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A

STUDIES IN DENSITY FUNCTIONAL THEORY

by

YILI LIU

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

1993

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## ABSTRACT

### STUDIES IN DENSITY FUNCTIONAL THEORY

by

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The method proposed by Krieger, Li and Iafrate (KLI) for the construction of the optimized effective potential (OEP) is examined to determine whether it can be significantly simplified while still retaining its high accuracy. The need for simplification arises because the KLI method may be difficult to employ in multi-atom calculations.

We construct a simplified KLI(SKLI) potential by approximating the  $V_w$  corresponding to the core electrons by the corresponding expression in the local spin density (LSD) approximation or the LSD with self interaction correction (SIC) while employing the HF  $V_w$  only for the occupied valence electron states. We show analytically that such an approximation continues to maintain the important analytic properties of both the OEP and KLI. The SKLI makes only a modest improvement over the LSD (or LSDSIC) in the calculation

of the total energy. However, calculations of  $\epsilon_{mo}$ , the energy eigenvalue of the highest occupied single particle state, and of  $\langle r^2 \rangle$ , are nearly identical to the OEP and KLI results demonstrating that the behavior of the valence electrons, which are important in molecular binding calculations, can be accurately predicted by this approximation. These conclusions are substantiated by performing similar calculations on negative ions.

We investigate correlation energy by extending the exactly soluble Laufer-Krieger model to the case of two electrons with parallel spin. We find the exact value of the total energy, the exchange-correlation energy, the exchange-correlation potential as well as the separate exchange and correlation contributions to these quantities and compare these results to various approximations. In exchange only case, the LSD, LSDSIC and the KLI method which constructs the OEP single potential from the effective single particle HF exchange potentials are examined. Also we test exchange-correlation functionals. We use the LSD, LSDSIC and HF to calculate the exchange energy and add the correlation energy by invoking the LSD, LSDSIC, GGA and GGA with SIC. The KLI method (with correlation) is employed to construct the OEP potential as the sum of the effective HF exchange potential and the LSD, LSDSIC, GGA, GGASIC correlation potential respectively.

O Lord, how manifold are thy works! In wisdom hast thou made  
them all; the earth is full of thy creatures.

-----Psalms 104:24

Give all my loves to my Creator.

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# CHAPTER 1

## Introduction

### 1.1 General Survey

The solution of the appropriate Schrodinger equation, in principle, provides the basis for the study of the properties of quantum many particle systems. In atoms, molecules and solids, an exact solution entails an accurate treatment of interparticle potentials, including the electron-electron, and electron-proton Coulomb interactions. However, for a system containing  $N$  electrons, the Schrodinger equation is a  $3N$  dimensional differential equation and analytic solutions are generally unavailable for  $N > 1$ . In fact, we are still not able to obtain an exact solution for even the two electron system, the helium atom, let alone an analytic result for solids containing electrons with  $N$  the order of  $10^{23}$ .

Therefore various approximations have been developed. Among these, the Thomas-Fermi<sup>[1][2]</sup>(TF), Hartree<sup>[3]</sup>, Hartree-Fock (HF)<sup>[4]</sup>, configuration interactions(CI)<sup>[5][6]</sup> and density functional theory(DFT)<sup>[7][8]</sup> are regarded as the most fundamental and useful ones.

Thomas and Fermi realized that statistical considerations can be used to approximate the distribution of electrons. The relation between  $n_0$  (the number of electron per unit volume) and  $K_F$  (the Fermi momentum) derived for a homogeneous electron gas is employed for an inhomogeneous electron gas by

replacing  $n_0$  by  $n(\mathbf{r})$  and  $K_F$  by  $K_F(\mathbf{r})$  i.e.  $n(\mathbf{r}) = [1/(3\pi^2)]K_F^3(\mathbf{r})$ . The corresponding kinetic energy,  $T_{TF}$ , becomes  $T_{TF} = (3/10)(3\pi^2)^{2/3} \int n(\mathbf{r})^{5/3} d\mathbf{r}$ , a functional of the density only. Dirac considered the exchange interaction between the electrons and thus the method was further improved as the Thomas-Fermi-Dirac method (TFD). Thomas-Fermi and related models constitute a direct approach for the calculation of the kinetic energy. This results in considerable simplicity--- instead of a  $3N$  dimensional wave function, the basic function in describing the system involves  $n(\mathbf{r})$  alone (only three dimensions). However, due to the fact that the highly non-local kinetic energy is replaced by a local functional of the density  $n(\mathbf{r})$ , the traditional Thomas-Fermi model is only a first approximation and it is difficult to systematically improve --- i.e. the resulting density does not exhibit the usual shell structure of the atom.

In the Hartree approximation, one solves the original Schrodinger equation by applying the variational principle and assuming a product wavefunction composed of single particle wavefunctions. The Pauli principle is satisfied by allowing only one electron to occupy each electron state. Each electron is considered as moving in the sum of the external potential and the average Coulomb field due to all other electrons. On the other hand, the Hartree-Fock method is derived by using the same technique except assuming the wavefunction to be a determinant of the single particle

wavefunctions. The wavefunction here is antisymmetric and it automatically satisfies the Pauli exclusion principle. Consequently the corresponding exchange energy, which arises from the reduction of the probability of two electrons with the same spin from approaching each other, only occurs in the HF method. As a result, the electron-electron Coulomb repulsion energy is reduced and the total energy is lowered. However, since the exchange potential in HF involves non-local terms, it is much more difficult to solve for the single particle wavefunctions in this case than in the Hartree case. Both Hartree and Hartree-Fock approximations correctly describe the shell structure of atoms.

When one is interested in higher accuracy, one finds that the exact wavefunction for a system of many interacting electrons is never a single determinant or a simple combination of a few determinants. The calculation of the error in the energy, which exists in HF, is called the correlation energy. The correlation energy arises because, due to the electron-electron repulsion, the total energy of the system will be reduced if electrons tend to avoid each other. Although the amount of correlation energy is usually small compared to the exchange energy in atoms, it becomes significant in many problems in which accurate quantitative results are required. The configuration interaction method will include the exchange and correlation interactions by expanding the wavefunction as a sum of many determinantal

wavefunctions with undetermined constants. The constants are obtained from employing the variational principle for the energy. In principle, this method is exact when the number of determinants in the expansion approaches infinity. However, it is impractical to employ on systems with a large number of electrons.

Thus, the above approximations for treating a multi--electron system are either not exact in principle or not practical to employ on systems consisting of a large number of electrons.

More recently, Hohenberg and Kohn<sup>[7]</sup> and Kohn and Sham<sup>[8]</sup> (KS) developed a new way to calculate the ground state density and ground state energy, called density functional theory. In this theory, instead of the complicated N-electron wavefunction, the electron density will be employed as the basic variable describing the system. Although the original idea comes from the Thomas Fermi approximation, DFT is significantly improved---it is in principle exact and it has been turned into a practical tool for rigorous calculations. Hohenberg and Kohn proved that the ground state energy of any system containing electrons moving in an external potential is a functional of the electron density. In particular they showed that the energy of the ground state of a many-electron system can be obtained as the minimum of the energy functional

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

where  $v(\mathbf{r})$  is a given external potential and  $F[n]$  is a universal functional of the density  $n(\mathbf{r})$ .  $F[n]$  is the sum of the kinetic energy functional  $T[n]$  and electron-electron interaction energy functional  $V_{ee}[n]$  which are also universal functionals of the density  $n(\mathbf{r})$ .

$$F[n] = T[n] + V_{ee}[n] \dots\dots\dots (1.2)$$

In 1965, Kohn and Sham developed an ingenious indirect approach to calculate  $T[n]$ . They thereby turned density functional theory into a practical tool for various calculations. Kohn and Sham invoked a corresponding noninteracting reference system which shared the same total electron density  $n(\mathbf{r})$  with the original interacting system. The kinetic energy in the noninteracting system is  $T_s[n]$  and it is  $T[n]$  in interacting system.

We can write (1.2) as:

$$F[n] = T_s[n] + J[n] + E_{xc}[n] \dots\dots\dots (1.3)$$

where  $J[n]$  is the classical coulomb energy functional i.e.

$$J[n] = \frac{1}{2} \int \frac{n(\mathbf{r}') n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \dots\dots\dots (1.4)$$

The exchange-correlation energy functional  $E_{xc}[n]$  can be written as:

$$E_{xc}[n] = T[n] - T_s[n] + V_{ee}[n] - J[n] \dots\dots\dots (1.5)$$

The exact ground state energy of the interacting system is

calculated from single particle orbitals describing noninteracting electrons moving in a local effective potential  $V_{\text{eff}}(\mathbf{r})$ , i.e.

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \dots\dots\dots (1.6)$$

$$V_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{\text{XC}}[n(\mathbf{r})] \dots\dots\dots (1.7)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \dots\dots\dots (1.8)$$

$v(\mathbf{r})$  is the external potential,  $V_H[n(\mathbf{r})]$  is the Hartree potential,  $V_{\text{xc}}[n(\mathbf{r})]$  is the functional derivative of the exchange-correlation energy with respect to the density  $n(\mathbf{r})$  and is a universal function of  $n(\mathbf{r})$ .

$$V_H = \int \frac{n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' \dots\dots\dots (1.9)$$

$$V_{\text{XC}}[n(\mathbf{r})] = \frac{\delta E_{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \dots\dots\dots (1.10)$$

The total energy of the system can be written as:

$$E = \sum_i^N \epsilon_i + E_{\text{XC}}[n] - \int V_{\text{XC}}[n(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \iint \frac{n(\mathbf{x}) n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{r} d\mathbf{r}' \dots\dots (1.11)$$

Kohn Sham theory merely provides for the existence of  $E_{\text{XC}}[n(\mathbf{r})]$ . However, it does not prescribe a method for its exact construction. So the search for an accurate  $E_{\text{XC}}[n]$  becomes the greatest challenge in the density functional

theory. As a first approximation to its construction, Kohn and Sham introduced a local density approximation (LDA)<sup>[8]</sup>. In this approximation, electronic properties are determined as a functional of the electron density by applying local relations appropriate for a homogeneous electron system. In the LDA, the total exchange and correlation energy of the electrons are approximated by results for the homogeneous spin-compensated electron gas.  $V_x$  in LDA equals 2/3 of the usual Slater exchange potential<sup>[9]</sup>. The LDA method was further improved by Von Barth and Hedin<sup>[10]</sup> to include spin effects in a local spin density (LSD) approximation. Improved accuracy was obtained by employing a gradient expansion approximation (GEA)<sup>[11][12]</sup> in early work.

Recently, Perdew et al<sup>[13]</sup> showed that the maximum occupied KS orbital energy eigenvalue is equal to the negative of the ionization energy of the system. Therefore, much effort has been devoted toward constructing  $V_{xc}$  which results in accurate calculations of the total energy  $E$ , the highest occupied eigenvalue  $\epsilon_m$  and the density  $n(\mathbf{r})$ . In order to accomplish this, in addition to LSD and GEA, the LSD with self interaction correction(LSDSIC)<sup>[14]</sup> and generalized gradient approximation (GGA)<sup>[15]</sup> developed by Perdew and coworkers are also often used. On the other hand, an accurate spin-polarized exchange only Kohn Sham potential  $V_{x\sigma}$  can be obtained from a consideration of the Optimized Effective Potential(OEP) method.<sup>[16][17]</sup>

Recently, Krieger, Li and Iafrate<sup>[18]</sup> analyzed the OEP intergral equation for the exchange only case and obtained a set of conditions which are satisfied by the exact Optimized Effective Potential. These conditions were employed to construct a very accurate approximation to the OEP, which we shall refer to as the KLI potential which is a single (spin polarized) potential and also an explicit functional of KS orbitals. This potential reduces to the exact KS result in the homogenous electron gas limit; it approaches  $-1/r$  as  $r \rightarrow \infty$ <sup>[18]</sup>; it yields highest occupied orbital eigenvalues  $\epsilon_m$  that satisfy Koopmans' theorem;<sup>[19]</sup> and exhibits an integer discontinuity when considered as a function of fractional occupancy of the highest energy occupied single potential state of a given spin projection<sup>[18]</sup> and  $\epsilon_m$  nearly exactly satisfies Janak's theorem<sup>[20]</sup>. The KLI potential is a remarkably accurate approximation to the exact OEP. The results provided by this method make a significant improvement in total energy, highest occupied energy eigenvalues and average of  $r^2$ , which is highly weighted by the density of valence electrons. They are in excellent agreement with both HF and exact OEP results.

The OEP method may be extended to find the optimized potential for any assumed form of  $E_{xc}[\varphi_i]$ . In addition, the KLI method for accurately approximating the corresponding OEP is easily extended to this case as well so that it is now possible to construct accurate orbital dependent

approximations to  $E_{xc}$ .

In 1986, Laufer and Krieger<sup>[21]</sup> gave an exactly soluble model consisting of two electrons with anti-parallel spin attracted to a common center by harmonic-oscillator forces with mutual Coulomb repulsion between electrons. They obtained the exact exchange and correlation energy and related potentials. The results can be used as a test of the efficacy of various functionals of  $E_{xc}$ .

## 1.2 Thesis Outline

The KLI method for exchange only provides a very accurate approximation to the exact OEP. However, it requires the calculation of all the HF overlap integrals thereby limiting its application in multi-atom calculations. On the other hand, the LSD is a simple and accurate approximation for core electrons. But it becomes less accurate when it is used to treat the valence electrons.

In chapter 2, we will develop a new simplified KLI (SKLI) approximation which is a simple and accurate approximation to the KLI method. In the exchange only case, we construct the simplified KLI potential by combining KLI with LSD--- corresponding to core electrons i.e. for inner orbitals, we make use of the LSD; we treat outer orbitals i.e. valence electrons according to the KLI prescription. We have performed calculations for atoms from  $Z=3$  to  $Z=56$ . The

results demonstrate that the total energy is moderately improved compared with LSD, and that the calculations of the highest occupied eigenvalues, the average value of  $r^2$  are very close to the exact HF and KLI values.

We employ the SKLI method for the calculation of negative ions and compare these results to those obtained by using the HF, OEP, KLI methods.<sup>[22]</sup> In the application of this method, the electron affinity (EA), which is defined as the difference between the total ground state energies of the corresponding atom A and the ion A<sup>-</sup>, the highest occupied energy eigenvalue and the total ground state energy of negative ions are obtained. We have shown that in atomic calculations, the SKLI method does yield results that are very close to those of HF, OEP and KLI with a significant reduction in the calculation of HF type overlap integrals.

In chapter 3, we will study the correlation energy. It has been known that although the correlation energy is generally much smaller than the exchange energy, it plays a significant role in describing the behavior of the valence electrons.

The HF method and OEP, KLI in exchange only approximation fail to give accurate electron affinity (EA) for many atoms. Sometimes these methods provide EA as a negative number<sup>[22]</sup> which implies that corresponding negative ion do not exist in nature even in those cases for which it has been experimentally observed.

This happens because of the fact that in those calculations correlation has been neglected. We have attempted to add the effect of correlation in both HF and KLI approximations. The results show that the existence of negative ions can be predicted correctly. EA,  $\epsilon_m$  and the total energy in the ground state are improved and are closer to the value provided by experiment than those obtained using the exchange only theory.

In Laufer and Krieger's paper,<sup>[21]</sup> the exact correlation potential was obtained by considering an exactly soluble model consisting of two electrons with antiparallel spin attracted to a common center by harmonic-oscillator forces with mutual Coulomb repulsion between the electrons. Recently O.V. Gritsenko and G.M.Zhidomirov<sup>[23]</sup> pointed out that the contribution of electrons with antiparallel spin to the correlation energy in atoms is much larger than the contribution of electrons with parallel spin.

In chapter 4, we will extend Laufer-Krieger model to find the ground state of a similar harmonic force system which consists of two electrons with parallel spin. The model is completely soluble. The exact ground state energy, exchange potential, correlation potential, KS single particle energy eigenvalues, exchange energy and correlation energy can be calculated.

Our calculation demonstrates that the contribution to the correlation energy from electrons with parallel spin is about

1/6 of the total correlation energy found by Laufer and Krieger. We choose  $r_s = [3/4\pi n(\mathbf{r})]^{1/3}$  as a variable, graph  $V_x[n(\mathbf{r})]$  vs  $r_s$  and  $V_c[n(\mathbf{r})]$  vs  $r_s$ , for various spring constants,  $K$ . We find that they are very similar in shape to  $V_x$  and  $V_c$  corresponding to antiparallel spin.

For the system consisting of two electrons with parallel spin, the KS equation is:

$$\left[-\frac{1}{2}\nabla^2 + U(\mathbf{r}) + V_{xc}[n(\mathbf{r})]\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \dots\dots\dots (1.12)$$

$$U(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \dots\dots\dots (1.13)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \dots\dots\dots (1.14)$$

Each different approximation provides a different  $V_{xc}$ . The equation can be solved by employing self-consistent calculations. We investigate the accuracy of LSD and LSDSIC, including exchange, correlation energy and related potentials by comparing them with the exact solutions. The accuracy of the KLI method is also tested for this two particle system. We take the HF exchange potential and the HF exchange potential plus the LSD, LSDSIC, GGA and GGASIC correlation potential respectively to construct the KLI single potentials (KLI in exchange only case and exchange-correlation case). The comparison of the results obtained by the KLI and the exact

solutions are given in thesis.

## CHAPTER 2

### Accurate Approximation For the Kohn-Sham Exchange Potential Using the SKLI Method

#### 2.1 Overview of the OEP and the KLI

The major problem in applying density functional theory for the calculation of the ground state properties of interacting electrons subject to an external potential is in obtaining an accurate exchange and correlation potential  $V_{XC}(\mathbf{r})$ , which is the functional derivative of the exchange--correlation energy function  $E_{XC}[n(\mathbf{r})]$  with respect to the electron density  $n(\mathbf{r})$ . Although Hohenberg and Kohn<sup>[7]</sup> have proved that  $E_{XC}[n]$  exists, none of the  $E_{XC}[n]$  that have been proposed results in accurate calculation of  $V_{XC}(\mathbf{r})$  in the region occupied by the valence electrons and beyond i.e. it is known that in the large  $r$  limit  $V_{XC} \rightarrow -1/r$ , whereas the proposed  $E_{XC}$  lead to  $V_{XC}$  which approach zero exponentially fast.

Earlier, Sharp and Horton<sup>[16]</sup> provided an alternative approach which we refer to as the Optimized Effective Potential method. In this method, the Optimized Effective Potential,  $V^o$ , is defined such that when  $V^o$  is employed in a single particle Schrodinger equation, the Slater determinant of the occupied eigenfunctions minimizes the expectation value of the total hamiltonian. In the spin polarized case, the optimized effective potential (OEP)  $V^o$ , is spin dependent and

the single particle eigenfunctions satisfy

$$-\frac{1}{2}\nabla^2\varphi_{i\sigma}^{\circ}(\mathbf{r})+V_{\sigma}^{\circ}(\mathbf{r})\varphi_{i\sigma}^{\circ}=\epsilon_{i\sigma}^{\circ}\varphi_{i\sigma}^{\circ}(\mathbf{r})\dots\dots(2.1)$$

$$V_{\sigma}^{\circ}(\mathbf{r})=V_H(\mathbf{r})+V_{ext}(\mathbf{r})+V_{XC\sigma}(\mathbf{r})\dots\dots(2.2)$$

If we only consider exchange, (2.2) will be:

$$V_{\sigma}^{\circ}(\mathbf{r})=V_H(\mathbf{r})+V_{ext}(\mathbf{r})+V_{X\sigma}^{\circ}(\mathbf{r})\dots\dots(2.3)$$

The Hartree-Fock exchange energy can be represented by using the eigenfunctions  $\varphi_{i\sigma}^{\circ}$  of (2.1):

$$E_x^{HF}[\varphi_{i\sigma}^{\circ}]=-\frac{1}{2}\sum_{\sigma}\sum_{ij}f_{i\sigma}f_{j\sigma}\iint\frac{\varphi_{i\sigma}^{\circ*}(\mathbf{r}')\varphi_{j\sigma}^{\circ*}(\mathbf{r}')\varphi_{i\sigma}^{\circ}(\mathbf{r})\varphi_{j\sigma}^{\circ}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\dots\dots(2.4)$$

where  $f_{i\sigma}$  is the fractional occupancy of the  $i\sigma$  state. In the exchange only case, we minimize the total energy with respect to the optimized effective potential  $V^{\circ}$ ((2.3)), and obtain the original equation for the optimized effective exchange potential generalized to the spin polarized case including fractional occupancy.

$$\sum_i f_{i\sigma}\int[V_{X\sigma}^{\circ}(\mathbf{r}')-v_{i\sigma}(\mathbf{r}')]G_{i\sigma}^{\circ}(\mathbf{r}',\mathbf{r})\varphi_{i\sigma}^{\circ*}(\mathbf{r}')\varphi_{i\sigma}^{\circ}(\mathbf{r})d\mathbf{r}'+C.C.=0\dots\dots(2.5)$$

here  $v_{i\sigma}(\mathbf{r})$  is the effective HF single-particle potential given by

$$V_{i\sigma}(\mathbf{r}) = \frac{1}{f_{i\sigma} \varphi_{i\sigma}^{\circ}(\mathbf{r})} \frac{\delta E_x^{HF}}{\delta \varphi_{i\sigma}^{\circ}(\mathbf{r})} = -\sum_j f_{j\sigma} \int \frac{\varphi_{j\sigma}^{\circ}(\mathbf{r}') \varphi_{j\sigma}^{\circ}(\mathbf{r}) \varphi_{i\sigma}^{\circ}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'| \varphi_{i\sigma}^{\circ}(\mathbf{r})} d\mathbf{r}' \dots (2.6)$$

and  $G_{i\sigma}^{\circ}(\mathbf{r}', \mathbf{r})$  is the Green's function

$$G_{i\sigma}^{\circ}(\mathbf{r}', \mathbf{r}) = \sum_j' \frac{\varphi_{j\sigma}^{\circ}(\mathbf{r}') \varphi_{j\sigma}^{\circ}(\mathbf{r})}{\varepsilon_{j\sigma}^{\circ} - \varepsilon_{i\sigma}^{\circ}} \dots (2.7)$$

where the sum is over all state for which  $\varepsilon_{j\sigma} \neq \varepsilon_{i\sigma}$ .

If we approximate  $\varepsilon_{j\sigma}^{\circ}$  in equation (2.7) by some mean energy  $\varepsilon_{j\sigma}$  and assume  $\varepsilon_{j\sigma}^{\circ} - \varepsilon_{i\sigma}^{\circ} = \Delta\varepsilon_{\sigma}$ , is independent of  $i$ , we obtain the approximation to  $G_{i\sigma}(\mathbf{r}', \mathbf{r})$ :

$$G_{i\sigma}(\mathbf{r}', \mathbf{r}) \approx \frac{1}{\Delta\varepsilon_{\sigma}} \sum_j' \varphi_{j\sigma}(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}) = \frac{1}{\Delta\varepsilon_{\sigma}} [\delta(\mathbf{r}', \mathbf{r}) - \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r})] \dots (2.8)$$

for non degenerate  $\{\varphi_{j\sigma}\}$ .

When eq (2.8) is substituted for  $G_{i\sigma}^{\circ}$  in eq(2.5), Krieger, Li and Iafrate<sup>[18]</sup> have shown that eq (2.5) may be exactly rewritten as:

$$V_{x\sigma}(\mathbf{r}) = \frac{\sum_j n_{j\sigma} V_{j\sigma}(\mathbf{r})}{\sum_j n_{j\sigma}(\mathbf{r})} + \frac{\sum_j n_{j\sigma} (\bar{V}_{x\sigma j} - \bar{V}_{i\sigma})}{\sum_j n_{j\sigma}(\mathbf{r})} \dots (2.9)$$

where the average values of  $V_{x\sigma}$  and  $v_{i\sigma}$  are both taken over the  $i\sigma$  state.

Then, if we require that  $V_{x\sigma} \rightarrow 0$  as  $r \rightarrow \infty$ , it follows that:

$$\bar{V}_{x\sigma m} = \bar{V}_{m\sigma} \dots\dots\dots (2.10)$$

where  $m\sigma$  denotes the highest energy occupied orbital with spin projection  $\sigma$ . So that eq (2.9) may be written

$$V_{x\sigma}(\mathbf{r}) = \frac{\sum_i n_{i\sigma} v_{i\sigma}(\mathbf{r})}{\sum_i n_{i\sigma}(\mathbf{r})} + \frac{\sum'_i n_{i\sigma} (\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})}{\sum_i n_{i\sigma}(\mathbf{r})} \dots\dots\dots (2.11)$$

It can be shown that eq (2.11) is consistent with eq (2.10) i.e. multiplying both side of (2.11) by  $n_\sigma(\mathbf{r}) = f_{i\sigma} |\varphi_{i\sigma}|^2$  and integrating over  $\mathbf{r}$ , we obtain eq (2.10).

On the other hand, analyzing the OEP equation in the exchange only case, we have:

$$\bar{V}_{x\sigma m}^o = \bar{V}_{m\sigma}^o \dots\dots\dots (2.12)$$

Eq (2.10) and eq (2.12) result in a series of important properties which are preserved by both the OEP and the KLI method: the highest occupied orbital eigenvalue  $\epsilon_{m\sigma}$  is exactly equal to the expectation value of the single particle HF hamiltonian corresponding to the  $m\sigma$  orbital  $\epsilon_{m\sigma}^{\text{HF}}$ . In addition,  $\epsilon_{m\sigma}$  is equal to the difference in the expectation values of the total energy for  $N$  particles and  $N-1$  particles (for unrelaxed orbitals), thus Koopmans' theorem is satisfied here. In the uniform electron gas limit, the exchange potential of the OEP, KLI, LSD and Slater will be related by  $V_{x\sigma}^o = V_{x\sigma}^{\text{KLI}} = V_{x\sigma}^{\text{LSD}} = 2/3 V_{x\sigma}^{\text{S}}$ . Janak's theorem for the highest energy occupied orbital eigenvalue is valid in the OEP and

approximately satisfied in the KLI approximation. Both  $V_{x\sigma}^0$  and  $V_{x\sigma}^{KLI} \rightarrow -1/r$  as  $r \rightarrow \infty$ .

The KLI is an accurate approximation of OEP and it yields precise results<sup>[18]</sup>. However, unlike the Kohn-Sham theory, in which the exchange-correlation potential is a functional of  $n(\mathbf{r})$  alone (or of  $n_\sigma$  in a spin polarized theory) the calculation of  $v_{i\sigma}(\mathbf{r})$  for each orbital is needed for its construction. That is time consuming and may limit its application for multi-atom systems.

The further development of the KLI method will be provided in this chapter.

## 2.2 Simplified KLI Method (SKLI):

We recall the local spin density (LSD) approximation which is an orbital independent approximation has been widely used. The LSD will take less time as compared with the KLI. However, when it is employed atomic calculation, two regions should be distinguished. These are:

1. The core region comprising orbitals of tightly bound electrons. This is a high density region with  $\nabla n_\sigma / K_F n_\sigma$  in which the LSD approximation is expected to be accurate.

2. The "surface" of atoms corresponding to the region occupied by the valence electrons. In this region the LSD can produce significant errors in the energy eigenvalue of the highest energy occupied orbital (for some atoms, above 40%

error).

Similarly, in the overlap regions of molecules, the LSD is less accurate than when it is employed to describe the electron distribution localized about the atomic nuclei.

In the atomic calculation, we can take advantage of the strength of both the LSD and the KLI method by combining the LSD with the KLI in a proper way. We show that using the KLI method to construct the OEP potential, accurate results can even be obtained by merely choosing  $v_{i\sigma}(\mathbf{r})$  for the core states as those given by the exchange potentials of the LSD, whereas the valence states  $v_{i\sigma}(\mathbf{r})$  continue to be those of HF. Here we get rid of the LSD approximation in the region where it fails by developing the KLI method to which we shall refer as Simplified KLI method (SKLI). In the SKLI, accurate results can also be achieved by replacing the LSD with self interaction correction (LSDSIC) potential to the LSD potential in the core region.<sup>[14]</sup>

In the exchange only case, the spin polarized potential in the SKLI,  $V_{x\sigma}$ , is constructed in a way which is similar to that of the KLI:

$$\tilde{V}_{x\sigma}(\mathbf{r}) = \frac{\sum_i n_{i\sigma}(\mathbf{r}) \tilde{v}_{i\sigma}(\mathbf{r})}{\sum_i n_{i\sigma}(\mathbf{r})} + \frac{\sum'_i n_{i\sigma}(\tilde{V}_{x\sigma i} - \tilde{v}_{i\sigma})}{\sum_i n_{i\sigma}(\mathbf{r})} \dots\dots\dots (2.13)$$

here,

for the inner orbitals:

$$\tilde{v}_{i\sigma} = v_{i\sigma}^{LSD}(\mathbf{r}) \dots\dots (2.14)$$

for the outer orbitals:

$$\tilde{v}_{i\sigma} = v_{i\sigma}(\mathbf{r}) \text{ (HF)} \dots\dots (2.15)$$

We can show that the solution of (2.13) satisfies:

$$\tilde{V}_{x\sigma m} = \bar{v}_{m\sigma} \dots\dots (2.16)$$

and (2.16) is exactly the relation which the KLI potential and the OEP satisfied in (2.10) and (2.11)

We will prove (2.16) as follows:

Multiplying both sides of (2.13) by

$$n_{\sigma} = \sum_i n_{i\sigma} = \sum_i f_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}) \phi_{i\sigma}(\mathbf{r})$$

and integrating over  $r$ , we apply (2.14) and (2.15) to core part and valence part separately,

$$\begin{aligned} \sum_{i(\text{core})} f_{i\sigma} \tilde{V}_{x\sigma i} + \sum_{i(\text{valence})} f_{i\sigma} \tilde{V}_{x\sigma i} &= \sum_{i(\text{core})} f_{i\sigma} \bar{v}_{i\sigma}^{LSD} + \sum_{i(\text{valence})} f_{i\sigma} \bar{v}_{i\sigma} \\ &+ \sum_{i(\text{core})} f_{i\sigma} (\tilde{V}_{x\sigma i} - \bar{v}_{i\sigma}^{LSD}) + \sum'_{i(\text{valence})} f_{i\sigma} (\tilde{V}_{x\sigma i} - \bar{v}_{i\sigma}) \end{aligned}$$

We simplify the equation as:

$$\sum_{i(\text{valence})} f_{i\sigma} \tilde{V}_{x\sigma i} = \sum_{i(\text{valence})} f_{i\sigma} \bar{v}_{i\sigma} + \sum'_{i(\text{valence})} f_{i\sigma} (\tilde{V}_{x\sigma i} - \bar{v}_{i\sigma}) \dots\dots (2.17)$$

the second term of equation (2.17) is the summation of all valence states except the highest occupied orbital. Equation

(2.17) is valid provided:

$$f_{m\sigma} \tilde{V}_{x\sigma m} = f_{m\sigma} \bar{V}_{m\sigma}$$

for any  $f_{m\sigma} > 0$ , thus

$$\tilde{V}_{x\sigma m} = \bar{V}_{m\sigma} \dots \dots \dots (2.18)$$

Let's substitute  $V_{x\sigma}$  into the OEP equation:

$$\left[ -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \tilde{V}_{x\sigma}(\mathbf{r}) \right] \varphi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r})$$

Since these wavefunctions are solutions obtained by employing  $V_{x\sigma}$  we should denote them by  $\varphi_{i\sigma}$  and eigenvalue by  $\epsilon_{i\sigma}$ , and  $\epsilon_{m\sigma}$  satisfies:

$$\epsilon_{m\sigma} = \int \varphi_{m\sigma}^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \tilde{V}_{x\sigma}(\mathbf{r}) \right] \varphi_{m\sigma}(\mathbf{r}) d\mathbf{r}$$

Using the relation in (2.18),

$$\epsilon_{m\sigma} = \int \varphi_{m\sigma}^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{m\sigma}(\mathbf{r}) \right] \varphi_{m\sigma}(\mathbf{r}) d\mathbf{r} = \int \varphi_{m\sigma}^*(\mathbf{r}) h_{m\sigma}^{HF} \varphi_{m\sigma}(\mathbf{r}) d\mathbf{r} = \bar{\epsilon}_{m\sigma}^{HF} \dots (2.19)$$

Where the single particle Hamiltonian corresponding to the orbital is evaluated using  $\{\varphi_{i\sigma}\}$  that are obtained by taking  $V_{x\sigma}$  as the exchange potential and (2.19) is valid only for the highest energy occupied orbital  $\varphi_{m\sigma}$  of spin projection  $\sigma$ .

