.6153	2.6106	2.6573
3p	2.5228	2.5048	2.5029	2.4981	2.5413
3d	2.2769	2.2844	2.2760	2.2883	2.3020
4s	0.8042	0.8317	0.8342	0.8297	0.8624
4p	0.6692	0.6775	0.6754	0.6762	0.7112
n	5.0792	5.0781	5.0744	5.0786	5.1013
Zn Atom					
1s	29.5121	29.5096	29.5099	29.5098	29.4854
2s	6.4671	6.4006	6.4021	6.4008	6.4530
2p	6.4018	6.4106	6.4034	6.4158	6.4177
3s	2.0401	2.0357	2.0409	2.0336	2.0742
3p	1.9044	1.9063	1.9063	1.9000	1.9368
4s	0.4419	0.4736	0.4777	0.4695	0.5162
3d	1.5305	1.5293	1.5181	1.5339	1.5557
n	4.7355	4.7344	4.7300	4.7354	4.7581

Figs. 8-10 show the deviations of the 4s,4p states and the density for the Kr atom. Figs. 11-13 are the 3d, 4s and the density for Zn.

These figures clearly indicate that the LSDSICI outer wavefunctions are always more similar to those of HF than are the other two

Table 19: Overlap integrals between the HF wavefunctions and the DFT wavefunctions for the Kr and Zn atoms.

nl	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom				
1s	0.999999	0.999999	0.999999	1.000000
2s	0.999981	0.999982	0.999981	0.999995
2p	0.999997	0.999997	0.999993	0.999996
3s	0.999866	0.999889	0.999855	0.999976
3p	0.999920	0.999912	0.999937	0.999957
3d	0.999967	0.999944	0.999984	0.999929
4s	0.999783	0.999718	0.999825	0.998517
4p	0.999815	0.999756	0.999965	0.999090
Zn atom				
1s	0.999999	0.999999	0.999999	0.999999
2s	0.999964	0.999966	0.999964	0.999990
2p	0.999997	0.999997	0.999994	0.999995
3s	0.999933	0.999962	0.999916	0.999954
3p	0.999972	0.999978	0.999986	0.999913
3d	0.999752	0.999536	0.999934	0.999820
4s	0.998161	0.997530	0.998693	0.989899

especially for the p and d states. The LSDSICI outer s state is also slightly improved over the LSDSICA but not so evident as the p and d orbitals. This can be easily understood if we recall that all the three exchange potentials and thus the effective potentials for the s orbital have the same expression. The difference produced in the wavefunctions is purely from the requirement of self-consistency.

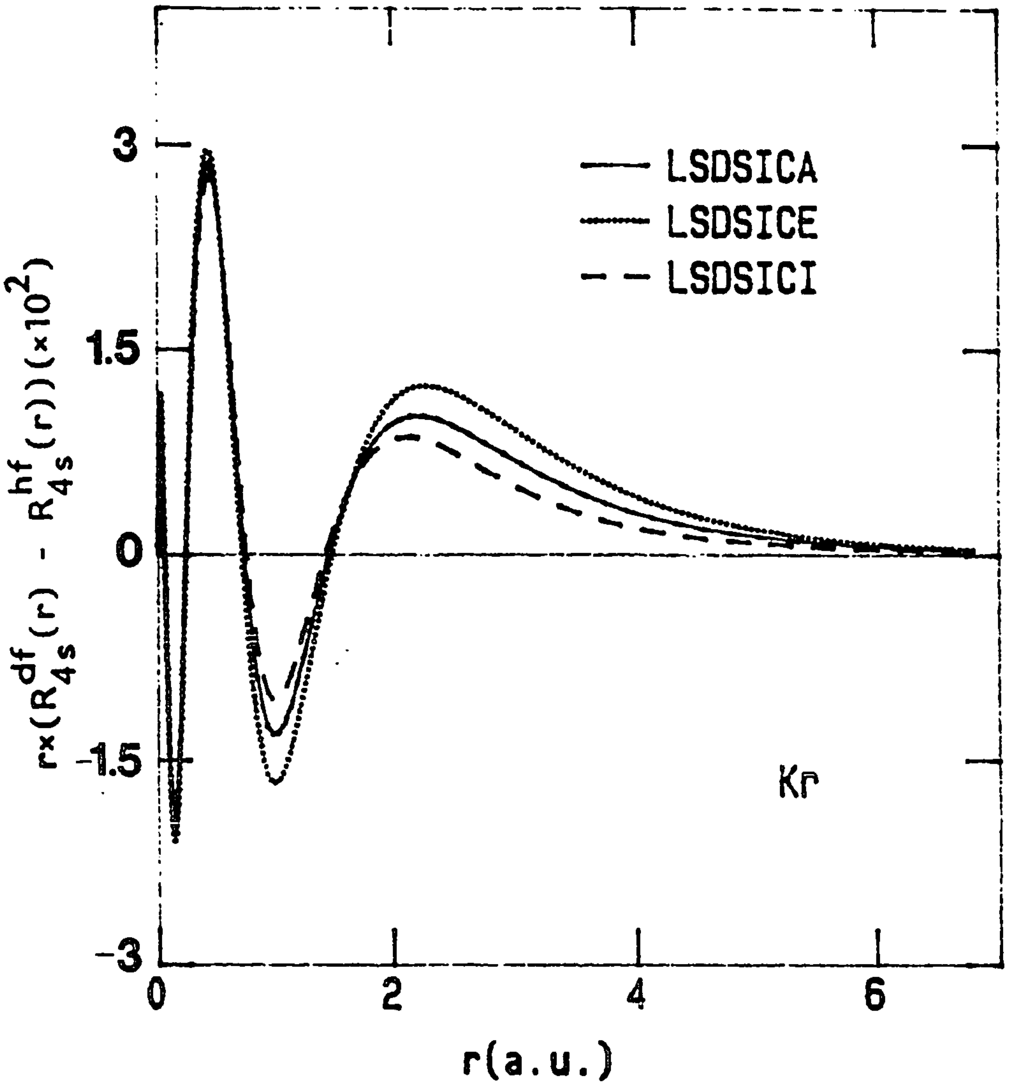

Figure 8: The deviations of the LSDSICA, LSDSICE and LSDSICI 4s wavefunctions from the HF for the Kr atom.

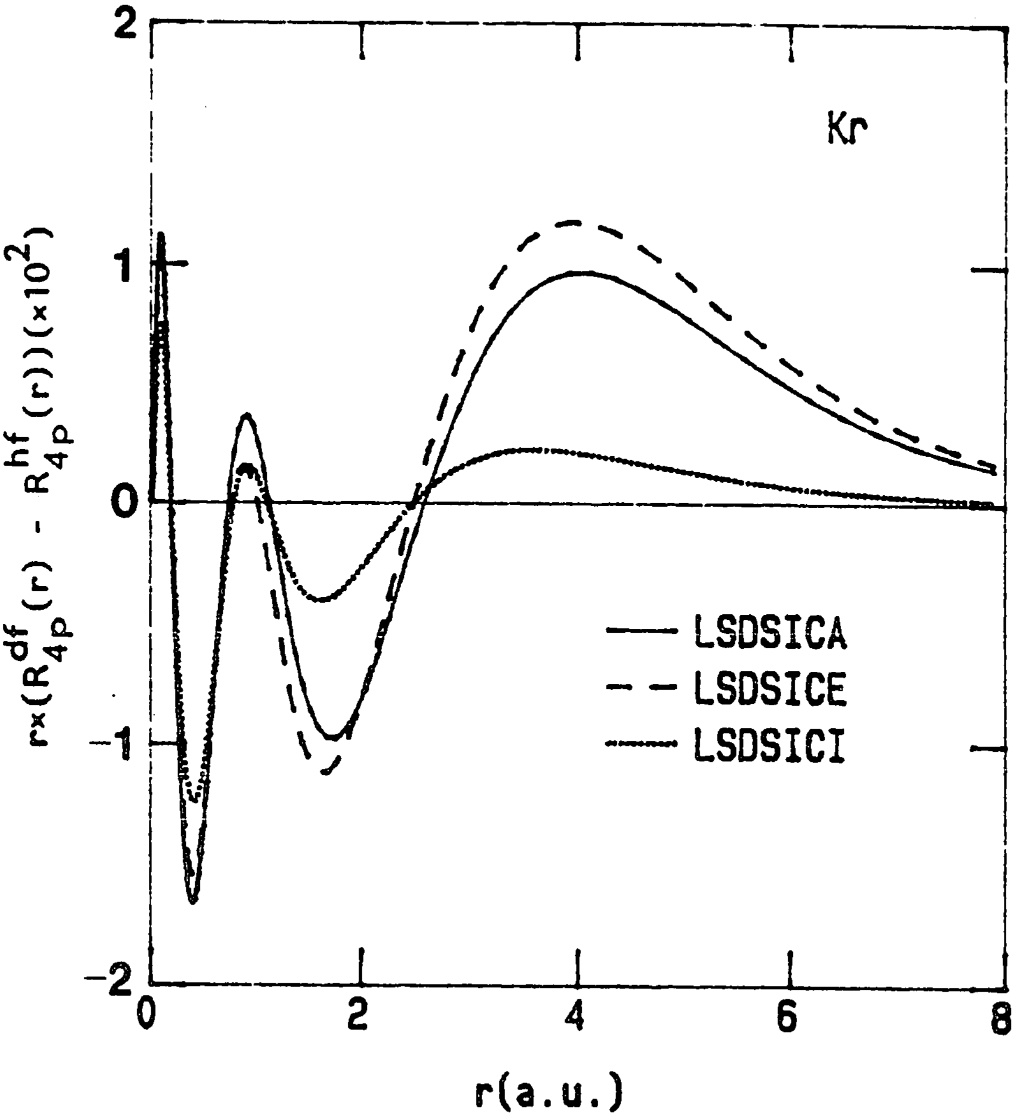

Figure 9: The deviations of the LSDSICA, LSDSICE and LSDSICI 4p wavefunctions from the HF for the Kr atom.

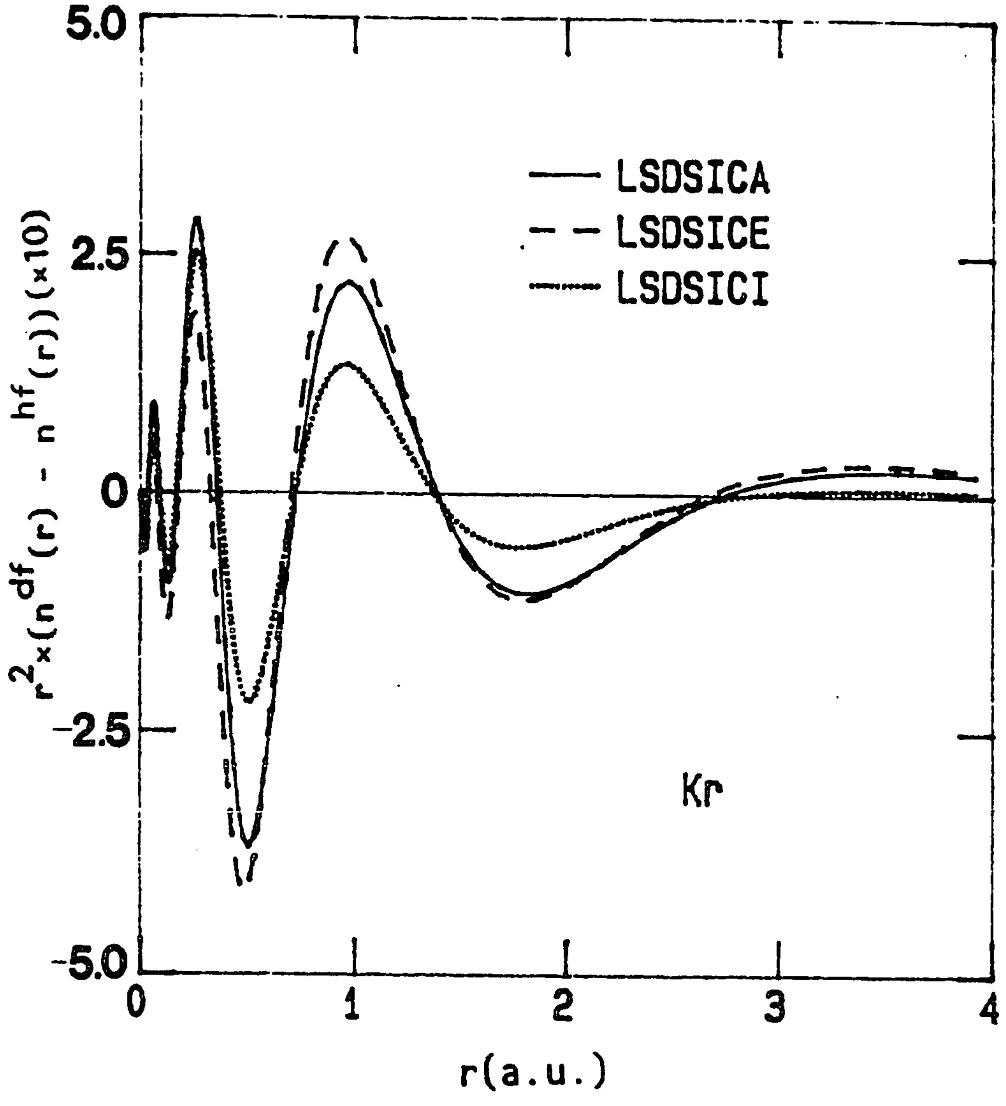

Figure 10: The deviations of the LSDSICA, LSDSICE and LSDSICI electron density from the HF for the Kr atom.

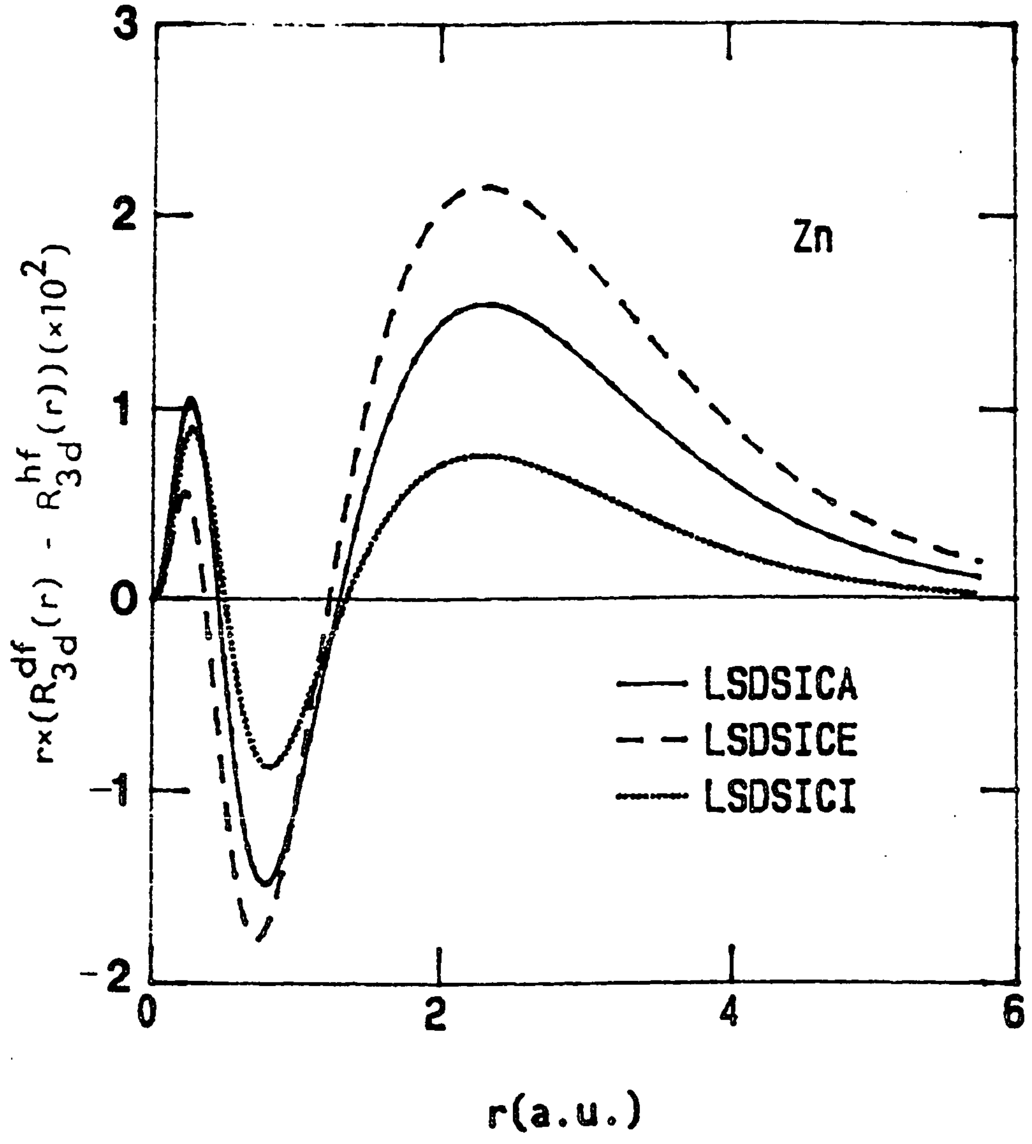

Figure 11: The deviations of the LSDSICA, LSDSICE and LSDSICI 3d wavefunctions from the HF for the Zn atom.

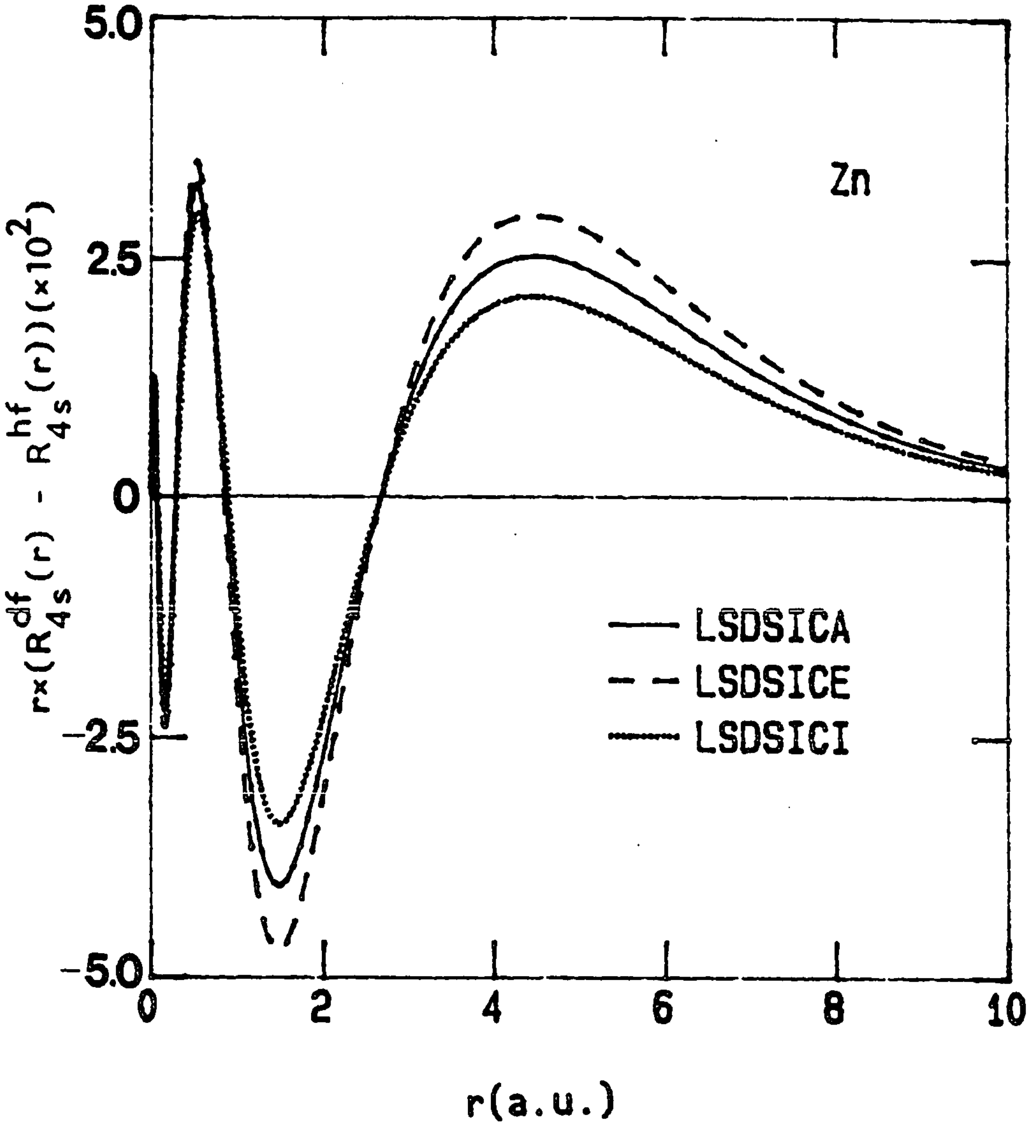

Figure 12: The deviations of the LSDSICA, LSDSICE and LSDSICI 4s wavefunctions from the HF for the Zn atom.

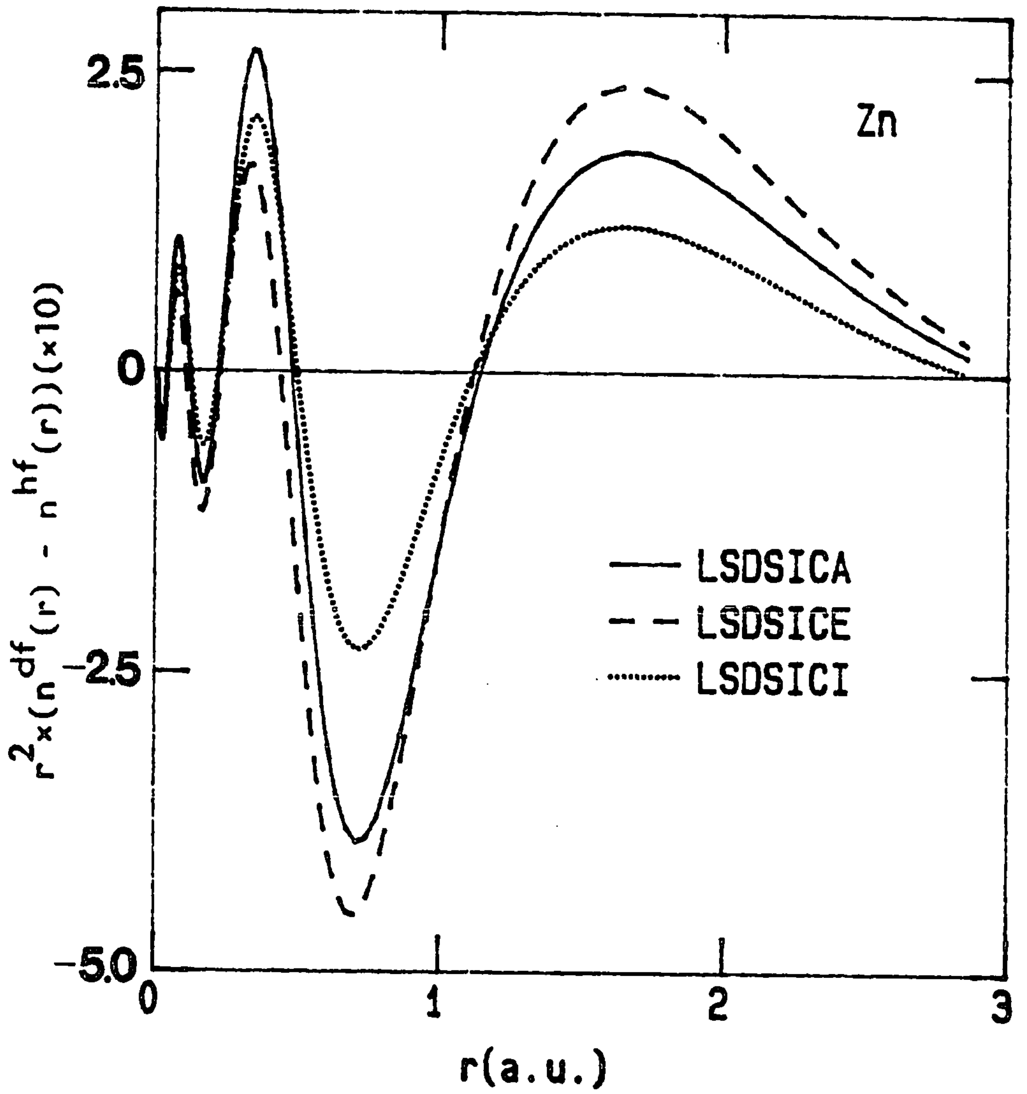

Figure 13: The deviations of the LSDSICA, LSDSICE and LSDSICI electron density from the HF for the Zn atom

Table 20: HF total energy expectation values for atoms.

The negative of the expectation values of the HF Hamiltonian using wavefunctions obtained from the various DFT schemes are listed. The exact HF total energies are also given(all in a.u.).

Atom	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Be	14.5730	14.5727	14.5727	14.5727	14.5700
Ne	128.547	128.539	128.541	128.540	128.528
Mg	199.615	199.604	199.606	199.606	199.585
Ar	526.818	526.802	526.803	526.807	526.765
Ca	676.758	676.741	676.742	676.746	676.692
Zn	1777.85	1777.81	1777.81	1777.83	1777.72
Kr	2752.06	2752.02	2752.02	2752.03	2751.91
Sr	3131.55	3131.51	3131.51	3131.52	3131.38
Cd	5465.13	5465.08	5465.07	5465.10	5464.90
Xe	7232.14	7232.09	7232.08	7232.10	7231.88

The most important evaluation of the quality of the wavefunctions might be the calculation of the expectation values of the HF total energy using the wavefunctions obtained from the various DFT approximations. In Table 20, we show these calculations for atoms. It can be seen that all calculations are quite good, some results for the large Z atoms are comparable with Talman's optimized orbital calculations. Those using the method of LSDSICI however, are particular good.

Table 21: Expectation values of the HF single particle hamiltonian compared with the HF results for the Kr and Zn atoms.

Listed are the negative values of ε_i(in Ry.)

nl	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Kr atom					
1s	1040.33	1040.30	1040.56	1040.26	1038.79
2s	139.806	139.769	139.962	139.700	138.684
2p	126.020	126.003	126.201	125.936	124.847
3s	21.699	21.706	21.794	21.648	21.145
3p	16.663	16.679	16.763	16.624	16.107
3d	7.650	7.678	7.759	7.623	7.089
4s	2.306	2.322	2.338	2.302	2.155
4p	1.048	1.056	1.067	1.042	0.922
Zn Atom					
1s	706.609	706.580	706.839	706.516	705.293
2s	88.723	88.705	88.908	88.626	87.776
2p	77.850	77.852	78.057	77.775	76.863
3s	11.276	11.314	11.413	11.246	10.869
3p	7.679	7.719	7.810	7.657	7.276
3d	1.565	1.594	1.664	1.542	1.206
4s	0.585	0.585	0.592	0.577	0.511

Finally, as we have done in Chapter 2 in comparing the HF, KS, LSD and SLA for the harmonic oscillator problems, we also calculate the expectation values of the HF single particle eigenvalues. It is found that all the ε_i ($i = 1, 2, \ldots.$) calculated for all the atoms using these LSDSIC type wavefunctions are very close to the exact ε_i^{hf}.

Table 22: Expectation values of the outermost orbital HF energy eigenvalues for atoms.

Listed are the negative values of ε_{max} The exact HF values are also given for comparison(in Ry.).

Atom	HF	LSDSICA	LSDSICE	LSDSICI	SLASICE
Be(2s)	0.6185	0.6196	0.6196	0.6196	0.6072
Ne(2p)	1.7008	1.7070	1.7353	1.6744	1.5942
Mg(3s)	0.5061	0.5027	0.5034	0.5017	0.4737
Ar(3p)	1.1820	1.1936	1.2064	1.1798	1.0820
Ca(4s)	0.3911	0.3860	0.3867	0.3849	0.3508
Zn(3d)	1.5651	1.5939	1.6641	1.5424	1.2062
(4s)	0.5850	0.5847	0.5921	0.5771	0.5114
Kr(4p)	1.0484	1.0560	1.0668	1.0419	0.9220
Sr(5s)	0.3569	0.3508	0.3517	0.3493	0.3080
Cd(4d)	1.5273	1.5410	1.5771	1.5168	1.1994
(5s)	0.5297	0.5326	0.5394	0.5253	0.4460
Xe(5p)	0.9146	0.9158	0.9247	0.9046	0.7836

Thus we have found a very efficient short cut in obtaining the removal energy of the system without relaxation(see Table 21 in which we present the results for the Kr and Zn atoms for all the ε_i thus calculated. Also see Table 22 where the ε_{max} values for all the atoms using this method are given.) When observing that the ε_i^{hf} do not satisfy the variational principle as the HF E_{tot} does, this result is indeed very interesting.

3.4.2 Harmonic Oscillators

As discussed earlier, when the LSDSICE method is employed, the harmonic oscillator systems show a distinctive feature from the atomic problem that, unlike the atomic case, the LSDSICE method yields E_{tot} and E_x which are in general not as accurate as those given by the LSDSICA(for the 8 electron problem). Since, as in the atomic problem, the ε^{df}_{max} given by this method are also slightly farther away from the ε^{hf}_{max} than those given by the LSDSICA, it thus appears that the LSDSICE method has improved nothing for the oscillator systems.

The LSDSICI method, on the other hand, as in the atomic case, can produces ε^{df}_{max} which are much closer to the ε^{hf}_{max} than the LSDSICA. Nevertheless, the direct calculations of the E_{tot} becomes poorer.

Just as what we have done for atoms previously, we will make a more detailed comparison in this subsection for the oscillator results from the different schemes. Especially we will study the qualities of the wavefunctions and the densities as compared with the HF results and employ the same technique as we did for atoms to calculate the approximate E_{tot} and ε^{hf}_{max} by using the DFT wavefunctions. (In those Tables in which we also list the KS results, it can be seen that the KS results are in general always closer to the HF results than those given by other DFT approximations with the exception of ε_{1s}).

Table 23: Orbital expectation values <r> for harmonic oscillator systems(in a.u.).

k	0.01	0.1	1	10	100
1s state					
HF	6.35678	2.98981	1.45806	0.74180	0.39121
KS	6.20876	2.93848	1.44200	0.73695	0.38973
LSDSICA	6.12094	2.89812	1.42710	0.73199	0.38815
LSDSICE	6.09674	2.89259	1.42598	0.73178	0.38811
LSDISIC	6.11242	2.89714	1.42704	0.73200	0.38815
SLASICE	6.20166	2.92755	1.43623	0.73467	0.38894
2p state					
HF	7.12016	3.52619	1.79835	0.94419	0.50781
KS	7.16950	3.54330	1.80370	0.94580	0.50830
LSDSICA	7.17605	3.54742	1.80529	0.94633	0.50846
LSDSICE	7.20207	3.55642	1.80832	0.94732	0.50879
LSDISIC	7.16879	3.54351	1.80367	0.94573	0.50826
SLASICE	7.10697	3.52070	1.79589	0.94319	0.50744
density					
HF	6.92931	3.39210	1.71328	0.89359	0.47866
KS	6.92931	3.39210	1.71328	0.89359	0.47866
LSDSICA	6.91227	3.38510	1.71074	0.89274	0.47838
LSDSICE	6.92574	3.39046	1.71274	0.89344	0.47862
LSDISIC	6.90469	3.38192	1.70951	0.89230	0.47823
SLASICE	6.88064	3.37241	1.70598	0.89106	0.47782

Tables 23-25 list the $<r>_i$, $<r^2>_i$ and $<1/r>_i$ (i = 1s, 2p, n(r)) values. Table 26 shows the overlap integral values for k = 10. From these Tables, it might be difficult to judge which scheme produces

Table 24: Orbital expectation values $<r^2>$ for harmonic oscillator systems(in a.u.).

k	0.01	0.1	1	10	100
1s state					
HF	45.03157	10.1658	2.45382	0.64092	0.17917
KS	43.16649	9.84232	2.40197	0.63268	0.17782
LSDSICA	42.37042	9.64541	2.36382	0.62595	0.17666
LSDSICE	42.07161	9.61192	2.36039	0.62561	0.17663
LSDSICI	42.27184	9.64020	2.36370	0.62596	0.17666
SLASICE	43.17153	9.79461	2.38749	0.62957	0.17723
2p state					
HF	54.72023	13.51921	3.53638	0.97868	0.28380
KS	55.34193	13.62704	3.55367	0.98143	0.28425
LSDSICA	55.60332	13.68450	3.56411	0.98320	0.28455
LSDSICE	55.97064	13.74819	3.57517	0.98513	0.28489
LSDSICI	55.36977	13.63615	3.55492	0.98152	0.28425
SLASICE	54.56055	13.48554	3.52836	0.97692	0.28345
n-density					
HF	52.29807	12.68086	3.26574	0.89424	0.25764
KS	52.29807	12.68086	3.26574	0.89424	0.25764
LSDSICA	52.29510	12.67473	3.26404	0.89389	0.25758
LSDSICE	52.49588	12.71412	3.27147	0.89525	0.25782
LSDSICI	52.09529	12.63716	3.25711	0.89263	0.25735
SLASICE	51.71329	12.56281	3.24314	0.89008	0.25689

the $\psi_i(r)$ and n(r) that more closely approximate to the HF results. However, if we calculate the expectation values of the HF total energy, it turns out that the LSDSICI wavefunctions give the E_{tot} that

Table 25: Orbital expectation values $<1/r>$ for harmonic oscillator systems(in a.u.).

k	0.01	0.1	1	10	100
1s state					
HF	0.18569	0.40717	0.85206	1.69398	3.23164
KS	0.19088	0.41447	0.86086	1.70367	3.24182
LSDSICA	0.19807	0.42670	0.87768	1.72376	3.26397
LSDSICE	0.19912	0.42772	0.87850	1.72434	3.26434
LSDSICI	0.19852	0.42695	0.87777	1.72378	3.26396
SLASICE	0.19293	0.41916	0.86850	1.71377	3.25363
2p state					
HF	0.15488	0.31539	0.62244	1.19077	2.22018
KS	0.15315	0.31296	0.61950	1.18754	2.21679
LSDSICA	0.15388	0.31373	0.62031	1.18841	2.21770
LSDSICE	0.15317	0.31274	0.61905	1.18691	2.21603
LSDSICI	0.15349	0.31341	0.62011	1.18833	2.21772
SLASICE	0.15545	0.31629	0.62383	1.19269	2.22252
n-density					
HF	0.16258	0.33834	0.67984	1.31657	2.47305
KS	0.16258	0.33834	0.67984	1.31657	2.47305
LSDSICA	0.16493	0.34197	0.68465	1.32225	2.47927
LSDSICE	0.16466	0.34149	0.68391	1.32127	2.47811
LSDSICI	0.16475	0.34180	0.68453	1.32219	2.47928
SLASICE	0.16482	0.34201	0.68500	1.32296	2.48029

are most close to the exact HF values(see Table 27). In addition, if we study Figs. 14-16, in which the differences $r \times (R_i^{df}(r) - R_i^{hf}(r))$ and $r^2 \times (n^{df}(r) - n^{hf}(r))$ are shown as a function of r, we can see

Table 26: Overlap integrals of the HF and SIC wavefunctions for harmonic oscillator systems with k=10(8 electrons).

nl	LSDSICA	LSDSICE	LSDSICI	SLASICE
1s	0.999863	0.999857	0.999863	0.999933
2p	0.999992	0.999985	0.999996	0.999990

that the LSDSICI wavefunctions are in general having the smallest deviations from the HF results. We can also see from the graphs that the differences of the deviations from the three LSDSIC schemes are mainly in the 2p states, those in the 1s state are so small that it is difficult to distinguish from each other.

In Table 28, we list the HF expectation values of the HF single particle eigenvalues for both the 1s and 2p states. As in the atomic case, they give a very good approximation to the exact ε_i^{hf}, but here an interesting result is that among all the LSDSIC results, the ε_{2p} from the LSDSICE method stands particularly accurate.

In Figure 17 we show the exchange potentials from the three SIC schemes as well as the effective HF exchange potential for the lowest 2p state with oscillator strength of k=10. We see from this graph how the LSDSICI mimics the HF in the region where the orbital density is large. This, we believe, is the main reason that the direct calculated

Table 27: HF total energy expectation values for harmonic oscillator systems(in a.u.).

k	0.01	0.1	1	10	100
HF	5.86236	13.57516	32.92404	84.58465	230.48278
KS	5.86326	13.57647	32.92567	84.58644	230.48471
LSDSICA	5.86415	13.57793	32.92766	84.58882	230.48734
LSDSICE	5.86449	13.57839	32.92818	84.58938	230.48792
LSDSICI	5.86413	13.57782	32.92746	84.58856	230.48704
SLASICE	5.86310	13.57639	32.92577	84.58675	230.48519

ε_{2p} from the LSDSICI are so close to the HF values. It can also be seen from the graph that the three potentials are all too large compared to the HF near the origin. This is due to the fact that the orbital density is zero there and thus the self-exchange in the LSD expression vanishes whereas the corresponding self-coulomb term is not. However, this difference does not significantly affect the p state solution because of the nullness of the p state there.

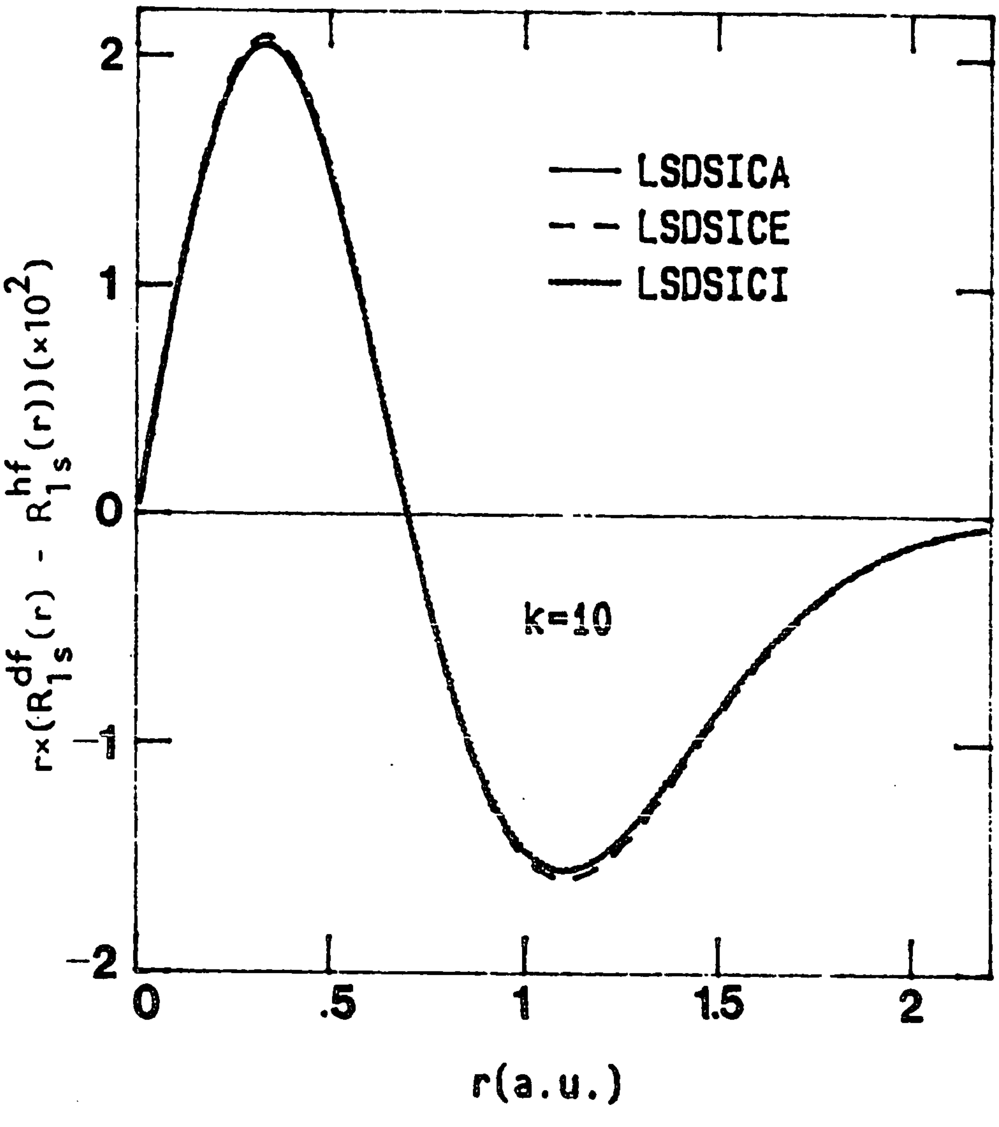

Figure 14: The deviations of the LSDSICA, LSDSICE and LSDSICI 1s wavefunctions from the HF for the harmonic oscillator system with k=10

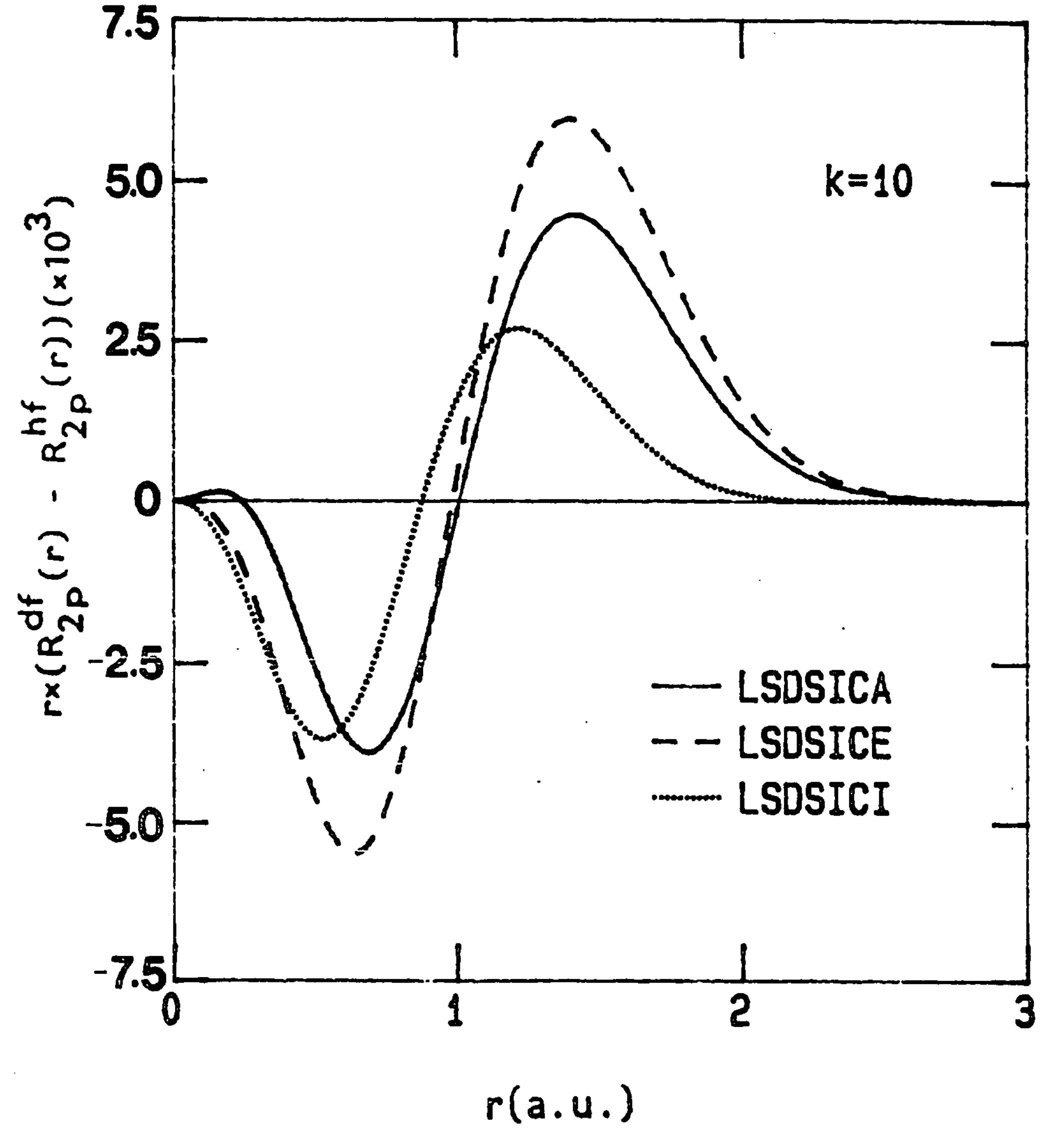

Figure 15: The deviations of the LSDSICA, LSDSICE and LSDSICI 2p wavefunctions from the HF for the harmonic oscillator system with k=10

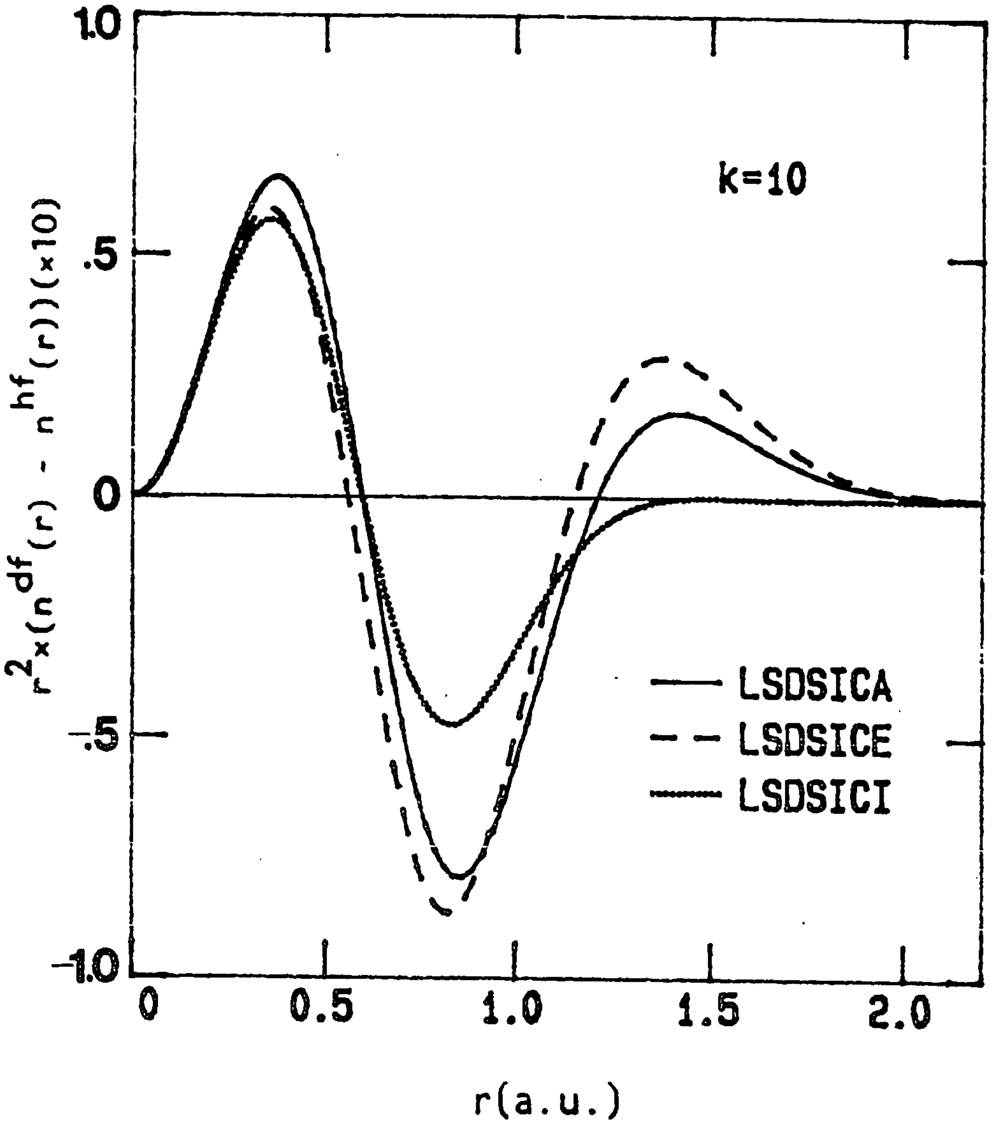

Figure 16: The deviations of the LSDSICA, LSDSICE and LSDSICI electron density from the HF for the harmonic oscillator system with k=10