In addition, it follows from:

$$E(N) - E_u(N-1) = \int \varphi_{m\sigma}^*(\mathbf{r}) h_{m\sigma}^{HF} \varphi_{m\sigma}(\mathbf{r}) d\mathbf{r}$$

where  $E(M)$  is the expectation value of total energy for the  $M$  particle system that  $E(N) - E_0(N-1) = \epsilon_{m\sigma}$ . The subscript  $u$  indicates the value calculated using the same orbitals as employed in the  $N$  particle calculation with the  $m\sigma$  orbital missing (unrelaxed). Thus Koopmans' theorem is satisfied for the highest occupied state in the SKLI.

Comparing (2.18) and (2.12), we see that the important property for the highest occupied orbital will be valid in both the KLI and the SKLI. The other properties derived from the above property will still be true -- Janak's theory will be approximately satisfied in the SKLI; in the uniform gas limit,  $V_{x\sigma} = V_{x\sigma}^{KLI} = V_{x\sigma}^{LSD} = 2/3 V_{x\sigma}^S$  and  $V_{x\sigma} \rightarrow -1/r$  as  $r \rightarrow \infty$ . Thus the SKLI maintains some important analytic properties satisfied by  $V_{x\sigma}^0$  and  $V_{x\sigma}^{KLI}$ . In order to determine whether it can serve as an accurate approximation to the OEP, it is necessary to perform numerical calculations on systems for which accurate OEP and KLI results exist.

### 2.3 Numerical Results

We have applied the SKLI method to calculate the properties of atoms whose atomic numbers range from  $Z=3$  to  $Z=56$  (for  $Z=2$ , the HF, OEP, KLI and SKLI are all identical). To each atom, the two states with the same spin projection as the highest occupied energy state and the same states with the opposite spin projection that are occupied are chosen as valence states, the HF exchange potential  $v_{i\sigma}(\mathbf{r})$  (HF) are

employed. The rest of the atom is considered as the core state. Two different approximations -- the LSD potential and the LSD with self interaction correction (LSDSIC) potential are used in describing core state.

Table (2.1) gives the total energy of all atoms by applying the SKLI method with the LSD in the core states. Table (2.2) gives the comparison of overestimates of total energy in the OEP, KLI, LSD, SKLI approximations. The results in table (2.1) and (2.2) show that the total energy calculated by employing the SKLI method is moderately improved compared with the LSD approximation (except Ga). The conclusion can be well understood -- changing the prescription for valence states from the LSD to HF will improve the energy, but the improvement would not be significant, because we still treat the core states in the LSD approximation which is highly weighted in total energy. Similarly, table (2.3) and (2.4) give the total energy and the comparison of overestimate of total energy in the OEP, KLI, LSDSIC and SKLI approximation with the LSDSIC in the core state. Figure 2.1 and Fig.2.2 display the relative overestimate in ppm of the total energy compared with the HF total energy according to table (2.2) and (2.4).

Fig.(2.3) and Fig.(2.4) are graphs of various exchange potential  $V_x$ . We can observe that exchange potential of the KLI is very close to those of the OEP. The exchange potential of the LSD is nearly too weak everywhere and approaches to zero too rapidly. The  $V_x$  of LSDSIC is too deep. However, the

exchange potential of the SKLI in the region where is close to core is almost identical to the  $V_x$  of the LSD or the LSDSIC,  $V_x$  of SKLI coincide with KLI in the outer region.

However, the calculations of  $\epsilon_{m\sigma}$  using the SKLI method are a significant improvement over the LSD results. As previously demonstrated by Krieger, Li and Iafrate, unlike the results of LSD, the  $\epsilon_{m\sigma}$  given by the KLI method are very close to both the  $\epsilon_{m\sigma}^{HF}$  and  $\epsilon_{m\sigma}^0$ . Since the SKLI method treats the highest orbital exactly the same as the KLI method, the  $\epsilon_{m\sigma}$  value in the SKLI is extremely close to those obtained in the KLI calculation, no matter whether we use the LSD or the LSDSIC approximation for the core states in the SKLI method.

Table(2.5) gives the results of  $\epsilon_{m\sigma}$  for different approximations. The SKLI here describes the core state by employing the LSD potential. The similar table(2.6) corresponds to the LSDSIC potential in the core states. Obviously, from tale(2.5) we find that the LSD makes a large error (around 40%) in  $\epsilon_{m\sigma}$ . It thus fails in describing the valence electrons which are important for chemical binding.

Similarly, from table (2.6) we use that the  $\epsilon_{m\sigma}$  given by the LSDSIC are a significant improvement over the LSD results, being generally only a few percent from the  $\epsilon_{m\sigma}^{HF}$  and  $\epsilon_{m\sigma}^0$ . However, they are significantly in error when compared with the  $\epsilon_{m\sigma}^{KLI}$  results as well as the SKLI results for  $\epsilon_{m\sigma}$  when the LSDSIC is employed only in the core state.

Furthermore, it is interesting to observe that the  $\epsilon_{m\sigma}$  calculated in the SKLI approximation are often closer to  $\epsilon_{m\sigma}^{HF}$  than those given by the KLI method. This arises because the KLI method tends to slightly overestimate the Hartree potential thus making  $\epsilon_{m\sigma}$  too small in magnitude. However, the LSD and LSDSIC approximations tend to be slightly too weak in the core region which results in a slightly weaker Hartree potential which tends to cancel the overestimate of  $V_H$  given by the KLI prescription.

Fig.(2.5) and Fig.(2.6) are the  $\epsilon_m / \epsilon_m^{HF}$  curves for halogen atoms corresponding to different approximations (the OEP, KLI, LSD(LSDSIC) and the SKLI). In Fig.(2.5) the SKLI method chooses the LSD potential in the core states, whereas in Fig.(2.6) the SKLI corresponding to the LSDSIC in the core. We can see from Fig.(2.5) and Fig.(2.6) that  $\epsilon_m$  obtained from the SKLI method is almost identical to those obtained from the KLI and OEP (<0.2%). However, the error in  $\epsilon_m$  is around 40% to 50% in the LSD and 5% to 10% in the LSDSIC respectively. Similar curves are shown in Fig.(2.7) and Fig.(2.8) for the atoms in the second column of periodic table (group IIA). These show that the difference between the OEP, KLI and SKLI is less than 0.6 %. However, for the LSD approximation, the error can be as large as 45%; for the LSDSIC approximation, the largest error is about 10%.

These results strongly support the conclusion that the SKLI method treats the valence states accurately. So the

highest occupied eigenvalues in the SKLI method are as accurate as the KLI and OEP.

We may also compare the accuracy of various approximations by examining the expectation value of  $\langle r^2 \rangle$  which is sensitive to the behavior of the density far from the nucleus. i.e. depends heavily on the valence charge distribution.

Table(2.7) and (2.8) are compilations of  $\langle r^2 \rangle$  calculated by applying different approximations. As we mentioned before, the SKLI potentials in table (2.7) and (2.8) choose the LSD and the LSDSIC as the core state potentials respectively. The results show that the OEP, KLI and SKLI give accurate results. If we compare the SKLI calculations for  $\langle r^2 \rangle$  with those of HF we find that the SKLI provides less than 0.14% difference for halogens and less than 0.66% difference for the atoms in group IIA. But both the LSD and the LSDSIC approximations produce much larger errors of unpredictable sign.

The Fig.(2.9) and Fig.(2.10) ( $\langle r^2 \rangle$  for halogens) and Fig.(2.11) and (2.12) ( $\langle r^2 \rangle$  for the group IIA atoms) demonstrate those errors. In halogens, the maximum error of  $\langle r^2 \rangle / \langle r^2 \rangle_{\text{HF}}$  is 7.3% in the LSD and 1.5% in the LSDSIC. However, in group IIA, the maximum error is 4.2% in the LSD and the LSDSIC.

To sum up, we see that by using the SKLI method, the approximate OEP potential can be easily constructed and the results are significantly improved comparing with the LSD and

the LSDSIC. Thus the SKLI provides a prescription for the calculation of the approximate OEP potential that maintains the high accuracy of the KLI method when applied to properties sensitive to the valence states i.e. the  $\epsilon_{m\sigma}$  and  $\langle r^2 \rangle$ , while producing modest improvements in the calculation of the total energy given by the LSD or LSDSIC approximation. As such it has the potential of providing an accurate but simple construction of the OEP for multi-atom calculations.

## CHAPTER 3

### Study of Negative Ions

An important test for any approximate density functional theory is its application to the negative ions. Earlier studies<sup>[24][25]</sup> show that the LSD approximation fails for most of the negative ions; it even can not yield a self-consistent field solution in those cases. The reason this is true is due to the fact that the valence electrons are weakly bound in many negative ions and the LSD approximation provides a large error when it is used to describe them. On the other hand, if we include the self-interaction correction in the LSD approximation (LSDSIC), a convergent result can be obtained. But LSDSIC is an orbital dependent multi-potential method rather than a single potential technique.

Krieger, Li and Iafrate have reported<sup>[22]</sup> that by employing the KLI single potential, the results are very close to those of HF and the OEP for negative ions.

In this chapter, we will apply the SKLI method to the negative ions and study the effects of the correlation energy in them.

#### 3.1 The SKLI Method and Negative Ions

The most important property associated with the negative ions is the electron affinity (EA). The definition of EA is the difference between the total ground state energies ( $E_{\text{tot}}$ ) of the corresponding atom A and negative ion A<sup>-</sup>.

$$EA = E_{tot}(A) - E_{tot}(A^-) \dots\dots\dots (3.1)$$

If the ion is stable, EA should be positive and EA is obtained by calculating  $E_{tot}(A)$  and  $E_{tot}(A^-)$  separately.

If we use HF theory to calculate EA from (3.1), the results are far from accurate, sometimes even predicting the wrong sign for EA<sup>[26][27]</sup>. This happens because of the fact that in HF theory, only the exchange energy has been included and the correlation energy, which plays a very important role in describing the behavior of the valence electrons, has been neglected. For the same reason, exchange only KS theory like the OEP and the KLI will not be able to provide an accurate approximation to EA for negative ions.

It has been shown<sup>[13]</sup> that in exact KS theory, the negative of the highest occupied energy eigenvalue  $-\epsilon_{mo}$  is exactly equal to EA, i.e.

$$EA = -\epsilon_{mo} \dots\dots\dots (3.2)$$

In exchange only KS theory, (3.2) will not be satisfied exactly. However, according to Koopmans' theorem  $-\epsilon_{mo}$  still can be considered as the removal energy without relaxation.

Nevertheless, one can always regard  $-\epsilon_{mo}$  as an approximation to EA in the exchange only case and calculations have shown<sup>[22]</sup> that in general  $-\epsilon_{mo}$  is a better approximation to EA than that given by (3.1).

Krieger, Li and Iafrate<sup>[18]</sup> applied the KLI method for the

calculation of the negative ions which include alkalis, halogens and some stable negative ions with incomplete 2p and 3p shells. We also apply the SKLI method to the corresponding negative ions. The highest occupied energy eigenvalues, the total energies and the electron affinities calculated from (3.1) for various negative ions are obtained. The results demonstrate that the SKLI method provides very close results for  $\epsilon_{m\sigma}$  to those of HF, the OEP and KLI. In addition, whereas the total energies of negative ions are higher in the SKLI than those of the HF, OEP and KLI, the EA of corresponding negative ions in the SKLI are still very close to those obtained by the HF, OEP and KLI. This result follows from the fact that the overestimate of the total energy for the atom and corresponding negative ions are nearly equal so the cancellation of these overestimates, in calculating EA by employing (3.1) will make the results of EA in the SKLI close to those of the HF, OEP and KLI.

### 3.2 Results and discussion

In table (3.1) we tabulate the highest occupied eigenvalues ( $-\epsilon_{m\sigma}$ ) obtained by applying the HF, LSDSIC, OEP, KLI, SKLI(LSD in core) and SKLI(LSDSIC in core) in the exchange-only approximation. For H-, the same results are obtained in all calculations since in this case OEP, KLI and SKLI are all exactly the same as the single HF  $V_x$ . For alkalis, we see that  $\epsilon_{m\sigma}$  of the SKLI are within 0.3% of the

KLI, within 1.7% of the OEP, and within 1.5% of the HF. But the LSDSIC are different from the above by as much as 12%. For halogens, the SKLI results are within 0.7% of the KLI, within 0.5% of the OEP, within 0.9% of the HF. Whereas the LSDSIC are, at most, 18.5% away from the above approximations. For ions with incomplete 2p and 3p shells, the SKLI results are all within 0.8% of the KLI, within 0.9% of the OEP and 3.9% (corresponding, however, to a difference of only 0.0016Ry) of the HF. But the maximum difference from the above of the LSDSIC is 24.8%. Since the valence states have been chosen by employing the HF prescription in the SKLI, the highest occupied eigenvalues,  $\epsilon_{mo}$ , which mainly depend upon the valence states contribution to the exchange potential are also very close to those of the HF, OEP and KLI.

As an approximation to EA, we can see that for alkalis, all  $-\epsilon_{mo}$  in the SKLI are too small compared with the experimental value. This is also true for LSDSIC. For halogens and ions with incomplete 2p and 3p shells, all  $-\epsilon_{mo}$  in the SKLI are too large.

On the other hand, in the LSDSIC approximation, all  $-\epsilon_{mo}$  for halogens underestimate EA except for F- and they overestimate EA in ions with incomplete 2p and 3p shells except Si- and S-.

Table (3.2) lists the total energy calculations of the negative ions. In alkalis (except Li) and halogens, the overestimate in the SKLI method are smaller than the LSDSIC if

either LSD or LSDSIC is employed to calculate the single particle potentials of the core electrons. But in the atoms with incomplete 2p and 3p shells, the overestimate in the LSDSIC is generally larger only if LSDSIC is employed in the core. The total energy overestimates in both the LSDSIC and SKLI are larger than those in the OEP and KLI.

In table (3.3), we display the calculation EA by using (3.1). Since HF fails to give an accurate value due to the neglect of the correlation energies, the OEP, KLI and SKLI which are using the same HF functional fail too. In those cases in which the negative ion has a higher energy than the neutral atom in the exchange-only approximation, the wrong sign (negative sign) for EA has been given.

Regardless of the accuracy of all the approximations to the exact results, if we only compare the SKLI results with the calculations of the HF, LSDSIC, OEP and KLI, we find that EA obtained by the SKLI method are closer to those of the HF, OEP and KLI than those obtained by the LSDSIC approximation.

Table (3.4) gives the comparison of  $\langle r^2 \rangle$  obtained by the HF, OEP, KLI and the SKLI. For alkalis  $\langle r^2 \rangle$  of the SKLI are within 0.36% of the KLI, within 0.15% of the OEP and 1.5% of the HF. Whereas the LSDSIC are different from the above by as much as 10.3%.

For the halogens, the SKLI are within 0.3% of the KLI, within 0.1% of the OEP, 0.2% of the HF. But the LSDSIC gives a 4.0% difference from the above approximations. Similar

results are shown for the ions with incomplete 2p and 3p shells. In these cases  $\langle r^2 \rangle$  of the SKLI are within 0.6% of the KLI, within 0.6% of the OEP and 0.65% of the HF. However, the maximum difference from the above in the LSDSIC is 14%.

Comparing table (3.1) and table (3.3) with the EA obtained from experiment as tabulated in table 3.5, we can see that in exchange only case,  $-\epsilon_{mo}$  is a better approximation to EA than those obtained by using (3.1). While for alkalis, all  $-\epsilon_{mo}$  are too small to account for EA, they are too large for halogens and atoms with incomplete 2p and 3p shells. For S-, all  $-\epsilon_{mo}$  in the HF, OEP, KLI and SKLI are in good agreement with the experimental EA, but  $-\epsilon_{mo}$  in the LSDSIC is too small.

Fig. 3.1 is the comparison of the total energy for the negative ions by employing the KLI, SKLI(LSDSIC in core) and LSDSIC. We can see that the SKLI and LSDSIC approximation overestimate the total energy more than the KLI. But the SKLI method improves the total energy moderately compared to the LSDSIC results.

Fig. 3.2 and Fig.3.3 corresponds to  $\epsilon_{mo}/\epsilon_{HF}$  for alkalis and halogens respectively. The  $\epsilon_{mo}$  given by the SKLI method is in good agreement with those given by the KLI method. In both figure whereas, the LSDSIC provides as much as an 18% error. For the halogens the highest occupied eigenvalues  $\epsilon_{mo}$  of the LSDSIC are lower than those in the SKLI and KLI, But

in alkalis , the reverse is true.

Fig.3.4 and fig.3.5 are average values of  $r^2$  corresponding to alkalis and halogens. We find the similar results:  $\langle r^2 \rangle$  of the SKLI and KLI are very close to each other, but  $\langle r^2 \rangle$  calculated by the LSDSIC approximation are significantly farther from the HF values.

### 3.3 Correlation Energy in Negative Ions

In the HF theory and the corresponding KLI method, the correlation energy has been neglected. As a result, when they are applied to negative ions, EA obtained from (3.1) are far from accurate. Even the wrong sign is sometimes predicted (see table3.3 )

To study the effects of correlations in negative ions, the LSD and LSDSIC correlations are added to the HF exchange energy. While the KLI potential will be constructed by using HF with the LSD correlation and HF with the LSDSIC correlation respectively.

In the LSD approximation, the correlation energy  $E_c[n]$  can be written as:

$$E_c[n_\sigma] = \sum_\sigma \int n_\sigma(\mathbf{r}) e_c[n_1(\mathbf{r}), n_1(\mathbf{r})] d\mathbf{r}$$

For  $e_c$  we use the Ceperly and Alder <sup>[28][29]</sup> results as parameterized by Perdew and Zunger<sup>[14]</sup> i.e.

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

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

Here, coefficients were given by Perdew and Zunger.  $r_s$  is defined by:

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

with  $n$  being the electron density and  $i$  can represent polarized and unpolarized cases.

For intermediate values of polarization, we employ the von-Barth-Hedin interpolation formula<sup>[30]</sup>:

$$e_c(n(\mathbf{r}), \zeta(\mathbf{r})) = e_c(n, \zeta=0) + [e_c(n, \zeta=1) - e_c(n, \zeta=0)] f(\zeta(\mathbf{r}))$$

here, the interpolation equation function is:

$$f(\zeta(\mathbf{r})) = \frac{(1 + \zeta(\mathbf{r}))^{4/3} + (1 - \zeta(\mathbf{r}))^{4/3} - 2}{2(2^{1/3} - 1)}$$

We also add the LSD correlation with self-interaction-correction(LSDSIC) to the HF and KLI.

Table (3.5) gives the highest occupied energy eigenvalues  $-\epsilon_{m\sigma}$  (including the effects of LSD and LSDSIC correlation respectively). Table (3.6) lists the total energy including correlation. Table(3.7) shows the electron affinity EA including the effects of the correlation energy. Here EA is given by employing (3.1).

From table(3.5) to (3.7) the following conclusions can be drawn:

(1) Compared with table(3.1) to table(3.3), we can see that the correlation energies make total energies significantly lower. Also table (3.6) demonstrates that the LSD correlation energy is larger in magnitude compared with the LSDSIC correlation results.

(2) After adding the correlation energies, the sign of EA is positive for all negative ions. Therefore, unlike in the exchange only case, the existence of negative ions can be consistently predicted.

(3) Compared with the experimental values, we can see from table (3.7) that the electron affinity EA in halogens and the ions with incomplete 2p and 3p shells are closer to those values than  $-\epsilon_{mv}$  in table (3.5). In alkalis, however, the  $-\epsilon_{mv}$  calculated with LSDSIC correlation are slightly closer to the EA than the EA given by equation(3.1). Generally speaking, when correlation energies are added , the results of EA from equation (3.1) will be a better approximation to the electron affinity than those of  $-\epsilon_{mv}$ .

(4) Comparing the calculations with LSD correlation and those with LSDSIC correlation given in table 3.7, we find that in alkalis and most halogens the electron affinity obtained by employing the LSDSIC correlation are closer to the experimental values than those with LSD correlation, whereas, in the ions with incomplete 2p and 3p subshells, the LSD

correlation makes the electron affinity somewhat closer to the experimental results, especially for the light ions. This arises because of cancellation of errors in the overestimate of the total energy of both atoms and corresponding ion when LSD correlation is employed. However, from table 3.5 we see that in all cases,  $-\epsilon_{m\sigma}$  given by LSDSIC correlation is a better approximation to EA.

(5) The KLI is an accurate approximation of the OEP and also an accurate approximation of the HF. The results from table (3.5) to (3.7) demonstrate that in the calculation of negative ions, the results obtained by adding correlation in the KLI prescriptions are still very close to those of the HF plus correlation.

## CHAPTER 4

### Test of Exchange-Correlation Functionals in an Exactly Soluble Model

As we saw in previous chapters, accurate calculational implementations of the density-functional theory are far from easy to achieve, because of the fact that no exact  $E_{xc}[n]$  has yet been proposed. To evaluate the various approximations, Laufer and Krieger<sup>[21]</sup> have given a comparison between LDA and the solution in an exactly soluble model consisting of two electrons with antiparallel spin attracted to a common center by harmonic-oscillator forces with mutual coulomb repulsion between the electrons. In this chapter, we extend the Laufer-Krieger model to find the exact solution of a similar harmonic force system which consists of two electrons with parallel spin. The solution will be used to study the contribution of electrons with parallel spin to the correlation energy and to evaluate the accuracy of various correlation functionals which include the local spin density (LSD) correlation, the LSD with self-interaction-correction (LSDSIC), the Generalized Gradient Approximation Correlation (GGA) and the GGA with self-interaction correction (GGASIC) correlation.

In each case in which the approximation for the exchange and/or correlation energy is orbital dependent, we employ the KLI method to construct the approximate OEP potential. The application of the various exchange-correlation energy

functionals is then compared to the exact results.

#### 4.1 The Model

We apply the same Laufer-Krieger model to two electrons with parallel spin attracted to a force center by a harmonic-oscillator potential. The hamiltonian of this system is:

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + \frac{1}{2} K (r_1^2 + r_2^2) + \frac{e^2}{|r_{12}|} \dots \dots (4.1)$$

Here  $r_i$  are the coordinates of electron  $i$  ( $i=1,2$ ) and  $K$  is a measure of the strength of the attractive center. To solve the above Schrodinger equation, we make a transformation to center of mass coordinate  $R$  and relative coordinate  $r$ . Here  $R = (r_1 + r_2)/2$ ,  $r = r_1 - r_2$  and  $r_1^2 + r_2^2 = [(2R)^2 + r^2]/2$ , the reduced mass is  $\mu = m/2$  and the total mass is  $M = 2m$ .

$$\psi(r_1, r_2) = \psi(R, r)$$

$$H(r_1, r_2) = H(R, r) = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + \frac{1}{4} K (r^2 + 4R^2) + \frac{e^2}{r}$$

Separating variables

$$\psi(r, R) = f(r) g(R)$$

and substituting into the previous equation and dividing both sides by  $\psi(r, R)$  yields,

$$\left[ -\frac{\hbar^2}{2M} \nabla_R^2 + KR^2 \right] g(R) = E_{cm} g(R)$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + \frac{1}{4}KR^2 + \frac{e^2}{r}\right] f(\mathbf{r}) = \varepsilon_{rel} f(\mathbf{r})$$

where  $E = E_{cm} + \varepsilon_{rel}$ .

In atomic units,  $e^2 = \hbar = m = 1$ , these equations can be written as

$$\left[-\frac{1}{4}\nabla_R^2 + KR^2\right] g(\mathbf{R}) = E_{cm} g(\mathbf{R}) \dots\dots (4.2)$$

$$\left[-\nabla_r^2 + \frac{1}{4}KR^2 + \frac{1}{r}\right] f(\mathbf{r}) = \varepsilon_{rel} f(\mathbf{r}) \dots\dots (4.3)$$

We can consider the wavefunction as a product of a spin part and a space part. In the Laufer-Krieger case ( $S=0$ ) the spin state is antisymmetric, the space part of the wavefunction is symmetric, so the wavefunction of the system is still antisymmetric and the Pauli principle is satisfied. But in our case, for two electrons with parallel spin,  $S=1$ . The spin part of the wave function is symmetric, so the space part should be antisymmetric, so that the system still satisfies the Pauli principle. Since interchanging  $\mathbf{r}_1$  and  $\mathbf{r}_2$  leaves  $\mathbf{R}$  unchanged, the ground state corresponding to  $S=0$  or  $S=1$  must correspond to the ground state of (4.2). Equation (4.2) is the equation of a spherical harmonic oscillator<sup>[21]</sup>. Thus

$$g(\mathbf{R}) = c \exp(-K^{1/2} R^2)$$

$$E_{cm} = 1.5 K^{\frac{1}{2}}$$

Under interchange of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ,  $\mathbf{r} \rightarrow -\mathbf{r}$ . Therefore in order to ensure that the total wavefunction is antisymmetric under interchange of electron coordinates we take for the solution of eq(4.3) the lowest odd solution i.e. the lowest lying p state.

If we take  $f(\mathbf{r}) = f(r)Y(\theta, \varphi)$ , then corresponding to a p state there are 3 degenerate states for Y:  $Y_{10}(\theta, \varphi)$ ,  $Y_{11}(\theta, \varphi)$  and  $Y_{1,-1}(\theta, \varphi)$ . They are equally weighted. The one dimensional equation for  $f(r)$  can be obtained by separating  $f(r)$  and  $Y(\theta, \varphi)$ :

$$-\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{df(r)}{dr} \right] + \left[ \frac{1}{4} K r^2 + \frac{1}{r} + \frac{l(l+1)}{r^2} \right] f(r) = \epsilon_{rel} f(r)$$

Since  $l=1$  corresponds to a p state,

$$-\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{df(r)}{dr} \right] + \left[ \frac{1}{4} K r^2 + \frac{1}{r} + \frac{2}{r^2} \right] f(r) = \epsilon_{rel} f(r) \dots (4.4)$$

The probability density that an electron is at  $\mathbf{r}_2$  is given by

$$P(\mathbf{r}_2) = \int |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1$$

Thus the electron density is given by:

$$n(\mathbf{r}_2) = 2 \int f^2(\mathbf{r}) g^2(\mathbf{R}) d\mathbf{r}_1$$

where  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ . For a fixed  $\mathbf{r}_2$ ,  $d\mathbf{r}_1 = d\mathbf{r}$  so

$$n(\mathbf{r}_2) = 2 \int f^2(\mathbf{r}) g^2\left(\frac{\mathbf{r}}{2} + \mathbf{r}_2\right) d\mathbf{r} = c^2 \int f^2(\mathbf{r}) e^{-2K\frac{1}{2}|\frac{\mathbf{r}}{2} + \mathbf{r}_2|^2} d\mathbf{r} = c^2 e^{-2K\frac{1}{2}r_2^2} \int e^{-\frac{K\frac{1}{2}r^2}{2}} e^{-2K\frac{1}{2}\mathbf{r} \cdot \mathbf{r}_2} f^2(\mathbf{r}) d\mathbf{r}$$

$$f^2(\mathbf{r}) = f^2(r)$$

Substituting  $f^2(r)$  into  $n(r_2)$ , and simplifying we obtain:

$$n(r_2) = A^2 e^{-2K\frac{1}{2}r_2^2} \int_{space} e^{-\frac{1}{2}K\frac{1}{2}r^2} e^{-2K\frac{1}{2}r r_2 \cos\theta} f^2(r) r^2 \sin\theta d\theta d\phi dr$$

where A is a constant . We can obtain  $n(r_2)$  by performing the angular integrals which yields

$$n(r_2) = B^2 (e^{-qr_2^2} / qr_2) \int_0^\infty f^2(r) e^{-\frac{qr^2}{4}} [e^{qr_2} - e^{-qr_2}] r dr \dots \dots (4.5)$$

where  $q = (4K)^{1/2}$ .

In the two electron case, the normalization factor  $B^2$  is obtained from  $\int n(r) 4\pi r^2 dr = 2$ .

We employ a numerical calculation to solve equation (4.4) to obtain  $\epsilon_{rel}$  and  $f(r)$ . Then:

$$E_{exact} = E_{cm} + \epsilon_{rel} = 1.5K^{\frac{1}{2}} + \epsilon_{rel} \dots \dots (4.6)$$

gives the exact total energy of electrons with parallel spin which includes both the exchange and correlation energy.

Also, equation(4.5) provides the exact electron density  $n(r)$ .

On the other hand, we can apply the KS equation to a system of two electrons with parallel spin.

$$\left[-\frac{1}{2}\nabla^2+V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r})\dots\dots(4.7)$$

If we write  $\psi_i(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\varphi)$  and  $u_{nl}(r)=rR_{nl}(r)$ , equation (4.7) may be written:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+V_{eff}(r)+\frac{l(l+1)}{2r^2}\right]u_{nl}=\epsilon_{nl}u_{nl}$$

In our system, we only consider two orbitals. For  $l=0$ ,  $u_{nl}=u_1$ ; for  $l=1$ ,  $u_{nl}=u_2$ . Equation (4.7) will be :

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+V_{eff}(r)\right]u_1=\epsilon_1u_1\dots\dots(4.8)$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+V_{eff}(r)+\frac{1}{r^2}\right]u_2=\epsilon_2u_2\dots\dots(4.9)$$

from (4.8)  $V_{eff}(r)=\epsilon_1+(1/2u_1)(d^2u_1/dr^2)$ . Substituting  $V_{eff}(r)$  into (4.9), we have

$$\left[-\frac{1}{2}\frac{d^2u_2}{dr^2}+\frac{1}{r^2}+\frac{1}{2u_1}\frac{d^2u_1}{dr^2}\right]u_2=(\epsilon_2-\epsilon_1)u_2\dots\dots(4.10)$$

here  $l=1$  (p state). Also

$$n(r)=\psi_1^2(r)+\psi_2^2(r)=u_1^2/r^2+u_2^2/r^2\dots\dots(4.11)$$

Substituting for  $u_1(r)$  in eq(4.10) in terms of  $u_2(r)$  and  $n(r)$

from equation (4.11), equation(4.10) can be solved self-consistently for  $\varepsilon=\varepsilon_2-\varepsilon_1$  and  $u_2(r)$  by employing the exact  $n(r)$  given by eq(4.5).

Since  $\varepsilon_{\max}=\varepsilon_2=E(N=2)-E(N=1)$ <sup>[13]</sup> and  $E(N=2)$  and  $E(N=1)$  are known exactly, then  $\varepsilon_2$  is known exactly and consequently once  $\varepsilon=\varepsilon_2-\varepsilon_1$  is obtained,  $\varepsilon_1$  is known exactly. Then from

$$V_{eff}=\varepsilon_1+\frac{1}{2u_1}\frac{d^2u_1}{dr^2}\dots\dots\dots(4.12)$$

we may obtain the exact exchange correlation potential  $V_{xc}$  exactly i.e.

$$V_{xc}=V_{eff}-\frac{1}{2}Kr^2-\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\dots\dots\dots(4.13)$$

Equation (4.13) provides the exact exchange -correlation potential for this two electron problem. We may consider  $V_{xc}$  as the sum of  $V_x$  and  $V_c$  which can be separately obtained as follows. We obtain the exact KS exchange potential  $V_x$  by first solving the HF equations for the exact HF exchange energy  $E_x$  and density,  $n^{HF}(\mathbf{r})$ . Using this density and the condition that the eigenvalue corresponding to the highest exchange-only KS occupied orbital satisfies  $\varepsilon_2^{KS}=\varepsilon_2^{HF}$ , we may obtain the exact KS  $V_x$  by performing the analogous procedure described by equation 4.7 through 4.13 for the exchange-only case. Then, by subtracting  $E_x$  and  $V_x$  from  $E_{xc}$  and  $V_{xc}$  respectively the exact  $E_c$  and  $V_c$  are obtained.