Table 28: Expectation values of the HF single particle eigenvalue for harmonic oscillator systems(in Ry.).

k	0.01	0.1	1	10	100
1s atate					
HF	1.09730	2.37667	5.21288	11.78827	28.06201
KS	1.09654	2.37552	5.21141	11.78660	28.06022
LSDSICA	1.09762	2.37764	5.21472	11.79092	28.06525
LSDSICE	1.09655	2.37583	5.21205	11.78746	28.06116
LSDSICI	1.09810	2.37844	5.21595	11.79257	28.06725
SLASICE	1.10003	2.38175	5.22087	11.79898	28.07479
2p state					
HF	1.17080	2.61379	6.01575	14.51644	37.18287
KS	1.17146	2.61480	6.01703	14.51789	37.18443
LSDSICA	1.17228	2.61650	6.01965	14.52124	37.18826
LSDSICE	1.17165	2.61542	6.01804	14.51914	37.18579
LSDSICI	1.17284	2.61733	6.02080	14.52269	37.18995
SLASICE	1.17387	2.61905	6.02337	14.52609	37.19398

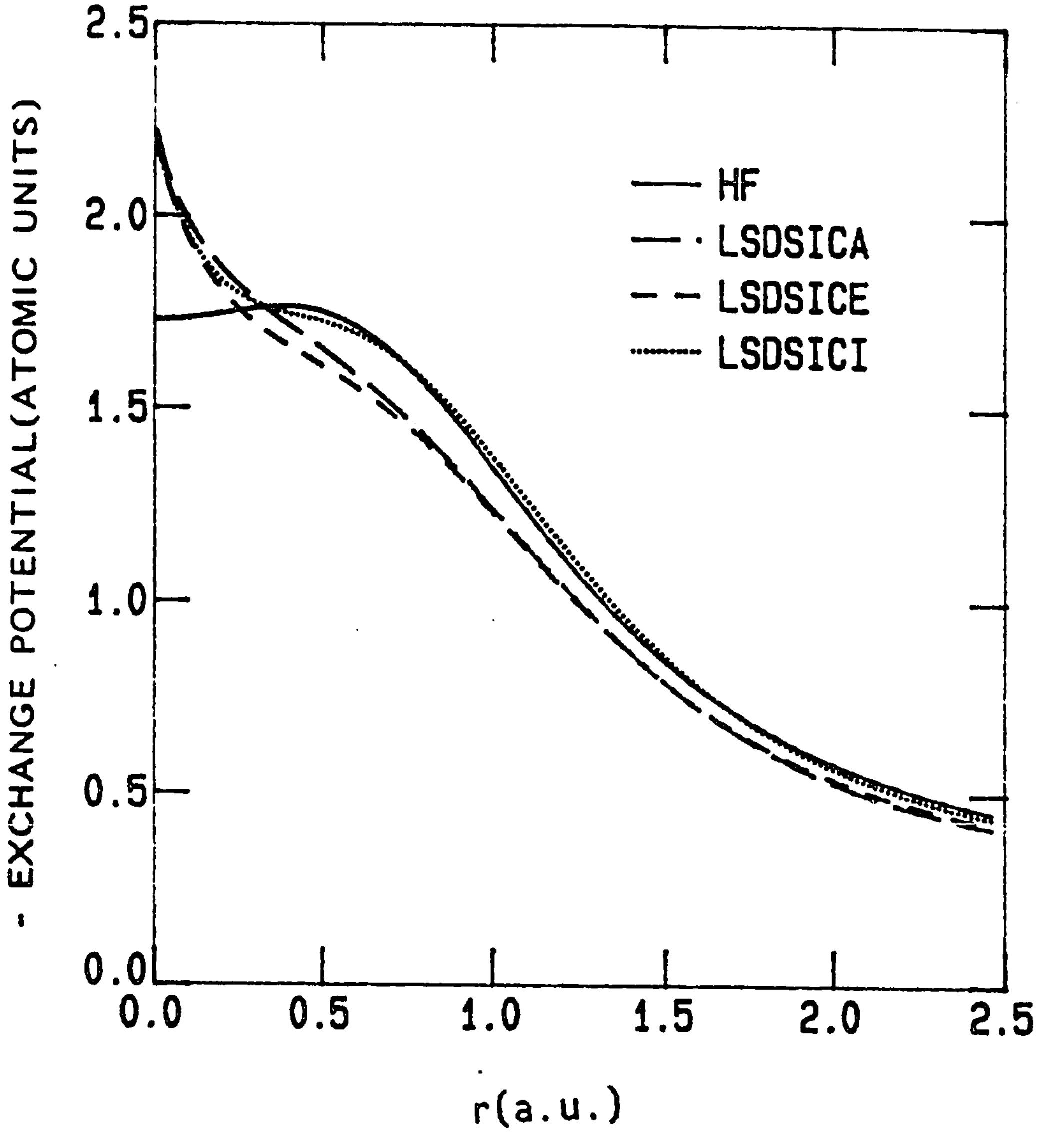

Figure 17: Comparison of the LSDSICA, LSDSICE and LSDSICI exchange potentials with the HF. The graphs are for the 2p states of the harmonic oscillator system with eight electrons.

3.5 Comparison of the LSDSIC and the SLASIC with HF

In view of the fact that many solid state calculations using the Xα method [37] [38] [39] [40] employ α which lie between the KS value α = 2/3 and the Slater value α = 1, it is interesting to study what results will be produced when one applies the SIC method to the Slater exchange.

Under SLA, the exchange potential in the Schrodinger type single particle equations assumes the following form:

$$v_x^{sla}(r) = -\kappa n(r)^{1/3}$$

where the coefficient in front of $n(r)^{1/3}$, $\kappa = -3/2((3/\pi)^{1/3}$ is 3/2 larger than the LSD values.

It is worth noting here that there is no corresponding SLA energy functional as for the LSD case. The so-called Slater total energy will be calculated by substituting the SLA wavefunctions into the LSD energy functional expression. By applying SIC to SLA we merely mean to write the exchange potential v_x^{sla} as:

$$v_x^{slasic(j)} = v_x^{sla}([n_\uparrow,n_\downarrow],r) - \{v_h([n_{nl}],r)+v_x^{sla}([n_{nl},0],r)\} \quad (3.13)$$

where (j) can be written in different forms as described in the previous sections, i.e., the SLASICA, SLASICE and SLASICI.

Using these expressions for the v_x^{sla}, we have solved the corresponding Schrodinger type equations self-consistently for both the atoms and the oscillator problems. Our calculations show that in all cases the results from the SLASICE are in general always superior to the other two when compared to the HF. So, in the following discussions of SLA exchange, we will show only those results obtained from the SLASICE scheme.

3.5.1 Results and Discussion

Most surprisingly, with the SLASICE scheme, the direct calculation of the outermost single particle eigenvalues for the noble gases and for the harmonic oscillators(in both cases they are corresponding to p states) turn out to be extremely close to the HF results. However, the ε_{max}, when they are not corresponding to the p or d states, are poorer than those given by the LSDSIC type calculations as compared to the HF values. These facts can be seen from Table 11, where we list all the ε_{max} calculated from the different schemes for both the atoms and the oscillator systems. Moreover, as we have observed in Chapter 2 for the SLA without SIC for the oscillator problem, the SLASICE ε_i of the inner orbitals are in general also closer to the ε_i^{hf} than are the ε_i obtained from the LSDSIC type calculations (see Tables 14-15). In addition, for atomic systems, even the direct calculation of the total energy using this meth-

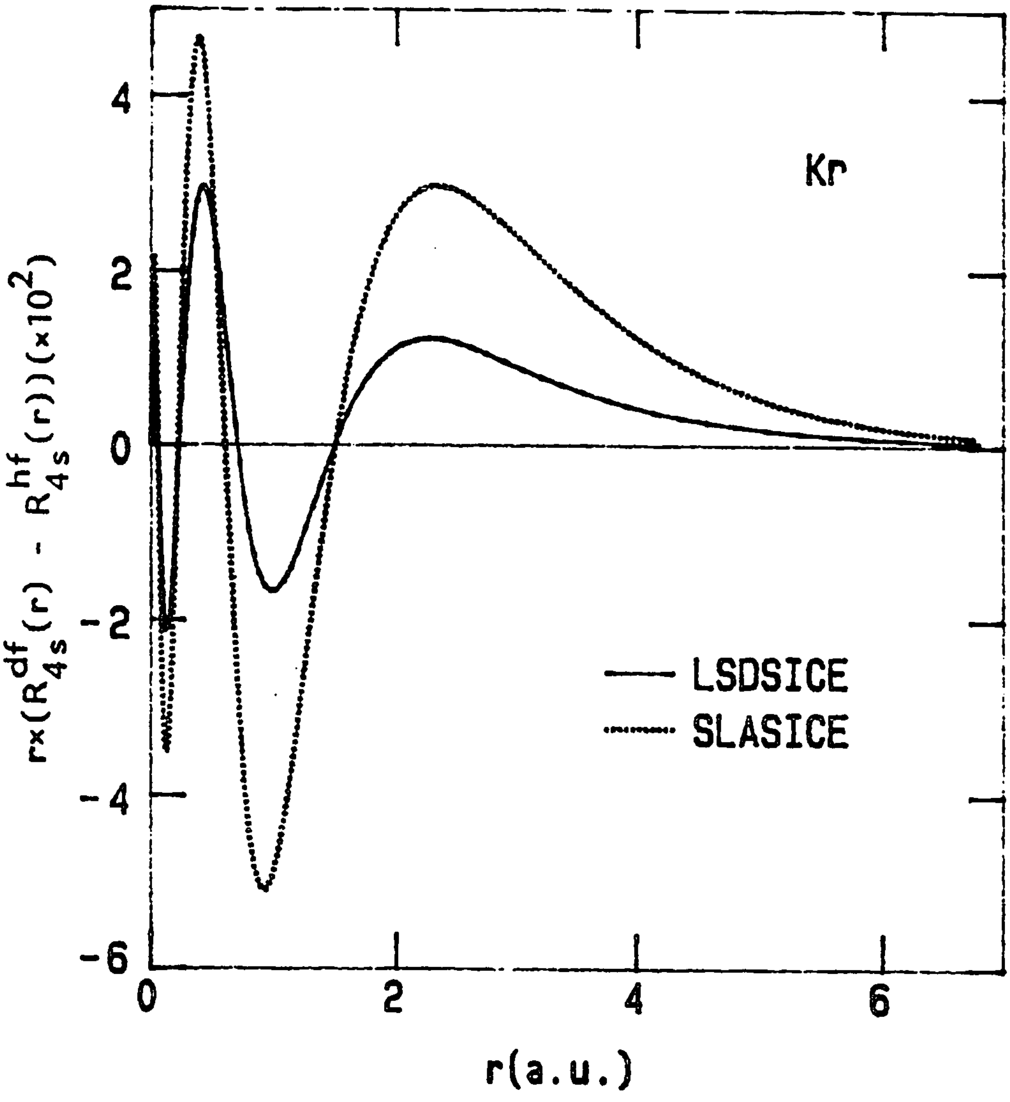

Figure 18: The deviations of the LSDSICA and SLASICE 4s wave-functions from the HF for the Kr atom

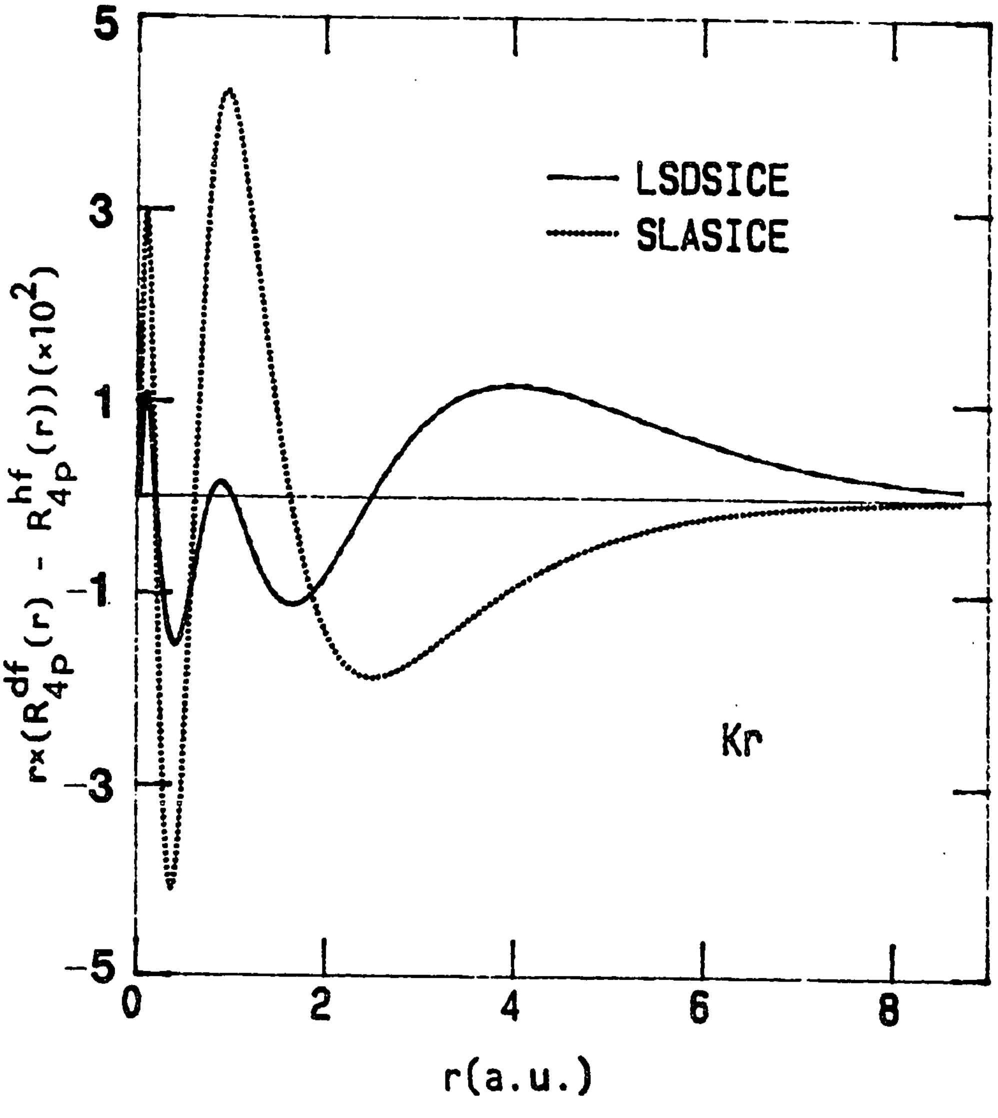

Figure 19: The deviations of the LSDSICA and SLASICE 4p wavefunctions from the HF for the Kr atom

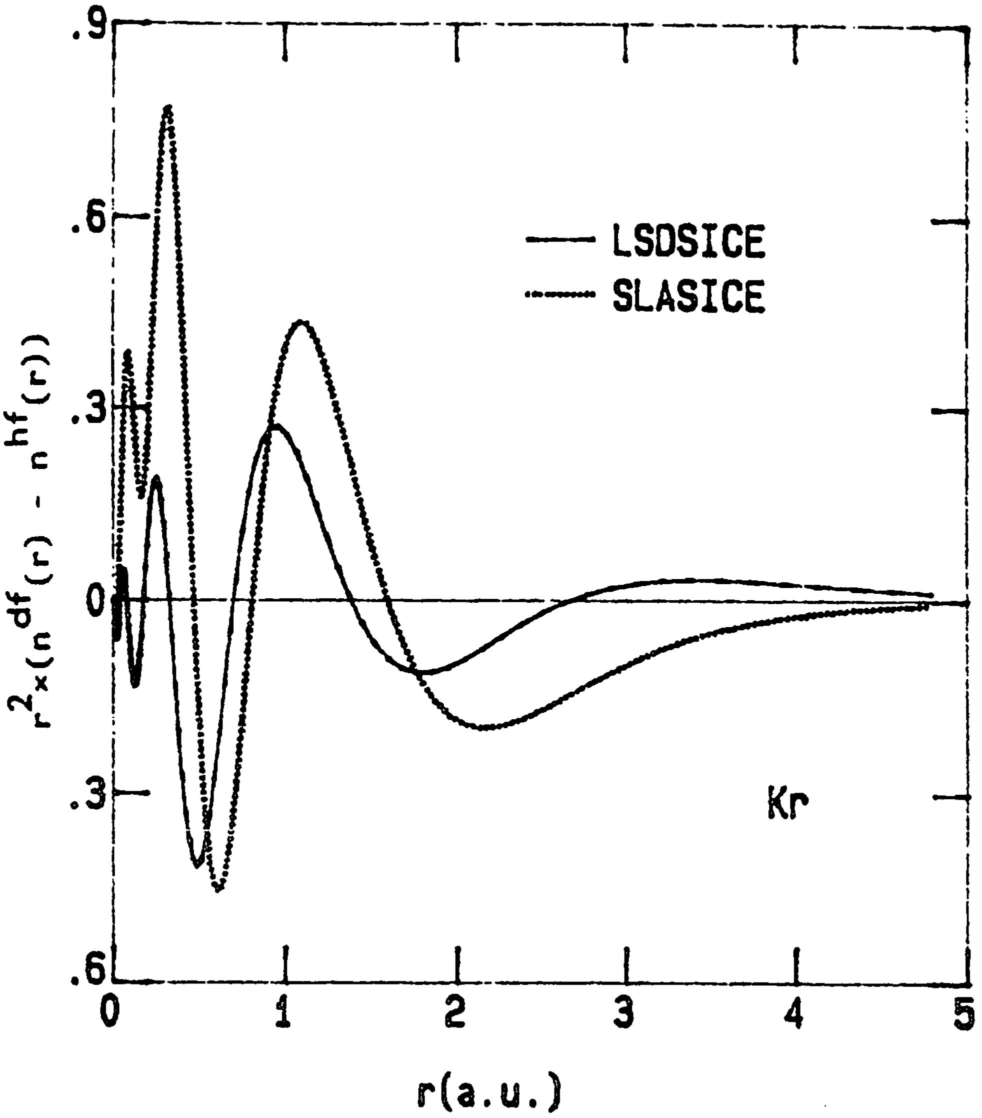

Figure 20: The deviations of the LSDSICA and SLASICE electron density from the HF for the Kr atom

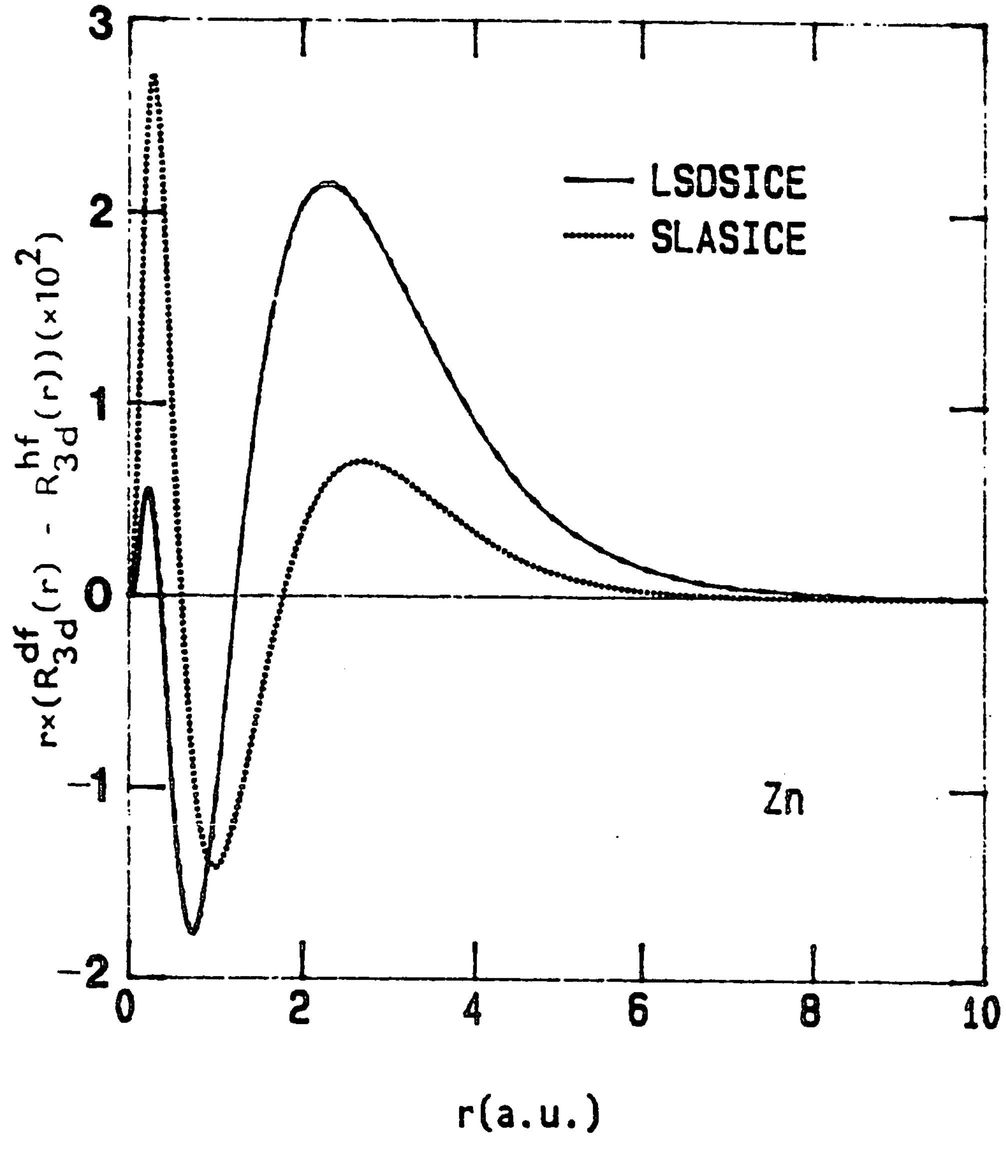

Figure 21: The deviations of the LSDSICA and SLASICE 3d wavefunctions from the HF for the Zn atom

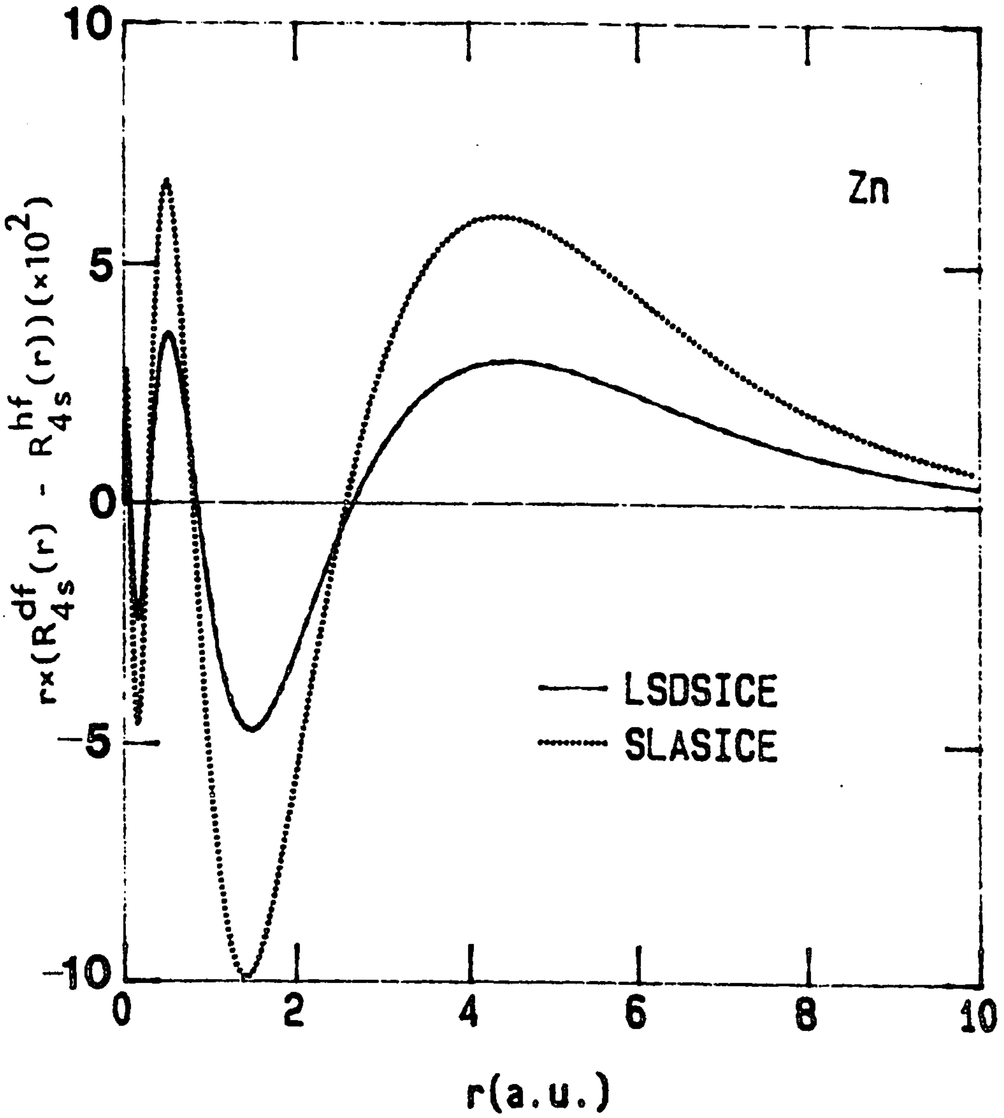

Figure 22: The deviations of the LSDSICA and SLASICE 4s wavefunctions from the HF for the Zn atom

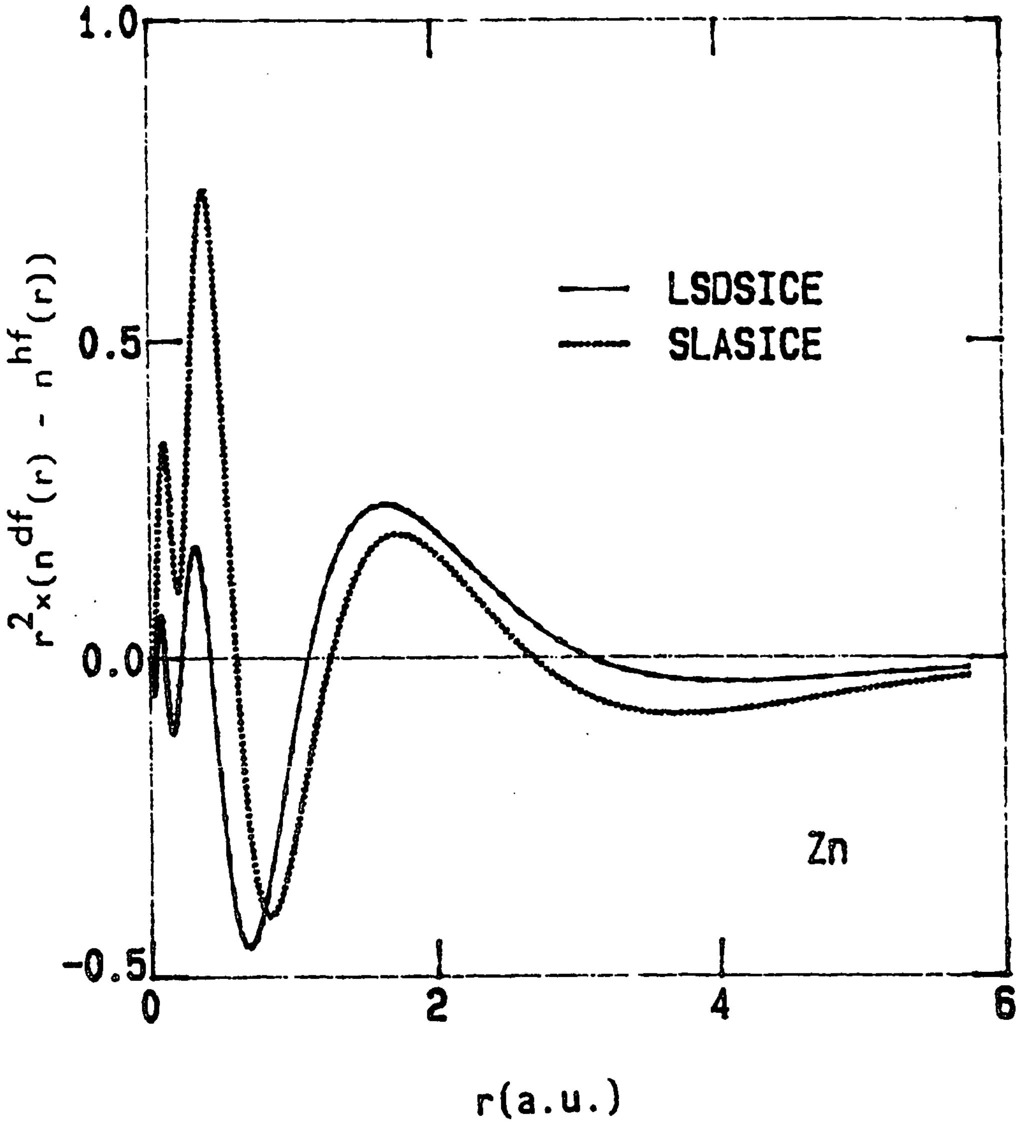

Figure 23: The deviations of the LSDSICA and SLASICE electron density from the HF for the Zn atom

od turns out to be very close to the HF results(although the definition for the SLASIC type E_{tot} may be ambiguous as discussed earlier). Such accuracy for the SLASICE E_{tot} is of course due to the fact that when we calculate the SLASICE E_{tot} we use the LSDSICE energy expression. As can be seen from Table 9, most of the LSDSICE E_{tot}(in fact the light atoms) are slightly too negative compared to the HF E_{tot}. According to the variational principle the SLASICE E_{tot} are always less negative than the LSDSICE E_{tot}. As a result, some of the SLASICE E_{tot}(light atoms) are even more close to the HF E_{tot} than those given by the LSDSICE method. However, the LSASICE E_{tot} for oscillator systems are very poor since the LSDSICE E_{tot} are too large which make the former even larger.

In Tables 16-19, 23-26, we have the $<r>_i$, $<r^2>_i$, $<1/r>_i$ values and the overlap integrals for both the atoms(Kr and Zn) and oscillator systems.

For atoms, it is seen from the Tables that the $<r^n>$ averages from the SLASICE are in general all significantly poorer than the corresponding LSDSIC type calculations especially those of the outer orbitals. The SLASICE overlap integrals are also slightly poorer than those given by the LSDSIC although they are also very close to one. These may be indications that the quality of its wavefunctions for atoms is poorer. One can further confirm this point when examining

Figs. 18-23 from which it is observed that the deviations of the SLASICE wavefunctions and density are significantly larger than the LSDSIC type wavefunctions and density. Because of the poorer quality of the SLASICE atomic wavefunctions, the expectation values of the HF total energy of the SLASICE are significantly higher than the corresponding LSDSIC type calculations(See Table 20). In addition, the expectation values of the HF single particle eigenvalues ε_i(including ε_{max} for the noble gases) are also gravely worsened from the exact HF than the LSDSIC ε_i although the direct SLASICE ε_i are in general closer to the ε_i^{hf} than the LSDSIC ε_i(refer to Table 21).

The result that the SLASICE HF expectation values ε_i are poorer than the LSDSIC ε_i could be understood when one considers the following:

$$\varepsilon_i = <\psi_i|h_i|\psi_i>$$

where h_i is the HF single particle hamiltonian operator for the ith state

$$h_i = -(1/2)\nabla^2 + v(r) + v_h(r) + v_{x,i}(r)$$

$$\delta\varepsilon_i = <\delta\psi_i|h_i|\psi_i> + <\psi_i|\delta h_i|\psi_i> + <\psi_i|h_i|\delta\psi_i> + O(\delta\psi_i)^2$$

$$= <\psi_i|\delta h_i|\psi_i> + \varepsilon_i\delta<\psi_i|\psi> + O(\delta\psi_i)^2$$

$$= \langle\psi_i|\delta h_i|\psi_i\rangle + O(\delta\psi_i)^2$$

since in the h_i, the $-(1/2)\nabla^2$ and v are independent of the density n(r), therefore

$$\delta h_i = \delta v_h + \delta v_x$$

we know $v_h >> v_x$ for system with a large number of electrons.

So $\delta h_i \simeq \delta v_h$

thus, $\delta\varepsilon_i \simeq \langle\psi_i|\delta v_h|\psi_i\rangle$

An examination of the separate contributions of each term in the calculation of ε_i shows that this conclusion is correct i.e. the error in ε_i is essentially equal to the difference between the expectation value of the Hartree potential as compared to the v_h in the HF approximation.

If we study Figs. 24-25, in which the differences of the v_h for the Kr and Zn atoms of various DFT from the HF are drawn, it is then quite clear that because of the significant difference of the $v_h^{slasice}$ from the v_h^{hf}, the $\varepsilon_i^{slasice}$ is very far away from the ε_i^{hf} Thus, although the overlap integrals of the SLA orbitals with the HF orbitals are just slightly farther away from unit than those of the

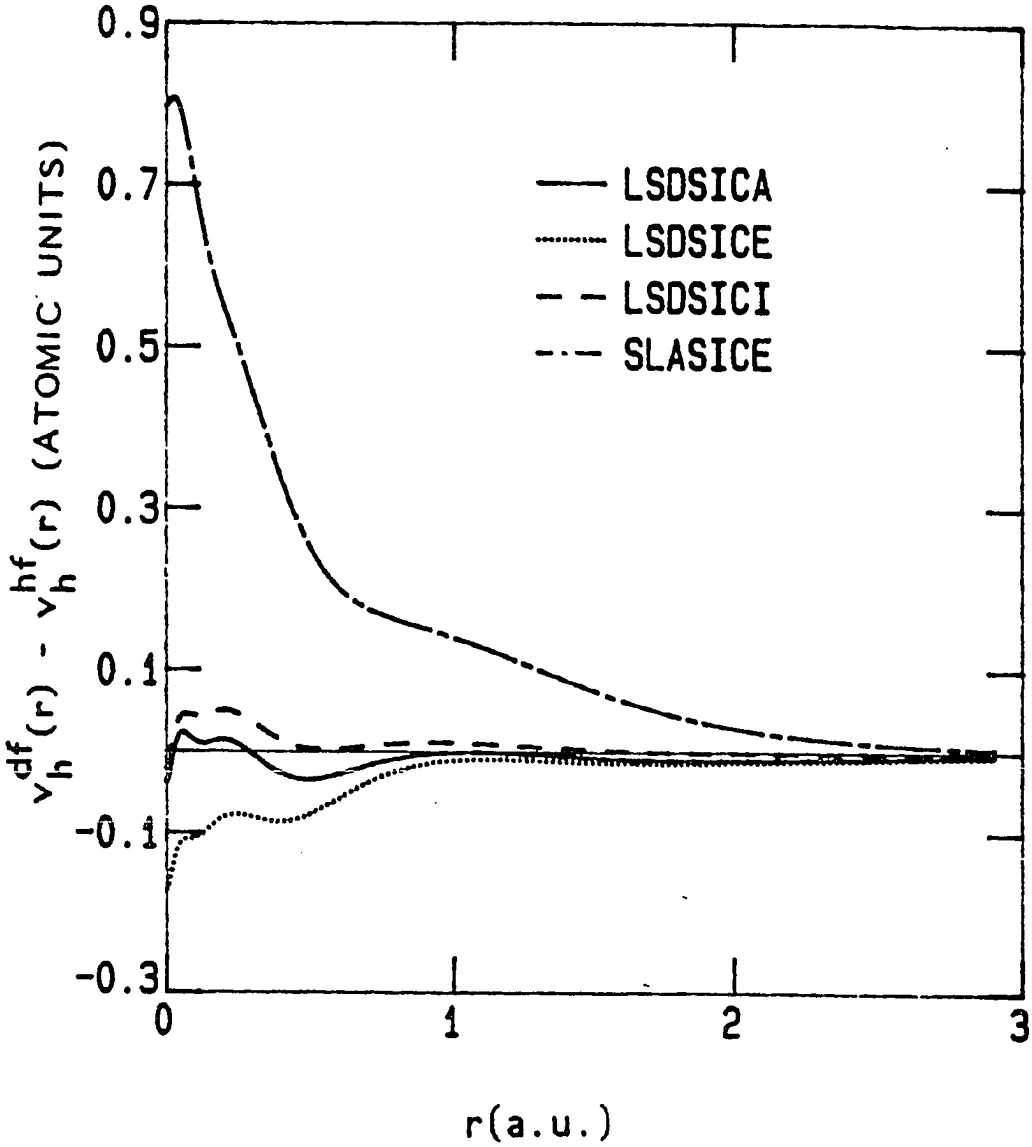

Figure 24: The deviations of the LSDSICA, LSDSICE, LSDSICI and SLASICE Hartree potentials with that of the HF for the Kr atom.

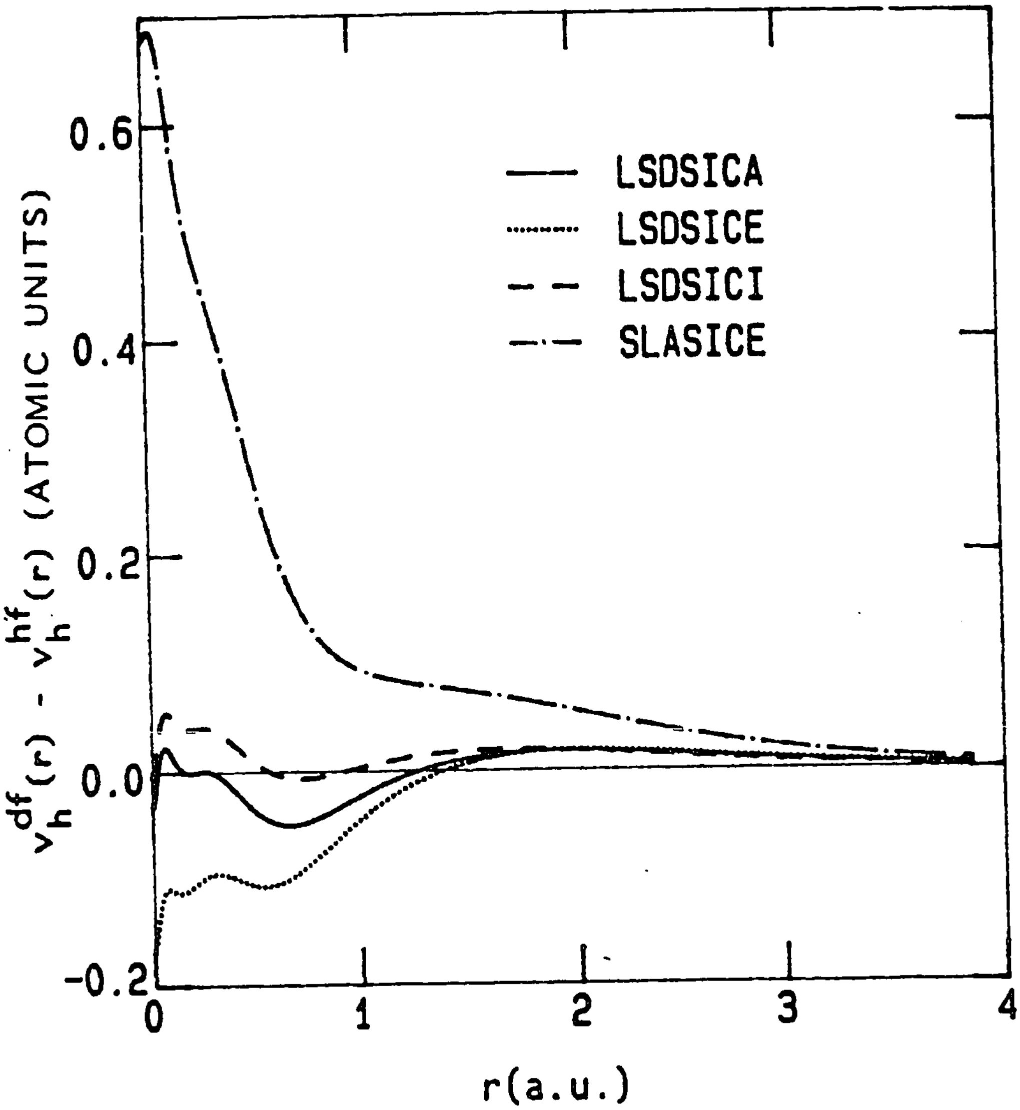

Figure 25: The deviations of the LSDSICA, LSDSICE, LSDSICI and SLASICE Hartree potentials with that of the HF for the Zn atom.

LSDSIC results, the v_x^{sla} gives rise to forces which are systematically too concentrated around the nucleus. This results in the $v_h^{slasice}$ being too large everywhere with the consequent raising of all the ε_i.

For harmonic oscillator systems, however, some peculiar results occur which make the results for this system very different from the atomic case. Among them, the most notable facts are 1) the SLASICE $<r^n>$ averages for the individual orbitals are closer to the HF results than those given by the LSDSIC. The overlap integrals are also closer to one. If we study Figs. 26-28, it can be seen that the SLASICE wavefunctions and density have smaller deviations than those of the LSDSIC. However, the SLASICE $<r^n>$ average values over the density turn out to be poorer because of the fact that although individual orbital SLASICE $<r^n>$ are closer to the HF values, the errors all have the same sign, whereas in the LSDSIC case the errors alternate in sign so that some of the errors are cancelled out. 2) From Table 10, it is seen that the fact that the SLASIC wavefunctions more closely approximate those of HF that the expectation values of the HF total energy are significantly more accurate than those obtained by using the LSDSIC wavefunctions.

One thing that is in common with the atomic problems is the result that the expectation values of the HF single particle eigenvalues are poorer than those given by the LSDSIC(see Table 28). As in the atomic case, the $v_h^{slasice}$ is to large everywhere as shown in Figure 29. As a result the expectation values of the HF single particle energy eigenvalue ε_i using the SLASICE orbitals are systematically too large and are in error by approximately the errors in the expectation values of the Hartree potential.

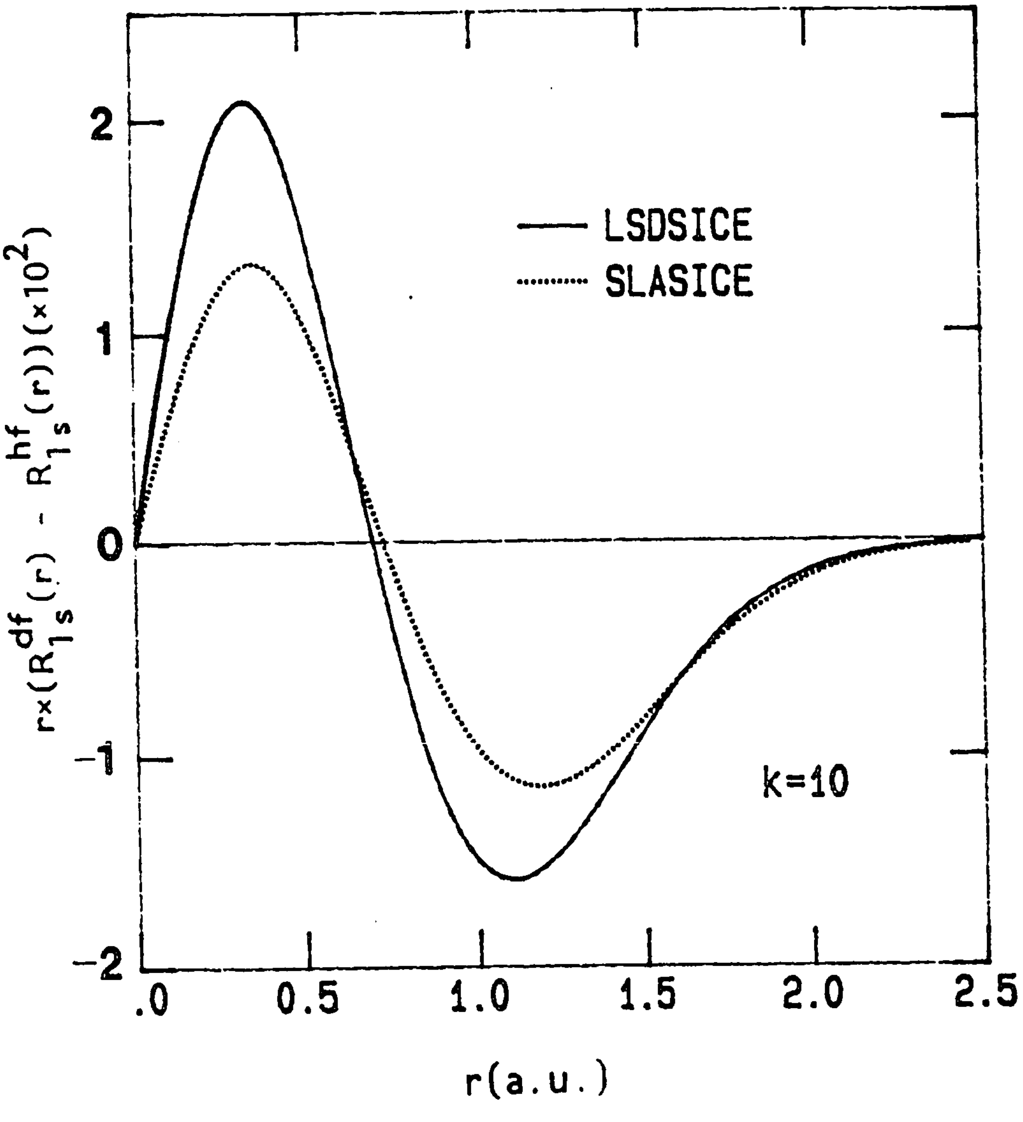

Figure 26: The deviations of the LSDSICA and SLASICE 1s wavefunctions from the HF for the harmonic oscillator system of k=10

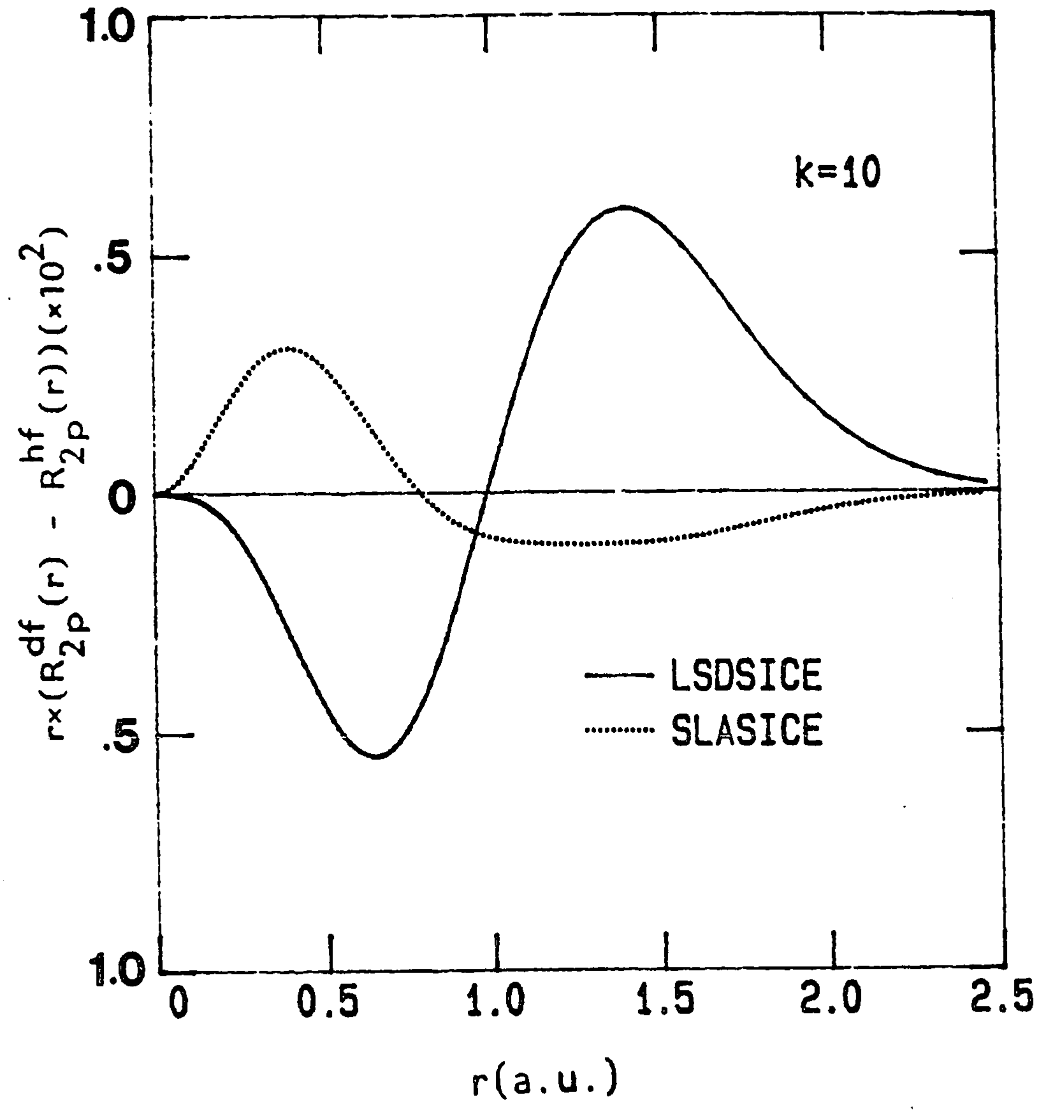

Figure 27: The deviations of the LSDSICA and SLASICE 2p wavefunctions from the HF for the harmonic oscillator system of k=10