#### 4.2 Exact $E_x, E_c, V_x$ and $V_c$

The exact correlation energy for various  $K$  is tabulated in table 4.1. The data demonstrate that although  $K$  changes by several orders of magnitude, the ratio of the correlation energy from parallel spin to those from the antiparallel spins as obtained by Laufer and Krieger is around 1:6, nearly independent of  $K$ . A similar result was observed by O.V. Gristenko and G.M. Zhidomiro(GZ)<sup>[23]</sup> for atoms. This suggests that the major part of the correlation energy for systems having electrons with both spin projections can be considered as arising from the interaction of the electrons with antiparallel spin.

In figure 4.1 and 4.2 we present the exact exchange potential  $V_x$  and correlation potential  $V_c$ . The shapes of  $V_x$  and  $V_c$  are similar to those of the antiparallel case but less negative in magnitude. Table 4.2 gives the overlap integral of the exact wavefunction and the wavefunction in the exchange only case. We can see the correlation potential plays a minor role in calculating the wavefunction.

This can be understood in view of the fact that electrons with parallel spin are forced to stay apart due to the Pauli principle whereas electrons with anti-parallel spin can more effectively reduce their repulsive coulomb energy by having their positions correlated in such a way that their relative distance are greater than in an uncorrelated state.

### 4.3 Test of Exchange-Correlation Functionals

In this section, the LSD, LSDSIC, GGA and GGASIC correlation energy functionals are added to the exchange energy functional of the system consisting of two electrons with parallel spin. The results are compared with the exact result for total energy, exchange and correlation potential, highest occupied energy eigenvalue,  $\langle r^2 \rangle$  and the electron density.

First, we study the system of two electrons with parallel spin in the exchange only case. Here, the LSDX, LSDSICX represent the corresponding approximation in the exchange only case whereas the KLIX represents the approximation which constructs the OEP single potential from the effective single particle HF exchange potential. (see eq.2.6)

Fig.4.3 gives us the percentage error in total energy for the exchange energy. The greatest error in the KLIX is only 0.006%. In the LSDSICX it is 0.09% whereas in the LSDX the error can be as great as 4.7%.

Fig.4.4 gives a graph of the highest occupied eigenvalue, for which the KLIX produces a maximum 0.2% error. However, the greatest error in the LSDSICX is 3.5%, whereas in the LSDX is about 20% ( $K=0.01$ ).

The comparison of  $\langle r^2 \rangle$  in the exchange only case are shown in Fig.4.5.  $\langle r^2 \rangle$  in the KLIX approximation is almost identical to that of the exact value -- Four significant figures after decimal point are identical in  $K=1,10,100$ ; three

significant figures after decimal point are identical in  $K=0.01, 0.1$ .  $\langle r^2 \rangle$  in the LSDSICX are very close to the KLIX whereas the greatest error in  $K=0.01$  is 0.1%. In the LSDX approximation, the maximum error is 3.03%.

These results are consistent with the conclusion which we arrived at in the previous chapter---in the exchange only case, the KLI is a very accurate approximation, the LSD approximation produces the largest error in the above three approximations.

In the LSD approximation the correlation energy  $E_c$  can be obtained by the formula discussed on page 35.

If we consider the self-interaction-correction(SIC) in the LSD correlation the LSD correlation energy functional with self interaction correction,  $E_c^{LSDSIC}$ , will be given by

$$E_c^{LSDSIC} = E_c^{LSD}[n_1, n_1] - \sum_{\alpha_s} E_c^{LSD}[n_{\alpha_s}, 0]$$

Perdew and Wang <sup>[31][32]</sup> have developed a Generalized Gradient Approximation (GGA) which adds a non-local correction to the LSD approximation.  $E_c^{GGA}$  (PW 91) will be:

$$E_c^{GGA}(PW91)[n_1, n_1] = \int d^3r n [e_c(r_s, \xi) + H(t, r_s, \xi)]$$

where

$$r_s = (3/4\pi n)^{1/3}, K_F = (3\pi^2 n)^{1/3}, K_s = (4K_F/\pi)^{1/2}, \xi = (n_1 - n_1) / n$$

$$g = [(1+\xi)^{2/3} + (1-\xi)^{2/3}] / 2, t = |\nabla n| / 2gK_s n$$

The function H equals  $H_0 + H_1$

$$H_0 = g^3 \frac{\beta^2}{2\alpha} \ln \left[ 1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right]$$

$$H_1 = \gamma [C_c(r_s) - C_c(0) - 3C_x/7] g^3 t^2 e^{-100g^4 (K_s^2/\kappa_s^2) t^2}$$

where

$$\alpha = 0.09, C_c(0) = 0.004235, C_x = -0.001667, \gamma = (16/\pi) (3\pi^2)^{1/3}, \beta = \gamma C_c(0)$$

$$A = \frac{2\alpha}{\beta} \frac{1}{e^{-2\alpha\epsilon_c(r_s, \xi) / (g^3 \beta^2)} - 1}$$

Accurate analytic representations are available for  $\epsilon_c(r_s, )$  and  $C(r_s)$  [32].

Similarly, if we apply the SIC method to the GGA, the GGA correlation energy functional can also be obtained from:

$$E_c^{GGASIC} = E_c^{GGA} [n_1, n_1] - \sum_{\alpha_\sigma} E_c^{GGA} [n_{\alpha_\sigma}, 0]$$

The correlation potential  $V_c$  can be obtained for  $E_c = E_c[n_\sigma]$  from

$$V_c = \frac{\delta E_c[n_\sigma]}{\delta n_\sigma}$$

The correlation potential for orbital dependent  $E_c$  can be

obtained by solving the OEP integral equation.

We test the exchange-correlation functionals as follows: we use the LSD, LSDSIC and HF to calculate the exchange energy.

We calculate the correlation energy by invoking the LSD, LSDSIC, GGA and GGASIC. The LSDC, HFC correspond to the LSD, HF approximation (for exchange) with the LSD correlation respectively. LSDSICXC and HF(SICC) correspond to the LSDSIC and HF approximation (for exchange) with LSDSIC correlation. However, KLIC, KLI(SICC) KLI(GC) and KLI(SICGC) correspond to an approximation which constructs the OEP potential as the sum of the effective HF exchange potential and the LSD, LSDSIC, GGA, GGASIC correlation potential respectively.

Fig.4.6 is a graph of the ratio of the calculated correlation energy in various approximations to the exact correlation energy ( $E_c/E_c(\text{exact})$ ) versus various  $K$ . In the HFC and KLIC,  $E_c/E_c(\text{exact})$  varies from 0.49 to 28. These results imply that the LSD correlation is a very inaccurate approximation. In the HF(SICC) and KLI(SICC), the  $E_c/E_c(\text{exact})$  is about 0.53 to 0.69 and 0.52 to 0.68 respectively. We observe that the LSDSIC correlation for two electrons with parallel spin is much better than the LSD. But it is slightly weak.

The KLI(GC) generates  $E_c/E_c(\text{exact})$  from 3.1 to 4.7. Therefore the GGA correlation is stronger compared with the exact result.  $E_c/E_c(\text{exact})$  in the KLI(SICGC) varies from 0.73

to 1.10. Especially, when we consider the region from  $K=1$  to  $K=10$  (that is the region similar to atomic density),  $E_c/E_c(\text{exact})$  varies from 0.93 to 1.02. We can conclude that the GGASIC correlation energy is significantly more accurate than any of the other approximations for this two electron problem.

Fig.4.7 and Fig.4.8 give the percentage error in the calculation of the total energy. All three approximations with the LSD correlation produce larger errors than those with the LSDSIC correlation functional. In the KLI method, KLIC has the greatest error, KLI(GC) has less error, KLI(SICC) is even more accurate, and KLI(SICGC) has the smallest error. The GGASIC correlation produces the most accurate results in total exchange-correlation energy. As we mentioned before, the HF and the KLIX are very accurate in the exchange only case. But HFC and KLIC produce a large error due to the inaccuracy of the LSD correlation. The LSD correlation is too deep, it cancels part of the error obtained in the LSD exchange only case and reduces the error in the total energy.

Fig.4.9 and 4.10(10.1,10.2) give the comparison of  $V_x$  and  $V_c$  respectively.  $V_x$  in KLIX is very close to exact  $V_x$ .  $V_x$  in LSDX is too weak everywhere.  $V_c$  of the LSDSIC correlation is close to exact  $V_c$ . However,  $V_c$  of the LSD is far from the exact  $V_c$ .  $V_c$  of the GGA correlation is better than those of the LSD, but it is still not as close as  $V_c$  of the LSDSIC.  $V_c$  of GGASIC oscillates but its average is better than  $V_c$  of the GGA.

Fig.4.11 and Fig.4.12 are the graphs of the  $\epsilon_m/\epsilon_m(\text{exact})$

versus K in exchange and correlation case. Various approximations with the LSD correlation generate maximum 16% error. Approximations with the LSDSIC correlation produce as great as 3% error. The greatest error in the KLI(GC) is 3% whereas it is 2% in the KLI(SICGC).

Fig.4.13 and 4.14 are graphs of comparison of  $\langle r^2 \rangle$  for exchange and correlation. The approximations with the LSD correlation produce as great as 1.6% error. However, the greatest error in approximations with the LSDSIC, GGA, GGASIC is less than 0.7%.

Fig.4.15, Fig.4.16 and Fig.4.17 are comparison of electron density. The electron density of the KLIC, KLI(SICC), LSDSICXC, KLI(SICGC) are larger than exact value in the core part. The electron density of the LSDC is smaller than the exact value. The electron density of HFC, HF(SICC) and KLI(GC) are close to the exact value.

From the above discussion, the conclusion can be arrived at as follows:

The LSD correlation produces the largest error; the GGA correlation has improved the LSD correlation; the LSDSIC correlation generates less error than the above; the GGASIC correlation produces the smallest error among these correlation energy functions.

**Table 2.1** Total Energy Calculated in Various Approximations  
(HF, OEP, KLI, LSD, SKLI (LSD in Core))

| Z  | ATOM | -E <sup>HF</sup> | -E <sup>OEP</sup> | -E <sup>KLI</sup> | -E <sup>LSD</sup> | -E <sup>SKLI</sup><br>(LSD) |
|----|------|------------------|-------------------|-------------------|-------------------|-----------------------------|
| 3  | Li   | 7.4328           | 7.4325            | 7.4324            | 7.4286            | 7.4324                      |
| 4  | Be   | 14.5730          | 14.5724           | 14.5723           | 14.5681           | 14.5723                     |
| 5  | B    | 24.5293          | 24.5283           | 24.5281           | 24.5228           | 24.5248                     |
| 6  | C    | 37.6900          | 37.6889           | 37.6887           | 37.6817           | 37.6853                     |
| 7  | N    | 54.4045          | 54.4034           | 54.4030           | 54.3933           | 54.3996                     |
| 8  | O    | 74.8136          | 74.8121           | 74.8117           | 74.8000           | 74.8081                     |
| 9  | F    | 99.4108          | 99.4092           | 99.4088           | 99.3948           | 99.4051                     |
| 10 | Ne   | 128.5471         | 128.5454          | 128.5448          | 128.5275          | 128.5410                    |
| 11 | Na   | 161.8590         | 161.8566          | 161.8559          | 161.8413          | 161.8514                    |
| 12 | Mg   | 199.6146         | 199.6116          | 199.6107          | 199.5973          | 199.6060                    |
| 13 | Al   | 241.8768         | 241.8733          | 241.8723          | 241.8593          | <del>241.8588</del>         |
| 14 | Si   | 288.8546         | 288.8507          | 288.8495          | 288.8364          |                             |
| 15 | P    | 340.7193         | 340.7150          | 340.7137          | 340.7000          | 340.7035                    |
| 16 | S    | 397.5063         | 397.5016          | 397.5002          | 397.4861          | 397.4902                    |
| 17 | Cl   | 459.4826         | 459.4776          | 459.4760          | 459.4614          | 459.4662                    |
| 18 | Ar   | 526.8175         | 526.8122          | 526.8105          | 526.7949          | 526.8007                    |
| 19 | K    | 599.1649         | 599.1591          | 599.1571          | 599.1426          | 599.1467                    |
| 20 | Ca   | 676.7582         | 676.7519          | 676.7497          | 676.7358          | 676.7397                    |
| 21 | Sc   | 759.7359         | 759.7277          | 759.7249          | 759.7092          | 759.7115                    |
| 22 | Ti   | 848.4066         | 848.3972          | 848.3942          | 848.3748          | 848.3813                    |
| 23 | V    | 942.8856         | 942.8760          | 942.8729          | 942.8501          | 942.8602                    |
| 24 | Cr   | 1043.3568        | 1043.3457         | 1043.3422         | 1043.3091         | 1043.3315                   |
| 25 | Mn   | 1149.8698        | 1149.8600         | 1149.8569         | 1149.8264         | 1149.8447                   |
| 26 | Fe   | 1262.4500        | 1262.4380         | 1262.4344         | 1262.4026         | 1262.4218                   |
| 27 | Co   | 1381.4186        | 1381.4056         | 1381.4018         | 1381.3662         | 1381.3896                   |
| 28 | Ni   | 1506.8732        | 1506.8598         | 1506.8560         | 1506.8171         | 1506.8441                   |
| 29 | Cu   | 1638.9642        | 1638.9523         | 1638.9481         | 1638.8958         | 1638.9371                   |

**Table 2.1** Continued

| Z  | ATOM | -E <sup>HF</sup> | -E <sup>OEP</sup> | -E <sup>KLI</sup> | -E <sup>LSD</sup> | -E <sup>SKLI</sup><br>(LSD) |
|----|------|------------------|-------------------|-------------------|-------------------|-----------------------------|
| 30 | Zn   | 1777.8481        | 1777.1111         | 1233.1234         | 1234.1234         | 1223.1233                   |
| 31 | Ga   | 1923.2612        | 1923.2487         | 1923.2454         | 1923.2046         | 1923.2043                   |
| 32 | Ge   | 2075.3603        | 2075.3483         | 2075.3453         | 2075.3088         | 2075.3095                   |
| 33 | As   | 2234.2399        | 2234.2281         | 2234.2251         | 2234.1914         | 2234.1934                   |
| 34 | Se   | 2399.8691        | 2399.8573         | 2399.8543         | 2399.8228         | 2399.8253                   |
| 35 | Br   | 2572.4418        | 2572.4300         | 2572.4269         | 2572.3970         | 2572.4001                   |
| 36 | Kr   | 2752.0550        | 2752.0430         | 2752.0398         | 2752.0108         | 2752.0149                   |
| 37 | Rb   | 2938.3576        | 2938.3455         | 2938.3421         | 2938.3152         | 2938.3180                   |
| 38 | Sr   | 3131.5457        | 3131.5334         | 3131.5299         | 3131.5042         | 3131.5074                   |
| 39 | Y    | 3331.6846        | 3331.6710         | 3331.6670         | 3331.6418         | 3331.6429                   |
| 40 | Zr   | 3539.0117        | 3538.9970         | 3538.9925         | 3538.9651         | 3538.9686                   |
| 41 | Nb   | 3753.6006        | 3753.5855         | 3753.5807         | 3753.5515         | 3753.5570                   |
| 42 | Mo   | 3975.5530        | 3975.5371         | 3975.5320         | 3975.4998         | 3975.5084                   |
| 43 | Tc   | 4204.7946        | 4204.7793         | 4204.7741         | 4204.7422         | 4204.7512                   |
| 44 | Ru   | 4441.5409        | 4441.5245         | 4441.5190         | 4441.4843         | 4441.4961                   |
| 45 | Rh   | 4685.8822        | 4685.8656         | 4685.8600         | 4685.8242         | 4685.8371                   |
| 46 | Pd   | 4937.9210        | 4937.9060         | 4937.9016         | 4937.8555         | 4937.8815                   |
| 47 | Ag   | 5197.6989        | 5197.6815         | 5197.6758         | 5197.6328         | 5197.6529                   |
| 48 | Cd   | 5465.1331        | 5465.1144         | 5465.1084         | 5465.0702         | 5465.0861                   |
| 49 | In   | 5740.1694        | 5740.1514         | 5740.1455         | 5740.1094         | 5740.1104                   |
| 50 | Sn   | 6022.9325        | 6022.9149         | 6022.9092         | 6022.8750         | 6022.8769                   |
| 51 | Sb   | 6313.4870        | 6313.4697         | 6313.4639         | 6313.4336         | 6313.4339                   |
| 52 | Te   | 6611.7856        | 6611.7683         | 6611.7625         | 6611.7344         | 6611.7349                   |
| 53 | I    | 6917.9814        | 6917.9642         | 6917.9582         | 6917.9297         | 6917.9313                   |
| 54 | Xe   | 7232.1384        | 7232.1210         | 7232.1150         | 7232.0859         | 7232.0893                   |
| 55 | Cs   | 7553.9338        | 7553.9165         | 7553.9103         | 7553.8838         | 7553.8853                   |
| 56 | Ba   | 7883.5438        | 7883.5226         | 7883.5201         | 7883.4922         | 7883.4963                   |

**Table 2.2** Comparison of Overestimate of SKLI(LSD in Core)  
Total Energy With the Other Approximations

| Z  | ATOM | $-E^{HF}$ | $E^{OEP}-E^{HF}$ | $E^{KLI}-E^{OEP}$ | $E^{LSD}-E^{OEP}$ | $E^{SKLI(LSD)}-E^{OEP}$ |
|----|------|-----------|------------------|-------------------|-------------------|-------------------------|
| 3  | Li   | 7.4328    | 0.3              | 0.1               | 3.9               | 0.1                     |
| 4  | Be   | 14.5730   | 0.6              | 0.1               | 4.3               | 0.1                     |
| 5  | B    | 24.5293   | 1.0              | 0.2               | 5.5               | 3.5                     |
| 6  | C    | 37.6900   | 1.1              | 0.2               | 7.2               | 3.6                     |
| 7  | N    | 54.4045   | 1.1              | 0.4               | 10.1              | 3.8                     |
| 8  | O    | 74.8136   | 1.5              | 0.4               | 11.7              | 4.0                     |
| 9  | F    | 99.4108   | 1.6              | 0.4               | 14.4              | 4.1                     |
| 10 | Ne   | 128.5471  | 1.7              | 0.6               | 17.9              | 4.4                     |
| 11 | Na   | 161.8590  | 2.4              | 0.7               | 15.3              | 5.2                     |
| 12 | Mg   | 199.6146  | 3.0              | 0.9               | 14.3              | 5.6                     |
| 13 | Al   | 241.8768  | 3.5              | 1.0               | 14.0              | 12.4                    |
| 14 | Si   | 288.8546  | 3.9              | 1.2               | 14.3              | 11.8                    |
| 15 | P    | 340.7193  | 4.3              | 1.3               | 15.0              | 11.5                    |
| 16 | S    | 397.5063  | 4.7              | 1.4               | 15.5              | 11.4                    |
| 17 | Cl   | 495.4826  | 5.0              | 1.6               | 16.2              | 11.4                    |
| 18 | Ar   | 526.8175  | 5.3              | 1.7               | 17.3              | 11.5                    |
| 19 | K    | 599.1649  | 5.8              | 2.0               | 16.5              | 12.4                    |
| 20 | Ca   | 676.7582  | 6.3              | 2.2               | 16.1              | 12.2                    |
| 21 | Sc   | 759.7359  | 8.2              | 2.8               | 18.5              | 16.2                    |
| 22 | Ti   | 848.4066  | 9.2              | 3.2               | 22.6              | 16.1                    |
| 23 | V    | 942.8856  | 9.6              | 3.1               | 25.9              | 15.8                    |
| 24 | Cr   | 1043.3568 | 11.1             | 3.5               | 36.6              | 14.2                    |
| 25 | Mn   | 1149.8698 | 9.8              | 3.1               | 33.6              | 15.3                    |
| 26 | Fe   | 1262.4500 | 12.0             | 3.6               | 35.4              | 16.2                    |
| 27 | Co   | 1381.4186 | 13.0             | 3.8               | 39.4              | 16.0                    |
| 28 | Ni   | 1506.8732 | 13.4             | 3.8               | 42.7              | 15.7                    |
| 29 | Cu   | 1632.9642 | 11.9             | 4.2               | 56.5              | 15.2                    |

**Table 2.2** Continued

| Z  | ATOM | $-E^{HF}$ | $E^{OEP}-E^{HF}$ | $E^{KLI}-E^{OEP}$ | $E^{LSD}-E^{OEP}$ | $E^{SKLI}(LSD)-E^{OEP}$ |
|----|------|-----------|------------------|-------------------|-------------------|-------------------------|
| 30 | Zn   | 1777.8481 | 13.7             | 3.7               | 51.0              | 15.1                    |
| 31 | Ga   | 1923.2612 | 12.5             | 3.3               | 44.1              | 44.4                    |
| 32 | Ge   | 2075.3603 | 12.0             | 3.0               | 39.5              | 38.8                    |
| 33 | As   | 2234.2399 | 11.8             | 3.0               | 36.7              | 34.7                    |
| 34 | Se   | 2339.8691 | 11.8             | 3.0               | 34.5              | 32.0                    |
| 35 | Br   | 2572.4418 | 11.8             | 3.1               | 33.0              | 29.9                    |
| 36 | Kr   | 2752.0550 | 12.0             | 3.2               | 32.2              | 28.1                    |
| 37 | Rb   | 2938.3576 | 12.1             | 3.4               | 30.3              | 27.5                    |
| 38 | Sr   | 3131.5457 | 12.3             | 3.5               | 29.2              | 26.0                    |
| 39 | Y    | 3331.6846 | 13.6             | 4.0               | 29.2              | 28.1                    |
| 40 | Zr   | 3539.0117 | 14.7             | 4.5               | 31.9              | 28.4                    |
| 41 | Nb   | 3753.6006 | 15.1             | 4.8               | 34.0              | 28.5                    |
| 42 | Mo   | 3975.5530 | 15.9             | 5.1               | 37.3              | 28.7                    |
| 43 | Tc   | 4204.7949 | 15.6             | 5.2               | 37.1              | 28.1                    |
| 44 | Ru   | 4441.5409 | 16.4             | 5.5               | 40.2              | 28.4                    |
| 45 | Rh   | 4685.8822 | 16.6             | 5.6               | 41.4              | 28.5                    |
| 46 | Pd   | 4937.9210 | 15.0             | 4.4               | 50.5              | 25.5                    |
| 47 | Ag   | 5197.6789 | 17.4             | 5.7               | 43.0              | 28.6                    |
| 48 | Cd   | 5465.1331 | 18.7             | 6.0               | 44.2              | 28.3                    |
| 49 | In   | 5740.1694 | 18.0             | 5.9               | 42.0              | 41.0                    |
| 50 | Sn   | 6022.9325 | 17.6             | 5.7               | 39.9              | 38.0                    |
| 51 | Sb   | 6313.4870 | 17.3             | 5.8               | 36.1              | 35.8                    |
| 52 | Te   | 6611.7856 | 17.3             | 5.8               | 33.9              | 33.4                    |
| 53 | I    | 6917.9814 | 17.2             | 6.0               | 34.5              | 32.9                    |
| 54 | Xe   | 7232.1384 | 17.4             | 6.0               | 35.1              | 31.7                    |
| 55 | Cs   | 7553.9338 | 17.3             | 6.2               | 33.7              | 31.2                    |
| 56 | Ba   | 7883.5438 | 21.2             | 2.5               | 30.4              | 26.3                    |

**Table 2.3** Total Energy Calculated in Various Approximations (HF, OEP, KLI, LSDSIC, SKLI (LSDSIC in Core))

| Z  | ATOM | -E <sup>HF</sup> | -E <sup>OEP</sup> | -E <sup>KLI</sup> | -E <sup>LSDSIC</sup> | -E <sup>SKLI</sup><br>(LSDSIC) |
|----|------|------------------|-------------------|-------------------|----------------------|--------------------------------|
| 3  | Li   | 7.4328           | 7.4325            | 7.4324            | 7.4322               | 7.4324                         |
| 4  | Be   | 14.5730          | 14.5724           | 14.5723           | 14.5717              | 14.5723                        |
| 5  | B    | 24.5293          | 24.5283           | 24.5281           | 24.5272              | 24.5279                        |
| 6  | C    | 37.6900          | 37.6889           | 37.6887           | 37.6869              | 37.6884                        |
| 7  | N    | 54.4045          | 54.4034           | 54.4030           | 54.3999              | 54.4027                        |
| 8  | O    | 74.8136          | 74.8121           | 74.8117           | 74.8022              | 74.8113                        |
| 9  | F    | 99.4108          | 99.4092           | 99.4088           | 99.4044              | 99.4083                        |
| 10 | Ne   | 128.5471         | 128.5454          | 128.5448          | 128.5390             | 128.5443                       |
| 11 | Na   | 161.8590         | 161.8566          | 161.8559          | 161.8495             | 161.8549                       |
| 12 | Mg   | 199.6146         | 199.6116          | 199.6107          | 199.6037             | 199.6091                       |
| 13 | Al   | 241.8768         | 241.8733          | 241.8723          | 241.8650             | 241.8663                       |
| 14 | Si   | 288.8546         | 288.8507          | 288.8495          | 288.8416             | 288.8436                       |
| 15 | P    | 340.7193         | 340.7150          | 340.7137          | 340.7048             | 340.7078                       |
| 16 | S    | 397.5063         | 397.5016          | 397.5002          | 397.4909             | 397.4942                       |
| 17 | Cl   | 459.4826         | 459.4776          | 459.4760          | 459.4661             | 459.4701                       |
| 18 | Ar   | 526.8175         | 526.8122          | 526.8105          | 526.7996             | 526.8044                       |
| 19 | K    | 599.1649         | 599.1591          | 599.1571          | 599.1458             | 599.1503                       |
| 20 | Ca   | 676.7582         | 676.7519          | 676.7497          | 676.7381             | 676.7430                       |
| 21 | Sc   | 759.7359         | 759.7277          | 759.7249          | 759.7126             | 759.7141                       |
| 22 | Ti   | 848.4066         | 848.3972          | 848.3942          | 848.3799             | 848.3836                       |
| 23 | V    | 942.8856         | 942.8760          | 942.8729          | 942.8440             | 942.8625                       |
| 24 | Cr   | 1043.3568        | 1043.3457         | 1043.3422         | 1043.3221            | 1043.3324                      |
| 25 | Mn   | 1149.8698        | 1149.8600         | 1149.8569         | 1149.8361            | 1149.8469                      |
| 26 | Fe   | 1262.4500        | 1262.4380         | 1262.4344         | 1262.4128            | 1262.4240                      |
| 27 | Co   | 1381.4186        | 1381.4056         | 1381.4018         | 1381.3881            | 1381.3917                      |
| 28 | Ni   | 1506.8732        | 1506.8598         | 1506.8560         | 1506.8297            | 1506.8462                      |
| 29 | Cu   | 1638.9642        | 1638.9523         | 1638.9481         | 1638.9203            | 1638.9392                      |

**Table 2.3** Continued

| Z  | ATOM | -E <sup>HF</sup> | -E <sup>OEP</sup> | -E <sup>KLI</sup> | -E <sup>LSD</sup> | -E <sup>SKLI</sup><br>(LSD) |
|----|------|------------------|-------------------|-------------------|-------------------|-----------------------------|
| 30 | Zn   | 1777.8481        | 1777.8344         | 1777.8307         | 1777.8006         | 1777.8214                   |
| 31 | Ga   | 1923.2612        | 1923.2487         | 1923.2454         | 1923.2172         | 1923.2181                   |
| 32 | Ge   | 2075.3603        | 2075.3483         | 2075.3453         | 2075.3181         | 2075.3196                   |
| 33 | As   | 2234.2399        | 2234.2281         | 2234.2251         | 2234.1983         | 2234.2008                   |
| 34 | Se   | 2399.8691        | 2399.8573         | 2399.8543         | 2399.8280         | 2399.8309                   |
| 35 | Br   | 2572.4418        | 2572.4300         | 2572.4269         | 2572.4010         | 2572.4045                   |
| 36 | Kr   | 2752.0550        | 2752.0430         | 2752.0398         | 2752.0138         | 2752.0182                   |
| 37 | Rb   | 2938.3576        | 2938.3455         | 2938.3421         | 2938.3166         | 2938.3206                   |
| 38 | Sr   | 3131.5457        | 3131.5334         | 3131.5299         | 3131.5048         | 3131.5094                   |
| 39 | Y    | 3331.6846        | 3331.6710         | 3331.6670         | 3331.6422         | 3331.6433                   |
| 40 | Zr   | 3539.0117        | 3538.9970         | 3538.9925         | 3538.9665         | 3538.9689                   |
| 41 | Nb   | 3753.6006        | 3753.5855         | 3753.5807         | 3753.5528         | 3753.5571                   |
| 42 | Mo   | 3975.5530        | 3975.5371         | 3975.5320         | 3975.4997         | 3975.5083                   |
| 43 | Tc   | 4204.7946        | 4204.7793         | 4204.7741         | 4204.7425         | 4204.7508                   |
| 44 | Ru   | 4441.5409        | 4441.5245         | 4441.5190         | 4441.4861         | 4441.4958                   |
| 45 | Rh   | 4685.8822        | 4685.8656         | 4685.8600         | 4685.8254         | 4685.8367                   |
| 46 | Pd   | 4937.9210        | 4937.9060         | 4937.9016         | 4937.8646         | 4937.8824                   |
| 47 | Ag   | 5197.6989        | 5197.6815         | 5197.6758         | 5197.6369         | 5197.6524                   |
| 48 | Cd   | 5465.1331        | 5465.1144         | 5465.1084         | 5465.0691         | 5465.0854                   |
| 49 | In   | 5740.1694        | 5740.1514         | 5740.1455         | 5740.1085         | 5740.1086                   |
| 50 | Sn   | 6022.9325        | 6022.9149         | 6022.9092         | 6022.8737         | 6022.8741                   |
| 51 | Sb   | 6313.4870        | 6313.4697         | 6313.4639         | 6313.4293         | 6313.4307                   |
| 52 | Te   | 6611.7856        | 6611.7683         | 6611.7625         | 6611.7289         | 6611.7305                   |
| 53 | I    | 6917.9814        | 6917.9642         | 6917.9582         | 6917.9255         | 6917.9275                   |
| 54 | Xe   | 7232.1384        | 7232.1210         | 7232.1150         | 7232.0828         | 7232.0855                   |
| 55 | Cs   | 7553.9338        | 7553.9165         | 7553.9103         | 7553.8787         | 7553.8816                   |
| 56 | Ba   | 7883.5438        | 7883.5226         | 7883.5201         | 7883.4890         | 7883.4926                   |

**Table 2.4** Comparison of Overestimate of SKLI(LSDSIC in Core) Total Energy With the Other Approximations

| Z  | ATOM | $-E^{HF}$ | $E^{OEP}-E^{HF}$ | $E^{KLI}-E^{OEP}$ | $E^{LSDSIC}-E^{OEP}$ | $E^{SKLI}(SIC)-E^{OEP}$ |
|----|------|-----------|------------------|-------------------|----------------------|-------------------------|
| 3  | Li   | 7.4328    | 0.3              | 0.1               | 0.3                  | 0.1                     |
| 4  | Be   | 14.5730   | 0.6              | 0.1               | 0.7                  | 0.1                     |
| 5  | B    | 24.5293   | 1.0              | 0.2               | 1.1                  | 0.4                     |
| 6  | C    | 37.6900   | 1.1              | 0.2               | 2.0                  | 0.5                     |
| 7  | N    | 54.4045   | 1.1              | 0.4               | 3.5                  | 0.7                     |
| 8  | O    | 74.8136   | 1.5              | 0.4               | 9.9                  | 0.8                     |
| 9  | F    | 99.4108   | 1.6              | 0.4               | 4.8                  | 0.9                     |
| 10 | Ne   | 128.5471  | 1.7              | 0.6               | 6.4                  | 1.1                     |
| 11 | Na   | 161.8590  | 2.4              | 0.7               | 7.1                  | 2.0                     |
| 12 | Mg   | 199.6146  | 3.0              | 0.9               | 7.9                  | 2.5                     |
| 13 | Al   | 241.8768  | 3.5              | 1.0               | 8.3                  | 7.0                     |
| 14 | Si   | 288.8546  | 3.9              | 1.2               | 9.1                  | 7.1                     |
| 15 | P    | 340.7193  | 4.3              | 1.3               | 10.2                 | 7.2                     |
| 16 | S    | 397.5063  | 4.7              | 1.4               | 10.7                 | 7.4                     |
| 17 | Cl   | 495.4826  | 5.0              | 1.6               | 11.5                 | 7.5                     |
| 18 | Ar   | 526.8175  | 5.3              | 1.7               | 12.6                 | 7.8                     |
| 19 | K    | 599.1649  | 5.8              | 2.0               | 13.3                 | 8.8                     |
| 20 | Ca   | 676.7582  | 6.3              | 2.2               | 13.8                 | 8.9                     |
| 21 | Sc   | 759.7359  | 8.2              | 2.8               | 15.1                 | 13.6                    |
| 22 | Ti   | 848.4066  | 9.2              | 3.2               | 17.5                 | 13.8                    |
| 23 | V    | 942.8856  | 9.6              | 3.1               | 32.0                 | 13.5                    |
| 24 | Cr   | 1043.3568 | 11.1             | 3.5               | 23.6                 | 13.3                    |
| 25 | Mn   | 1149.8698 | 9.8              | 3.1               | 23.9                 | 13.1                    |
| 26 | Fe   | 1262.4500 | 12.0             | 3.6               | 25.2                 | 14.0                    |
| 27 | Co   | 1381.4186 | 13.0             | 3.8               | 17.5                 | 13.9                    |
| 28 | Ni   | 1506.8732 | 13.4             | 3.8               | 30.1                 | 13.6                    |
| 29 | Cu   | 1632.9642 | 11.9             | 4.2               | 32.0                 | 13.1                    |

**Table 2.4** Continued

| Z  | ATOM | $-E^{HF}$ | $E^{OEP}-E^{HF}$ | $E^{KLI}-E^{OEP}$ | $E^{LSDSIC}-E^{OEP}$ | $E^{SKLI}(SI C)-E^{OEP}$ |
|----|------|-----------|------------------|-------------------|----------------------|--------------------------|
| 30 | Zn   | 1777.8481 | 13.7             | 3.7               | 33.8                 | 13.0                     |
| 31 | Ga   | 1923.2612 | 12.5             | 3.3               | 31.5                 | 30.6                     |
| 32 | Ge   | 2075.3603 | 12.0             | 3.0               | 30.6                 | 28.7                     |
| 33 | As   | 2234.2399 | 11.8             | 3.0               | 29.8                 | 27.3                     |
| 34 | Se   | 2339.8691 | 11.8             | 3.0               | 29.3                 | 26.4                     |
| 35 | Br   | 2572.4418 | 11.8             | 3.1               | 29.0                 | 25.5                     |
| 36 | Kr   | 2752.0550 | 12.0             | 3.2               | 29.2                 | 24.8                     |
| 37 | Rb   | 2938.3576 | 12.1             | 3.4               | 28.9                 | 24.9                     |
| 38 | Sr   | 3131.5457 | 12.3             | 3.5               | 28.6                 | 24.0                     |
| 39 | Y    | 3131.6846 | 13.6             | 4.0               | 28.8                 | 27.7                     |
| 40 | Zr   | 3539.0117 | 14.7             | 4.5               | 30.5                 | 28.1                     |
| 41 | Nb   | 3753.6006 | 15.1             | 4.8               | 32.7                 | 28.4                     |
| 42 | Mo   | 3975.5530 | 15.9             | 5.1               | 37.4                 | 28.8                     |
| 43 | Tc   | 4204.7949 | 15.6             | 5.2               | 36.8                 | 28.5                     |
| 44 | Ru   | 4441.5409 | 16.4             | 5.5               | 38.4                 | 28.7                     |
| 45 | Rh   | 4685.8822 | 16.6             | 5.6               | 40.2                 | 28.9                     |
| 46 | Pd   | 4937.9210 | 15.0             | 4.4               | 41.4                 | 23.6                     |
| 47 | Ag   | 5197.6989 | 17.4             | 5.7               | 44.6                 | 29.1                     |
| 48 | Cd   | 5465.1331 | 18.7             | 6.0               | 45.3                 | 28.7                     |
| 49 | In   | 5740.1694 | 18.0             | 5.9               | 42.6                 | 42.8                     |
| 50 | Sn   | 6022.9325 | 17.6             | 5.7               | 41.2                 | 40.8                     |
| 51 | Sb   | 6313.4870 | 17.3             | 5.8               | 40.4                 | 39.0                     |
| 52 | Te   | 6611.7856 | 17.3             | 5.8               | 39.4                 | 37.8                     |
| 53 | I    | 6917.9814 | 17.2             | 6.0               | 38.7                 | 36.7                     |
| 54 | Xe   | 7232.1384 | 17.4             | 6.0               | 38.2                 | 35.5                     |
| 55 | Cs   | 7553.9338 | 17.3             | 6.2               | 37.8                 | 34.9                     |
| 56 | Ba   | 7883.5438 | 21.2             | 2.5               | 37.6                 | 34.0                     |

**Table 2.5** Comparison of Highest Occupied Eigenvalue Obtained in SKLI(LSD in Core) With Other Approximations

| Z  | ATOM | $\epsilon_{ms}^{HF}$ | $\epsilon_{ms}^{OEP}$ | $\epsilon_{ms}^{KLI}$ | $\epsilon_{ms}^{LSD}$ | $\epsilon_{ms}^{SKLI}$ |
|----|------|----------------------|-----------------------|-----------------------|-----------------------|------------------------|
| 3  | Li   | 0.3927               | 0.3926                | 0.3924                | 0.2009                | 0.3924                 |
| 4  | Be   | 0.6185               | 0.6185                | 0.6177                | 0.3401                | 0.6177                 |
| 5  | B    | 0.5219               | 0.6194                | 0.6191                | 0.2402                | 0.6216                 |
| 6  | C    | 0.8711               | 0.8705                | 0.8698                | 0.3920                | 0.8713                 |
| 7  | N    | 1.1418               | 1.1423                | 1.1409                | 0.5526                | 1.1417                 |
| 8  | O    | 1.0187               | 1.0153                | 1.0138                | 0.4193                | 1.0158                 |
| 9  | F    | 1.3475               | 1.3469                | 1.3449                | 0.6519                | 1.3456                 |
| 10 | Ne   | 1.7008               | 1.7014                | 1.6988                | 0.8861                | 1.6987                 |
| 11 | Na   | 0.3644               | 0.36426               | 0.3640                | 0.1934                | 0.3649                 |
| 12 | Mg   | 0.5061               | 0.5060                | 0.5048                | 0.2843                | 0.5059                 |
| 13 | Al   | 0.4200               | 0.4189                | 0.4171                | 0.1724                | 0.4189                 |
| 14 | Si   | 0.5947               | 0.5933                | 0.5915                | 0.2872                | 0.5932                 |
| 15 | P    | 0.7842               | 0.7831                | 0.7810                | 0.4066                | 0.7825                 |
| 16 | S    | 0.7281               | 0.7273                | 0.7253                | 0.3485                | 0.7270                 |
| 17 | Cl   | 0.9467               | 0.9460                | 0.9436                | 0.5083                | 0.9449                 |
| 18 | Ar   | 1.1820               | 1.1816                | 1.1786                | 0.6676                | 1.1795                 |
| 19 | K    | 0.2953               | 0.2954                | 0.2954                | 0.1609                | 0.2958                 |
| 20 | Ca   | 0.3911               | 0.3913                | 0.3901                | 0.2227                | 0.3908                 |
| 21 | Sc   | 0.4331               | 0.4354                | 0.4381                | 0.2658                | 0.4412                 |
| 22 | Ti   | 0.4203               | 0.4191                | 0.4161                | 0.2406                | 0.4176                 |
| 23 | V    | 0.4317               | 0.4307                | 0.4272                | 0.2461                | 0.4286                 |
| 24 | Cr   | 0.4441               | 0.4483                | 0.4551                | 0.3021                | 0.4557                 |
| 25 | Mn   | 0.4521               | 0.4512                | 0.4472                | 0.2560                | 0.4484                 |
| 26 | Fe   | 0.4843               | 0.4845                | 0.4835                | 0.2876                | 0.4857                 |
| 27 | Co   | 0.5111               | 0.5113                | 0.5108                | 0.3123                | 0.5123                 |
| 28 | Ni   | 0.5371               | 0.5374                | 0.5366                | 0.3337                | 0.5373                 |
| 29 | Cu   | 0.4793               | 0.4810                | 0.4880                | 0.3176                | 0.4884                 |

**Table 2.5 Continued**

| Z  | ATOM | $g_{m\sigma}^{HF}$ | $g_{m\sigma}^{OEP}$ | $g_{m\sigma}^{KLI}$ | $g_{m\sigma}^{LSD}$ | $g_{m\sigma}^{SKLI}$ |
|----|------|--------------------|---------------------|---------------------|---------------------|----------------------|
| 30 | Zn   | 0.5850             | 0.5855              | 0.5837              | 0.3707              | 0.5843               |
| 31 | Ga   | 0.4176             | 0.4150              | 0.4116              | 0.1703              | 0.4226               |
| 32 | Ge   | 0.5758             | 0.5734              | 0.5706              | 0.2789              | 0.5790               |
| 33 | As   | 0.7404             | 0.7382              | 0.7355              | 0.3858              | 0.7422               |
| 34 | Se   | 0.6708             | 0.6688              | 0.6669              | 0.3317              | 0.6722               |
| 35 | Br   | 0.8550             | 0.8532              | 0.8509              | 0.4682              | 0.8555               |
| 36 | Kr   | 1.0484             | 1.0468              | 1.0440              | 0.5997              | 1.0480               |
| 37 | Rb   | 0.2762             | 0.2766              | 0.2768              | 0.1528              | 0.2771               |
| 38 | Sr   | 0.3569             | 0.3573              | 0.3564              | 0.2055              | 0.3570               |
| 39 | Y    | 0.4103             | 0.4144              | 0.4168              | 0.2588              | 0.4192               |
| 40 | Zr   | 0.4125             | 0.4189              | 0.4256              | 0.2802              | 0.4255               |
| 41 | Nb   | 0.4321             | 0.4378              | 0.4446              | 0.2911              | 0.4438               |
| 42 | Mo   | 0.4461             | 0.4512              | 0.4582              | 0.2991              | 0.4571               |
| 43 | Tc   | 0.4061             | 0.4055              | 0.4031              | 0.2348              | 0.4037               |
| 44 | Ru   | 0.4437             | 0.4474              | 0.4534              | 0.2930              | 0.4529               |
| 45 | Rh   | 0.4427             | 0.4458              | 0.4513              | 0.2892              | 0.4511               |
| 46 | Pd   | 0.6720             | 0.6702              | 0.6725              | 0.2379              | 0.6705               |
| 47 | Ag   | 0.4420             | 0.4443              | 0.4490              | 0.2831              | 0.4492               |
| 48 | Cd   | 0.5297             | 0.5310              | 0.5301              | 0.3357              | 0.5302               |
| 49 | In   | 0.3954             | 0.3932              | 0.3904              | 0.1689              | 0.3984               |
| 50 | Sn   | 0.5315             | 0.5295              | 0.5272              | 0.2650              | 0.5332               |
| 51 | Sb   | 0.6715             | 0.6694              | 0.6673              | 0.3571              | 0.6718               |
| 52 | Te   | 0.6022             | 0.6004              | 0.5992              | 0.3095              | 0.6029               |
| 53 | I    | 0.7554             | 0.7537              | 0.7521              | 0.4234              | 0.7551               |
| 54 | Xe   | 0.7146             | 0.9129              | 0.9109              | 0.5314              | 0.9133               |
| 55 | Cs   | 0.2478             | 0.2483              | 0.2486              | 0.1388              | 0.2486               |
| 56 | Ba   | 0.3151             | 0.3155              | 0.3148              | 0.1828              | 0.3150               |

**Table 2.6** Comparison of Highest Occupied Eigenvalue Obtained in SKLI(LSDSIC in Core) With Other Approximations

| Z  | ATOM | $\epsilon_{mo}^{HF}$ | $\epsilon_{mo}^{OEP}$ | $\epsilon_{mo}^{KLI}$ | $\epsilon_{SICmo}^{LSD}$ | $\epsilon_{mo}^{SKLI}$ |
|----|------|----------------------|-----------------------|-----------------------|--------------------------|------------------------|
| 3  | Li   | 0.3927               | 0.3926                | 0.3924                | 0.3913                   | 0.3924                 |
| 4  | Be   | 0.6185               | 0.6185                | 0.6177                | 0.6164                   | 0.6177                 |
| 5  | B    | 0.5219               | 0.6194                | 0.6191                | 0.5794                   | 0.6199                 |
| 6  | C    | 0.8711               | 0.8705                | 0.8698                | 0.8248                   | 0.8702                 |
| 7  | N    | 1.1418               | 1.1423                | 1.1409                | 1.0726                   | 1.1410                 |
| 8  | O    | 1.0187               | 1.0153                | 1.0138                | 0.9577                   | 1.0140                 |
| 9  | F    | 1.3475               | 1.3469                | 1.3449                | 1.2904                   | 1.3448                 |
| 10 | Ne   | 1.7008               | 1.7014                | 1.6988                | 1.6156                   | 1.6984                 |
| 11 | Na   | 0.3644               | 0.36426               | 0.3640                | 0.3729                   | 0.3647                 |
| 12 | Mg   | 0.5061               | 0.5060                | 0.5048                | 0.5122                   | 0.5058                 |
| 13 | Al   | 0.4200               | 0.4189                | 0.4171                | 0.3830                   | 0.4176                 |
| 14 | Si   | 0.5947               | 0.5933                | 0.5915                | 0.5494                   | 0.5920                 |
| 15 | P    | 0.7842               | 0.7831                | 0.7810                | 0.7164                   | 0.7813                 |
| 16 | S    | 0.7281               | 0.7273                | 0.7253                | 0.6875                   | 0.7260                 |
| 17 | Cl   | 0.9467               | 0.9460                | 0.9436                | 0.8945                   | 0.9440                 |
| 18 | Ar   | 1.1820               | 1.1816                | 1.1786                | 1.0986                   | 1.1787                 |
| 19 | K    | 0.2953               | 0.2954                | 0.2954                | 0.3075                   | 0.2958                 |
| 20 | Ca   | 0.3911               | 0.3913                | 0.3901                | 0.4010                   | 0.3907                 |
| 21 | Sc   | 0.4331               | 0.4354                | 0.4381                | 0.4575                   | 0.4406                 |
| 22 | Ti   | 0.4203               | 0.4191                | 0.4161                | 0.4306                   | 0.4173                 |
| 23 | V    | 0.4317               | 0.4307                | 0.4272                | 0.4421                   | 0.4283                 |
| 24 | Cr   | 0.4441               | 0.4483                | 0.4551                | 0.4755                   | 0.4552                 |
| 25 | Mn   | 0.4521               | 0.4512                | 0.4472                | 0.4630                   | 0.4481                 |
| 26 | Fe   | 0.4843               | 0.4845                | 0.4835                | 0.5071                   | 0.4852                 |
| 27 | Co   | 0.5111               | 0.5113                | 0.5108                | 0.5415                   | 0.5119                 |
| 28 | Ni   | 0.5371               | 0.5374                | 0.5366                | 0.5415                   | 0.5373                 |
| 29 | Cu   | 0.4793               | 0.4810                | 0.4880                | 0.5373                   | 0.4882                 |

**Table 2.6** Continued

| Z  | ATOM | $\epsilon_{m\sigma}^{HF}$ | $\epsilon_{m\sigma}^{OEP}$ | $\epsilon_{m\sigma}^{KLI}$ | $\epsilon_{m\sigma}^{LSD}$ | $\epsilon_{m\sigma}^{SKLI}$ |
|----|------|---------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|
| 30 | Zn   | 0.5850                    | 0.5855                     | 0.5837                     | 0.6242                     | 0.5843                      |
| 31 | Ga   | 0.4176                    | 0.4150                     | 0.4116                     | 0.3808                     | 0.4158                      |
| 32 | Ge   | 0.5758                    | 0.5734                     | 0.5706                     | 0.5296                     | 0.5740                      |
| 33 | As   | 0.7404                    | 0.7382                     | 0.7355                     | 0.6711                     | 0.7382                      |
| 34 | Se   | 0.6708                    | 0.6688                     | 0.6669                     | 0.6382                     | 0.6691                      |
| 35 | Br   | 0.8550                    | 0.8532                     | 0.8509                     | 0.8069                     | 0.8528                      |
| 36 | Kr   | 1.0484                    | 1.0468                     | 1.0440                     | 0.9683                     | 1.0456                      |
| 37 | Rb   | 0.2762                    | 0.2766                     | 0.2768                     | 0.2905                     | 0.2771                      |
| 38 | Sr   | 0.3569                    | 0.3573                     | 0.3564                     | 0.3690                     | 0.3569                      |
| 39 | Y    | 0.4103                    | 0.4144                     | 0.4168                     | 0.2588                     | 0.4193                      |
| 40 | Zr   | 0.4125                    | 0.4189                     | 0.4256                     | 0.4586                     | 0.4259                      |
| 41 | Nb   | 0.4321                    | 0.4378                     | 0.4446                     | 0.4785                     | 0.4442                      |
| 42 | Mo   | 0.4461                    | 0.4512                     | 0.4582                     | 0.4943                     | 0.4574                      |
| 43 | Tc   | 0.4061                    | 0.4055                     | 0.4031                     | 0.4269                     | 0.4038                      |
| 44 | Ru   | 0.4437                    | 0.4474                     | 0.4534                     | 0.4965                     | 0.4532                      |
| 45 | Rh   | 0.4427                    | 0.4458                     | 0.4513                     | 0.4965                     | 0.4514                      |
| 46 | Pd   | 0.6720                    | 0.6702                     | 0.6725                     | 0.6687                     | 0.6708                      |
| 47 | Ag   | 0.4420                    | 0.4443                     | 0.4490                     | 0.4966                     | 0.4494                      |
| 48 | Cd   | 0.5297                    | 0.5310                     | 0.5301                     | 0.5714                     | 0.5303                      |
| 49 | In   | 0.3954                    | 0.3932                     | 0.3904                     | 0.3629                     | 0.3959                      |
| 50 | Sn   | 0.5315                    | 0.5295                     | 0.5272                     | 0.4887                     | 0.5316                      |
| 51 | Sb   | 0.6715                    | 0.6694                     | 0.6673                     | 0.6063                     | 0.6706                      |
| 52 | Te   | 0.6022                    | 0.6004                     | 0.5992                     | 0.5758                     | 0.6021                      |
| 53 | I    | 0.7554                    | 0.7537                     | 0.7521                     | 0.7124                     | 0.7551                      |
| 54 | Xe   | 0.7146                    | 0.9129                     | 0.9109                     | 0.8416                     | 0.9128                      |
| 55 | Cs   | 0.2478                    | 0.2483                     | 0.2486                     | 0.2624                     | 0.2487                      |
| 56 | Ba   | 0.3151                    | 0.3155                     | 0.3148                     | 0.3277                     | 0.3151                      |

**Table 2.7** Comparison of  $\langle r^2 \rangle$  Calculated in SKLI (LSD in Core With the Other Approximations

| Z  | ATOM | $\langle r^2 \rangle_{\text{HF}}$ | $\langle r^2 \rangle_{\text{OEP}}$ | $\langle r^2 \rangle_{\text{KLI}}$ | $\langle r^2 \rangle_{\text{LSD}}$ | $\langle r^2 \rangle_{\text{SKLI}}$ |
|----|------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------------------|
| 3  | Li   | 6.2080                            | 6.2145                             | 6.1974                             | 6.4685                             | 6.1974                              |
| 4  | Be   | 4.3297                            | 4.3316                             | 4.3255                             | 4.4809                             | 4.3255                              |
| 5  | B    | 3.1674                            | 3.1690                             | 3.1724                             | 3.3918                             | 3.1614                              |
| 6  | C    | 2.2966                            | 2.2967                             | 2.2969                             | 2.4543                             | 2.2918                              |
| 7  | N    | 1.7252                            | 1.7253                             | 1.7240                             | 1.8461                             | 1.7215                              |
| 8  | O    | 1.4029                            | 1.4032                             | 1.4039                             | 1.5108                             | 1.4015                              |
| 9  | F    | 1.1386                            | 1.1386                             | 1.1395                             | 1.2211                             | 1.1371                              |
| 10 | Ne   | 0.9372                            | 0.9372                             | 0.9367                             | 1.0036                             | 0.9358                              |
| 11 | Na   | 2.4673                            | 2.4708                             | 2.4574                             | 2.4506                             | 2.4531                              |
| 12 | Mg   | 2.4676                            | 2.4693                             | 2.4610                             | 2.4575                             | 2.4567                              |
| 13 | Al   | 2.5756                            | 2.5772                             | 2.5798                             | 2.6668                             | 2.5695                              |
| 14 | Si   | 2.3037                            | 2.3042                             | 2.3068                             | 2.3788                             | 2.2996                              |
| 15 | P    | 2.0173                            | 2.0174                             | 2.0188                             | 2.0856                             | 2.0139                              |
| 16 | S    | 1.8267                            | 1.8269                             | 1.8281                             | 1.8847                             | 1.8240                              |
| 17 | Cl   | 1.6264                            | 1.6265                             | 1.6273                             | 1.6774                             | 1.6242                              |
| 18 | Ar   | 1.4464                            | 1.4465                             | 1.4467                             | 1.4889                             | 1.4445                              |
| 19 | K    | 2.6936                            | 2.6939                             | 2.6785                             | 2.6087                             | 2.6755                              |
| 20 | Ca   | 2.8283                            | 2.8282                             | 2.8174                             | 2.7503                             | 2.8143                              |
| 21 | Sc   | 2.5334                            | 2.5258                             | 2.5057                             | 2.4788                             | 2.5012                              |
| 22 | Ti   | 2.2838                            | 2.2792                             | 2.2581                             | 2.2367                             | 2.2538                              |
| 23 | V    | 2.0721                            | 2.0693                             | 2.0502                             | 2.0317                             | 2.0471                              |
| 24 | Cr   | 1.5691                            | 1.5529                             | 1.5226                             | 1.6059                             | 1.5203                              |
| 25 | Mn   | 1.7325                            | 1.7313                             | 1.7167                             | 1.7041                             | 1.7148                              |
| 26 | Fe   | 1.5869                            | 1.5832                             | 1.5595                             | 1.5543                             | 1.5544                              |
| 27 | Co   | 1.4608                            | 1.4584                             | 1.4336                             | 1.4277                             | 1.4299                              |
| 28 | Ni   | 1.3504                            | 1.3485                             | 1.3254                             | 1.3187                             | 1.3224                              |
| 29 | Cu   | 1.1074                            | 1.1020                             | 1.0741                             | 1.1148                             | 1.2277                              |

**Table 2.7** Continued

| Z  | ATOM | $\langle r^2 \rangle_{\text{HF}}$ | $\langle r^2 \rangle_{\text{OEP}}$ | $\langle r^2 \rangle_{\text{KLI}}$ | $\langle r^2 \rangle_{\text{LSD}}$ | $\langle r^2 \rangle_{\text{SKLI}}$ |
|----|------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------------------|
| 30 | Zn   | 1.1660                            | 1.1648                             | 1.1453                             | 1.1392                             | 1.1431                              |
| 31 | Ga   | 1.3218                            | 1.3223                             | 1.3188                             | 1.3448                             | 1.3129                              |
| 32 | Ge   | 1.2999                            | 1.2997                             | 1.2990                             | 1.3264                             | 1.2941                              |
| 33 | As   | 1.2436                            | 1.2432                             | 1.2433                             | 1.2736                             | 1.2396                              |
| 34 | Se   | 1.2130                            | 1.2130                             | 1.2135                             | 1.2377                             | 1.2102                              |
| 35 | Br   | 1.1582                            | 1.1581                             | 1.1588                             | 1.1803                             | 1.1561                              |
| 36 | Kr   | 1.0981                            | 1.0980                             | 1.0985                             | 1.1196                             | 1.0964                              |
| 37 | Rb   | 1.8422                            | 1.8409                             | 1.8298                             | 1.7712                             | 1.8296                              |
| 38 | Sr   | 2.0016                            | 2.0006                             | 1.9923                             | 1.9294                             | 1.9896                              |
| 39 | Y    | 1.8841                            | 1.8765                             | 1.8699                             | 1.8404                             | 1.8665                              |
| 40 | Zr   | 1.5449                            | 1.5318                             | 1.5301                             | 1.5828                             | 1.5276                              |
| 41 | Nb   | 1.4374                            | 1.4285                             | 1.4210                             | 1.4643                             | 1.4191                              |
| 42 | Mo   | 1.3420                            | 1.3355                             | 1.3245                             | 1.3647                             | 1.3231                              |
| 43 | Tc   | 1.4832                            | 1.4818                             | 1.4737                             | 1.4572                             | 1.4724                              |
| 44 | Ru   | 1.2294                            | 1.2252                             | 1.2097                             | 1.2358                             | 1.2094                              |
| 45 | Rh   | 1.1749                            | 1.1715                             | 1.1558                             | 1.1745                             | 1.1553                              |
| 46 | Pd   | 0.9265                            | 0.9268                             | 0.9292                             | 0.9987                             | 0.9288                              |
| 47 | Ag   | 1.0750                            | 1.0728                             | 1.0577                             | 1.0666                             | 1.0571                              |
| 48 | Cd   | 1.1325                            | 1.1312                             | 1.1180                             | 1.1065                             | 1.1172                              |
| 49 | In   | 1.2549                            | 1.2544                             | 1.2512                             | 1.2587                             | 1.2500                              |
| 50 | Sn   | 1.2602                            | 1.2594                             | 1.2586                             | 1.2702                             | 1.2567                              |
| 51 | Sb   | 1.2356                            | 1.2349                             | 1.2350                             | 1.2511                             | 1.2331                              |
| 52 | Te   | 1.2275                            | 1.2272                             | 1.2277                             | 1.2387                             | 1.2258                              |
| 53 | I    | 1.1977                            | 1.1973                             | 1.1980                             | 1.2081                             | 1.1964                              |
| 54 | Xe   | 1.1602                            | 1.1600                             | 1.1607                             | 1.1716                             | 1.1592                              |
| 55 | Cs   | 1.7776                            | 1.7757                             | 1.7662                             | 1.7017                             | 1.7641                              |
| 56 | Ba   | 1.9399                            | 1.9384                             | 1.9309                             | 1.8597                             | 1.9294                              |

Table 2.8 Comparison of  $\langle r^2 \rangle$  Calculated in SKLI (LSDSIC in Core With the Other Approximations

| Z  | ATOM | $\langle r^2 \rangle_{\text{HF}}$ | $\langle r^2 \rangle_{\text{OEP}}$ | $\langle r^2 \rangle_{\text{KLI}}$ | $\langle r^2 \rangle_{\text{LSDSIC}}$ | $\langle r^2 \rangle_{\text{SKLI}}$ |
|----|------|-----------------------------------|------------------------------------|------------------------------------|---------------------------------------|-------------------------------------|
| 3  | Li   | 6.2080                            | 6.2145                             | 6.1974                             | 6.2594                                | 6.1974                              |
| 4  | Be   | 4.3297                            | 4.3316                             | 4.3255                             | 4.3457                                | 4.3255                              |
| 5  | B    | 3.1674                            | 3.1690                             | 3.1724                             | 3.1899                                | 3.1697                              |
| 6  | C    | 2.2966                            | 2.2967                             | 2.2969                             | 2.3143                                | 2.2954                              |
| 7  | N    | 1.7252                            | 1.7253                             | 1.7240                             | 1.7476                                | 1.7233                              |
| 8  | O    | 1.4029                            | 1.4032                             | 1.4039                             | 1.4217                                | 1.4033                              |
| 9  | F    | 1.1386                            | 1.1386                             | 1.1385                             | 1.1554                                | 1.1382                              |
| 10 | Ne   | 0.9372                            | 0.9372                             | 0.9367                             | 0.9509                                | 0.9365                              |
| 11 | Na   | 2.4673                            | 2.4708                             | 2.4574                             | 2.3918                                | 2.4538                              |
| 12 | Mg   | 2.4676                            | 2.4693                             | 2.4610                             | 2.4129                                | 2.4571                              |
| 13 | Al   | 2.5756                            | 2.5772                             | 2.5798                             | 2.6022                                | 2.5761                              |
| 14 | Si   | 2.3037                            | 2.3042                             | 2.3068                             | 2.3372                                | 2.3041                              |
| 15 | P    | 2.0173                            | 2.0174                             | 2.0188                             | 2.0566                                | 2.0169                              |
| 16 | S    | 1.8267                            | 1.8269                             | 1.8281                             | 1.8558                                | 1.8261                              |
| 17 | Cl   | 1.6264                            | 1.6265                             | 1.6273                             | 1.6508                                | 1.6257                              |
| 18 | Ar   | 1.4464                            | 1.4465                             | 1.4467                             | 1.4701                                | 1.4445                              |
| 19 | K    | 2.6936                            | 2.6939                             | 2.6785                             | 2.5770                                | 2.6762                              |
| 20 | Ca   | 2.8283                            | 2.8282                             | 2.8174                             | 2.7289                                | 2.8147                              |
| 21 | Sc   | 2.5334                            | 2.5258                             | 2.5057                             | 2.4469                                | 2.5004                              |
| 22 | Ti   | 2.2838                            | 2.2792                             | 2.2581                             | 2.2076                                | 2.2531                              |
| 23 | V    | 2.0721                            | 2.0693                             | 2.0502                             | 2.0050                                | 2.0465                              |
| 24 | Cr   | 1.5691                            | 1.5529                             | 1.5226                             | 1.5365                                | 1.5206                              |
| 25 | Mn   | 1.7325                            | 1.7313                             | 1.7167                             | 1.6805                                | 1.7144                              |
| 26 | Fe   | 1.5869                            | 1.5832                             | 1.5595                             | 1.5315                                | 1.5548                              |
| 27 | Co   | 1.4608                            | 1.4584                             | 1.4336                             | 1.4070                                | 1.4301                              |
| 28 | Ni   | 1.3504                            | 1.3485                             | 1.3254                             | 1.2997                                | 1.3226                              |
| 29 | Cu   | 1.1074                            | 1.1020                             | 1.0741                             | 1.2058                                | 1.0726                              |