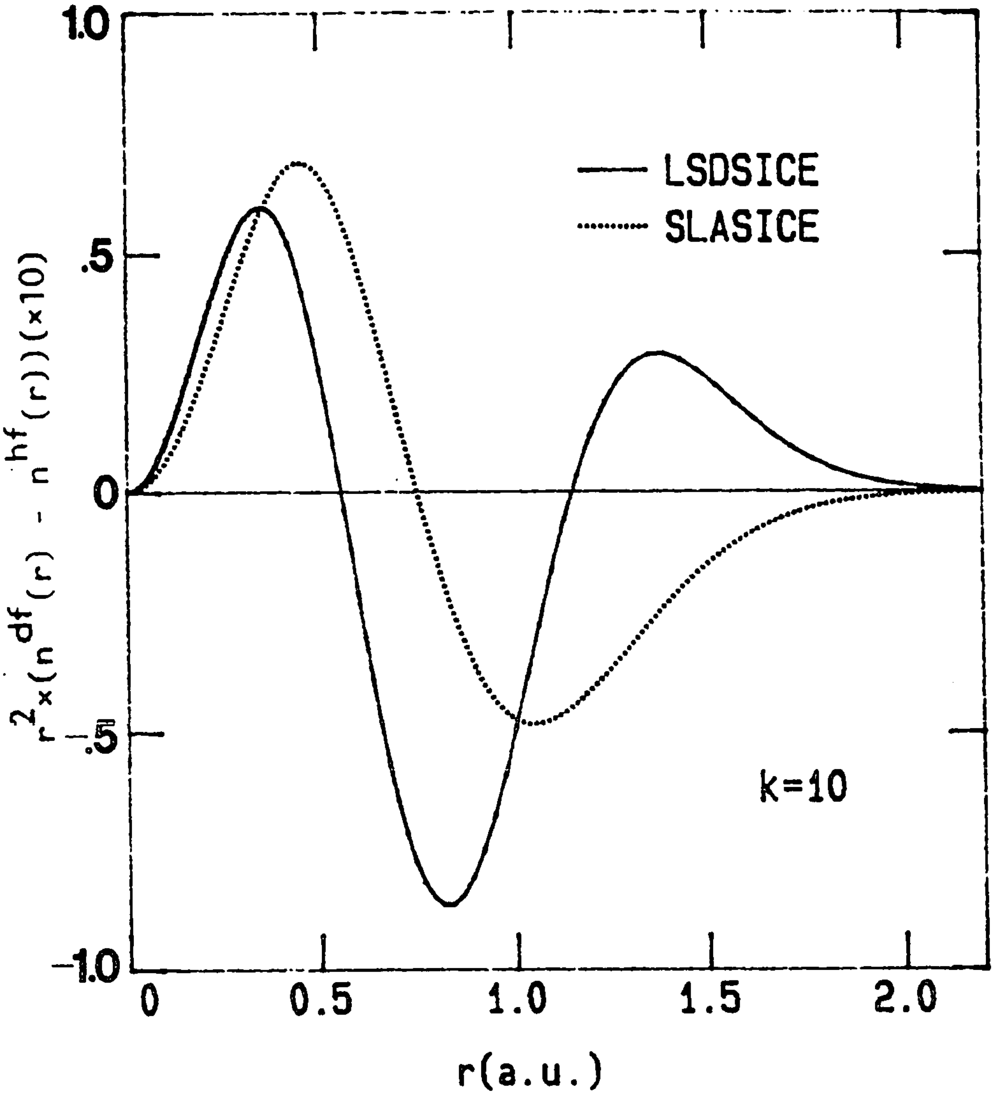

Figure 28: The deviations of the LSDSICA and SLASICE electron density from the HF for the harmonic oscillator system of k=10

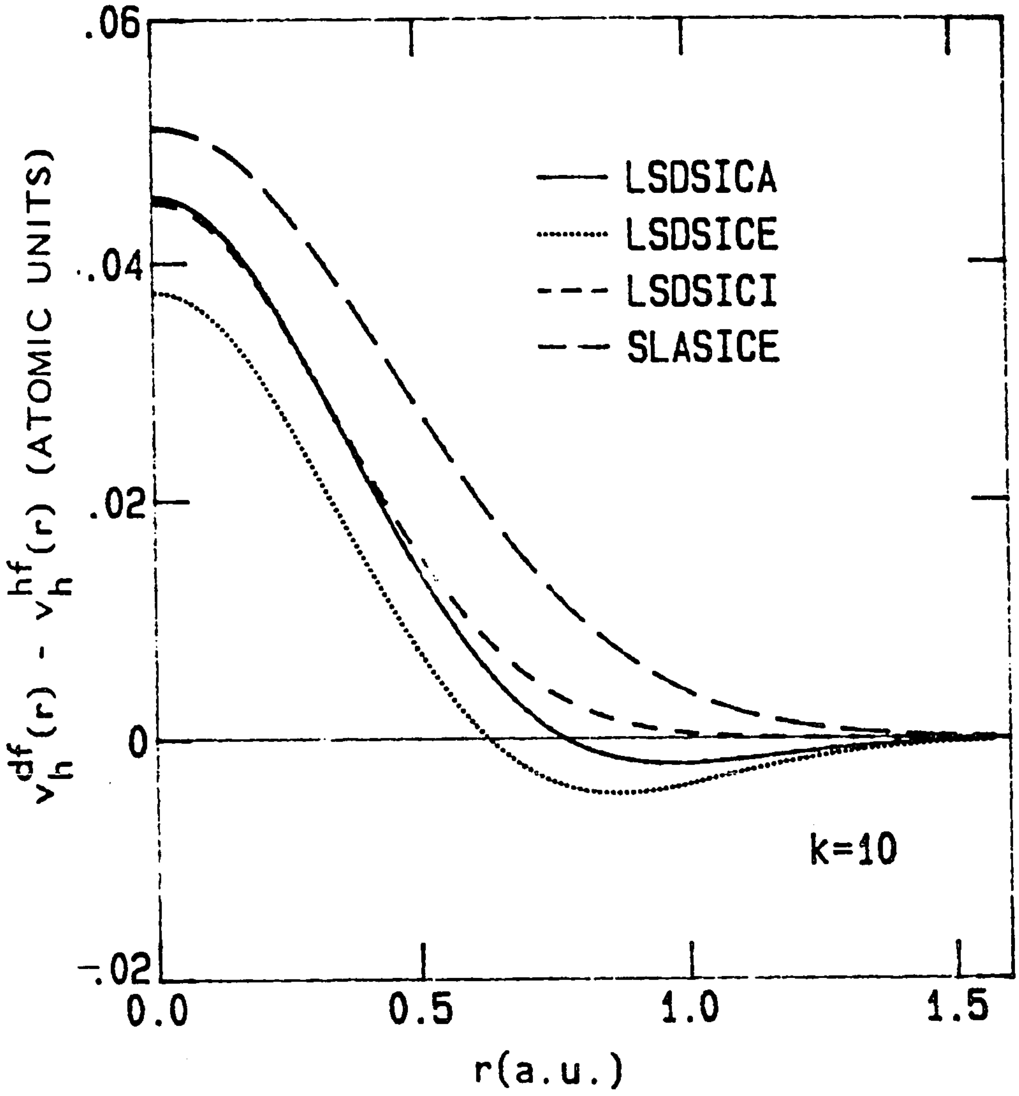

Figure 29: The deviations of the DFT and SLASICE Hartree potentials with that of the HF for the harmonic oscillator system of k=10

Chapter IV

Study of the Gradient Expansion Method and Beyond

The various LSDSIC approximations discussed in the previous chapter all reduced to the LSD approximation in the delocalized electron limit as found in the description of the valence and conduction band wavefunctions discribed by Bloch waves. There is currently a renewed interest in going beyond the LSD approximation for treating delocalized electron states in solids.

One such method is given by the gradient expansion technique. This method was initially proposed by Hohenberg and Kohn, who suggested that for a system with density that varies slowly over distances such as the Fermi wavelength, a non-local correction in the form of an expansion in gradients of the density can be added to the LDA, i.e., in the exchange-only case

$$E_x[n] = E_x^{l\,sd}[n] - C_x \int |\nabla n|^2 n^{-4/3} dr \qquad (4.1)$$

to order of $O(|\nabla n|^2)$.

The most controversial issue about this expression is the determination of the coefficient in front of the $|\nabla n|^2$ term, i.e. the C_x.

Herman et al [24] find its value by fitting the DFT total energy to the HF. But later, Sham derived from first principles a result that was about one fifth as large. By a more elaborate consideration, Langreth and Mehl [41] [42] concluded that C_x equals $C_{lm.} = 1.52C_s$ where

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

is the Sham result. Values of 8/7, 10/9 C_s were also reported over the years by other investigators [43] [44].

Recently, expansions have been given which express the exchange density functional beyond (4.1). Perdew and Wang [25] [26], after analyzing the exchange hole in real space, obtain a formula:

$$E_x[n] = A_x \int n^{4/3} F(\xi) dr$$

where

$$F(\xi) = (1 + 1.296\xi^2 + 14\xi^4 + 0.2\xi^6)^{1/15}$$

$$\xi = |\nabla n|/(2k_F n)$$

$$A_x = -0.73856 \text{ a.u.} \quad \text{and} \quad k_F = (3\pi^2 n)^{1/3}$$

Becke [45] and others [46] [47] have also proposed different forms for $F(\xi)$ by fitting it to the exact exchange energy-densities.

In this chapter, we will consider GEA approximations which involve only ξ^2, but start from a different consideration. We will then compare our results with the HF as well as with other versions of GEA.

4.1 Construction of Convergent GEA Potential

It is well known that the usual GEA exchange potential has an unphysical behavior that it is divergent both at the origin and at infinity. The singularity behavior of the terms involving $\nabla^2 n/n^{4/3}$ at r=0 has been formerly observed by Ma and Brueckner [48] in dealing with the correlation energy problem. Nevertheless, this singularity(at $r = 0$ as $1/r$), as pointed out by Herman et al, does not significantly influence the solutions of the wavefunctions except perhaps the s states. However, the divergence problem at infinity does greatly affect the final results and must be removed before a reasonable solution can be obtained. The common practice which was first employed by Herman et al, is to multiply the v_x by a a convergent factor which, when expanded for small ξ, gives the original expression but for large r makes the original expression convergent.

If, however, we recall that the GEA is valid only for slowly varying density or small ξ, we realize that there are actually an infinite number of possibilities in choosing the GEA forms which, when expanded for small ξ, give the usual expression but are otherwise different from (3.1). The simplest form may be the following

$$E_x[n] = \int n(r)\varepsilon_x[n]dr = A_x\int n^{4/3}(1 + B_x\xi^2/\alpha)^\alpha dr \qquad (4.2)$$

with the relationship for A_x, B_x and the C_x mentioned previously such that

$$C_x = A_xB_x \qquad (4.3)$$

the corresponding exchange potential is:

$$v_x(r) = \delta E_x[n]/\delta n$$

or

$$v_x[n(r)] = v_x^{(1)}[n(r)] + v_x^{(2)}[n(r)] \qquad (4.4)$$

$$v_x^{(1)}[n(r)] = v_x^{1\,da}[n(r)]f^\alpha[n(r)]$$

$$v_x^{(2)}[n(r)] = -v_x^{1\,da}[n(r)](3B_x/2n^{5/3})f^{\alpha-1}[n(r)]g[n(r)]$$

where

$$v_x^{1\,da}[n(r)] = -(3/\pi)^{1/3}n^{1/3}(r)$$

is the LSD exchange potential and

Table 29: Comparisons of the exchange energy calculations between the usual GEA and the new GEA.

The calculations are performed with the HF densities. GEAO, LMO are the usual GEA and LM results quoted from [26], GEAN and LMN mean the new GEA form i.e. Eq.(4.2), with $\alpha = 1/2$. These notations will only be used here. Listed are the negative of the exchange energy values and in atomic units.

Atom	HF	GEAO	GEAN	LMO	LMN
Be	2.67	2.50	2.49	2.60	2.58
Ne	12.11	11.55	11.52	11.82	11.80
Ar	30.19	28.86	28.83	29.39	29.34
Zn	69.70	67.36	67.33	68.25	68.21
Kr	93.9	90.7	90.7	91.8	91.8
Xe	179.1	173.9	173.8	175.6	175.6

$$f[n(r)] = 1 + B_x|\nabla n|^2/(\alpha n^{8/3})$$

$$g[n(r)] = \nabla^2 n + 2(1-\alpha)f^{-1}[n(r)]\{1-f[n(r)]\}\{n''-4n'^2/(3n)\}$$

with

$$n' = dn/dr$$

$$n'' = d^2n/d^2r$$

No matter what values we chose for α, when Eq.(4.2) expanded for small ξ Eq.(4.1) is always recovered. In particular, we can chose the value of α such that both v_x and ε_x are finite at infinity. We find the largest such value for α is 1/2. i.e. both ε_x and v_x will converge at the infinity limit for $\alpha \leq 1/2$(Refer to Appendix D for the derivation and proof). Unfortunatly, no value can remove the divergence at $r = 0$.

Our actual calculations show this method can produce almost identical results as the usual GEA when $C_x = C_s$ and LM when $C_x = C_{LM}$ with $\alpha = 1/2$ for both cases(see Table 29). For α less than 1/2, however, the results get poorer when compared with the HF. So, in the following discussion, when we use the expressions GEA and LM we will mean the expression (4.2) with the corresponding coefficients C_s and C_{lm} and the value of $\alpha = 1/2$.

4.2 Applying SIC to GEA

Perdew and Zunger [22] suggested the application of the SIC method to the GEA, but to our knowledge, no such calculations have been performed. In view of the fact that LSDSIC is quite successful in improving the LSD , it is indeed a quite enticing problem to pursue.

With SIC applied to the GEA, the exchange energy functional becomes:

$$E_x[n_\uparrow,n_\downarrow] = E_x^{gea}[n_\uparrow,n_\downarrow] - \Sigma_{\alpha\sigma}\delta_{\alpha\sigma} \tag{4.5}$$

with

$$\delta_{\alpha\sigma} = U[n_{\alpha\sigma}] + E_x^{gea}[n_{\alpha\sigma},0]$$

and the exchange potential is derived as:

$$v_x(r) = v_x^{gea}([n_\uparrow,n_\downarrow],r) - v_h[n_{\alpha\sigma}] - v_x^{gea}([n_{\alpha\sigma},0],r) \tag{4.6}$$

with v_x^{gea} expressed as Eq.(4.4).

Once again, our new expression for the exchange energy shows the advantage of this formulation. In the usual expression, the inclusion of the additional SIC terms in the gradient expansions poses not only the problems of divergence at the origin and infinite limits as for the non-corrected GEA, but also that they are singular at the nodes of the single particle wavefunctions. Moreover, the latter singularity can not be removed by the simple method of multiplying by a convergent factor. This may be why the GEASIC has not previously been implemented. However, by employing our new expression, all these singularities, except at the origin, which plays no important role as we discussed earlier, are automatically avoided as long as we chose $\alpha \leq 1/5$(See Appendix D for the derivation of the α values in GEA + SIC). So, using our new GEA form, we have no ambiguities in performing the GEASIC calculations.

Table 30: Total energies from the GEASIC calculations. The HF, GEA and the LSDSICA values have also been appended(in a.u.).

Atoms($-E_{tot}$)

Atom	HF	GEA	LSDSICA	GEASIC
Be	14.5730	14.3930	14.5799	14.5685
Ne	128.547	127.976	128.862	128.709
Mg	199.615	198.847	200.031	199.806
Ar	526.818	525.476	527.607	527.071
Ca	676.758	675.236	677.684	677.021
Zn	1777.85	1775.59	1780.19	1778.78
Kr	2752.06	2748.93	2754.96	2752.95
Sr	3131.55	3128.19	3134.67	3132.44
Cd	5465.13	5460.67	5469.59	5466.14
Xe	7232.14	7226.91	7237.27	7232.95

Oscillators(8 electrons)(E_{tot})

k	HF	GEA	LSDSICA	GEASIC
.01	5.86236	5.88987	5.86781	5.87500
.1	13.5752	13.6377	13.5780	13.5940
1	32.9240	33.0519	32.9167	32.9500
10	84.5846	84.8317	84.5538	84.6196
100	230.483	230.945	230.407	230.531

Table 31: Outmost single particle eigenvalues from the GEASIC compared with the HF and LSDSICA(in Ry.)

The GEA results are not quoted here because they are just as poor as those given by LSD and are nowhere near the HF values.

Atoms($-\varepsilon_{max}$)

Atom	HF	LSDSICA	GEASIC
Be(2s)	0.6185	0.6157	0.6088
Ne(2p)	1.7008	1.6144	1.6045
Mg(3s)	0.5061	0.5118	0.5012
Ar(3p)	1.1820	1.0982	1.0374
Ca(4s)	0.3911	0.4009	0.3901
Zn(3d)	1.5651	1.4684	1.4730
(4s)	0.5850	0.6238	0.6048
Kr(4p)	1.0484	0.9682	0.9553
Sr(5s)	0.3569	0.3689	0.3579
Cd(4d)	1.5273	1.4019	1.4018
(5s)	0.5297	0.5711	0.5519
Xe(5p)	0.9146	0.8413	0.8280

Oscillators(8 electrons)(ε_{max})

k	HF	LSDSICA	GEASIC
.01	1.1708	1.1874	1.1878
.1	2.6138	2.6451	2.6462
1	6.0158	6.0729	6.0757
10	14.516	14.619	14.625
100	37.183	37.367	37.379

We have self-consistently solved the GEASIC equations for both atoms and harmonic oscillator problems. The calculations are per-

Table 32: HF expectation values for the total energies from the GEASIC calculations(in a.u.).

Atoms($-E_{tot}$)

Atom	HF	GEA	LSDSICA	GEASIC
Be	14.5730	14.5714	14.5727	14.5725
Ne	128.547	128.533	128.539	128.540
Mg	199.615	199.603	199.604	199.605
Ar	526.818	526.802	526.802	526.802
Ca	676.758	676.743	676.741	676.741
Zn	1777.85	1777.79	1777.81	1777.81
Kr	2752.06	2752.02	2752.02	2752.01
Sr	3131.55	3131.51	3131.51	3131.50
Cd	5465.13	5465.08	5465.08	5465.07
Xe	7232.14	7232.10	7232.09	7232.08

Oscillators(8 electrons)(E_{tot})

k	HF	GEA	LSDSICA	GEASIC
.01	5.86236	5.86455	5.86415	5.86369
.1	13.5752	13.5776	13.5779	13.5772
1	32.9240	33.9268	32.9277	32.9268
10	84.5846	84.5876	84.5888	84.5879
100	230.483	230.486	230.487	230.486

formed within the LSDSICA scheme, i.e. as PZ did we replace all $n_{\alpha\sigma}(r)$ by its spherical average or the radial part $n_{nl}(r)$. The total energies for atoms thus obtained are considerablly closer to the HF values than either the GEA or the LSDSICA results as can be seen from Table 30. The outermost single particle eigenvalues are in a mixed situation. For atoms having the s orbital as the highest lying state, the ε_{max}^{df} given by the GEASIC are in general improved compared to those given by the LSDSICA. The ε_{max}^{df} corresponding to the p state(or more precisely the inert gases) are slightly farther away from the ε_{max}^{hf} (see Table 31 for comparison). When examining the expectation values of the HF total energies in Table 32, it can be seen that the E_{tot} calculated from the GEASIC wavefunctions are almost identical with those obtained from using the LSDSICA wavefunctions(they are only slightly poorer than the LSDSICA results). This indicates that the quality of the GEASIC wavefunctions are as good as the LSDSICA results. At this point, it may worth noting that the expectation values of the HF E_{tot} calculated from the GEA(without SIC) wavefunctions becomes more and more accurate when the number of the electrons get larger i.e. with Z increasing the GEA E_{tot} changes from being less accurate than those of the LSDSICA for lighter atoms to the GEA E_{tot} that is more accurate than the LSDSICA results(this is in fact also the case for the results of the LSD without SIC as compared to the LSDSIC results which we did not list in this thesis).

The results for the harmonic oscillator systems are, however, not so encouraging. The direct calculations of both the E_{tot} and the ε_{max}^{df} are poorer than those given by the LSDSICA(they are nevertheless, still better than the GEA alone results). One thing that is the best for the GEASIC, among the others, the GEA and LSDSICA, perhaps is the result that the expectation values of the HF E_{tot} calculated from its wavefunctions are closer to the HF values.

4.3 Fitted GEA potentials

As stated at the beginning of this chapter, the theoretically derived value for the coefficient of the first gradient correction term is found to be approximately a factor five too small to give accurate results when compared with the HF. Now that we have a different expression for the GEA which reduces to the usual GEA only in the limit of small $\xi \equiv |\nabla n|/(2k_F n)$, it is interesting to ask what value its coefficient should have in order to fit the HF results.

For atomic problems we find this value varies from $2.19C_s$ for Be to $2.67C_s$ for Xe. For harmonic oscillator problems with eight particles, the values lie between $1.97C_s$ and $2.35C_s$ for the k range from 0.01 to 100. At k=10, which has the density corresponding to the atomic electron density, the $C_x = 2.34C_s$ --- not far from the value for the Neon atom with 10 electrons($C_x = 2.27C_s$).

It thus appears that the coefficient for the first gradient correction depends more strongly on the number of electrons than on the forms of the external potential or equivalently on the shapes of the density.

Table 33: The optimized parameters in fitting the HF total energies.

The C_x values are defined in Eq.(4.4) in units of C_s. The values inside the brackets are the negative values of the corresponding exchange energies(in a.u.). SCF means the calculation is performed self-consistently. HF means the calculation is performed with the HF density.

Atoms

Atom	GEA(HF)	GEA(SCF)	GEAL(HF)
Be	2.199(2.67)	2.187(2.66)	4.020(2.67)
Ne	2.290(12.11)	2.267(12.04)	3.122(12.11)
Mg	2.385(15.99)	2.371(15.95)	3.157(15.99)
Ar	2.499(30.19)	2.488(30.15)	3.267(30.19)
Ca	2.504(35.21)	2.494(35.19)	3.217(35.21)
Zn	2.432(69.70)	2.405(69.45)	2.883(69.70)
Kr	2.593(93.86)	2.581(93.76)	3.072(93.86)
Sr	2.609(101.95)	2.599(101.88)	3.071(101.95)
Cd	2.638(148.91)	2.625(148.78)	3.082(148.91)
Xe	2.679(179.10)	2.670(179.03)	3.125(179.10)

Harmonic oscillators(8 electrons)

k	GEA(HF)	GEA(SCF)	GEAL(HF)
.01	2.064(.7958)	1.965(.7990)	-2.26(.7958)
.1	2.237(1.607)	2.187(1.607)	-2.57(1.607)
1	2.318(3.155)	2.291(3.154)	-2.73(3.154)
10	2.351(6.020)	2.335(6.017)	-2.87(6.020)
100	2.363(11.21)	2.354(11.20)	-2.98(11.21)

Table 33 illustrates the optimized C_x values for atoms as well as for Harmonic oscillators. By optimization we mean that the total energy thus calculated using the GEA energy functional is equal to the corresponding HF value. Also included in the Table are the C_x values determined by using the HF density instead of the self-consistent density. The C_x thus calculated have a small deviation from the exact one due to the self-consistency requirement. The self-consistent optimized GEA exchange energies also deviate from the HF by a small amount for the same reason as seen in the same Table.

We have also performed a least square fit to this GEA form for both the atoms and the harmonic oscillator systems. It is found that when the C_x value is equal to $2.375C_s$ for atoms or $2.257C_s$ for oscillators, the errors in the E_x(compared to HF) are less than 1%. Actually, for oscillator systems, even when we use the atomic fitting value of $C_x = 2.375C_s$, the errors in the GEA1 calculation of E_x are also less than 1% and are more accurate than the corresponding PW results. (See Tables 34-36 column GEA1 and compare to the HF results quoted there). It should also noted that the calculation of the GEA exchange energies is not very sensitive to the exact value of the parameters i.e. an increase in C_x of 10% results in an increase of $(-E_x)$ by $\simeq 0.5\%$. Thus if we made a least squares fit to the errors in E_x(instead of to the % errors)we would obtain a value of $C_x \simeq 2.6C_s$ with GEA1 results very close to the PW for all atoms.

Table 34: Comparisons of the least square fit GEA exchange energies with the HF and PW results(Atoms)

The values in column GEA1 are the fitted results from Eq.(4.2) with the fitted parameter $C_x = 2.375C_s$ The values in column GEA2 are calculated from Eq.(4.7) with the fitted parameter $C_x = 3.26C_s$. Those in column GEA3 are the fitted results from Eq.(4.8) with the parameters $\beta_1 = 6.34$, $\beta_2 = 25.43$. and γ determined from Eq.(4.9) which insures that Eq.(4.8) reduces to the Sham result when $\xi \equiv |\nabla n|/(2k_F n)$ is very small. All calculations are performed with the HF densities and energies are in units of a.u. and are listed as $-E_x$.

Atom	HF	PW	GEA1	GEA2	GEA3
Be	2.67	2.68	2.69	2.62	2.68
Ne	12.11	12.22	12.15	12.15	12.14
Mg	15.99	16.11	15.99	16.03	16.00
Ar	30.19	30.29	30.08	30.18	30.13
Ca	35.21	35.34	35.08	35.24	35.05
Zn	69.70	69.94	69.55	70.10	69.87
Kr	93.86	93.85	93.43	94.14	93.97
Sr	101.95	101.91	101.47	102.25	101.97
Cd	148.9	148.7	148.2	149.29	148.5
Xe	179.1	178.6	178.2	179.43	178.1

We note here that in the usual GEA expression, as long as we assume that the density vanishes at infinity, which is certainly true for any finite system as for atoms or molecules, or it satisfies periodic boundary conditions as for the solid, there is no difference in writing the gradient term in the exchange energy density as $C_x|\nabla n|^2/n^{4/3}$ or as $3C_x\nabla^2 n/n^{1/3}$ since using the method of integra-

Table 35: The GEA exchange energies for harmonic oscillator systems calculated by using the atomic fitting parameters.

The GEA1, GEA2 and GEA3 have the same meanings as in Table 34 with $C_x = 2.375C_s$ in GEA1, $C_x = 3.262C_s$ in GEA2, $\beta_1 = 6.34$ and $\beta_2 = 25.43$ in GEA3. All calculations are performed with the HF densities and energies are in units of a.u. and are listed as $-E_x$.

k	HF	PW	GEA1	GEA2	GEA3
.01	.7958	.7864	.8036	.7292	.7948
.1	1.607	1.583	1.613	1.489	1.631
1	3.155	3.107	3.161	2.946	3.246
10	6.020	5.930	6.024	5.649	6.249
100	11.21	11.04	11.21	10.55	11.69

Table 36: Comparisons of the least square fit GEA exchange energies with the HF and PW results(Oscillators).

The GEA1, GEA2 and GEA3 have the same meanings as in Table 34 with $C_x = 2.257C_s$ in GEA1, $C_x = -2.585C_s$ in GEA2, $\beta_1 = 1.72$ and $\beta_2 = 10.89$ in GEA3. All calculations are performed with the HF densities and energies are in units of a.u. and are listed as $-E_x$.

k	HF	PW	GEA1	GEA2	GEA3
.01	.7958	.7864	.8007	.8115	.7955
.1	1.607	1.583	1.608	1.607	1.606
1	3.155	3.107	3.150	3.134	3.157
10	6.020	5.930	6.004	5.952	6.024
100	11.21	11.04	11.17	11.03	11.23

tion by parts, they can transform to one another. However, this is no longer the case for our new form for the GEA. A square root in the expression prevents its argument from transforming to a different expression. We therefore have an entirely different GEA expression(we will denote it by GEAL):

$$E_x[n] = A_x \int n^{4/3} |1 + 3B_x \nabla^2 n/(\alpha n^{5/3})|^{\alpha} dr \tag{4.7}$$

instead of

$$E_x[n] = A_x \int n^{4/3} (1 + B_x \xi^2/\alpha)^{\alpha} dr$$

The factor 3 arises in (4.7) to guarantee that when $\xi \equiv |\nabla n|/(2k_F n)$ is small, the expression will recover to the usual GEA after an integration by parts. The absolute values taken in Eq.(4.7) will prevent the argument from becoming negative, but otherwise will make no difference when $\xi << 1$.

To test this expression, we have calculated the expectation values for the exchange energies using the HF densities. The B_x is determined by $B_x = C_s/A_x$ such that when ξ is far less than one Eq.(4.7) reduces to the Sham result. The α value is fixed to be 1/2 in order that E_x given in (4.7) is finite in the infinity limit(refer to Appendix C part D.5). The results, however, are not as good as those using the gradient form(see Table 37).

Table 37: Exchange energies from the GEAL calculations(in a.u.). The HF and GEA values have also been quoted for comparison.

All calculations are performed with the HF densities and listed as $-E_x$.

Atoms

Atom	HF	GEA	GEAL
Be	2.67	2.49	2.44
Ne	12.11	11.52	11.45
Mg	15.99	15.22	15.14
Ar	30.19	28.83	28.72
Ca	35.21	33.67	33.56
Zn	69.70	67.33	67.20
Kr	93.86	90.7	90.54
Sr	101.95	98.56	98.40
Cd	148.9	144.4	144.2
Xe	179.10	173.8	173.6

Harmonic oscillators(8 electrons)

k	HF	GEA	GEAL
.01	.7958	.7665	.7438
.1	1.607	1.542	1.503
1	3.155	3.025	2.956
10	6.020	5.770	5.647
100	11.21	11.74	10.52

Nevertheless, when we fit to the HF total energies for each atom we obtain a series values for $C_x = A_x/B_x$, which seems to change more smoothly than does the gradient form. Actually, except for the

Be atom and Zn atom which have C_x values of $4.02C_s$ and $2.88C_s$ respectively, all other atoms considered have very close C_x values, they vary from $3.12C_s$ for Zn to $3.27C_s$ for Ar as compared to $2.27C_s$ for Ne and $2.67C_s$ for Xe using the gradient expression. A least square fit to all atoms yields a value for C_x that is $3.26C_s$. The E_x values thus fitted for all atoms of concern are within 1% of the HF results.(without considering the Be atom, the fit can be even better.) A disappointing fact for this Laplacian expression is that when applied to the harmonic oscillator problems, the values of C_x turn out to be very different from those for atoms, and in fact, are negative numbers(The errors in the E_x thus calculated are also less than 1%). When we use the atomic fitting value of $C_x = 3.26C_s$, the errors are much larger. See the results in Tables 34-35. column GEA2 and the HF for comparison.

An examination of Table 33 shows how the C_x values varies for atoms as well as for harmonic oscillators.

We have also tested the expression

$$E_x[n] = \gamma A_x \int (1+\beta_1 B_x \xi^2/\alpha)^\alpha dr$$

$$+ (1-\gamma)A_x \int |1 + 3\beta_2 B_x \nabla^2 n/(\alpha n^{5/3})|^\alpha dr \qquad (4.8)$$

where

$$\gamma\beta_1 + (1-\gamma)\beta_2 = 1 \qquad (4.9)$$

i.e. a combination of the gradient expression and Laplacian expression. The coefficients β_1, β_2 and γ are related such that when $\xi \equiv |\nabla n|/(2k_F n)$ is a small number, it reduces to the usual LSD + GEA expression with Sham's coefficient.

A least square fitting to a series of atoms gives $\beta_1 = 6.34$ and $\beta_2 = 25.43$ and the γ is determined from Eq.(4.9). The value of α is fixed to be 1/2. The fitted exchange values are tabulated in Table 34 column GEA3.

Surprisingly, both the C_{gra} and C_{lapl} turn out to be very different from the separately optimized C_{gra} and C_{lapl}.

For purposes of comparison, in Tables 34-36, we also include the results of Perdew and Wang's GGA and the exact HF and GEA1 and GEA2 results discussed previously.

The fitted values using Eq.(4.8) represent much improved results compared with the usual GEA and are as good as PW for all the atoms tested(actually, the GEA1 and GEA2 results are also as good as those given by PW).

The drawback for such fitting is, of course, we do not have a physical explanation for the magnitude of these coefficients.

In Table 36 we present the similar fitting results for harmonic oscillator system with eight electrons. It is found that the E_x calculated using the PW formula have quite large errors compared with ours. However, the fitting parameters for this system are quite different from those of the atoms. When we use the atomic fitting values of β_1 and β_2, the errors becomes as large as those calculated from PW's formula(For small k our results are more accurate, but for large k ours become poorer. See Table 35).

The fact that we are able to treat two systems i.e atoms and oscillators enables us to see that a parameterization of the GEA that is successful in one case may not be successful in the other. The fact that the correct exchange energy functional must be universal i.e. it must apply to all systems independent of the nature of the external potential, enables us to conclude that the most successful GEA is GEA1 which is generally accurate to within one percent of the exact exchange energy for $C_x = 2.375C_s$

4.4 A New Exchange Energy Functional

Finally, we go beyond the gradient expansion and study the exchange energy functional derived directly from a single particle density matrix for an arbitrarily rapidly varying spherically symmetric density.

In general, the single particle density matrix $n(r_1,r_2)$ corresponding to a Slater determinant for an arbitrary number of electrons can be written :

$$n(r_1,r_2) = \Sigma_k\psi_k^*(r_1)\psi_k(r_2) \tag{4.10}$$

where $\psi_k(r)$ are the single particle wavefuntions and the $n(r_1,r_2)$ satisfies

$$\int n(r_1,r')n(r',r_2)dr' = n(r_1,r_2) \tag{4.11}$$

with the diagonal element equal to the electron density:

$$n(r,r) = n(r), \tag{4.12}$$

It is natural to write the $n(r_1,r_2)$ as

$$n(r_1,r_2) = n^{\frac{1}{2}}(r_1)n^{\frac{1}{2}}(r_2)f(r_1,r_2) \tag{4.13}$$

with $f(r_1,r_1) = 1$ in order to insure that (4.12) be satisfied.

Then Eq.(4.11) is equivalent to

$$\int f(r_1,r')f(r',r_2)n(r')dr' = f(r_1,r_2) \tag{4.14}$$

If it is possible to make a variable transformation in the integration

$$R = R(r) \tag{4.15}$$

or

$$r = r(R) \tag{4.15'}$$

such that

$$dR = n(r)/n_0 dr \tag{4.16}$$

and $f(\mathbf{r},\mathbf{r}') = F(\mathbf{R},\mathbf{R}')$, where n_0 is the average density of the system with total number of electrons $N = \int n(\mathbf{r})d\mathbf{r}$ and volume V i.e. $n_0 = N/V$. We then have

$$\int F(R,R')F(R',R'')n_0 dR' = F(R,R'') \tag{4.17}$$

Comparing with Eq.(4.14), we see, in the **R** space, that F(R,R') satisfies the same relationships as the function $f(\mathbf{r},\mathbf{r}')$ does in the **r** space, with, however, a special property that it is for a system with constant density. Thus we have a solution for Eq.(4.17), i.e the plane wave result

$$n(r_1,r_2) = n^{\frac{1}{2}}(r_1)n^{\frac{1}{2}}(r_2)F(R_1,R_2) \tag{4.18}$$

where

$$F(R_1,R_2) = (1/2)F_1[k_F^{(0)}|R_1-R_2|]$$

$$F_1(x) = 3(\sin(x)-x\cos(x))/x^3$$

$$k_F^{(0)} = (3\pi^2 n_0)^{1/3}$$

For a spherically symmetric density, i.e. $n(\mathbf{r}) = n(r)$, we can take $\mathbf{R} = R(r)$ only, in which case the solution of Eq.(4.16) is

$$R(r) = [\int_0^r (3n(r')/n_0)r'^2 dr']^{1/3} \tag{4.19}$$

with Θ and Φ equal to θ and ϕ respectively.

It may be argued that the solution of the integral equation (4.11) might not be unique. However, our solution at least reduces to the plane wave result in the constant density limit.

It is worth noting that, for a spherically symmetric density, the above result may also be derived by employing the Harriman [27] orbitals(the equal density orbitals), which reduce to the plane wave solutions in the limit n → const. That is, if we write:

$$\psi_k(r) = (n(r)/N)^{\frac{1}{2}}\exp(ik\cdot R(r)) \tag{4.20}$$

with R(r) defined as in Eq.(4.19) and the conditions

$$\int\psi^*_{k'}(r)\psi_k(r)dr$$

$$= (1/V)\int\exp\{-(k-k')\cdot R\}dR$$

$$= \delta_{k,k'}$$

i.e. the k's are exactly those corresponding to the usual plane waves with the upper limit $k_F^{(0)} = (3\pi^2 n_0)^{1/3}$, we can then calculate the density matrix as

$$n(r_1,r_2) = \Sigma_k\psi^*_k(r_1)\psi_k(r_2)\theta(k_F-k)$$

$$= (1/2)(n(r_1)n(r_2))^{\frac{1}{2}}F_1(|\chi(r_1)-\chi(r_2)|)$$

where F_1 is defined as before and

$$\chi(r) = [(9\pi/4)\int_{r'<r} n(r')dr']^{1/3}\hat{r}$$

which is exactly the same result as Eq.(4.18) when the relations R = R(r), $\Phi = \phi$ and $\Theta = \theta$ are applied.

With this density matrix, we can then study the exchange energy as given by the usual HF expression:

$$E_x[n] = - \int n^2(r,r')/|r-r'|drdr'$$

or

$$E_x[n] = - (1/4)\int\int n(r)n(r')F_1^2\ (|\chi(r)-\chi(r')|)/|r-r'|drdr' \quad (4.21)$$

where $\chi(r)$ is defined as before, which is a functional of the density only.

We want to stress here, that although there have been constructions of the exchange energy functional using the Harriman orbitals by other investigators [49] [50] [51] [52] [53], ours is a set of Harriman orbitals which has a vector form for the wave vector k and exactly reduces to the plane wave solutions when n(r) = const. The original Harriman orbitals are of the form

$$\psi_k(r) = (n(r)/N)^{\frac{1}{2}}\exp(-kq(r))$$

with

$$q(r) = \int 4\pi r'^2 n(r')dr'.$$

Here the k value is one dimensional and the states do not reduce to the usual free electron states in the constant density limit. As a result, they accommodate far too few electrons for a fixed k, and the kinetic energy calculated using the expression

$$T_s = \Sigma_k \int |\nabla\psi_k(r)|^2 dr$$

is too large for the system considered [49].

Taking the functional derivative of $E_x[n]$ given by (4.21) with respect to n(r), we then find the exchange potential:

$$v_x(r) = v_x^{(1)}(r) + v_x^{(2)}(r)$$

where

$$v_x^{(1)}(r) = -(1/2)\int n(r')F_1^2(|\chi(r)-\chi(r')|)/|r-r'|dr'$$

$$v_x^{(2)}(r) = -(27\pi/4)\int\int dr_1 dr_2 \{n(r_1)n(r_2)/|r_1-r_2| \times$$
$$Z(|\chi(r_1)-\chi(r_2)|)G(r_1,r_2,r)\}$$

with

$$Z(x) = (\sin(x)-x\cos(x))\sin(x)/x^6 - 3(\sin(x)-x\cos(x))^2/x^8$$

$$G(r_1,r_2,r) = \{\chi^{-1}(r_2) - [\chi(r_1)/\chi^2(r_2)]\hat{r}_1\cdot\hat{r}_2\}\theta(r_2-r)$$

When $r \to \infty$, it is easily verified that the exchange potential $v_x \to -1/r$ unlike the usual LSD result in which v_x goes to zero exponentially.

Table 38: Negative of the Exchange energies from the density matrix methods as compared with the HF and the LSD results.

The values in column DM1 are the results calculated from Eq.(4.21), those in DM2 are from Eq.(4.25), DM3 from Eq.(4.26) and DM4 from Eq.(4.27). All calculations are performed with the HF densities. Energies are in atomic units.

Atom	HF	LSD	DM1	DM2	DM3	DM4
Be	2.67	2.31	1.36	2.37	2.99	2.67
Ne	12.1	11.0	7.60	11.3	12.9	12.1
Mg	16.0	14.6	10.3	14.9	17.0	15.9
Ar	30.2	27.9	20.3	28.4	31.5	29.8
Ca	35.2	32.6	23.9	33.3	36.7	34.8
Zn	69.7	65.6	50.1	66.8	71.8	69.1
Kr	93.9	88.6	68.6	90.1	96.2	92.8
Sr	102.0	96.4	74.9	98.0	104.4	100.7
Cd	148.9	141.5	111.4	143.8	151.8	147.2
Xe	179.1	170.6	135.1	173.1	182.3	176.9

We therefore have obtained the exchange potential from a density matrix which exactly satisfies Eq.(4.11) whose diagonal elements are n(r) where n(r) is arbitrary, a condition only approximately satisfied by LDA. It might therefore be expected that the derived v_x could be an improvement over the $v_x^{l\,sd}$ not only in the limit of large r but for all r. However, actual applications to atoms produce results which are quite disappointing. In Table 38 column DM1, we show the exchange energy values for a series of atoms calculated using this method by employing the HF density. The results are much poorer than those given by the LSD.

It is quite puzzling at first, when one sees that an elaborate construction which takes account of the density and reduces to the plane-wave solutions in the constant density limit does not improve things. However, if one compares the derivations of the LDA and the present derivation of the expression for the exchange energy, then it is understandable that the expression given by the Harriman orbitals will not necessarily be an improvement over that of LDA.

Consider the construction of the LDA. By calculating the density matrix using the plane waves and summing over all the occupied orbitals up to $k_F = (3\pi^2 n_0)^{1/3}$, we get the expression for the exchange energy:

$$E_x[n] = -(1/4)\int n_0^2 F_1^2(k_F|r_1-r_2|)/|r_1-r_2|dr_1dr_2 \qquad (4.22)$$

Notice, the above expression is not the LSD expression yet unless we make an approximation that all n_0 be replaced by $n(R)$ with $R = (r_1 + r_2)/2$, i.e.

$$E_x^{l\,da}[n] = -(1/4)\int n^2(R)F_1^2(k_F(R)|r_1-r_2|)/|r_1-r_2|dr_1dr_2. \qquad (4.23)$$

Then after a transformation of the integration variables

$$dr_1dr_2 = drdR$$

where

$$r = r_1 - r_2$$

and performing the integration on r, the usual LSD form is obtained.

On the other hand, the construction of the new exchange energy functional has the same procedure, except that the orbitals employed take account of the varying density and as a result, one obtains an expression for the exchange energy given by Eq.(4.21)

Comparing (4.23) and (4.21), when $n(r) = \text{const}$, we see,they are identical, but for $n \neq \text{const}$, the two expressions for the exchange energy will in general be different.

Now if we write a formula for the exchange energy:

$$E_x[n] = -(1/4)\int n_0^2F_1^2(g(r_1,r_2))/|r_1-r_2|dr_1dr_2 \tag{4.24}$$

with $g(r_1,r_2)$ an unknown function, then we can see the LDA is equivalent to approximating the $g(r_1,r_2)$ by $k_F(R)|r_1-r_2|$ and the constant n_0^2 by $n^2(R)$, whereas the Harriman exchange, on the contrary, is equivalent to replace $g(r_1,r_2)$ by $|\chi(r_1)-\chi(r_2)|$ and n_0^2 by $n(r_1)n(r_2)$.

From this point of view, it is indeed very difficult to appreciate which approximation is more appropriate. Perhaps it is because that in LDA, when we replace the $g(r_1,r_2)$ by $k_F(R)|r_1-r_2|$, with $R = (r_1 + r_2)/2$, it implies the importance of the overlap of the two wavefunctions in the contribution to the exchange energy and this makes it quite successful.

This analysis suggests that it might be fruitful to consider other approximations to the g function. The only condition required is that it should reduce to the plane wave result in the constant density limit. (The condition that the hole charge density which is defined as

$$\rho(r_1,r_2) = -n^2(r_1,r_2)/n(r_1)$$

which should be integrated to -1

$$\int\rho(r_1,r_2)dr_2 = -1$$

may be a more stringent criterion [55] [56].)

Whereas the LDA stresses the importance of the overlap density, a simple and more appropriate consideration is perhaps that the exchange energy should also depend on the density of the interacting electrons at the corresponding positions. Bearing this in mind, we can then construct an exchange energy functional by simply replacing the $g(r_1,r_2)$ by $(3\pi^2(n(r_1) + n(R) + n(r_2))/3)^{1/3}|r_1-r_2|$ and n_0 by the expression $(n(r_1) + n(R) + n(r_2))/3$. Thus we have

$$E_x = -(1/4)\int\int dr_1 dr_2 [(n(r_1)+n(r_2)+n(R))/3)]^2 \times$$

$$F_1^2[((n(r_1)+n(r_2)+n(R))/3)^{1/3} a|r_1-r_2|]/|r_1-r_2| \qquad (4.25)$$

with

$$a = (3\pi^2)^{1/3}$$

The application to atoms using this expression(we will call it DM2) indeed improves the results over the LSD. Moreover, when we replace the n_0^2 by $n^2(R)$ and keep the argument in the g function as in Eq.(4.25) so that

$$E_x = -(1/4)\int\int dr_1 dr_2 \{n^2(R)\times$$

$$F_1^2[((n(r_1)+n(r_2)+n(R))/3)^{1/3} a|r_1-r_2|]/|r_1-r_2|\}, \qquad (4.26)$$

the results are also better than the LSD although in this case the values are too large in magnitude(we will call it DM3). We have also tried many other different forms for the $g(r_1,r_2)$ function. Among them the following expression for the $E_x[n]$ produce the E_x values that are particularly close to the HF, i.e.

$$E_x = -(1/4)\int\int dr_1 dr_2 [(n(r_1)+n(r_2)+7n(R))/9)]^2 \times$$

$$F_1^2[((n(r_1)+n(r_2)+n(R))/3)^{1/3} a|r_1-r_2|]/|r_1-r_2| \qquad (4.27)$$

We can see from Table 38 that the exchange energies thus calculated (denoted as DM4) are a significant improvement when compared to the LSD results as well as the results obtained from the DM1, DM2 and DM3.

The drawback of such approximations is, of course, that it is much more difficult to calculate than the LSD because of the three fold integration. However, with the application of the Monto Carlo method, the labor is greatly reduced.

The best approximation to the $g(r_1,r_2)$ is not known yet. However, the improvement we have obtained over the LDA results by making a reasonable approximation for $g(r_1,r_2)$ suggests that further progress in obtaining an accurate density functional for E_x may be made by further application of this idea.