**Table 2.8** Continued

| Z  | ATOM | $\langle r^2 \rangle_{\text{HF}}$ | $\langle r^2 \rangle_{\text{OEP}}$ | $\langle r^2 \rangle_{\text{KLI}}$ | $\langle r^2 \rangle_{\text{LSDSIC}}$ | $\langle r^2 \rangle_{\text{SKLI}}$ |
|----|------|-----------------------------------|------------------------------------|------------------------------------|---------------------------------------|-------------------------------------|
| 30 | Zn   | 1.1660                            | 1.1648                             | 1.1453                             | 1.1226                                | 1.1432                              |
| 31 | Ga   | 1.3218                            | 1.3223                             | 1.3188                             | 1.3140                                | 1.3132                              |
| 32 | Ge   | 1.2999                            | 1.2997                             | 1.2990                             | 1.3072                                | 1.2949                              |
| 33 | As   | 1.2436                            | 1.2432                             | 1.2433                             | 1.2608                                | 1.2402                              |
| 34 | Se   | 1.2130                            | 1.2130                             | 1.2135                             | 1.2258                                | 1.2110                              |
| 35 | Br   | 1.1582                            | 1.1581                             | 1.1588                             | 1.1710                                | 1.1568                              |
| 36 | Kr   | 1.0981                            | 1.0980                             | 1.0985                             | 1.1124                                | 1.0969                              |
| 37 | Rb   | 1.8422                            | 1.8409                             | 1.8298                             | 1.7560                                | 1.8274                              |
| 38 | Sr   | 2.0016                            | 2.0006                             | 1.9923                             | 1.9217                                | 1.9900                              |
| 39 | Y    | 1.8841                            | 1.8765                             | 1.8699                             | 1.8213                                | 1.8656                              |
| 40 | Zr   | 1.5449                            | 1.5318                             | 1.5301                             | 1.5396                                | 1.5276                              |
| 41 | Nb   | 1.4374                            | 1.4285                             | 1.4210                             | 1.4302                                | 1.4189                              |
| 42 | Mo   | 1.3420                            | 1.3355                             | 1.3245                             | 1.3365                                | 1.3229                              |
| 43 | Tc   | 1.4832                            | 1.4818                             | 1.4737                             | 1.4434                                | 1.4718                              |
| 44 | Ru   | 1.2294                            | 1.2252                             | 1.2097                             | 1.2100                                | 1.2092                              |
| 45 | Rh   | 1.1749                            | 1.1715                             | 1.1558                             | 1.1516                                | 1.1551                              |
| 46 | Pd   | 0.9265                            | 0.9268                             | 0.9292                             | 0.9606                                | 0.9290                              |
| 47 | Ag   | 1.0750                            | 1.0728                             | 1.0577                             | 1.0474                                | 1.0569                              |
| 48 | Cd   | 1.1325                            | 1.1312                             | 1.1180                             | 1.0945                                | 1.1169                              |
| 49 | In   | 1.2549                            | 1.2544                             | 1.2512                             | 1.2431                                | 1.2478                              |
| 50 | Sn   | 1.2602                            | 1.2594                             | 1.2586                             | 1.2611                                | 1.2555                              |
| 51 | Sb   | 1.2356                            | 1.2349                             | 1.2350                             | 1.2458                                | 1.2323                              |
| 52 | Te   | 1.2275                            | 1.2272                             | 1.2277                             | 1.2340                                | 1.2253                              |
| 53 | I    | 1.1977                            | 1.1973                             | 1.1980                             | 1.2049                                | 1.1959                              |
| 54 | Xe   | 1.1602                            | 1.1600                             | 1.1607                             | 1.1695                                | 1.1589                              |
| 55 | Cs   | 1.7776                            | 1.7757                             | 1.7662                             | 1.6950                                | 1.7636                              |
| 56 | Ba   | 1.9399                            | 1.9384                             | 1.9309                             | 1.8586                                | 1.9288                              |

**Table 3.1** Highest Occupied Eigenvalue ( $-\epsilon_m$  in Ry)

| Z                                    | ION | HF     | OEP    | KLI    | SKLI<br>LSD in<br>Core | SKLI<br>LSDSIC<br>in Core | LSDSIC |
|--------------------------------------|-----|--------|--------|--------|------------------------|---------------------------|--------|
| <b>Hydrogen</b>                      |     |        |        |        |                        |                           |        |
| 1                                    | H-  | .09244 | .09244 | .09244 | .09244                 | .09244                    | .09244 |
| <b>Alkalis</b>                       |     |        |        |        |                        |                           |        |
| 3                                    | Li- | .02908 | .02905 | .02891 | .02891                 | .02891                    | .02918 |
| 11                                   | Na- | .02670 | .02667 | .02634 | .02642                 | .02639                    | .02786 |
| 19                                   | K-  | .02064 | .02065 | .02031 | .02036                 | .02034                    | .02229 |
| 37                                   | Rb- | .01906 | .01911 | .01876 | .01880                 | .01878                    | .02102 |
| <b>Halogens</b>                      |     |        |        |        |                        |                           |        |
| 9                                    | F-  | .03620 | .03620 | .3609  | .3605                  | .3606                     | .3207  |
| 17                                   | Cl- | .3006  | .2995  | .2987  | .2989                  | .2986                     | .2523  |
| 35                                   | Br- | .2787  | .2765  | .2759  | .2778                  | .2763                     | .2305  |
| 53                                   | I-  | .2583  | .2559  | .2557  | .2570                  | .2564                     | .2106  |
| <b>Ions with incomplete P Shells</b> |     |        |        |        |                        |                           |        |
| 5                                    | B-  | .05314 | .05252 | .05257 | .05299                 | .05269                    | .04193 |
| 6                                    | C-  | .1562  | .1588  | .1556  | .1559                  | .1557                     | .1278  |
| 8                                    | O-  | .1434  | .1427  | .1421  | .1426                  | .1421                     | .1286  |
| 13                                   | Al- | .04124 | .03992 | .03654 | .03975                 | .03962                    | .03101 |
| 14                                   | Si- | .1241  | .1221  | .1219  | .1221                  | .1219                     | .09444 |
| 15                                   | S-  | .1551  | .1539  | .1535  | .1539                  | .1536                     | .1341  |

**Table 3.2** Total Energy (in Ry) ( $-E_{\text{total}}$ )

| Z  | ION | HF                                   | OEP        | KLI        | SKLI<br>LSD in<br>Core | SKLI<br>LSDSIC<br>in Core | LSDSIC     |
|----|-----|--------------------------------------|------------|------------|------------------------|---------------------------|------------|
|    |     | <b>Hydrogen</b>                      |            |            |                        |                           |            |
| 1  | H-  | 0.9759                               | 0.9759     | 0.9759     | 0.9759                 | 0.9759                    | 0.9759     |
|    |     | <b>Alkalis</b>                       |            |            |                        |                           |            |
| 3  | Li- | 14.8565                              | 14.8557    | 14.8556    | 14.8556                | 14.8556                   | 14.8486    |
| 11 | Na- | 323.7103                             | 323.7050   | 323.7034   | 323.6942               | 323.7006                  | 323.6892   |
| 19 | K-  | 1198.3238                            | 1198.3117  | 1198.3075  | 1198.2867              | 1198.2938                 | 1198.2830  |
| 37 | Rb- | 5876.7098                            | 5876.6850  | 5876.6780  | 5976.6297              | 5876.6350                 | 5876.6248  |
|    |     | <b>Halogens</b>                      |            |            |                        |                           |            |
| 9  | F-  | 198.9189                             | 198.9155   | 198.9144   | 198.9068               | 198.9134                  | 198.9022   |
| 17 | Cl- | 919.1539                             | 919.1433   | 919.1401   | 919.1199               | 919.1279                  | 919.1170   |
| 35 | Br- | 5145.1254                            | 5145.0477  | 5145.0413  | 5144.9871              | 5144.9959                 | 5144.9857  |
| 53 | I-  | 13836.1518                           | 13836.1162 | 13836.1040 | 13836.0500             | 13836.0423                | 13836.0355 |
|    |     | <b>Ions with incomplete P Shells</b> |            |            |                        |                           |            |
| 5  | B-  | 49.0386                              | 49.0366    | 49.0360    | 49.0291                | 49.0356                   | 49.0322    |
| 6  | C-  | 75.4206                              | 75.4183    | 75.4177    | 75.4107                | 75.4171                   | 75.4109    |
| 8  | O-  | 149.5862                             | 149.5829   | 149.5820   | 149.5744               | 149.5811                  | 149.5726   |
| 13 | Al- | 483.7575                             | 483.7502   | 483.7481   | 483.7249               | 483.7359                  | 483.7315   |
| 14 | Si- | 577.7801                             | 577.7716   | 577.7692   | 577.7475               | 577.7571                  | 577.7500   |
| 15 | S-  | 795.0789                             | 795.0691   | 795.0661   | 795.0457               | 795.0540                  | 795.0451   |

**Table 3.3** Electron Affinities as Calculated From  
 $EA = E_{\text{total}}(A) - E_{\text{total}}(A^-)$

| Z                                    | ION | HF     | OEP    | KLI    | SKLI<br>LSD in<br>Core | SKLI<br>LSDSIC<br>in Core | LSDSIC |
|--------------------------------------|-----|--------|--------|--------|------------------------|---------------------------|--------|
| <b>Hydrogen</b>                      |     |        |        |        |                        |                           |        |
| 1                                    | H-  | -.0241 | -.0241 | -.0241 | -.0241                 | -.0241                    | -.0241 |
| <b>Alkalis</b>                       |     |        |        |        |                        |                           |        |
| 3                                    | Li- | -9.04  | -9.26  | -9.30  | -9.30                  | -9.30                     | -9.28  |
| 11                                   | Na- | -7.64  | -8.30  | -8.44  | -8.56                  | -8.53                     | -9.81  |
| 19                                   | K-  | -5.90  | -6.54  | -6.72  | -6.73                  | -6.74                     | -8.60  |
| 37                                   | Rb- | -5.36  | -6.00  | -6.24  | -6.16                  | -6.20                     | -8.36  |
| <b>Halogens</b>                      |     |        |        |        |                        |                           |        |
| 9                                    | F-  | .0972  | .0971  | .0969  | .0966                  | .0969                     | .0934  |
| 17                                   | Cl- | .1887  | .1880  | .1880  | .1875                  | .1877                     | .1848  |
| 35                                   | Br- | .1889  | .1887  | .1875  | .1870                  | .1871                     | .1838  |
| 53                                   | I-  | .1890  | .1878  | .1875  | .1873                  | .1872                     | .1844  |
| <b>Ions with incomplete P Shells</b> |     |        |        |        |                        |                           |        |
| 5                                    | B-  | -.0200 | -.0201 | -.0202 | -.0206                 | -.0203                    | -.0222 |
| 6                                    | C-  | .0406  | .0405  | .0404  | .0402                  | .0404                     | .0371  |
| 8                                    | O-  | -.0411 | -.0412 | -.0414 | -.0418                 | -.0414                    | -.0317 |
| 13                                   | Al- | .0039  | .0035  | .0035  | .0031                  | .0033                     | .0015  |
| 14                                   | Si- | .071   | .0703  | .0702  | .0697                  | .0700                     | .0667  |
| 15                                   | S-  | .0664  | .0658  | .0658  | .0653                  | .0655                     | .0634  |

**Table 3.4** Expectation Values of  $\langle r^2 \rangle$  Under Total Densities as Obtained From HF, OEP, KLI, SKLI and LSDSIC

| Z                                    | ION | HF     | OEP    | KLI    | SKLI<br>LSD in<br>Core | SKLI<br>LSDSIC<br>in Core | LSDSIC |
|--------------------------------------|-----|--------|--------|--------|------------------------|---------------------------|--------|
| <b>Hydrogen</b>                      |     |        |        |        |                        |                           |        |
| 1                                    | H-  | 9.4111 | 9.4111 | 9.4111 | 9.4111                 | 9.4111                    | 9.4111 |
| <b>Alkalis</b>                       |     |        |        |        |                        |                           |        |
| 3                                    | Li- | 22.043 | 22.077 | 22.112 | 22.112                 | 22.112                    | 21.861 |
| 11                                   | Na- | 8.769  | 8.796  | 8.819  | 8.787                  | 8.795                     | 8.254  |
| 19                                   | K-  | 8.079  | 8.089  | 8.106  | 8.087                  | 8.091                     | 7.354  |
| 37                                   | Rb- | 5.036  | 5.034  | 5.038  | 4.959                  | 4.972                     | 4.516  |
| <b>Halogens</b>                      |     |        |        |        |                        |                           |        |
| 9                                    | F-  | 1.598  | 1.598  | 1.599  | 1.597                  | 1.599                     | 1.662  |
| 17                                   | Cl- | 2.135  | 2.135  | 2.140  | 2.136                  | 2.138                     | 2.219  |
| 35                                   | Br- | 1.484  | 1.484  | 1.489  | 1.483                  | 1.486                     | 1.536  |
| 53                                   | I-  | 1.479  | 1.478  | 1.483  | 1.479                  | 1.479                     | 1.517  |
| <b>Ions with incomplete P Shells</b> |     |        |        |        |                        |                           |        |
| 5                                    | B-  | 6.6660 | 6.6649 | 6.7012 | 6.6541                 | 6.6890                    | 7.3150 |
| 6                                    | C-  | 3.7331 | 3.7310 | 3.7401 | 3.7291                 | 3.7373                    | 3.9622 |
| 8                                    | O-  | 2.1582 | 2.1582 | 2.1633 | 2.1577                 | 2.1623                    | 2.2493 |
| 13                                   | Al- | 5.4514 | 5.4717 | 5.5530 | 5.5218                 | 5.5439                    | 6.2144 |
| 14                                   | Si- | 3.6551 | 3.6562 | 3.6839 | 3.6697                 | 3.6791                    | 3.9519 |
| 15                                   | S-  | 2.5583 | 2.5586 | 2.5683 | 2.5614                 | 2.5651                    | 2.6664 |

**Table 3.5** Highest Occupied Eigen values ( $-\epsilon_m$  in Ry)  
(Including Correlation)

| Z                                    | ION | HF with<br>LSD<br>Corr. | HF with<br>LSDSIC<br>Corr. | KLI with<br>LSD Corr. | KLI with<br>LSDSIC<br>Corr. | experi-<br>mental<br>Value |
|--------------------------------------|-----|-------------------------|----------------------------|-----------------------|-----------------------------|----------------------------|
| <b>Hydrogen</b>                      |     |                         |                            |                       |                             |                            |
| 1                                    | H-  | .1570.                  | .1250                      | .1570                 | .1250                       | .0554                      |
| <b>Alkalis</b>                       |     |                         |                            |                       |                             |                            |
| 3                                    | Li- | .07181                  | .05024                     | .07162                | .05001                      | .04542                     |
| 11                                   | Na- | .06830                  | .04733                     | .06776                | .04687                      | .04027                     |
| 19                                   | K-  | .05842                  | .03931                     | .05792                | .03889                      | .03686                     |
| 37                                   | Rb- | .05577                  | .03720                     | .05533                | .03684                      | .03571                     |
| <b>Halogens</b>                      |     |                         |                            |                       |                             |                            |
| 9                                    | F-  | .4573                   | .4190                      | .4561                 | .4180                       | .2498                      |
| 17                                   | Cl- | .3869                   | .3527                      | .3848                 | .3509                       | .2658                      |
| 35                                   | Br- | .3622                   | .3293                      | .3592                 | .3265                       | .2473                      |
| 53                                   | I-  | .3385                   | .3073                      | .3357                 | .3047                       | .2248                      |
| <b>Ions with incomplete P Shells</b> |     |                         |                            |                       |                             |                            |
| 5                                    | B-  | .09811                  | .06959                     | .09733                | .06881                      | .0204                      |
| 6                                    | C-  | .2059                   | .1731                      | .2053                 | .1724                       | .0928                      |
| 8                                    | O-  | .2613                   | .2248                      | .2598                 | .2233                       | .1074                      |
| 13                                   | Al- | .07865                  | .05385                     | .07667                | .05205                      | .0324                      |
| 14                                   | Si- | .1684                   | .1396                      | .1660                 | .1373                       | .1018                      |
| 15                                   | S-  | .2495                   | .2175                      | .2477                 | .2158                       | .1527                      |

**Table 3.6** Total Energy ( $-E_{\text{total}}$  in Ry) (Including Correlation)

| Z  | ION | HF with<br>LSD Corr.                 | HF with<br>LSDSIC<br>Corr. | KLI with<br>LSD Corr. | KLI with<br>LSDSIC<br>Corr. |
|----|-----|--------------------------------------|----------------------------|-----------------------|-----------------------------|
|    |     | <b>Hydrogen</b>                      |                            |                       |                             |
| 1  | H-  | 1.1260                               | 1.0529                     | 1.1260                | 1.0529                      |
|    |     | <b>Alkalis</b>                       |                            |                       |                             |
| 3  | Li- | 15.2235                              | 15.0448                    | 15.2225               | 15.0439                     |
| 11 | Na- | 325.3696                             | 324.6524                   | 325.3637              | 324.6474                    |
| 19 | K-  | 1201.3506                            | 1200.0645                  | 1201.3343             | 1200.0629                   |
| 37 | Rb- | 5883.4478                            | 5880.7315                  | 5883.4160             | 5880.7290                   |
|    |     | <b>Halogens</b>                      |                            |                       |                             |
| 9  | F-  | 200.3017                             | 199.7119                   | 200.2972              | 199.7075                    |
| 17 | Cl- | 921.8929                             | 920.7354                   | 921.8791              | 920.7347                    |
| 35 | Br- | 5151.4803                            | 5148.9230                  | 5151.4492             | 5148.9028                   |
| 53 | I-  | 13846.3737                           | 13842.3445                 | 13846.3262            | 13842.3376                  |
|    |     | <b>Ions with incomplete P Shells</b> |                            |                       |                             |
| 5  | B-  | 49.6660                              | 49.3652                    | 49.6635               | 49.36227                    |
| 6  | C-  | 76.1848                              | 75.8148                    | 76.1819               | 75.8120                     |
| 8  | O-  | 150.7643                             | 150.2513                   | 150.7601              | 150.2472                    |
| 13 | Al- | 485.7137                             | 484.8564                   | 485.7067              | 484.8559                    |
| 14 | Si- | 579.8942                             | 578.9622                   | 579.8843              | 578.9602                    |
| 15 | S-  | .2495                                | .2175                      | .2477                 | .2158                       |

**Table 3.7** Electron Affinities  $E_A = E_{\text{total}}(A) - E_{\text{total}}(A^-)$   
(Including Correlation)

| Z                                    | ION | HF with<br>LSD<br>Corr. | HF with<br>LSDSIC<br>Corr. | KLI with<br>LSD Corr. | KLI with<br>LSDSIC<br>Corr. | experi-<br>mental<br>Value |
|--------------------------------------|-----|-------------------------|----------------------------|-----------------------|-----------------------------|----------------------------|
| <b>Hydrogen</b>                      |     |                         |                            |                       |                             |                            |
| 1                                    | H-  | .0812                   | .0546                      | .0812                 | .0546                       | .0554                      |
| <b>Alkalis</b>                       |     |                         |                            |                       |                             |                            |
| 3                                    | Li- | .0572                   | .0382                      | .0568                 | .0379                       | .04542                     |
| 11                                   | Na- | .0546                   | .0360                      | .0538                 | .0354                       | .04027                     |
| 19                                   | K-  | .0488                   | .0315                      | .0480                 | .0315                       | .03686                     |
| 37                                   | Rb- | .0472                   | .0290                      | .0462                 | .0302                       | .03571                     |
| <b>Halogens</b>                      |     |                         |                            |                       |                             |                            |
| 9                                    | F-  | .2037                   | .1703                      | .2034                 | .1700                       | .2498                      |
| 17                                   | Cl- | .2828                   | .2495                      | .2821                 | .2530                       | .2658                      |
| 35                                   | Br- | .2795                   | .2418                      | .2781                 | .2501                       | .2473                      |
| 53                                   | I-  | .2754                   | .2288                      | .2740                 | .2476                       | .2248                      |
| <b>Ions with incomplete p Shells</b> |     |                         |                            |                       |                             |                            |
| 5                                    | B-  | .0273                   | .0032                      | .0272                 | .0030                       | .0204                      |
| 6                                    | C-  | .0934                   | .0653                      | .0932                 | .0651                       | .0928                      |
| 8                                    | O-  | .0725                   | .0416                      | .0722                 | .0413                       | .1074                      |
| 13                                   | Al- | .0403                   | .0165                      | .0423                 | .0213                       | .0324                      |
| 14                                   | Si- | .1165                   | .0868                      | .1157                 | .0913                       | .1018                      |
| 15                                   | S-  | .1662                   | .1400                      | .1655                 | .1384                       | .1527                      |

Table 4.1 Exact Correlation Energies for Various K

| K  | 0.01   | 0.1     | 1.0     | 4.0     | 10.0     | 100.0    |
|--|--------|---------|---------|---------|----------|----------|
| $E_{cm} = 1.5K^{1/2}$                        | 0.15   | .47434  | 1.5     | 3.0     | 4.74342  | 15.0     |
| $E_{rel}^{II}$                               | .40317 | 1.07354 | 3.01508 | 5.73513 | 8.83434  | 26.66458 |
| $E_{exact}^{II}$                             | .55317 | 1.54788 | 4.51508 | 8.73513 | 13.57776 | 41.66459 |
| $E_{HF}^{II}$                                | .55917 | 1.55461 | 4.52228 | 8.74252 | 13.58524 | 41.67223 |
| $E_{C=}^{II} = E_{exact}^{II} - E_{HF}^{II}$ | -.0060 | -.00673 | -.00720 | -.00739 | -.00748  | -.00764  |
| $E_{rel}^{II}$                               | .3500  | .86171  | 2.23012 | 4.05786 | 6.09034  | 17.44864 |
| $E_{exact}^{II}$                             | .5000  | 1.33605 | 3.73012 | 7.05786 | 10.83376 | 32.44865 |
| $E_{HF}^{II}$                                | .52904 | 1.37218 | 3.77146 | 7.10146 | 10.87853 | 32.49553 |
| $E_{C=}^{II} = E_{exact}^{II} - E_{HF}^{II}$ | -.0291 | -.03613 | -.04134 | -.04360 | -.04477  | -.04688  |
| $\frac{E_{C=}^{II}}{E_{C}^{II}}$             | 4.843  | 5.366   | 5.746   | 5.904   | 5.987    | 6.134    |

Table 4.2 Overlap of Wavefunction  
(Exchange Only and Exact KS)

|    | K=0.01   | K=0.1    | K=1.0    | K=40.0   | K=100.0  |
|----|----------|----------|----------|----------|----------|
| 1S | 0.999940 | 0.999981 | 0.999994 | 0.999998 | 0.999999 |
| 2P | 0.999935 | 0.999980 | 0.999994 | 0.999998 | 0.999999 |