Finally, one additional interesting point worth noting here is that the first gradient expansion coefficient for Eq.(4.25), Eq.(4.26) and Eq.(4.27) diverges(see Appendix E), which is a result that is also true for the HF exchange energy as proved by Kleiman [28] and Geldart et al [29]. The agreement here may not be accidental.

Chapter V

Study of the Effect of Correlation

In the previous Chapters, we have restricted ourselves to the study of exchange-only DFT. The effect of correlation has been ignored completely. In this way, we have been able to test the various approximations for the exchange and see how good they are in accounting for the exact exchange-only KS results i.e. the total energy, the highest occupied orbital single particle eigenvalue and the electron density which are actually all equal to the corresponding HF results.

It has been known that although the correlation effect plays a relatively minor role as compared to that of the exchange in calculating the total energies of the atoms and other finite electronic systems like harmonic oscillator problems, it becomes quite vital in correctly describing the motions of the valence electrons in atoms. As an example, without considering correlation, the HF method is quite successful in giving the total energies of atoms which are within a percent of the exact experimental values or the CI results. On the other hand, when dealing with problems concerning the valence electrons like the electron affinities, the HF method fails in the sense that the calculated total energies for some negative ions are even less negative than those of the corresponding atom, i.e. the electron affinities assume negative values and so the negative ions are unstable although they actually exist in nature. By adding the correlation effects, such failures disappear and the ions become stable, and in addition, the total energies also more closely approximate the exact results.

In this Chapter, we will extend our previous work to include the correlation effects and compare the results thus obtained with the experimental values. Since the exact results for electron systems with a harmonic potential are not available, we will be concerned with atomic problems only. The harmonic oscillator system is fictitious and thus no experimental values exist. Of course, one can always make a CI calculations and thus have an 'exact' result, but it is very tedious and will not be attempted here.

5.1 DFT with exchange and correlation

In the LDA, the correlation energy can be written

$$E_c[n] = \int e_c[n(r)]n(r)dr$$

where e_c is the correlation energy density per electron, just as the case in describing the LDA exchange energy. (Throughout our study, we will assume that the exchange correlation functional can be separated as exchange plus correlation).

There have been many different expressions for e_c. In our study, however, we will use the one proposed by Ceperly and Alder [57] [58] and parameterized by Perdew and Zunger [22], i.e.

$$e_c^i = A^i \ln(r_s) + B^i + C^i r_s \ln(r_s) + D^i r_s \quad (r_s < 1)$$

$$e_c^i = \gamma^i/(1 + \beta_1^i \sqrt{r_s} + \beta_2^i) \quad (r_s > 1)$$

where r_s is defined by

$$n = (4\pi r_s^3/3)^{-1}$$

with n being the electron density and i can represent U(unpolarized) and P(polarized) cases. The coefficients were given by Perdew and Zunger [22].

With correlation included, the energy functional becomes:

$$E[n] = T[n] + U_h[n] + U_{ext}[n] + E_x[n] + E_c[n]$$

And the correlation potential is

$$v_c(r) = \delta E_c[n]/\delta n$$

or

$$v_c^i = A^i \ln(r_s) + (B^i - 1/3A^i) + 2/3C^i r_s \ln(r_s) + 1/3(2D^i - C^i) r_s \quad (r_s < 1)$$

$$v_c^i = e_c^i(1 + 7/6\beta_1^i \sqrt{r_s} + 4/3\beta_2^i r_s)/(1 + \beta_1^i \sqrt{r_s} + \beta_2^i r_s) \quad (r_s > 1)$$

When PZ's self interaction correction method is applied, we have

$$E^{sic(i)}[n] = T[n] + U_h[n] + U_{ext}[n] + E_x^{sic(i)}[n] + E_c^{sic}[n]$$

where

$$E_x^{sic(i)}[n_\uparrow, n_\downarrow] = E_x^{l\,sd}[n_\uparrow, n_\downarrow] - \Sigma_{\alpha\sigma}\delta_{\alpha\sigma}^{(i)}$$

with

$$\delta_{\alpha\sigma}^{(i)} = U_h^{(i)}[n_{\alpha\sigma}] + \beta E_x^{l\,sd}[n_{\alpha\sigma}, 0]$$

and

$$E_c^{sic} = E_c^{l\,sd}[n_\uparrow, n_\downarrow] - \Sigma_{\alpha\sigma} E_c^{l\,sd}[n_{\alpha\sigma}, 0]$$

the parameter (i) represents the three different SIC treatments for the exchange energy functional discussed in Chapter 3 i.e. the LSDSICA, LSDSICE and LSDSICI. We do not make any further refinement on the correlation energy functional in the belief that any such corrections are very small in comparing with the uncorrected e_c which is itself a small contribution compared with exchange and other terms of the potential energy.

With these functionals, the single particle equations can be derived just as we did for the exchange-only case in Chapter 3, i.e.

$$[-(1/2)\nabla^2 + v_{\alpha\sigma}^{sic}(r)]\psi_{\alpha\sigma}(r) = \varepsilon_{\alpha\sigma}^{sic}\psi_{\alpha\sigma}(r)$$

with

$$v_{\alpha\sigma}^{sic}(r) = v(r) + v_h([n],r) + v_{xc,\alpha\sigma}^{sic}$$

$$v_{xc,\alpha\sigma}^{sic} = v_{x,\alpha\sigma}^{sic} + v_{c,\alpha\sigma}^{sic}$$

here, v_h, v and $v_{x,\alpha\sigma}^{sic}$ are defined as in Chapter 3, and $v_{c,\alpha\sigma}^{sic}$ is

$$v_{c,\alpha\sigma}^{sic} = v_c^{lsd}[n_\uparrow,n_\downarrow] - v_c^{lsd}[n_{\alpha\sigma},0]$$

5.2 Treating Exchange Exactly

Kohn and Sham in their original paper suggested that one can write the exchange correlation functional as

$$E_{xc} = E_x + E_c$$

with E_x defined as

$$E_x = -(1/2)\Sigma_{ij}\int\int\psi_i^*(r)\psi_i(r')\psi_j^*(r')\psi_j(r)drdr'/|r-r'|$$

i.e. in a sense, the exchange is now treated exactly as in the HF approximation, but with $\psi_i(r)$ replaced by the density functional wavefunctions. Then it is only the correlation part in the functional which needs to be approximated.

In essence, one can say that by treating exchange exactly, this method is equivalent to solving the HF equations with correlations included(HFC)(When the SIC technique is applied to the HFC to correct for the self-interaction in the approximation of correlation functional, one has the HFCSIC).

We know from the discussion in Chapter 2 that this so-called exact treatment for the exchange is not equivalent to the exchange as defined in the exact KS exchange-only theory. However, from our previous argument, it is also known that these different definitions for the exchange produce values which are not very far from each other(at least for finite systems like atoms and oscillators), so we expect $e_c[n(r)]$ to be essentially equivalent to the e_c in a theory in which the exchange energy is written in terms of a density functional.

Baroni and Tuncel [34] have employed this method to calculate the total energies and the electron affinities for atoms. It is quite successful in that it further improves the total energy calculations over the other versions of DFT calculations as compared to the exact experimental values and is able to predict the stable negative ions which the HF method failed to do. However, one thing which was not given by them and is of importance as we have previously mentioned is that we do not know if the highest occupied orbital single particle eigenvalue calculated this way will also be accurate i.e. whether it will closely approximate the electron ionization energy.

We thus perform similar calculations here, but instead of using the finite basis set method [59] as they used which involves errors due to the incomplete expansion of the HF orbitals, we employ a method which solves the HF equations exactly in numerical form as described by C.F.Fischer [60].

5.3 Results and Discussion

5.3.1 Total Energy

In this subsection, we compare the total energy calculations of the various schemes. Table 39 lists the E_{tot} of the HF, LSD, LSDSICA, LSDSICE, LSDSICI, HFC and HFCSIC as well as the experimental values(corrected for relativistic and reduced mass effects) given by Clementi [61] in the first column.

First, if we compare the results from the local density approximations(including various SIC) to the experimental results, it can be seen that Perdew and Zunger's LSDSICA is in general an improvement

Table 39: Total energies of atoms with complete sub-shells compared with the experimental values.

The LSD, HFC, HFCSIC, LSDSICA, LSDSICE and LSDSICI results are reported together with the experimental values which are quoted from [61]. Notice that Baroni Tuncel [34] have reported the HFC and HFCSIC results before. However, they are slightly different from ours because of the different numerical approaches as explained in the text. Energies are in a.u. and listed as $-E_{tot}$.

Atom	Expt.	HF	HFC	HFCSIC
Be	14.67	14.57	14.80	14.69
Ne	128.93	128.55	129.29	128.97
Mg	200.05	199.62	200.50	200.12
Ar	527.60	526.82	528.24	527.64
Ca		676.76	678.33	677.66
Zn		1777.85	1780.50	1779.43
Kr		2752.06	2755.32	2754.00
Sr		3131.55	3134.98	3133.58
Cd		5465.13	5469.18	5467.85
Xe		7232.14	7237.32	7235.22

Atom	LSD	LSDSICA	LSDSICE	LSDSICI
Be	14.45	14.70	14.70	14.70
Ne	128.23	129.29	129.04	129.35
Mg	199.13	200.54	200.21	200.65
Ar	525.94	528.43	527.72	528.74
Ca	675.73	678.60	677.76	678.97
Zn	1776.56	1781.78	1779.64	1782.45
Kr	2750.13	2756.93	2753.93	2757.97
Sr	3129.44	3136.73	3133.47	3137.89
Cd	5462.37	5472.36	5467.31	5474.11
Xe	7228.84	7240.43	7234.30	7242.61

over the LSD. However, whereas the LSD underestimates the $|E_{tot}|$, the LSDSICA gives the E_{tot} which is too negative. On the other hand, the LSDSICE, which had appropriately taken account of the angular dependence of the wavefunctions in the calculation of the exchange energy, considerably reduces the errors of the LSDSICA and gives the E_{tot} which is in fair agreement with the experimental value. The LSDSICI, which correctly approximates the intra-shell exchange in the large r region, however, overestimates the exchange energy and produces the total energy that is even more negative than that of LSDSICA. Thus, the comparisons of the total energy calculations show a completely similar pattern as we have seen in the exchange-only case. It thus appears that the inclusion of correlation does not significantly affect the relative accuracy of these different approximations.

We now examine the results obtained from the HF calculations(i.e. the HF and HF including correlation effect). We list these E_{tot} in Table 39 where the E_{tot} for the three SIC methods with correlation included are displayed. It is observed that whereas the HF(without correlation) gives upper bounds for the system total energy, the HF with correlation but without SIC yields E_{tot} that are too negative. It is the E_{tot} from the HFCSIC which takes account of the correlation and does not contain any self-interaction terms which is closest to the experimental results. Thus once more the importance of the requirement of SIF(i.e. in an exact DFT theory, the total energy functional is strictly self-interaction-free.) is shown.

Furthermore, we notice that the HFCSIC E_{tot} are even more accurate than the results given by the LSDSICE method. Observing that the errors in the HFCSIC E_{tot} are actually less than half of the errors produced by the LSDSICE and recalling that the errors in the HFCSIC E_{tot} are purely due to the incorrect description of the correlation effect, it is then understood that the major errors in the LSDSICE are still due to the inappropriate approximation to the exchange energy.

Finally, we calculate the overlap integrals of the wavefunctions. Since we do not have the exact KS results, the overlaps were calculated between the pure HF wavefunctions and those with correlation included. The purpose of such calculations is to see how much correlation will affect the wavefunctions as well as the total density.

When examining Table 40 for the results of the HFC and HFCSIC, one can see that most of the values are larger than or equal to .9999995. Thus the correlation changes the wavefunctions only slightly. If we further examine the results for the LSD and LSDSIC type calculations and compare the values with those in the exchange-only calculations(refer Table 19), surprisingly, it is found that the values obtained from those with correlation are more close to one than

Table 40: Overlap integrals between the HF wavefunctions and the DFT wavefunctions for the Kr atom. Refer Eq.(2.18).

These are the overlap integrals between the DFT wavefunctions with correlation and the HF wavefunctions.

nl	HFC	HFCSIC	LSD
1s	1.000000	1.000000	0.999999
2s	1.000000	1.000000	0.999983
2p	1.000000	1.000000	0.999998
3s	1.000000	1.000000	0.999903
3p	1.000000	1.000000	0.999942
4s	0.999989	0.999997	0.999687
3d	1.000000	1.000000	0.999930
4p	0.999930	0.999972	0.999889

nl	LSDSICA	LSDSICE	LSDSICI
1s	0.999999	0.999999	0.999999
2s	0.999981	0.999982	0.999981
2p	0.999997	0.999997	0.999993
3s	0.999869	0.999892	0.999858
3p	0.999923	0.999915	0.999939
4s	0.999756	0.999685	0.999802
3d	0.999967	0.999946	0.999983
4p	0.999892	0.999866	0.999956

those without i.e it appears that the DFT wavefunctions(with correlation) are more similar to the HF(without correlation) than those exchange-only DFT wavefunctions. Therefore, it might be concluded that actually the approximation to the correlation accounts for part of the exchange interaction which is missing in the LSD or LSDSIC approximation to the exchange energy. In any event, the fact that the HF orbitals(without correlation) are so similar to the DFT wavefunctions (with correlation) suggests that the E_{tot} of any system for which the HF orbitals are known may be accurately obtained by adding $E_c[n]$ to E_{hf} with n(r) given by the HF density.

5.3.2 Comparison of the Top Eigenvalue with the Experimental Ionization Energy

As is well known, the agreement of the total energy as well as the total electron density with the experimental values form the important criteria to judge the accuracy of any exchange and correlation approximation. However, as we have discussed previously, a more stringent test of any approximation for the exchange and correlation functional is that it must also produce the ε^{df}_{max} that is in fair agreement with the experimental ionization energy. In the previous subsection, we discussed the relative accuracies of the total energies of the various approximation schemes. It is found that the ones which accurately approximate the exchange in the exchange-only case, also give the E_{tot} which are in fair agreement with the experimental total energy. In this subsection, we will compare the top eigenvalues produced by the various approximate methods with the ionization energy obtained from experiment to see if the same trend follows.

Table 41: Comparison of the outmost orbital eigenvalues with the measured first ionization potentials.

Listed are the negative of the ε_{max} (in Ry.). Expt. values are quoted from [62] and conversions of units from eV to Ry. (1 Ry. = 13.6 eV) have been made.

Atom	Expt.	HF	HFC	HFCSIC
Be(2s)	.658	.619	.697	.661
Ne(2p)	1.59	1.70	1.82	1.77
Mg(3s)	.562	.506	.579	.545
Ar(3p)	1.16	1.18	1.29	1.24
Ca(4s)	.449	.391	.456	.426
Zn(4s)	.691	.585	.664	.629
Kr(4p)	1.03	1.05	1.15	1.11
Sr(5s)	.419	0.36	.420	.391
Cd(5s)	.661	.530	.607	.573
Xe(5p)	.892	.915	1.01	.972

Atom	LSD	LSDSICA	LSDSICE	LSDSICI
Be(2s)	.412	.657	.657	.657
Ne(2p)	.996	1.68	1.65	1.79
Mg(3s)	.351	.550	.551	.549
Ar(3p)	.765	1.16	1.14	1.24
Ca(4s)	.283	.436	.437	.435
Zn(4s)	.446	.669	.677	.660
Kr(4p)	.693	1.03	1.02	1.10
Sr(5s)	.264	.403	.404	.402
Cd(5s)	.409	.616	.623	.609
Xe(5p)	.620	.898	.889	.967

In Table 41, we list the ε_{max} values obtained from the various schemes with inclusion of correlation along with the experimental ionization energy values. The HF values, which are without correlation, are also tabulated for further comparison.

In Chapter 3, it is found that whereas the LSDSICE gives E_{tot} which is an improvement over that of the LSDSICA and is fairly close to the HF value, the corresponding ε_{max}^{df} is nontheless poorer and even further away from the exact ε_{max}^{hf} than the LSDSICA. On the other hand, since the LSDSICI fairly approximates the exchange potential, the ε_{max}^{df} thus produced is much closer to the exact ε_{max}^{ks} which is equal to ε_{max}^{hf}, than those of the LSDSICA or LSDSICE. However, the E_{tot} becomes too negative and is less accurate than even the E_{tot} of LSDSICA.

Here, we can see from Table 41 that for noble gases with outermost orbitals being the p orbitals, the ε_{max}^{df} produced by LSDSICA and LSDSICE are the ones which most closely approximate the experimental ionization energy. The ε_{max}^{df} given by LSDSICI are too negative. For atoms with a highest lying s state, the ε_{max}^{df} calculated from all the three LSDSIC schemes are too small in magnitude to give the right results although the ε_{max}^{df} from the LSDSICE and LSDSICA are still slightly better than those given by LSDSICI. Most noteworthy, for noble gases, the ε_{max}^{df} obtained from HFC and HFCSIC, which are the HF plus correlation without and with the SIC method applied, are much poorer than those given by the LSDSICA and LSDSICE. Actually, for these atoms the ε_{max}^{hf} produced by pure HF with no correlation included at all approximates the exact experimental ionization value quite well. It should be noted, however, that $-\varepsilon^{hf}_{max}$ is not the exact ionization energy in an exchange-only theory, i.e. it is the ionization energy neglecting any relaxation of the N - 1 electron system(Koopman's theorem). If the ionization energy is calculated by taking the difference E(N-1) - E(N) then the exact exchange-only ionization energg generally does not approximate the experimental results as well as $-\varepsilon^{hf}_{max}$. In other words, leaving out the relaxation effects approximately cancels the omission of the correlation effects for the rare gas atoms with respect to the calculation of the ionization energy, but not the total energy. For atoms with highest lying s states, the HF(without correlation) $|\varepsilon^{df}_{max}|$ are too small, even with the inclusion of the correlation, the $|\varepsilon^{df}_{max}|$ produced by the HFC and HFCSIC are still not large enough(Nevertheless, for these atoms, from Table 41 it can be seen that the ε^{df}_{max} given by the HFC are the best ones).

Thus, it appears that for atoms with highest lying p orbitals, although one needs the contribution from the correlation energy to lower the system total energy in order to agree with the experimental value, the exact correlation potential, which is the functional derivative of the correlation energy functional, on the other hand, should be such that it hardly makes any significant contribution to the single particle eigenvalues. In other words, the exact correlation potential might change sign or be very small through the configuration space. However, for atoms with highest lying s states, not only do we need the inclusion of correlation to lower the system total energy, but also that it should contribute a substantial part in giving the correct ε_{max}^{df} that is equal to the negative of the first ionization potential of the atom.

The current approximation to the correlation effect, especially the correlation potential, is evidently in error. However, from our study, especially the results of LSDSICA and LSDSICE, it can be seen that many of the errors due to the correlation are cancelled by the errors from the exchange, thus the approximations to exchange and correlation taken together are more accurate than each one separately. Most significantly, with correlation included, the slightly modified LSDSICA, the LSDSICE(which treats the angular integrations in the E_x exactly) stands as the most accurate calculation scheme which produces generally good results for all the properties of concern, i.e. the total energy, the electron density as well as the maximum single particle energy eigenvalue.

Appendix A

The Exchange-Only HK and KS Theory

In this appendix, we show that the HK and KS theory for exchange-only is exist, in which the HF density, n(r), plays the role of the fundamental variable describing the system and with this density the HK and KS energy functional assumes its minimum value which is the HF ground state total energy.

Let Ψ_{HF} be a determinant of single particle states $\{\psi_i\}$ (i = 1, 2,....N) that minimizes the expectation value of the N particle Hamiltonian. Then

$$E_{hf}\{\psi_i\} = E^0\{\psi_i\} + \int v(r)n(r)dr \tag{A.1}$$

where

$$E^0\{\psi_i\} \equiv -(1/2)\Sigma_i\int\psi_i^*\nabla^2\psi_i dr + (1/2)\int\int drdr'n(r)n(r')/|r-r'|$$

$$- (1/2)\Sigma_{ij}\int\int drdr'\psi_i^*(r)\psi_i(r')\psi_j^*(r')\psi_j(r)/|r-r'| \tag{A.3}$$

$$n(r) = \Sigma_i|\psi_i(r)|^2 \tag{A.4}$$

and v(r) is the external potential.

we shell assume that the HF ground state is non-degenerate. [This is not of course always the case i.e. open shell atoms will not satisfy this condition. However, we can consider v(r) to include the effects of an infinitesimal symmetry breaking term which will lift the ground state degeneracy]. We now show, in analogy to the theorem of HK, that the external potential v(r) is a functional of the HF ground state density n(r)

Consider any two external potential v and v' with corresponding sets of ground state orbitals $\{\psi_i\}$ and $\{\psi'_i\}$. Then $E_{hf}\{\psi_i\}$ is given by Eq.(A.2) and

$$E'_{hf}\{\psi'_i\} = E^0\{\psi'_i\} + \int v'(r)n'(r)dr \tag{A.5}$$

Now it follows from the HF equations for the single particle orbitals that if $v - v' \neq$ const., the sets $\{\psi_i\}$ and $\{\psi'_i\}$ cannot be identical. It then follows from the minimum property of $E_{hf}\{\psi_i\}$ and $E'_{hf}\{\psi'_i\}$ and the assumption that the ground states are non-degenerate that

$$E_{hf}\{\psi'_i\} > E_{hf}\{\psi_i\}$$

i.e.

$$E^0\{\psi'_i\} + \int v(r)n'(r)dr > E^0\{\psi_i\} + \int v(r)n(r)dr \tag{A.6}$$

and

$$E'_{hf}\{\psi_i\} > E'_{hf}\{\psi'_i\}$$

i.e.

$$E^0\{\psi_i\} + \int v'(r)n(r)dr > E^0\{\psi_i'\} + \int v'(r)n'(r)dr \qquad (A.7)$$

so

$$\int v(r)(n'-n)dr > E^0\{\psi_i\} - E^0\{\psi_i'\} > \int v'(r)(n'-n)dr$$

or

$$\int [v(r)-v'(r)][n'(r)-n(r)]dr > 0 \qquad (A.8)$$

But if $n'(r) = n(r)$, this is impossible. Thus, for a given $n(r)$ there is at most one $v(r)$ (up to an additive constant). Therefore $v(r)$ is uniquely determined by $n'(r)$.

The single particle orbitals satisfy the HF equations

$$\{-(1/2)\nabla^2 + v + v_h\}\psi_i - \Sigma_j \int dr'\psi_j(r)\psi_j^*(r')\psi_i(r')/|r-r'| = \varepsilon_i^{hf}\psi_i \qquad (A.9)$$

where $v_h = v_h[n]$ is the usual Hartree potential. Then since v is uniquely determined by $n(r)$, the $\psi_i(r)$, $i = 1,2....N$ are functionals of $n(r)$ and it follows from Eq.(A.1) that $E^0\{\psi_i\} = F[n]$ where $F[n]$ is a universal functional of the HF density $n(r)$. We may then define, for a given $v(r)$ the HF energy functional

$$E_{hf}^{(v)}[n] \equiv \int v(r)n(r)dr + F[n] \qquad (A.10)$$

Then, for the correct HF ground state density n(r), $E_{hf}^{(v)}[n] = E_{hf}$. Furthermore, it follows from applying the variational principle to the HF energy in exactly the same way as done by HK for the exact energy, that $E_{hf}^{(v)}[n]$ given by Eq.(A.10) assumes its minimum value for the correct n(r) for any n(r) associated with some other potential v'(r).

Finally, it follows using the arguments of KS that we may write

$$E_{hf}^{(v)}[n] = T_s[n] + \int v(r)n(r)dr$$

$$+ (1/2)\int\int drdr'n(r)n(r')/|r-r'| + E_x[n] \qquad (A.11)$$

where $T_s[n]$ is the kinetic energy of a system of non-interacting electrons with density n(r) and $E_x[n]$ is by definition the exchange energy of a HF system with density n(r). SInce $T_s[n]$ is a unique functional of n(r). Again using the same arguments as KS we obtain the KS exchange only single particle equations

$$[- (1/2)\nabla^2 + v(r) + v_h(r) + v_x[n(r)]]\psi_{xi}(r) = \varepsilon_{xi}\psi_{xi}(r) \qquad (A.12)$$

where

$$v_x[n(r)] \equiv \delta E_x[n(r)]/\delta n(r) \qquad (A.13)$$

and

$$n(r) = \Sigma_i|\psi_{xi}(r)|^2 \qquad (A.14)$$

If $E_x[n]$ were known exactly the solutions of Eq.(A.12) with n(**r**) given by Eq.(A.14) would provide the exact density n(**r**). In addition, $T_s[n]$ could be evaluated from Eq.(A.12) which when substituted into Eq.(A.11) would yield an equation analogous to that for the exact HF energy. Equations (A.11)-(A.14) are exactly the same as the usual KS equations for the orbitals and the density if the correlation part of E_{xc} is neglected. However, the foregoing analysis demonstrates that the resultant density is exactly equal to the HF density and the exact HF energy can be obtained as a functional of this density.

Appendix B

Significance of the Exchange-Only KS Outermost Eigenvalue

According to Payne [23], (as we have also shown in Appendix A) in an exact exchange-only theory, the KS ground state total energy is exactly equal to the corresponding HF ground state total energy and the KS density is equal to the corresponding HF density i.e $E^{hf}_{tot} = E^{ks}_{tot}$ and $n^{ks}(r) = n^{hf}(r) = n(r)$. We show here, in addition, that if the system is spherically symmetric, the exchange-only KS highest occupied single particle eigenvalue ε^{ks}_{max} is also equal to the corresponding HF ε^{hf}_{max}, i.e. the ε^{ks}_{max} has the physical meaning that it is the electron removal energy without relaxation.

Consider the single particle equations of the highest occupied states in both the HF and KS schemes

$$\{-(1/2)\nabla^2 + v + v_h + v^{hf}_{x,max}\}\psi^{hf}_{max} = \varepsilon^{hf}_{max}\psi^{hf}_{max} \tag{B.1}$$

$$\{-(1/2)\nabla^2 + v + v_h + v^{ks}_{x}\}\psi^{ks}_{max} = \varepsilon^{ks}_{max}\psi^{ks}_{max} \tag{B.2}$$

where v is the external potential, v_h, the Hartree potential, v_x^{ks}, the KS exchange potential and $v_{x,max}^{hf}$, the effective HF exchange potential corresponding to the highest occupied orbital as defined in the following

$$v_{x,max}^{hf} = -\Sigma_{\alpha\sigma}\{\int dr'\psi_{\alpha\sigma}^{*}(r')\psi_{max}(r')\}\psi_{\alpha\sigma}(r)/\psi_{max}(r) \tag{B.3}$$

With σ sums over only those states which have the same spin projection as ψ_{max}.

Solving for ε_{max}^{hf} and ε_{max}^{ks}, we have

$$\varepsilon_{max}^{hf} = -(1/2)(\nabla^2\psi_{max}^{hf})/\psi_{max}^{hf} + v + v_h + v_{x,max}^{hf} \tag{B.4}$$

$$\varepsilon_{max}^{ks} = -(1/2)(\nabla^2\psi_{max}^{ks})/\psi_{max}^{ks} + v + v_h + v_x^{ks} \tag{B.5}$$

As $r \rightarrow \infty$, $v_h \rightarrow 0$, $v_{x,max}^{hf} \rightarrow 0$ and $v_x^{ks} \rightarrow 0$. (for atoms, $v \rightarrow 0$ as well, for harmonic oscillator systems, however, it does not.)

Thus we have

$$\varepsilon_{max} = \lim_{r\rightarrow\infty}\{-(1/2)(\nabla^2\psi_{max})/\psi_{max} + v(r)\}$$

in both cases.

In a spherically symmetric system

$$n(r) = \Sigma_{\alpha\sigma}|\psi_{\alpha\sigma}(r)|^2 = 2\Sigma_{nl}(2l+1)|R_{nl}(r)|^2$$

where R_{nl} is the radial wavefunction for the subshell with quantum number nl.

For a finite system, the electron density as $r \to \infty$ is determined by the asymptotic behavior of the occupied orbital with the highest energy in both the HF and exchange-only KS theories, since the other orbitals decay exponentially faster.

Thus as $r \to \infty$, we have

$$R_{max}(r) \sim n^{\frac{1}{2}}(r)/(4l+2)$$

for both the HF and KS cases.

Therefore

$$\begin{aligned}
\varepsilon^{hf}_{max} &= \lim_{r\to\infty}\{-1/(2r^2)(d/dr)(r^2 dR^{hf}_{max}/dr)/R^{hf}_{max} + v\} \\
&= \lim_{r\to\infty}\{-1/(2r^2)(d/dr)(r^2 dn^{\frac{1}{2}}(r)/dr)/n^{\frac{1}{2}}(r) + v\} \\
&= \lim_{r\to\infty}\{-1/(2r^2)(d/dr)(r^2 dR^{ks}_{max}/dr)/R^{ks}_{max} + v\} \\
&= \varepsilon^{ks}_{max}
\end{aligned}$$

Appendix C

Derivation of the Non-Adjustable Constants in LSDSICE and LSDSICI

In this appendix, we derive the values of the coefficients β_l and $\gamma_{ll'}$ in both the LSDSICE and LSDSICI expressions for the exchange energy. These coefficients will occur when we appropriately integrate the angular dependent parts of the wavefunctions in the expression for E_x.

C.1 LSDSICE

It is known from our discussion in Chapter 3 that with the self-interaction-correction applied, the exchange energy has the form

$$E_x^{sic}[n_\uparrow,n_\downarrow] = E_x^{app}[n_\uparrow,n_\downarrow] - (\delta_{\alpha\sigma}^{(1)} + \delta_{\alpha\sigma}^{(2)}) \qquad (C.2)$$

$$\delta_{\alpha\sigma}^{(1)} = \Sigma_{\alpha\sigma} E_x^{app}[n_{\alpha\sigma},0] \qquad (C.3)$$

$$\delta_{\alpha\sigma}^{(2)} = (1/2)\Sigma_{\alpha\sigma} U_h[n_{\alpha\sigma},0] \qquad (C.4)$$

where E_x^{app} is the approximation for the exchange energy functional and U_h is the Hartree energy.

In LSD

$$E_x^{lsd}[n_{\alpha\sigma},0] = -A_x \int n_{\alpha\sigma}^{4/3}(r)dr \tag{C.5}$$

with $A_x = 3/4(3/\pi)^{1/3}$ being a constant.

If we assume

$$\psi_{\alpha\sigma}(r) = R_{nl}(r)f_{lm}(\theta,\phi), \tag{C.6}$$

then, the expression for $\delta_{\alpha\sigma}^{(1)}$ for systems with filled subshells becomes

$$\begin{aligned}\delta_{\alpha\sigma}^{(1)} &= \Sigma_{\alpha\sigma} E_x^{lsd}[n_{\alpha\sigma},0] \\ &= -2A_x^{4/3}\Sigma_{nl}\int R_{nl}^{8/3}(r)r^2dr\bullet\Sigma_m\int|f_{lm}(\Omega)|^{8/3}d\Omega \\ &= -2A_x^{4/3}\Sigma_{nl}\int n_{nl}^{4/3}(r)dr(2l+1)\beta_l\end{aligned} \tag{C.7}$$

where $n_{nl}(r) = R_{nl}^2(r)$, is the normalized radial density such that

$$\int n_{nl}(r)dr = 1 \tag{C.8}$$

and

$$\beta_l = \Sigma_m\int|f_{lm}(\Omega)|^{8/3}d\Omega/(4\pi(2l+1)) \tag{C.10}$$

With Cartesian orbitals, the $f_{lm}(\Omega)$ assume the following forms

$l = 0$: $\{1\}$

$l = 1$: $\sqrt{3}\{x, y, z\}/r$

$l = 2$: $\{\sqrt{15}xy, \sqrt{15}yz, \sqrt{15}zx, \sqrt{5/4}(3z^2-r^2), \sqrt{15/4}(x^2-y^2)\}/r^2$

It is then easy to calculate the β_l by using (C.10). We find

$\beta_0 = 1$

$\beta_1 = 1.18$

$\beta_2 = 1.24$

For $\delta^{(2)}_{\alpha\sigma}$, we have

$$\delta^{(2)}_{\alpha\sigma} = (1/2)\Sigma_{\alpha\sigma}\int\int n_{\alpha\sigma}(r)n_{\alpha\sigma}(r')/|r-r'|drdr'$$

$$= \Sigma_{nlm}\int\int n_{nl}(r)n_{nl}(r')|f_{lm}(\Omega)|^2|f_{lm}(\Omega')|^2drdr'$$

$$= 4\pi\Sigma_{nlm}\int\int drdr'\{r^2r'^2n_{nl}(r)n_{nl}(r')\times$$

$$\Sigma_{l'm'}(r_<^{l'}/r_>^{l'+1})|\int[|f_{lm}(\Omega)|^2Y_{l'm'}(\Omega)d\Omega]|^2/(2l'+1)\}$$

$$= \Sigma_{nl}\{(2l+1)\int\int n_{nl}(r)n_{nl}(r')\Sigma_{l'}(r_<^{l'}/r_>^{l'+1})drdr'\gamma_{ll'}\} \qquad (C.11)$$

where

$$\gamma_{ll'} = 4\pi\Sigma_{mm'}|\int[|f_{lm}(\Omega)|^2Y_{l'm'}(\Omega)d\Omega/4\pi]|^2/[(2l+1)(2l'+1)] \qquad (C.12)$$

By employing the Cartesian orbitals given previously for $f_{lm}(\Omega)$ and expressing them in terms of $Y_{lm}(\Omega)$, we obtain, after a tedious calculations of terms like

$$\int d\Omega Y_{lm}(\Omega) Y_{l'm'}(\Omega) Y_{k,-m-m'}(\Omega)$$

which is equal to [63] [64]

$$(2l+1)(2l'+1)/[4\pi(2k+1)]C(lml'm',k\ m+m')C(l0l'0,k0)$$

with C being the Clebsch-Gordon coefficients, that

$$\gamma_{00} = 1$$

$$\gamma_{10} = 1, \quad \gamma_{11} = 4/25$$

$$\gamma_{20} = 1, \quad \gamma_{21} = 4/49, \quad \gamma_{22} = 4/49$$

C.2 LSDSICI

When treating the intra-shell exchange exactly at large r, the $\delta^{(1)}_{\alpha\sigma}$ term will remain the same as that in LSDSICE, however, the $\delta^{(2)}_{\alpha\sigma}$ will be modified to

$$\delta^{(2)}_{\alpha\sigma} = \Sigma_{nl}\{\Sigma_{mm'}\int\int n_{nl}(r)n_{nl}(r')f^{*}_{lm}(\Omega)f_{lm}(\Omega')f^{*}_{lm'}(\Omega')f_{lm'}(\Omega)/|r-r'|drdr'$$

$$= \Sigma_{nl}\{(2l+1)\int\int n_{nl}(r)n_{nl}(r')\Sigma_{l'}(r_<^{l'}/r_>^{l'+1})drdr'\gamma_{ll'}\} \qquad (C.13)$$

where

$$\gamma_{ll'} = 4\pi\Sigma_{mm'm''}|\int f^{*}_{lm}(\Omega)f_{lm'}(\Omega)Y_{l''m''}(\Omega)d\Omega/4\pi|^{2}/[(2l+1)(2l'+1)] \quad (C.14)$$

Thus, we have a double sum over m and m' on $f_{lm}(\Omega)$ and $f_{lm'}(\Omega)$ instead of only one as in dealing with the LSDSICE problem. Nevertheless, the calculations of $\gamma_{ll'}$ are straight forward. By performing similar calculations as in C.1 for LSDSICE, we obtain

$\gamma_{00} = 1$

$\gamma_{10} = 1, \quad \gamma_{11} = 2/5$

$\gamma_{20} = 1, \quad \gamma_{21} = 2/7, \quad \gamma_{22} = 2/7$

Appendix D

Values of Alpha in the New GEA

We determine in this appendix the values of α in our GEA expression given in Chapter 4 which could avoid the singularities of the exchange density and exchange potential as r approaches infinity. In addition, we will also calculate the α values, such that when the SIC is applied to this GEA, the singularities of the exchange potential at the nodes of the wavefunctions are also removed. Finally, we show that when $\alpha < 1/2$ the exchange energy density as written in Eq.(4.7) will be finite as r approaches infinity.

Consider the expressions for the e_x and v_x

$$e_x[n(r)] = \varepsilon_x^{lda}[n(r)]f^{\alpha}[n(r)] \tag{D.1}$$

$$v_x[n(r)] = v_x^{(1)}[n(r)] + v_x^{(2)}[n(r)] \tag{D.2}$$

$$v_x^{(1)}[n(r)] = v_x^{lda}[n(r)]f^{\alpha}[n(r)] \tag{D.3}$$

$$v_x^{(2)}[n(r)] = -v_x^{lda}[n(r)](3B_x/2n^{5/3})f^{\alpha-1}[n(r)]g[n(r)] \tag{D.4}$$

where

$$\varepsilon_x^{l\,da}[n(r)] = -3/4(3/\pi)^{1/3}n^{1/3}(r) \qquad (D.5)$$

and

$$v_x^{l\,da}[n(r)] = -(3/\pi)^{1/3}n^{1/3}(r) \qquad (D.6)$$

are the LSD exchange density and exchange potential respectively and

$$f[n(r)] = 1 + B_x|\nabla n|^2/(\alpha n^{8/3})$$

$$g[n(r)] = \nabla^2 n + 2(1-\alpha)f^{-1}[n(r)]\{1-f[n(r)]\}\{n''-4n'^2/(3n)\}$$

with

$$n' = dn/dr$$

$$n'' = d^2n/dr^2$$

Comparing the e_x and $v_x^{(1)}$, they have exactly the same form except for the coefficients. Thus in the following discussions, we will only consider the v_x expression. The convergence of e_x is automatically guaranteed once α is chosen such that $v_x^{(1)}$ converges.

D.1 Convergence as r approaches infinity

It is known that in a finite system, $n(\mathbf{r}) \to 0$ as $r \to \infty$. For atoms, $n(r)$ goes to zero as $\exp(-ar)$ and for harmonic oscillator problem, it goes as $\exp(-br^2)$, where a and b are positive constants.

We thus can write $n(\mathbf{r}) \sim \exp(-ar^n)$ to denote both atoms (n=1) and harmonic oscillator system (n=2) situations.

Since we are only concerned with systems having spherical symmetry i.e. $n(\mathbf{r}) = n(r)$, we then have $|\nabla n| = |dn/dr| = n'$ and $\nabla^2 n = n'' + 2n'/r$.

As $r \to \infty$

$$n' \sim \exp(-ar^n)$$

$$n'' \sim \exp(-ar^n)$$

$$v_x^{lda} \sim n^{1/3} = \exp(-ar^n/3)$$

$$f[n(r)] \sim [n'^2/n^{8/3}] = \exp(2ar^n/3)$$

Consider the expression for $v_x^{(1)}$ first. As $r \to \infty$, we have

$$v_x^{(1)} \sim \exp(-ar^n/3)\exp(2a\alpha r^n/3) = \exp[-(1/3-2\alpha/3)ar^n]$$

In order to have $v_x^{(1)}$ converge as r approaches infinity, we must have

$$1/3 - 2\alpha/3 > 0$$

or

$$\alpha < 1/2$$

As for $v_x^{(2)}$, since

$$v_x^{(2)} = \exp(-ar^n/3)\exp(2ar^n(\alpha-1)/3)\exp(5ar^n/3)\exp(-ar^n)$$

$$= \exp(-(1-2\alpha)ar^n/3)$$

similarly, we obtain

$$\alpha < 1/2$$

Thus, as long as $\alpha < 1/2$, both the e_x and v_x will approach zero as $r \to \infty$

D.2 At r = 0

Since $n(0) \neq 0$ and $n'(0) \neq 0$ for atoms, it is observed, from the expression for v_x, that there is a term $\nabla^2 n = n'' + 2n'/r$ which is singular as $1/r$ at $r = 0$ and this singularity can not be removed no matter what value we chose for α. However, from the argument by Herman et al, that the singularity of $1/r$ of the exchange potential at $r=0$ does not significantly affect the solutions of the Schrodinger equations except perhaps the s-like wavefunctions. The only thing we need to insure, therefore, is that for $\alpha < 1/2$, $v_x \sim r^b$ with $b \geq -1$.

For the v_x considered above, we have already observed that $v_x \sim 1/r$, as $r \to 0$. However, if we consider the GEA with SIC applied, there will be additional terms involving the orbital density $n_{\alpha\sigma}$ which is zero at $r = 0$ and we must chose α such that the v_x is no more singular than r^{-1} when $r \to 0$.

In general, for states with angular momentum number l,

$$n_{\alpha\sigma} \sim r^{2l}$$

$$n'_{\alpha\sigma} \sim r^{2l-1}$$

$$n''_{\alpha\sigma} \sim r^{2l-2}$$

$$v_x^{\mathrm{lda}} \sim r^{2l/3}$$

$$f[n(r)] \sim r^{(2l-1)} r^{-16l/3} = r^{-(2+4l/3)}$$

Thus

$$v_x^{(1)} \sim r^{4l/3} r^{-(2+4l/3)\alpha}$$

and

$$4l/3 - (2 + 4l/3)\alpha \geq -1$$

or

$$\alpha \leq (1 + 4l/3)/(2 + 4l/3) = (3 + 4l)/(6 + 4l) \leq 1/2$$

For $v_x^{(2)}$

$$v_x^{(2)} \sim r^{-10l/3} r^{-(2+4l/3)(\alpha-1)} r^{2l/3} r^{2l-2}$$

$$= r^{2l/3-(2+4l/3)\alpha}$$

Therefore

$$2l/3 - (2 + 4l/3)\alpha \geq -1$$

or

$$\alpha \geq (1+2l/3)/(2+4l/3) = (3+2l)/(6+4l) \leq 1/2$$

Thus, $\alpha < 1/2$ always satisfies the condition that v_x and e_x be no more singular than r^{-1} as $r \to 0$.

D.3 At $r = r_0$, the node of the orbital wavefunction

To apply SIC in GEA, not only should the singularity problems of e_x and v_x at r equals zero and infinity be appropriately handled, one must also correctly deal with the possible singularities of the e_x and v_x at the nodes of the single particle wavefunctions. As $r \to r_0$, $n_{\alpha\sigma} \sim (r-r_0)^2$. If we make a transformation $\rho = r - r_0$, we will then have a completely similar situation as in dealing with r=0 case with the special value of $l = 1$, except now we have to chose the value for α such that the singularity in entirely removed instead of just requiring it not be more singular than r^{-1}. We have

$$v_x^{(1)} \sim \rho^{21/3-(2+41/3)\alpha}$$

$$= \rho^{2/3-101/3}$$

or

$$\alpha \le 1/5$$

For $v_x^{(2)}$

$$v_x^{(2)} \to \rho^{21/3-(2+41/3)\alpha}$$

$$= \rho^{2/3-10\alpha/3}$$

Thus we obtain $\alpha \le 1/5$ as well for $v_x^{(2)}$

D.4 Discussion of the GEA exchange functional in terms of the Laplacian form(GEAL)

In this subsection we will only consider the convergence problem for the exchange density for this formalism(ref Eq.(4.7) in the text), since we do not plan to solve self-consistently the Schrodinger equation. Instead, we will merely calculate the expectation values of the exchange energy using the HF densities and therefore the exchange potential is not needed.

Consider the following

$$e_x[n(r)] = \varepsilon_x^{1\,da}|1 + 3B_x\nabla^2 n/(\alpha n^{5/3})|^{\alpha}$$

As in discussing the e_x in the gradient form in the previous subsections, we need to consider the behavior of this e_x at 1) as $r \to \infty$ and 2) at $r = 0$.

However, if we observe that $\nabla^2 n/n^{5/3}$ actually has the same asymptotic behavior as $|\nabla n|^2/n^{8/3}$ both at infinity and at $r = 0$(except perhaps the s states for which the GEAL e_x is no more singular than $1/r$ anyway and pose no problems), it is then easy to reach the same conclusion which we have drawn for the e_x in the gradient form i.e the values of $\alpha < 1/2$ will guarantee that the GEAL e_x has no singularity as $r \to \infty$ and to be no more singular than r^{-1} at $r = 0$.

D.5 Conclusion

From the previous discussion, we may make the following conclusions.

(1) Without SIC, the values of $\alpha < 1/2$ will guarantee our GEA form for both the exchange energy density and exchange potential to have no singularity at infinity and actually to approach zero. In application, the value of $\alpha = 1/2$ can be used since we can chose α arbitrarily close to 1/2 and in computer calculation, there is no difference if we chose 1/2 or 0.49999999999.

(2) In applying SIC technique to this GEA, the value of α should be further reduced, i.e. $\alpha \leq 0.2$, in order that there are no singularities at the nodes of the wavefunctions.

(3) The values of $\alpha < 1/2$ will also insure that the e_x in the Laplacian form behaves appropriately.

Appendix E

Discussion of the Gradient Expansion for Two New Exchange Energy Functionals

We show in this appendix that the following three expressions for the exchange energy have no gradient expansion.

$$E_x = -(1/4)\int\int dr_1 dr_2 n^2(R)\times$$

$$F[((n(r_1)+n(r_2)+n(R))/3)^{1/3}ar]/|r_1-r_2| \qquad (E.1)$$

$$E_x = -(1/4)\int\int dr_1 dr_2 [(n(r_1)+n(r_2)+n(R))/3)]^2\times$$

$$F[((n(r_1)+n(r_2)+n(R))/3)^{1/3}ar]/|r_1-r_2| \qquad (E.2)$$

$$E_x = -(1/4)\int\int dr_1 dr_2 [(n(r_1)+n(r_2)+7n(R))/9)]^2\times$$

$$F[((n(r_1)+n(r_2)+n(R))/3)^{1/3}ar]/|r_1-r_2| \qquad (E.3)$$

where

$$a = (3\pi^2)^{1/3}$$

$$r_1 + r_2 = 2R$$

$$r_1 - r_2 = r$$

$$F(x) = 9[(\sin(x)-x\cos(x))/x^3]^2$$

thus

$$r_1 = R + r/2$$

$$r_2 = R - r/2$$

To order of $O(\nabla^2)$

$$n(R+r/2) = n(R) + R\cdot\nabla n(R)/2 + rr:\nabla\nabla n(R)/8$$

$$n(R-r/2) = n(R) - r\cdot\nabla n(R)/2 + rr:\nabla\nabla n(R)/8$$

$$(n(r_1)+n(r_2)+n(R))/3 = n(R) + rr:\nabla\nabla n(R)/12$$

$$(n(r_1)+n(r_2)+7n(R))/9 = n(R) + rr:\nabla\nabla n(R)/36$$

Therefore, expression (E.1) becomes

$$E_x = - (1/4)\int\int n^2(R)F[(n(R) + rr:\nabla\nabla n(R)/12)^{1/3}ar]drdR/r$$

$$= - (1/4)\int\int n^2F[k_F(R)r + k_F(R)rr:\nabla\nabla n(R)/(36n(R))]drdR/r$$

$$= E_x^{l\,da} - (1/16)\int\int n(R)k_F(R)F'(k_Fr)rr:\nabla\nabla n(R)drdR$$

$$= E_x^{l\,da} - (\pi/12)\int n(R)\nabla^2 n(R)/k_F^4(R)dR\cdot\int x^4F'(x)dx$$

$$= E_x^{l\,da} + (\pi I_0/3)\int n(R)\nabla^2 n(R)/k_F^4(R)dR$$

where

$$I_0 = \int x^3 F(x)dx$$

It is easily shown, by integration by parts, that

$$I_0 = \int dx[\sin^2(x)/x]$$

which is divergent as ln(x) $(x \to 0)$, and therefore, there is no gradient expansion for expression (E.1).

Similarly, we can show that expression (E.2) can be written

$$E_x = E_x^{1\,da} - (\pi I_0/6)\int n(R)\nabla^2 n(R)/k_F^4(R)dR$$

and expression (E.3) as

$$E_x = E_x^{1\,da} + (\pi I_0/6)\int n(R)\nabla^2 n(R)/k_F^4(R)dR$$

which are also divergent due to I_0, so no gradient expansion exists for (E.2) and (E.3) either.

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