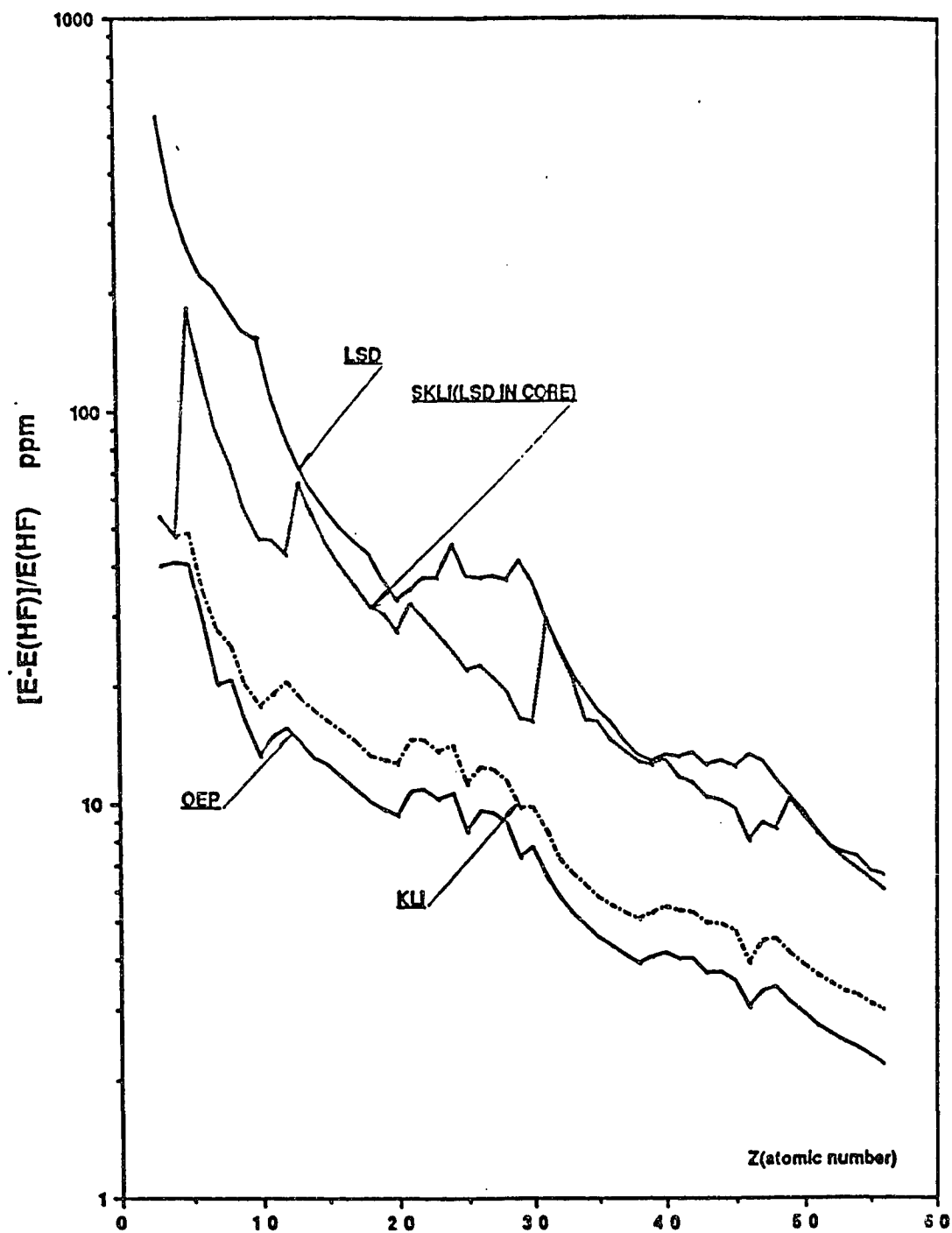


Fig. 2.1 Overestimate of Total Energy

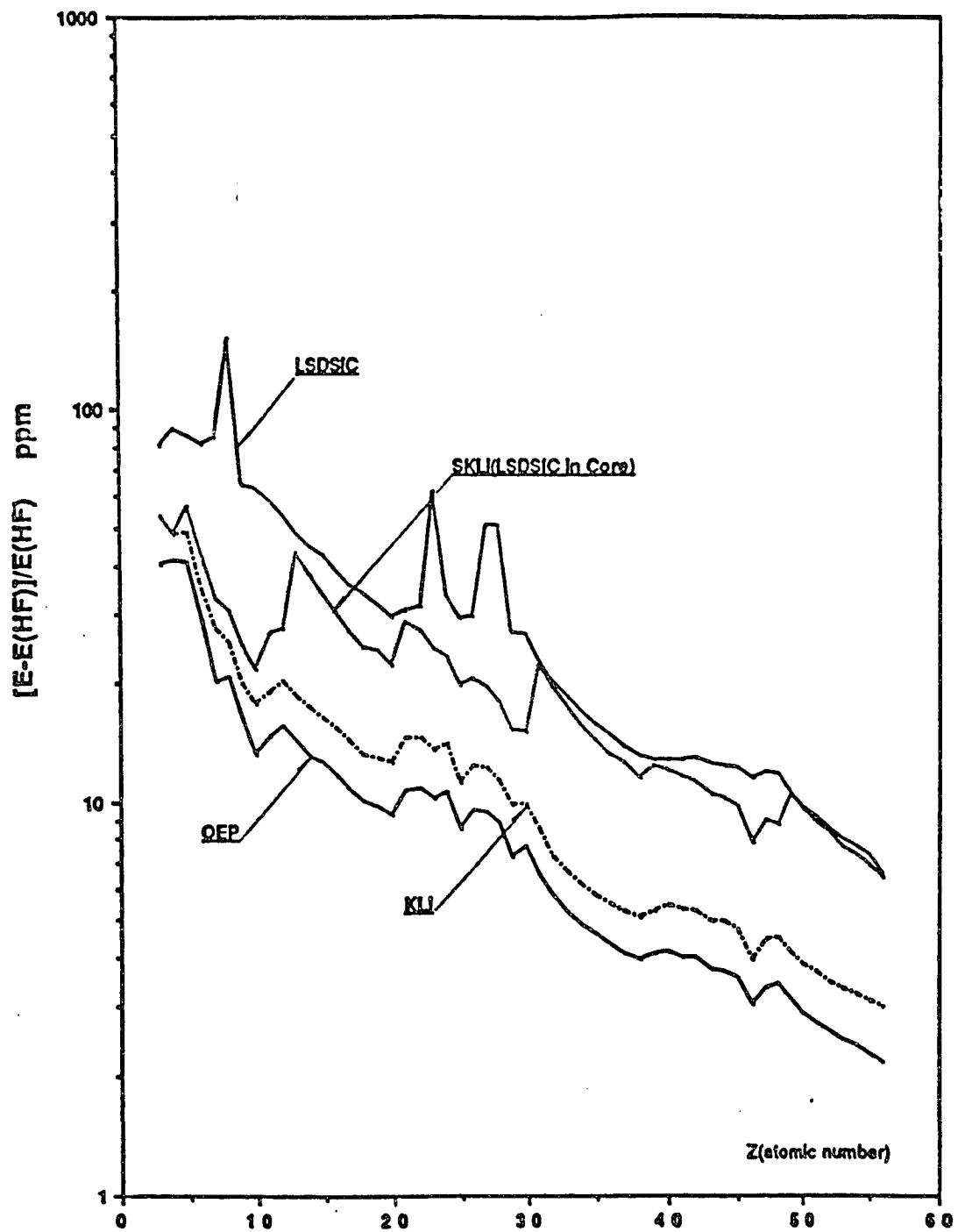


Fig. 2.2 Overestimate of Total Energy

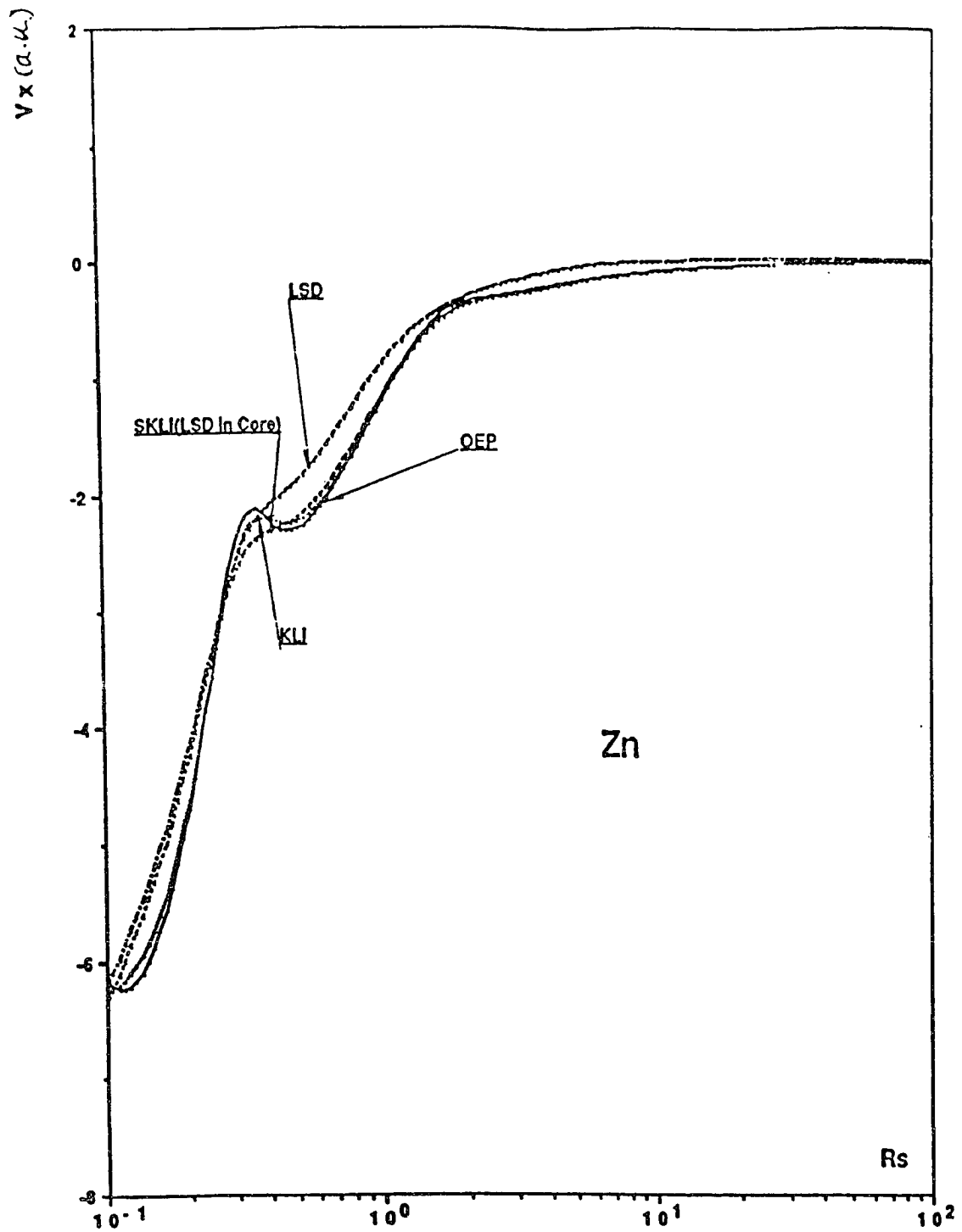


Fig.2.3 Comparison of  $V_x$

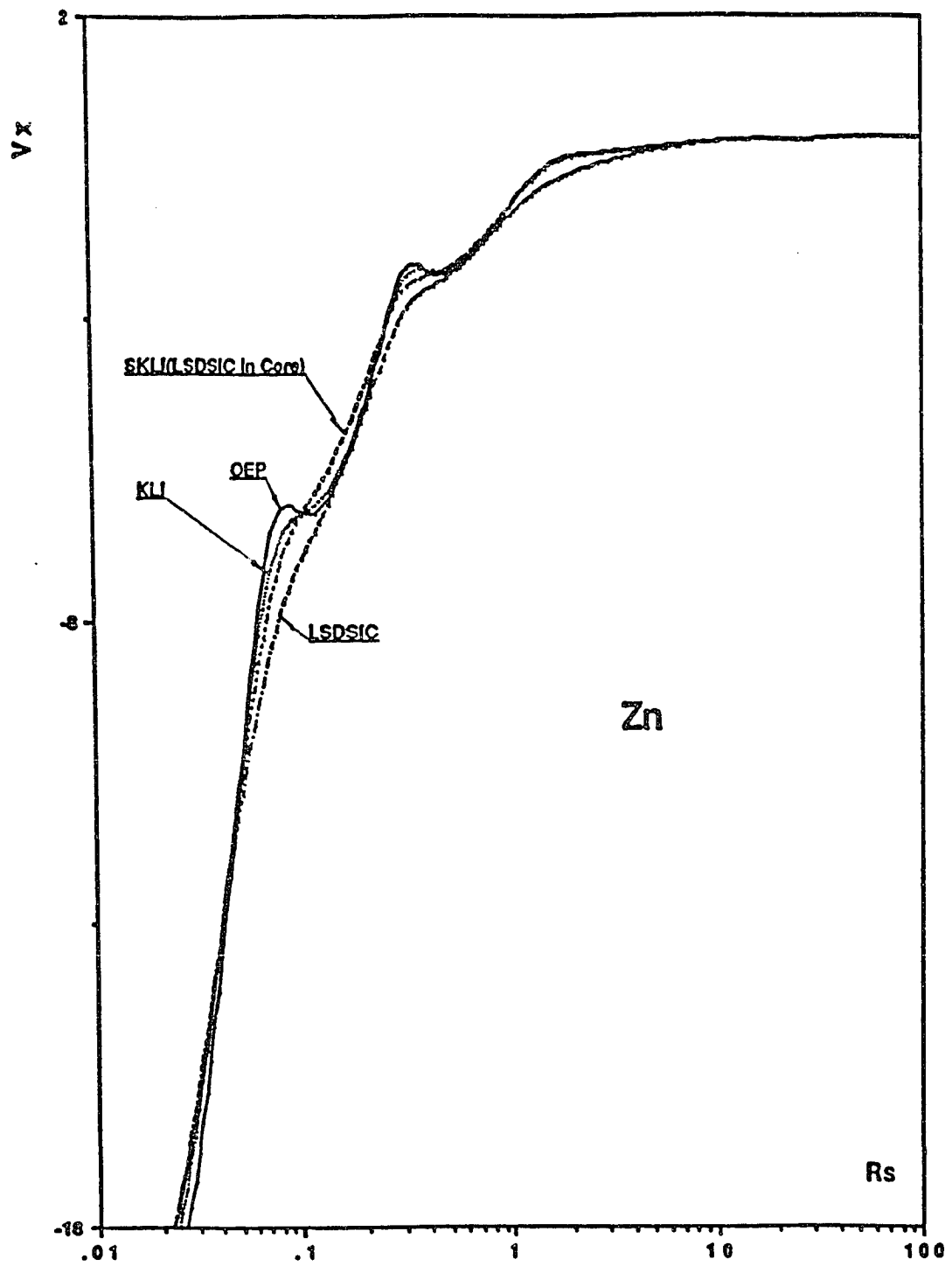


Fig. 2.4 Comparison of  $V_x$

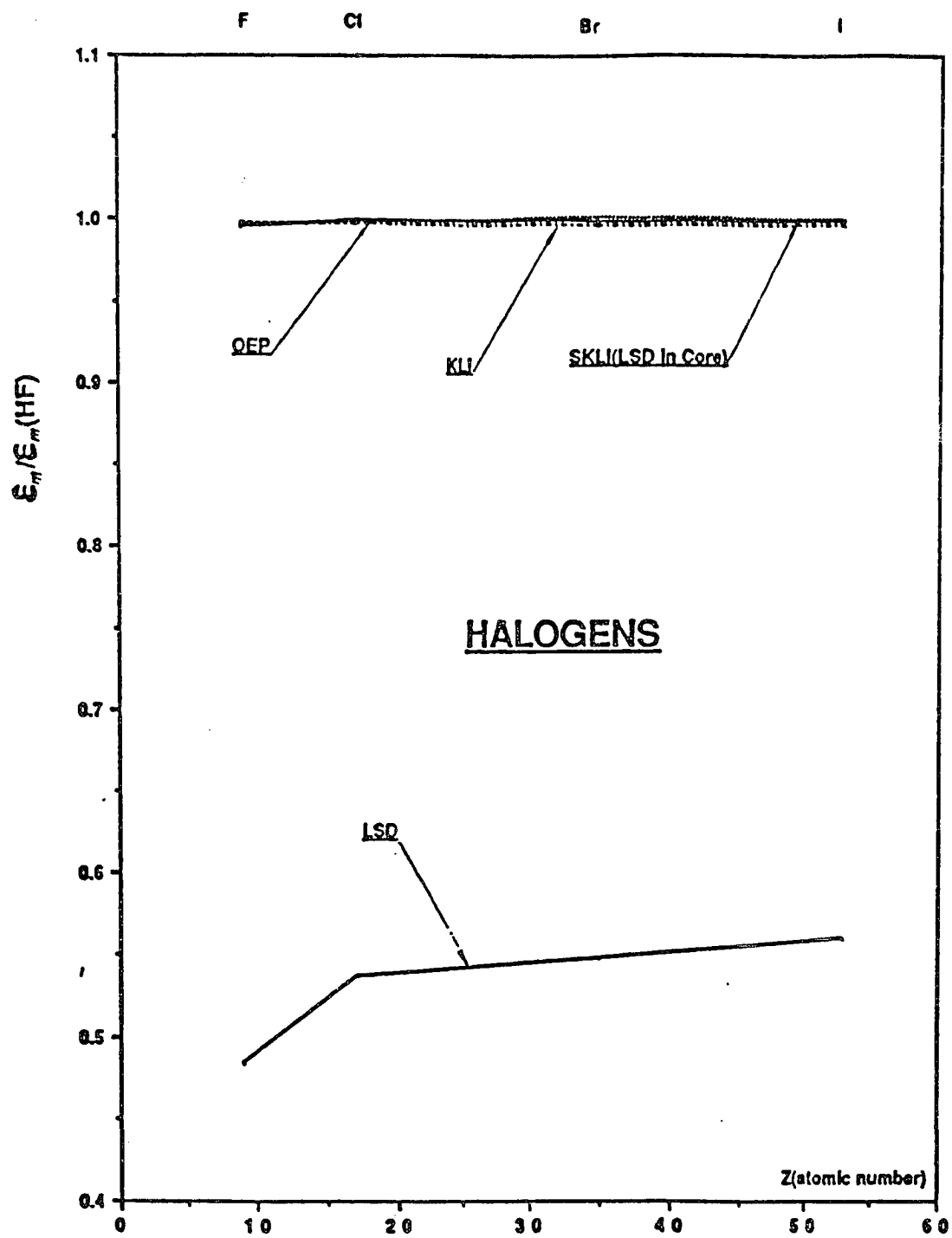


Fig. 2.5 Comparison of Highest Occupied Energy Eigenvalues

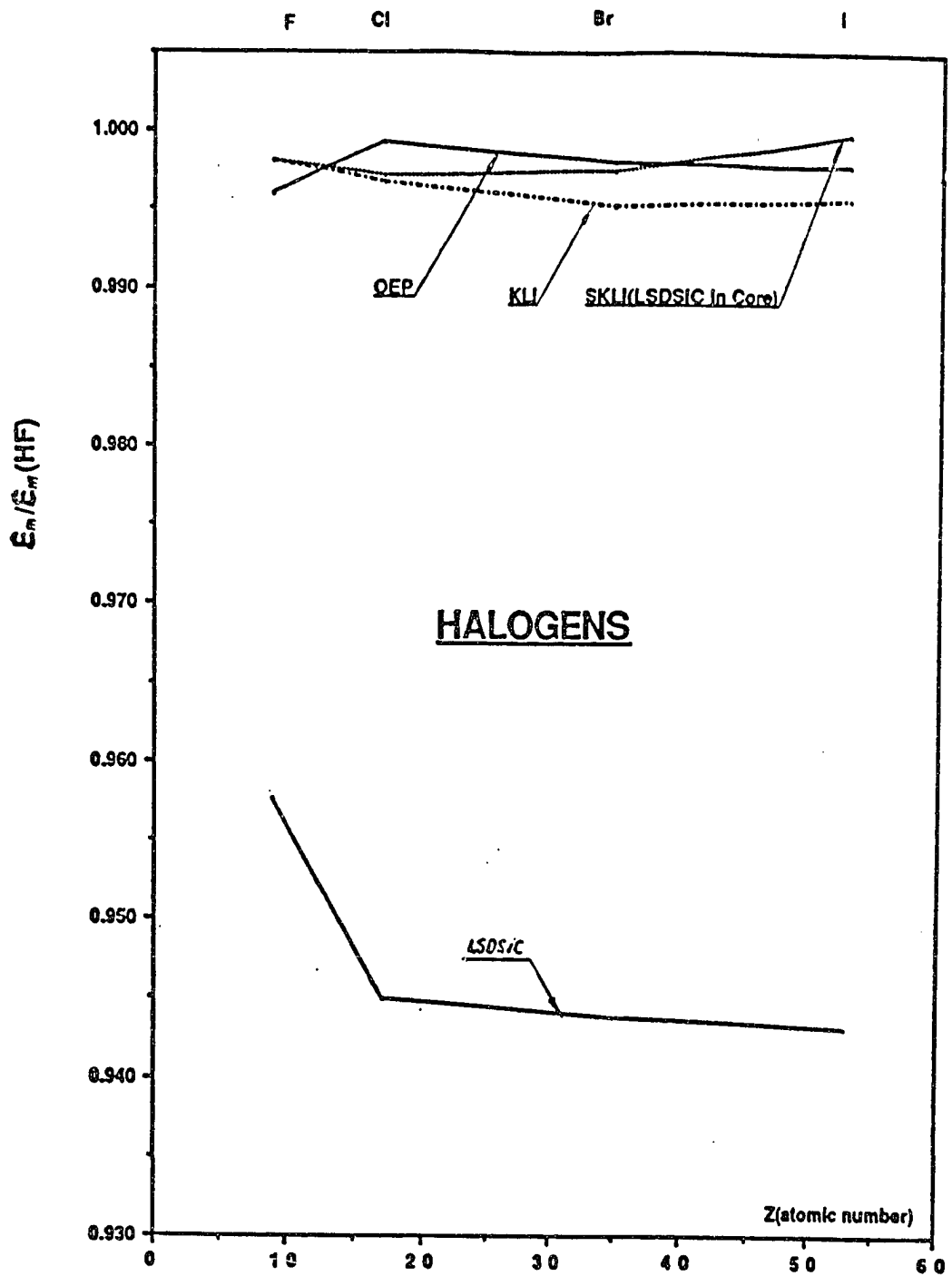


Fig. 2.6 Comparison of Highest Occupied Energy Eigenvalues

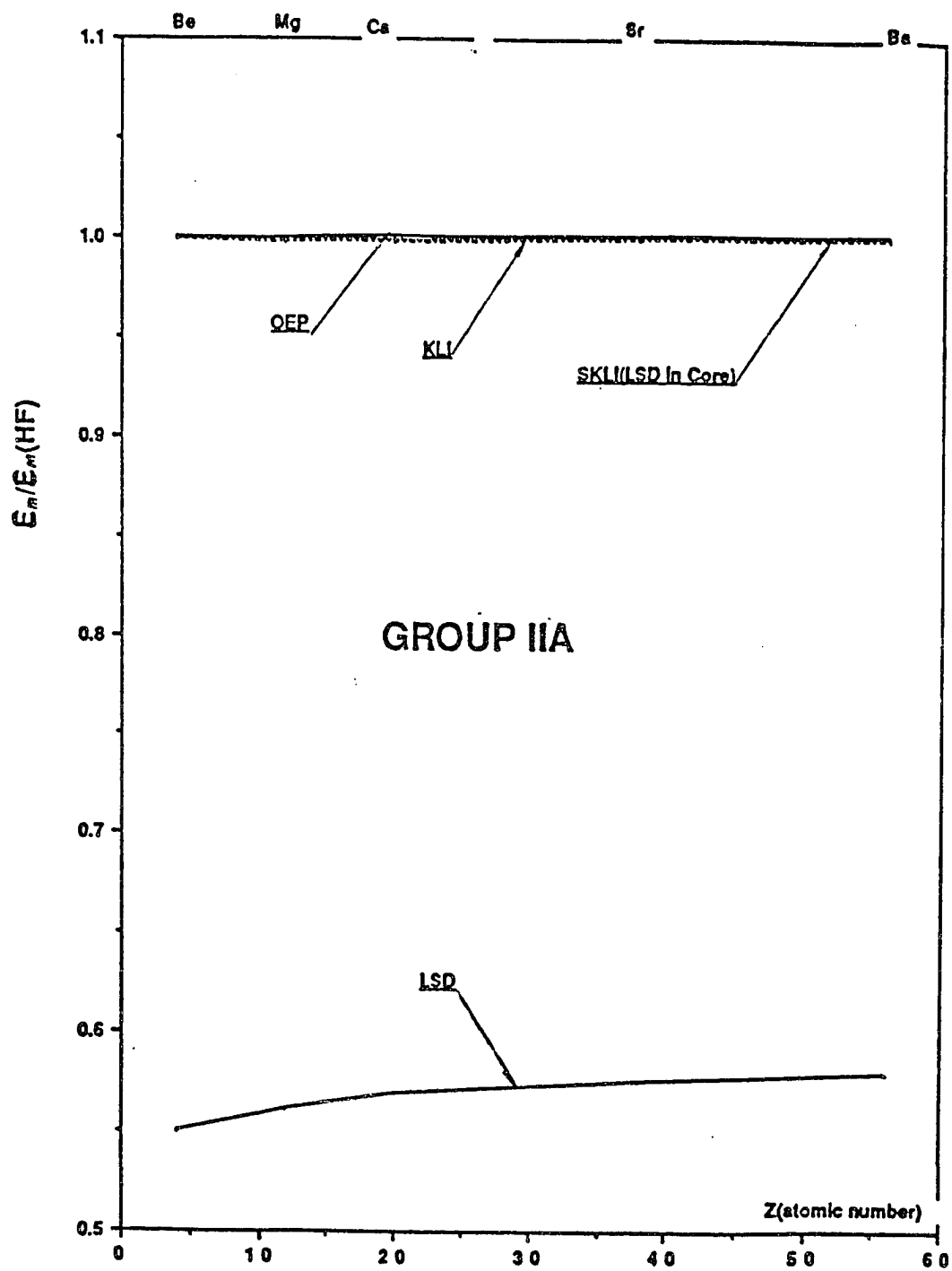


Fig. 2.7 Comparison of Highest Occupied Energy Eigenvalues

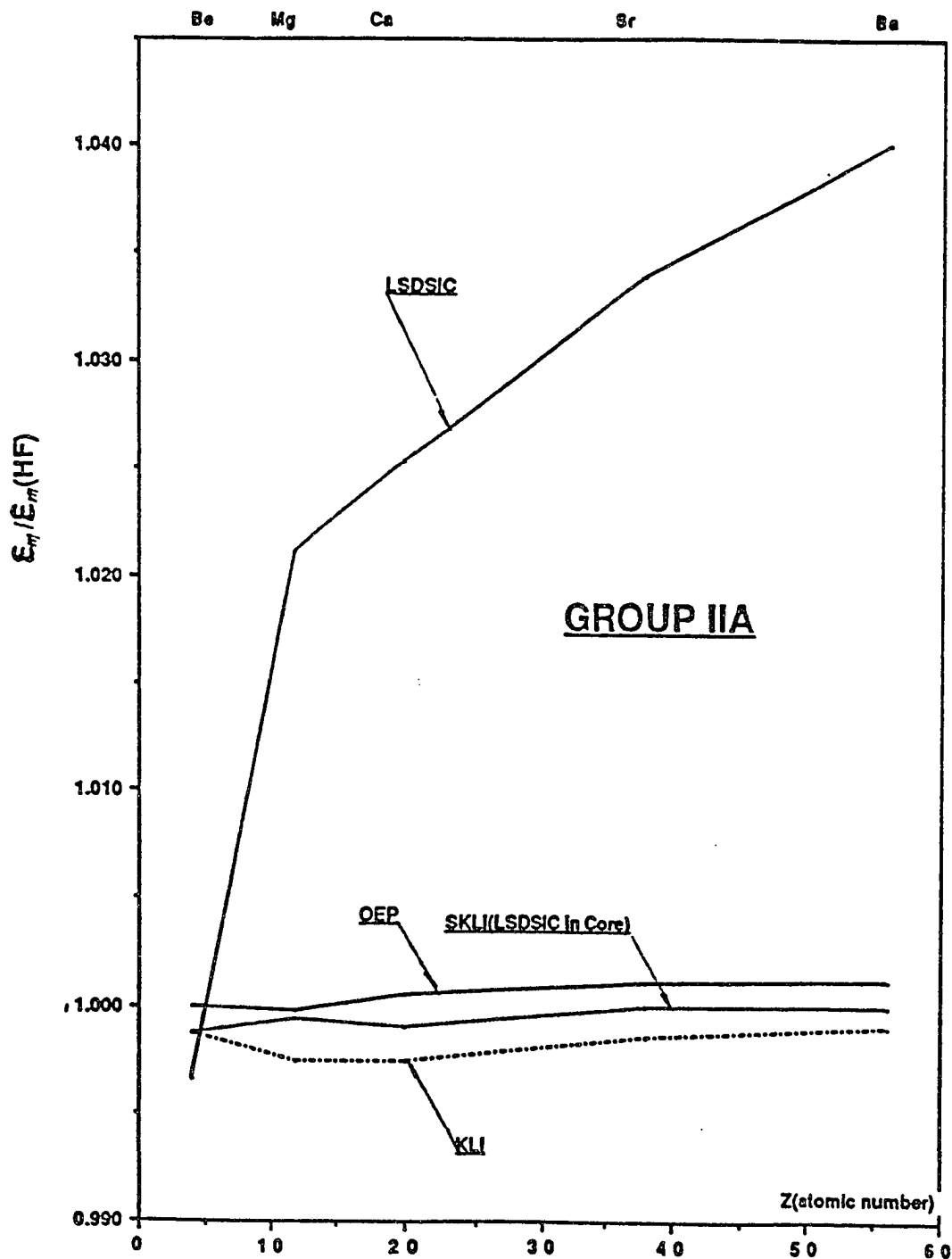


Fig.2.8 Comparison of Highest Occupied Energy Eigenvalues

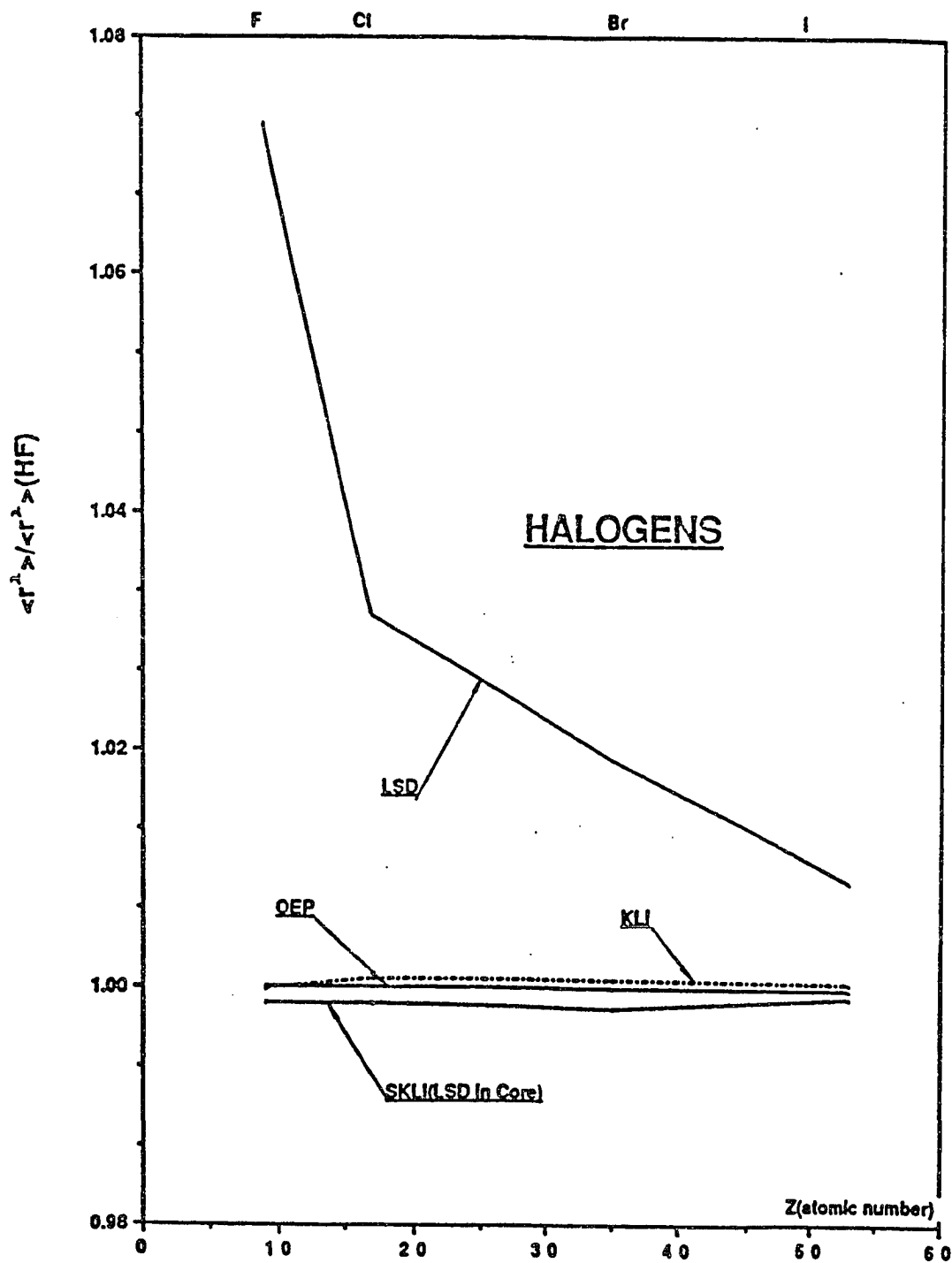


Fig. 2.9 Comparison of  $\langle r^2 \rangle$

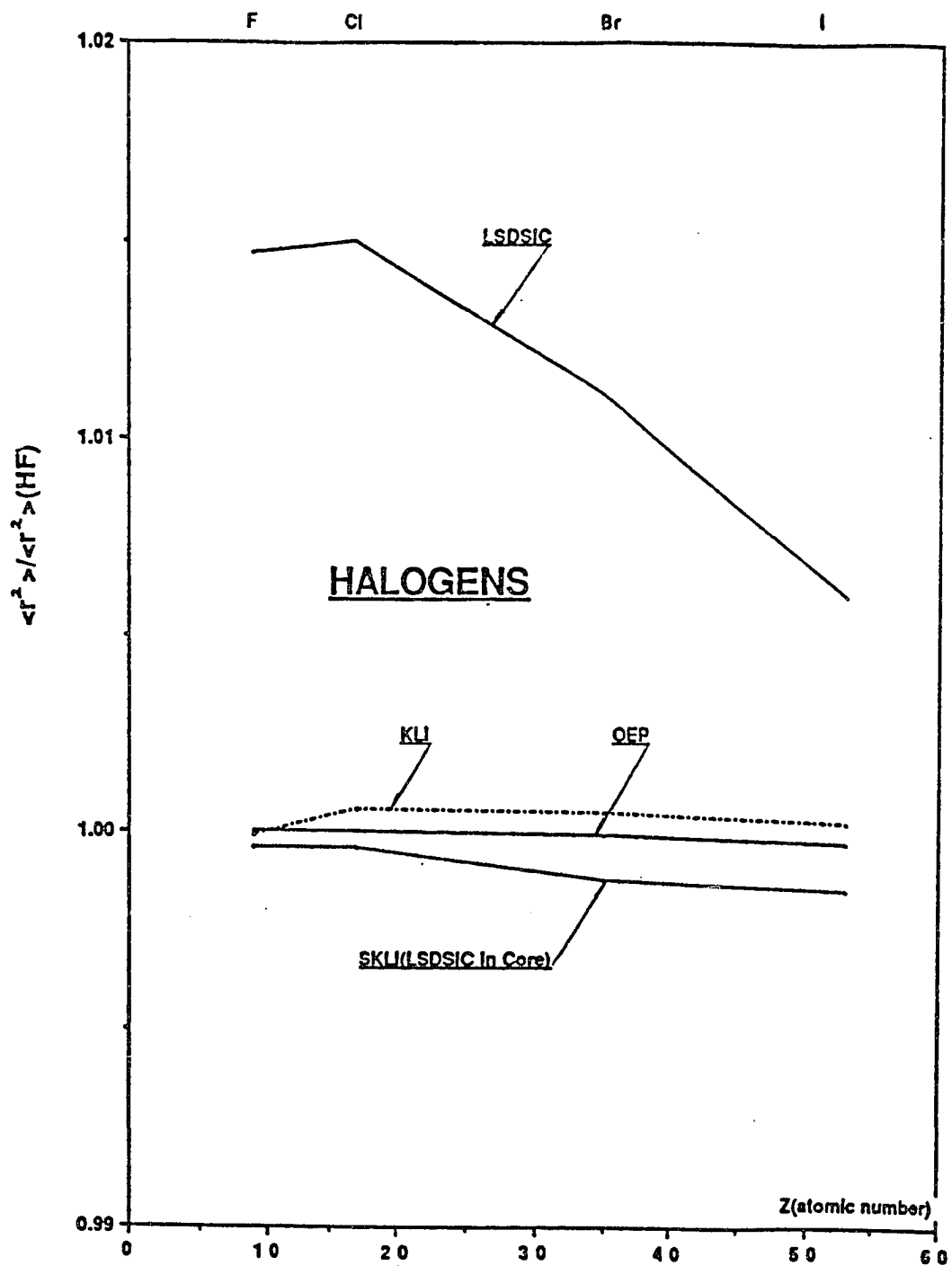


Fig. 2.10 Comparison of  $\langle r^2 \rangle$

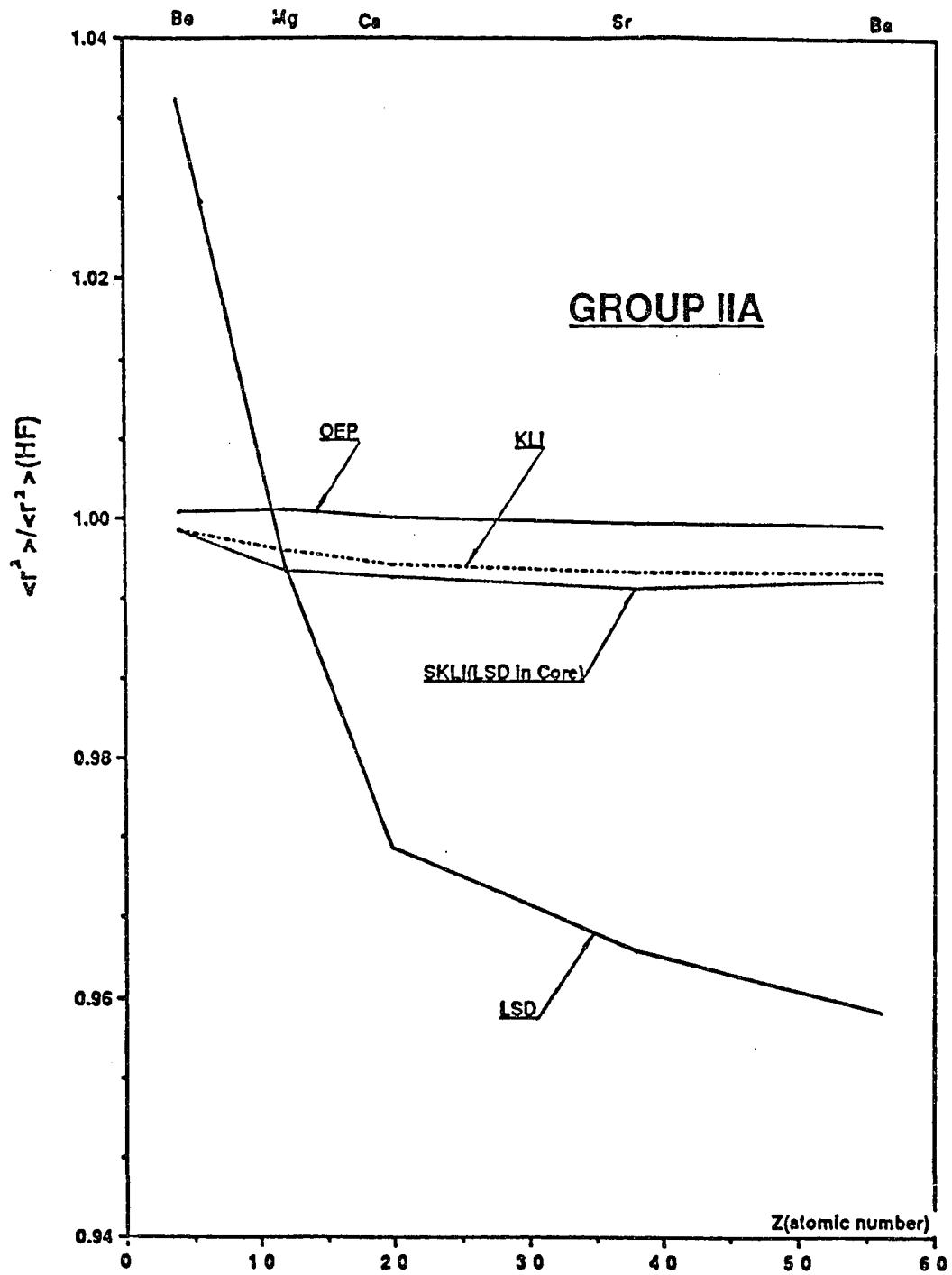


Fig.2.11 Comparison of  $\langle r^2 \rangle$

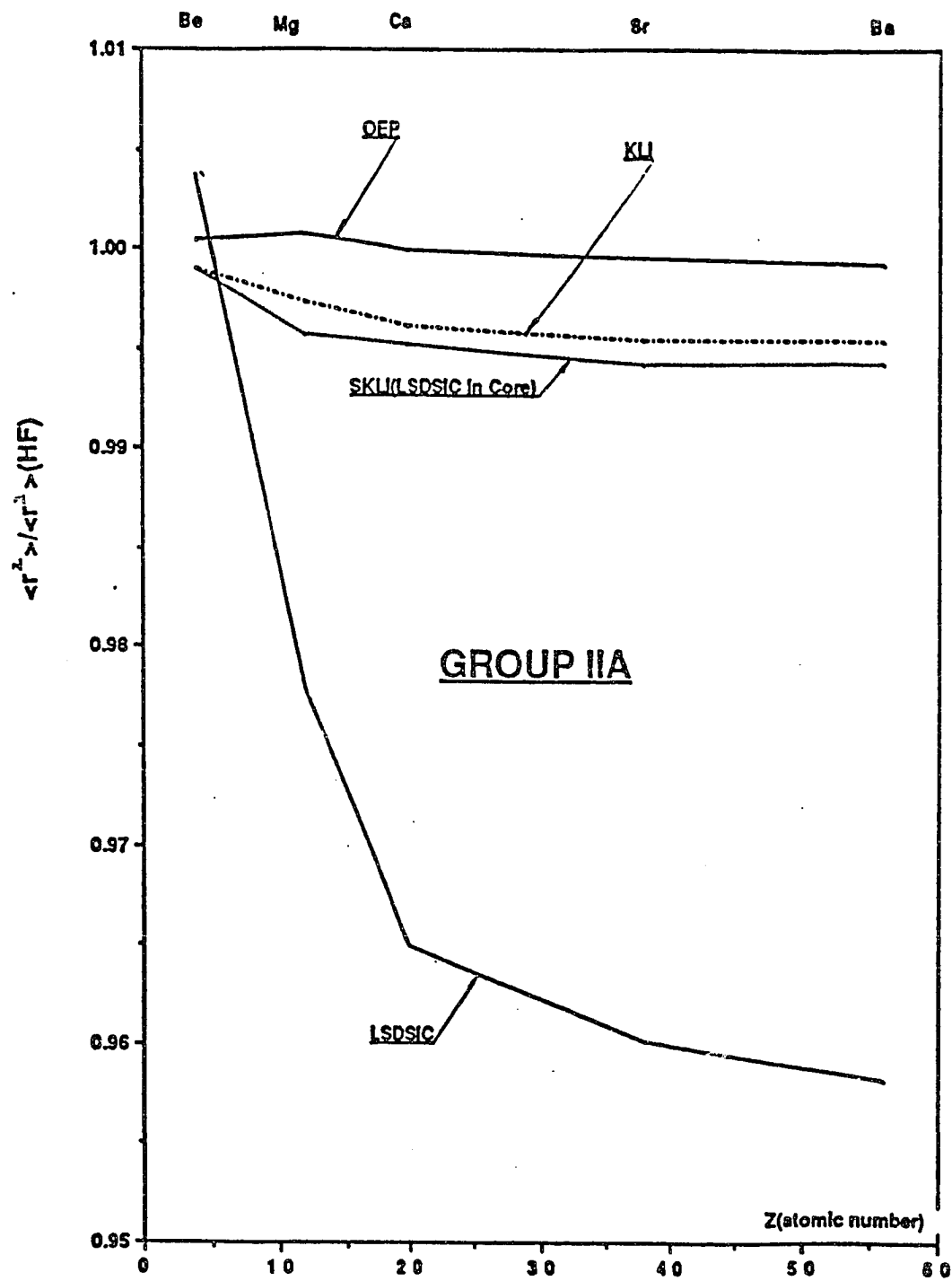


Fig. 2.12 Comparison of  $\langle r^2 \rangle$

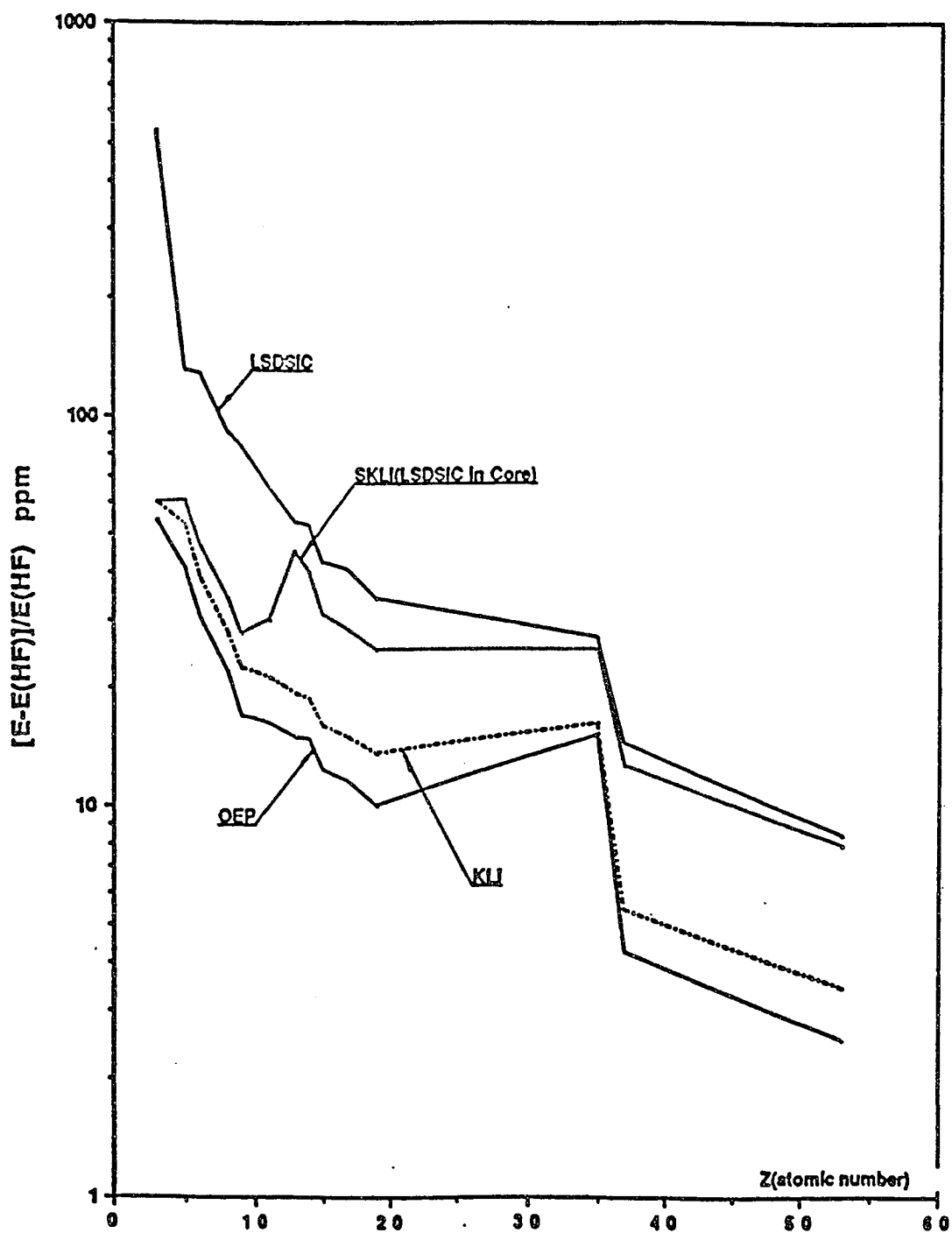


Fig.3.1 Overestimate of Total Energy in Negative Ions

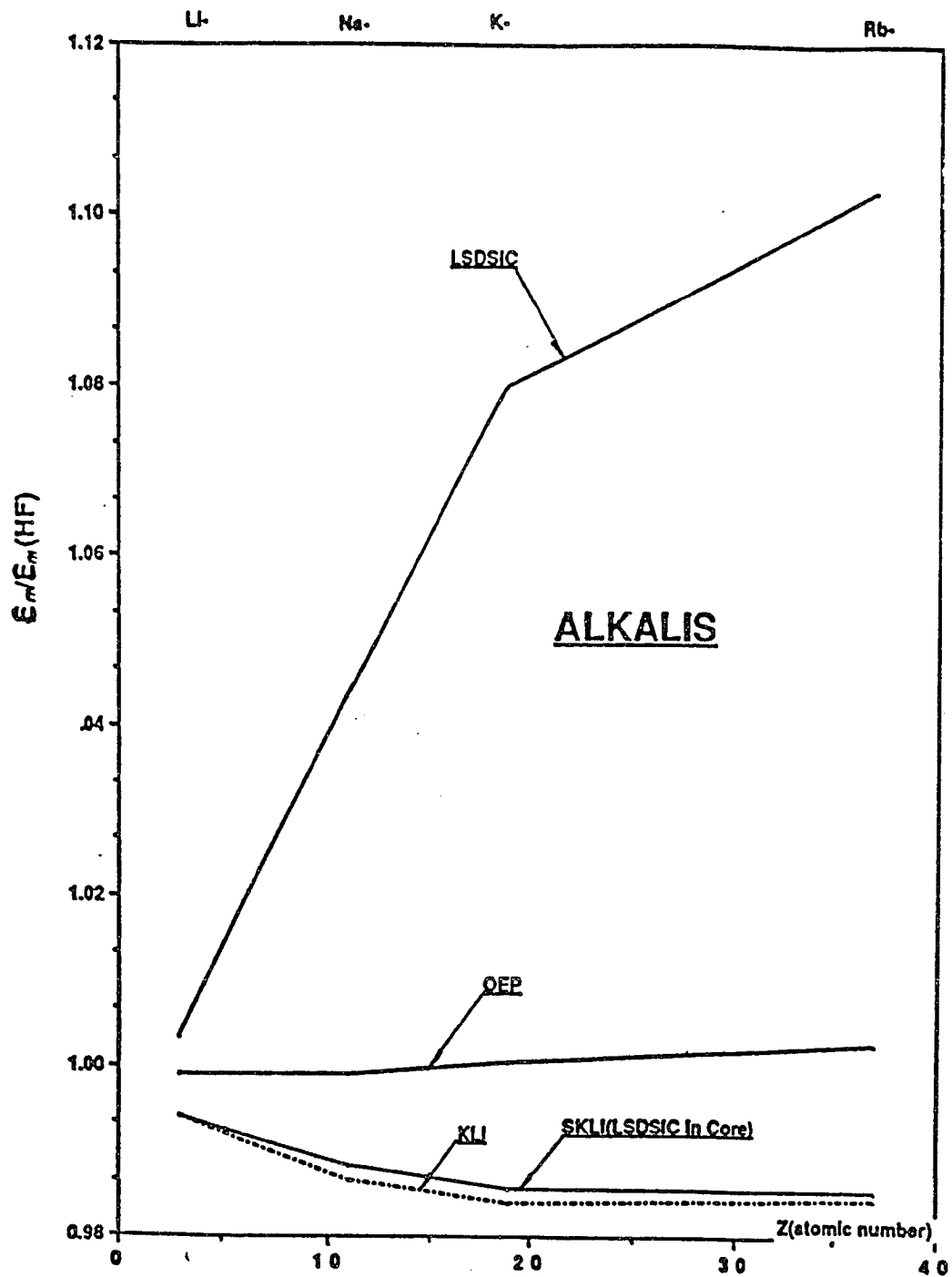


Fig.3.2 Comparison of Highest Occupied Energy Eigenvalues

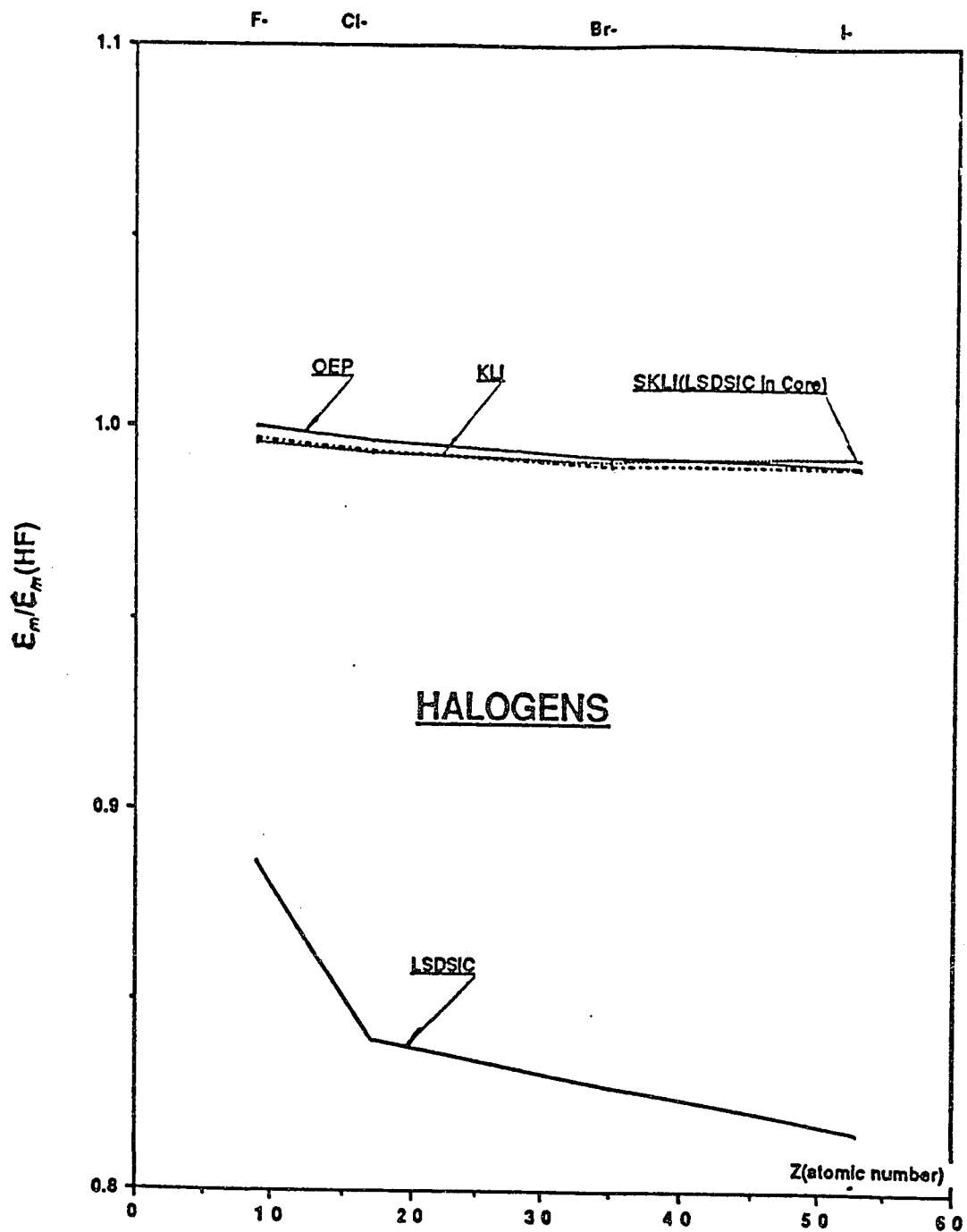


Fig.3.3 Comparison of Highest Occupied Energy Eigenvalue

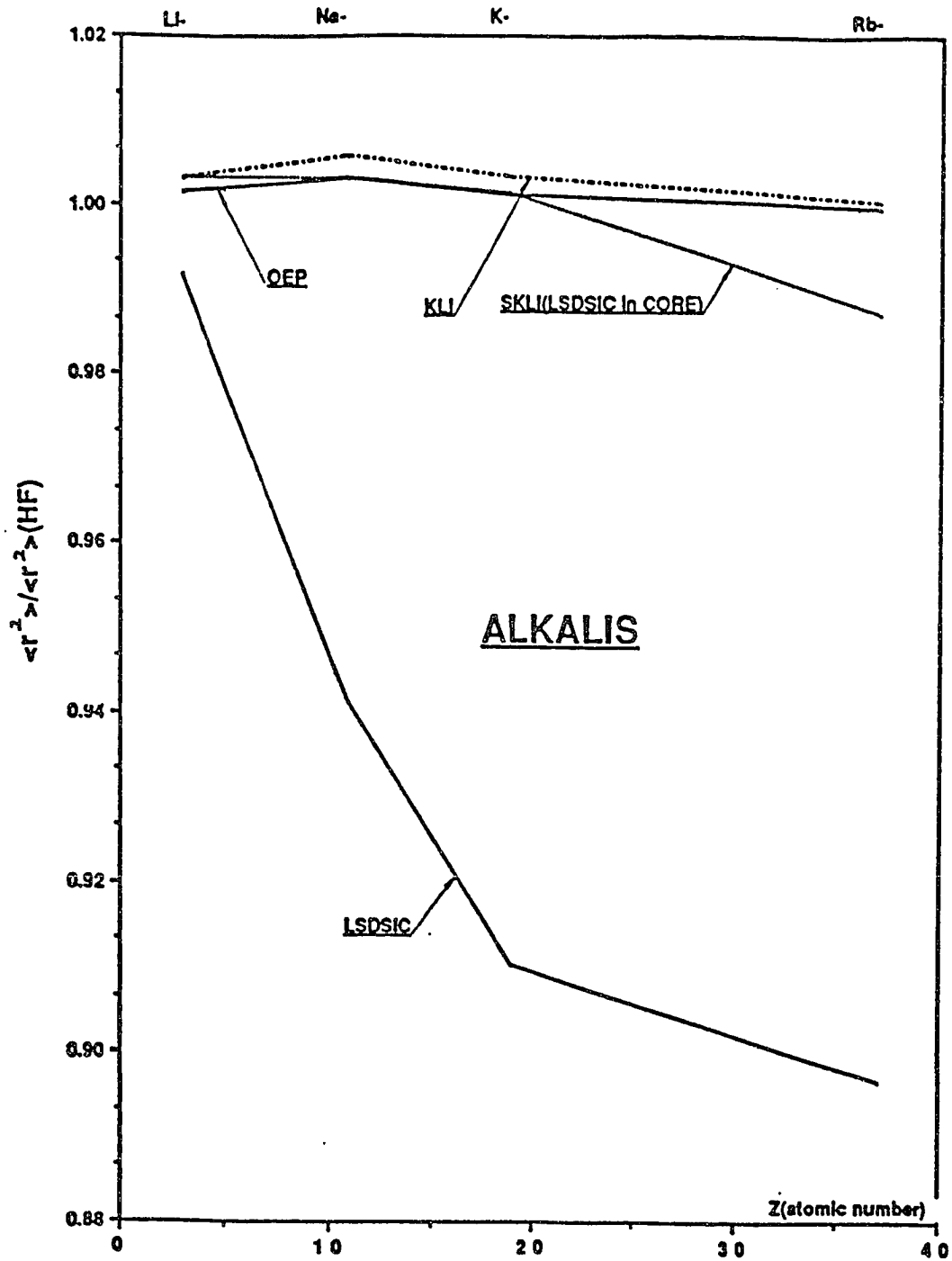


Fig.3.4 Comparison of  $\langle r^2 \rangle$

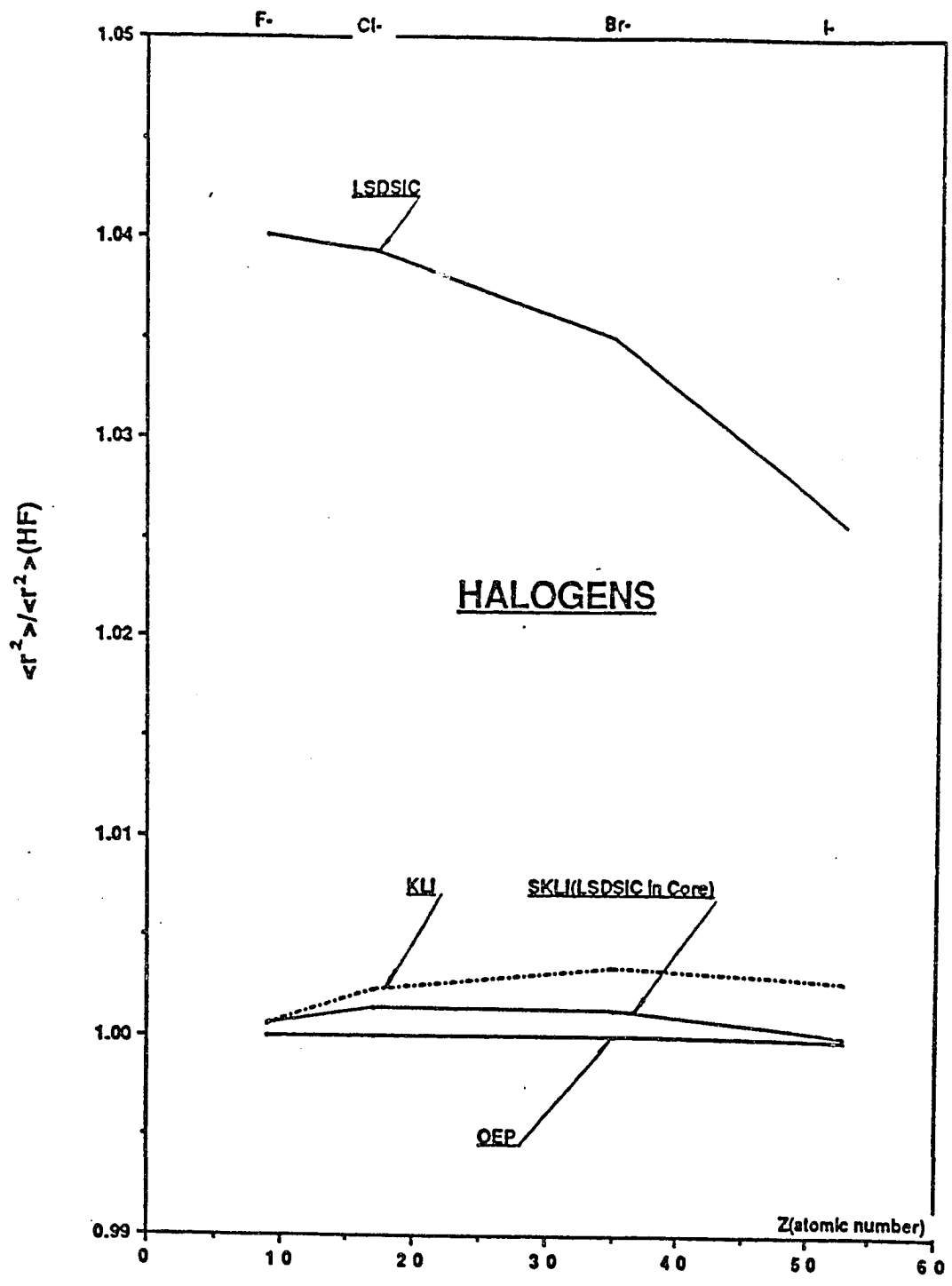


Fig.3.5 Comparison of  $\langle r^2 \rangle$

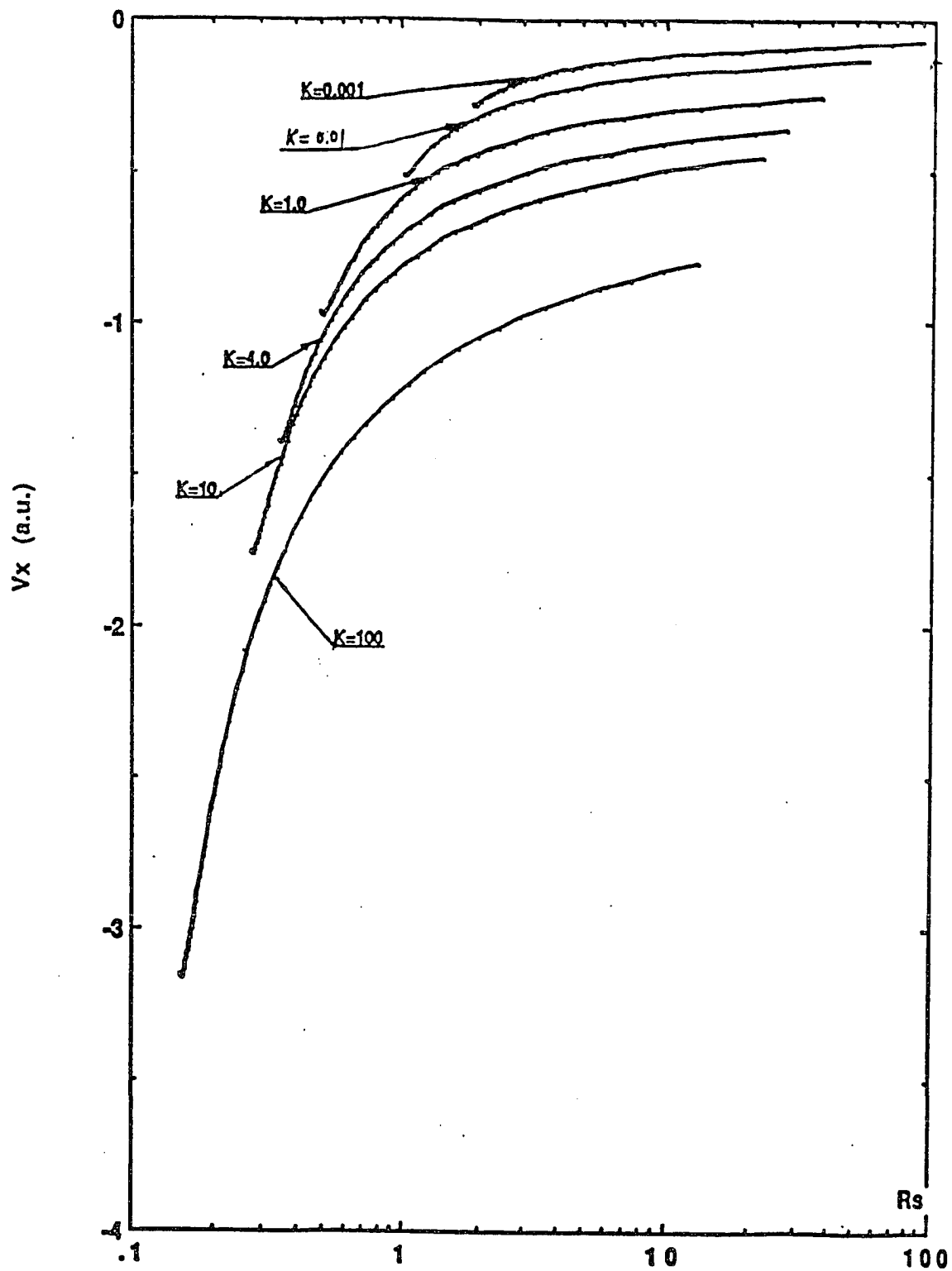


Fig.4.1 Exact  $V_x$

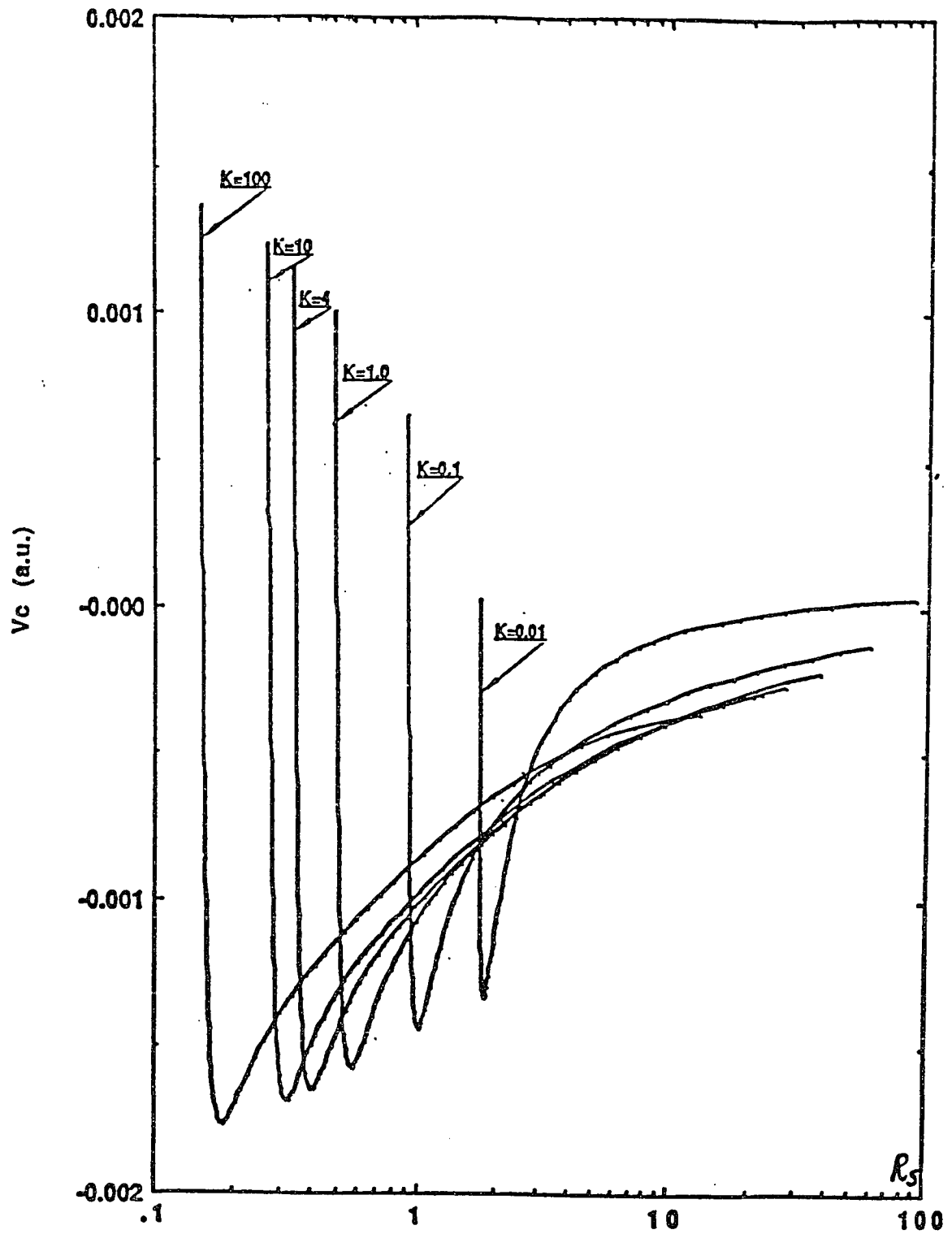


Fig.4.2 Exact  $V_c$

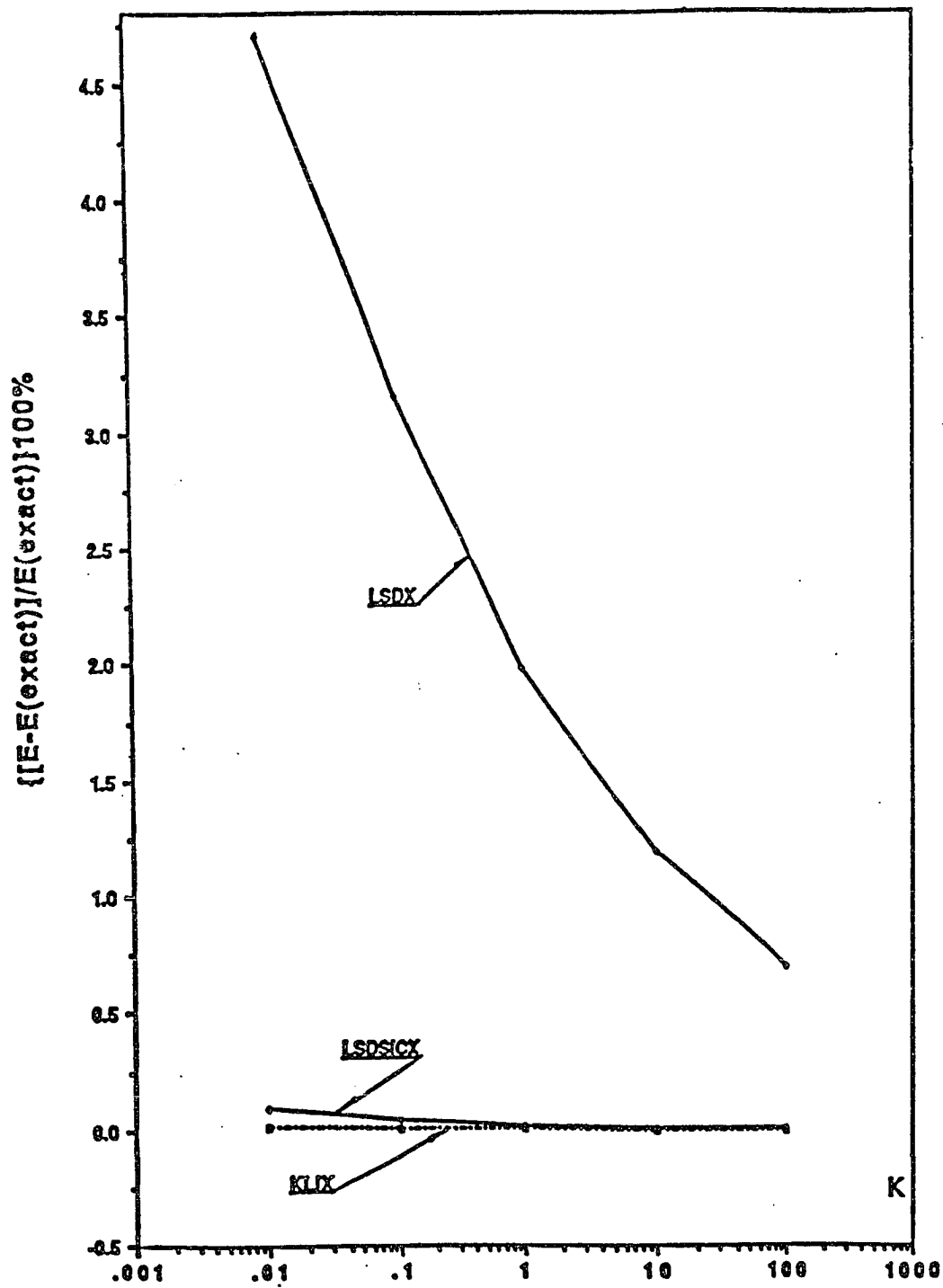


Fig.4.3 Percentage Error in Total Energy for Exchange Only

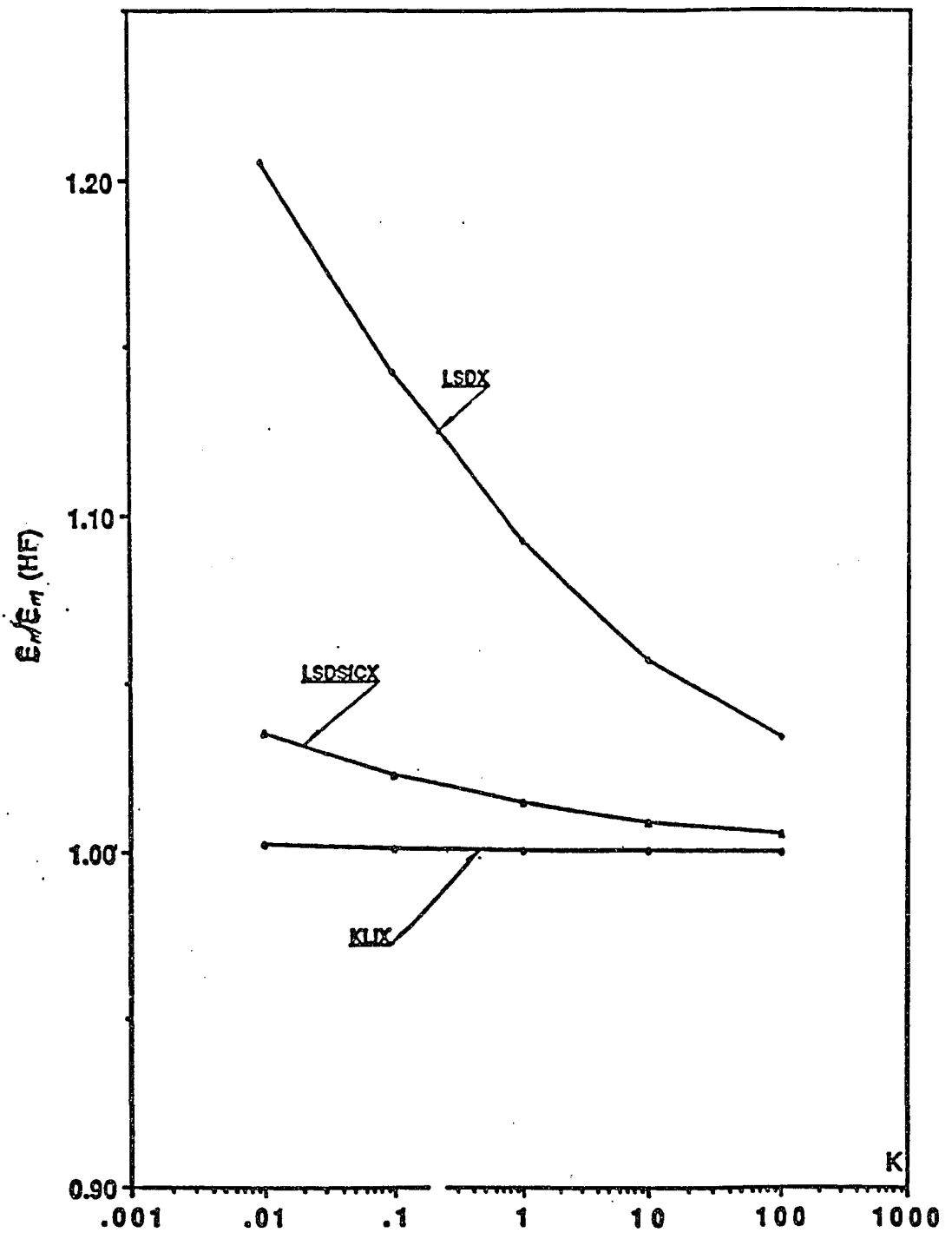


Fig.4.4 Highest Occupied Energy Eigenvalues (Exchange Only)

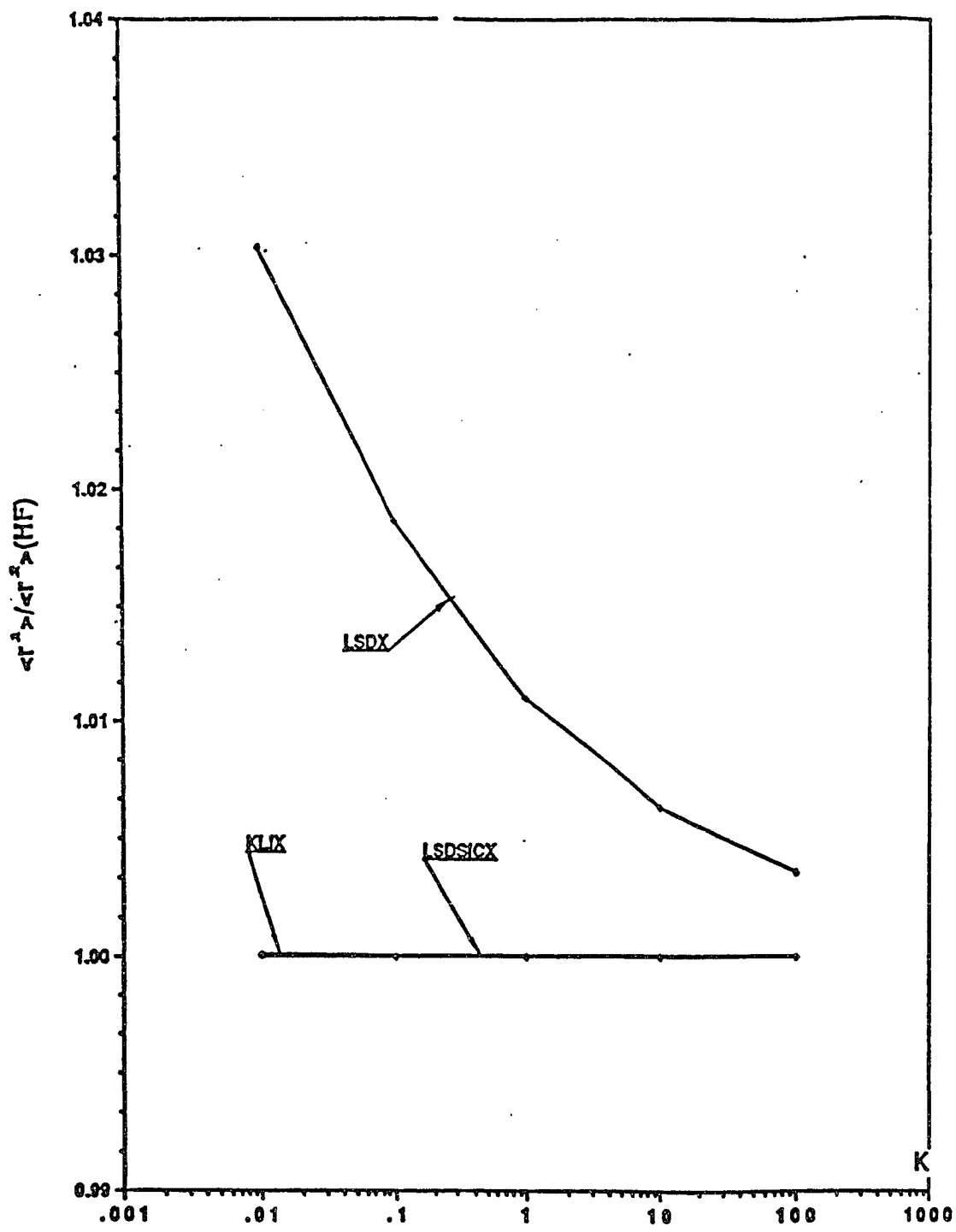


Fig.4.5 Comparison of  $\langle r^2 \rangle$  (Exchange Only)

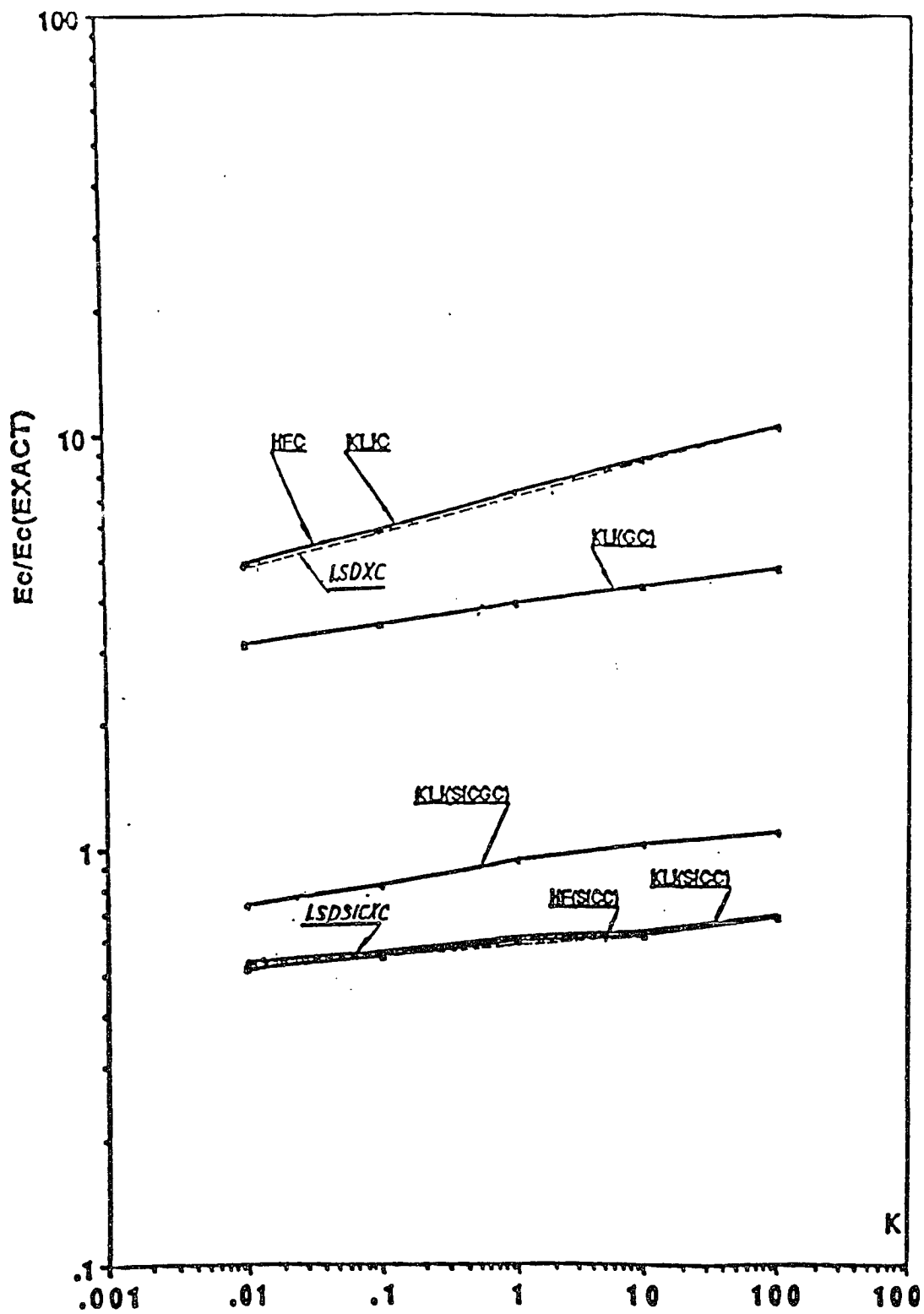


Fig.4.6 Comparison of Correlation Energy

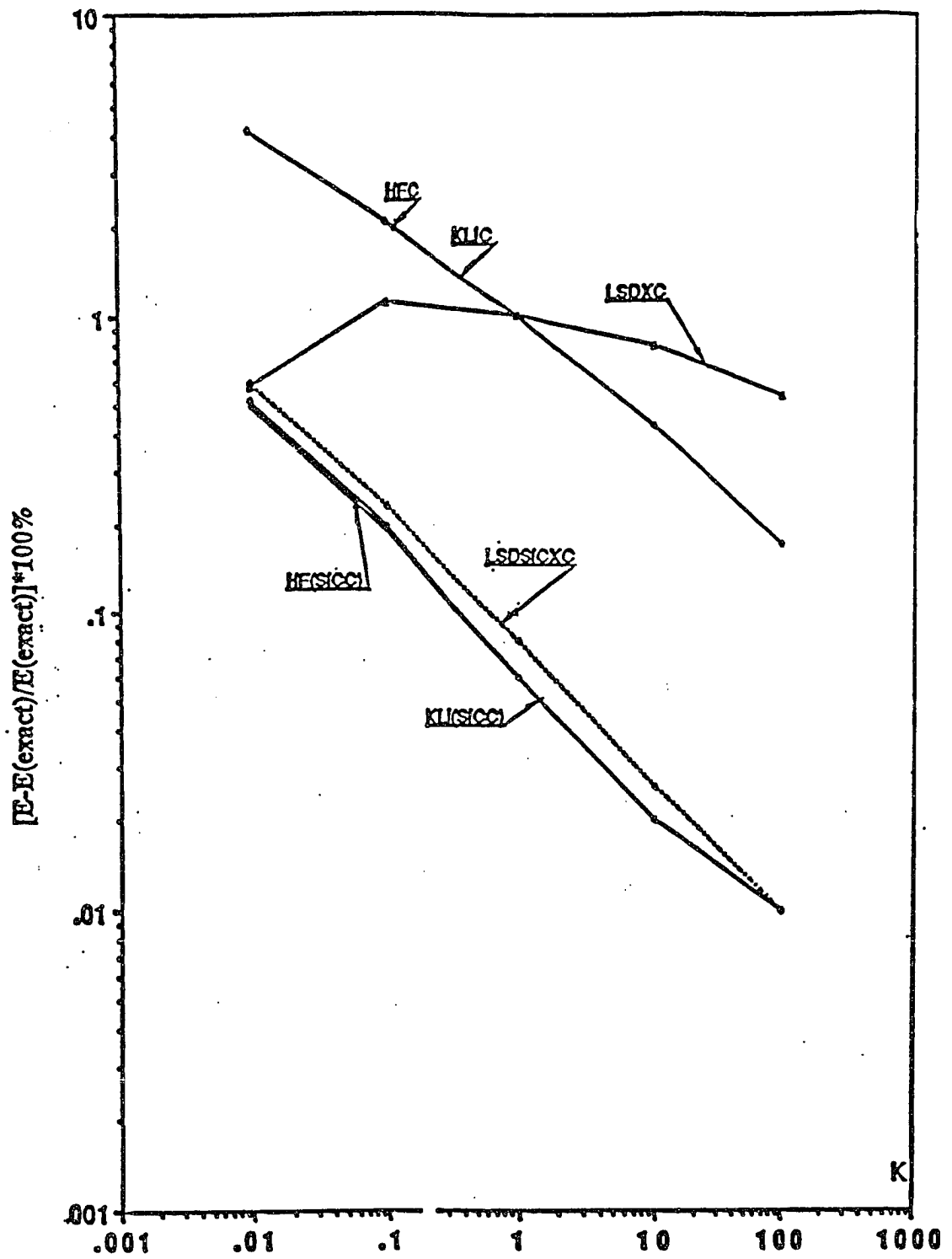


Fig.4.7 Percentage Error in Total Energy Including Exchange and Correlation

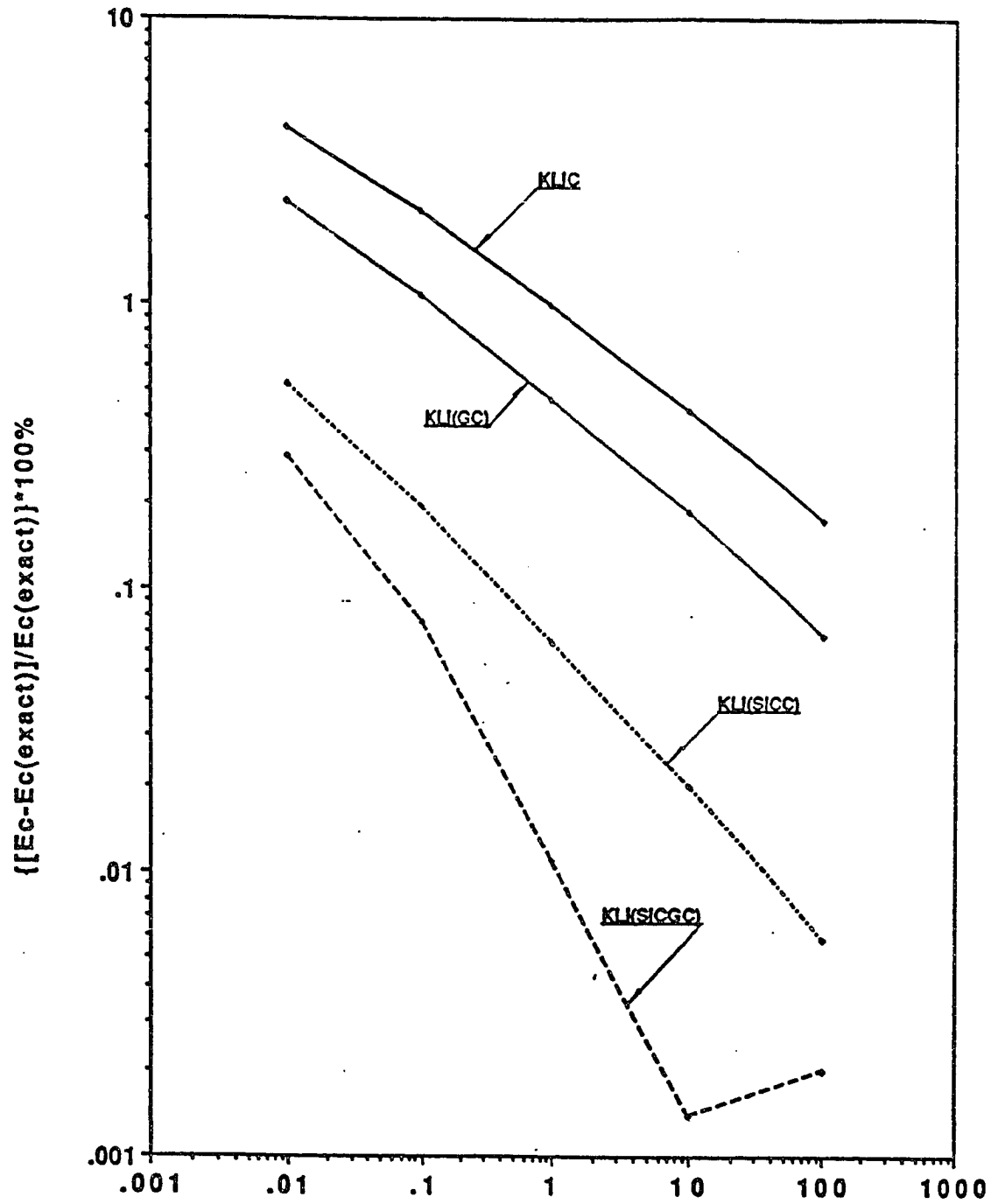


Fig.4.8. Percentage Error of Total Energy (KLI With Correlation)

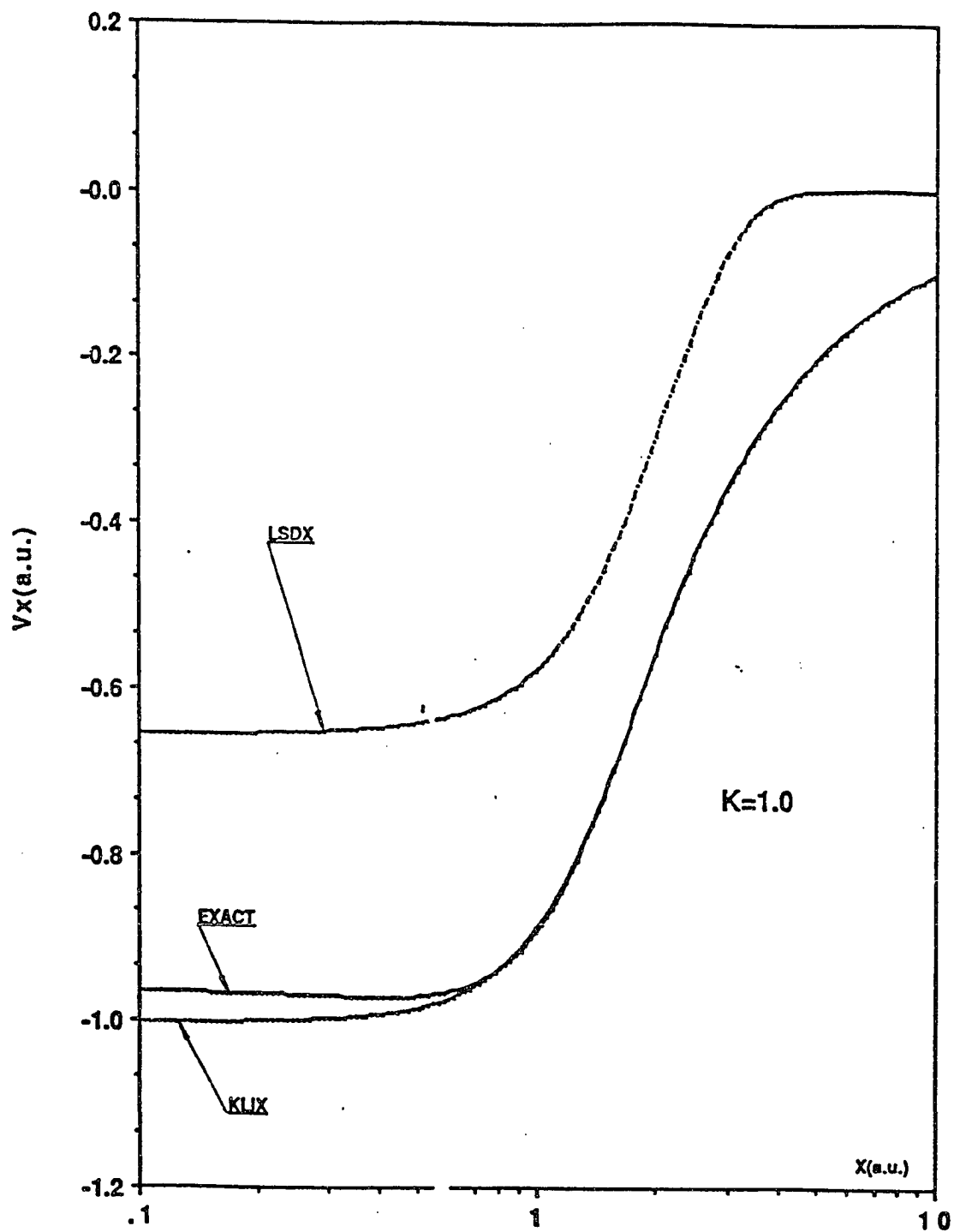


Fig.4.9 Comparison of  $V_x$

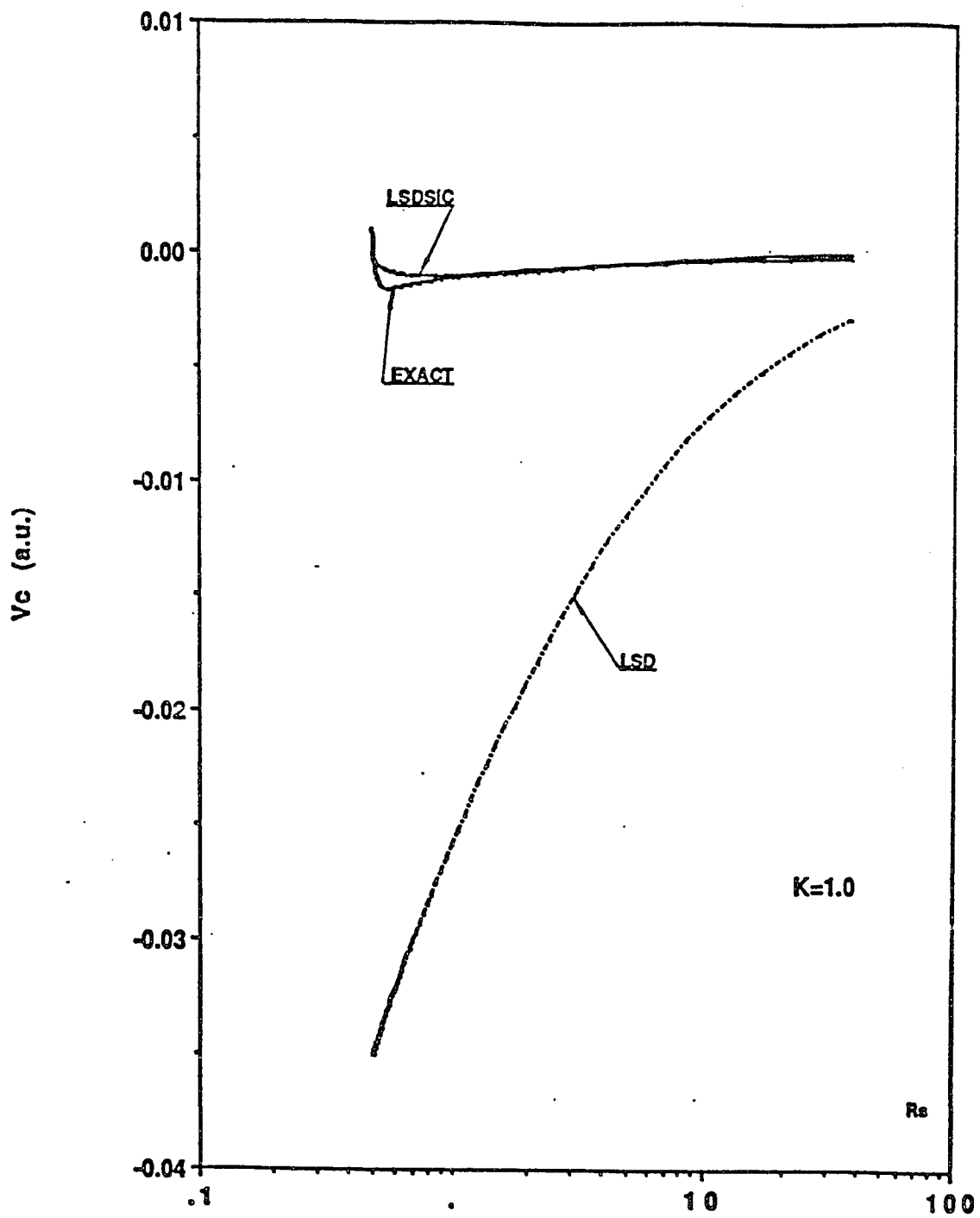


Fig.4.10.1 Comparison of  $V_c$

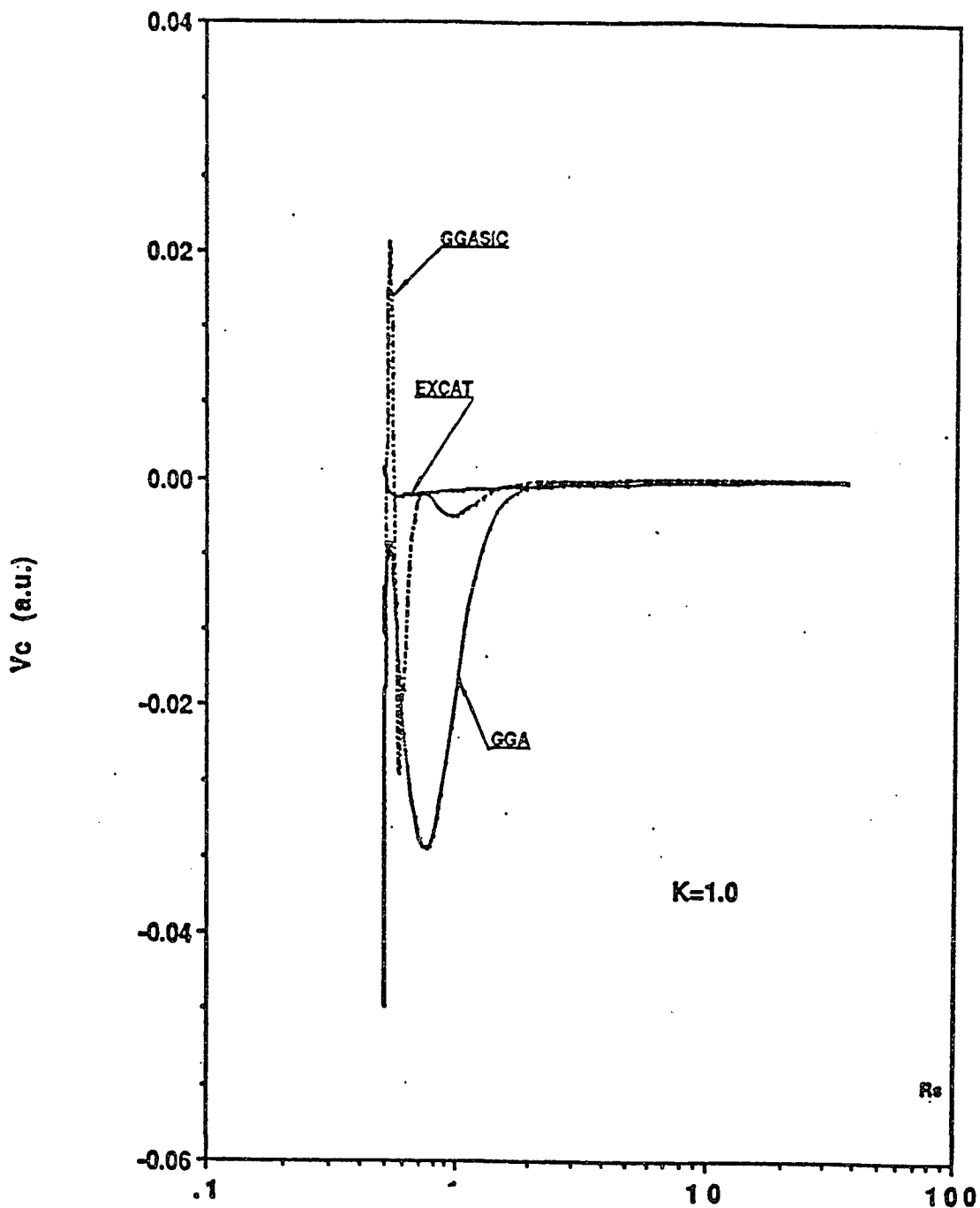


Fig.4.10.2 Comparison of  $V_c$

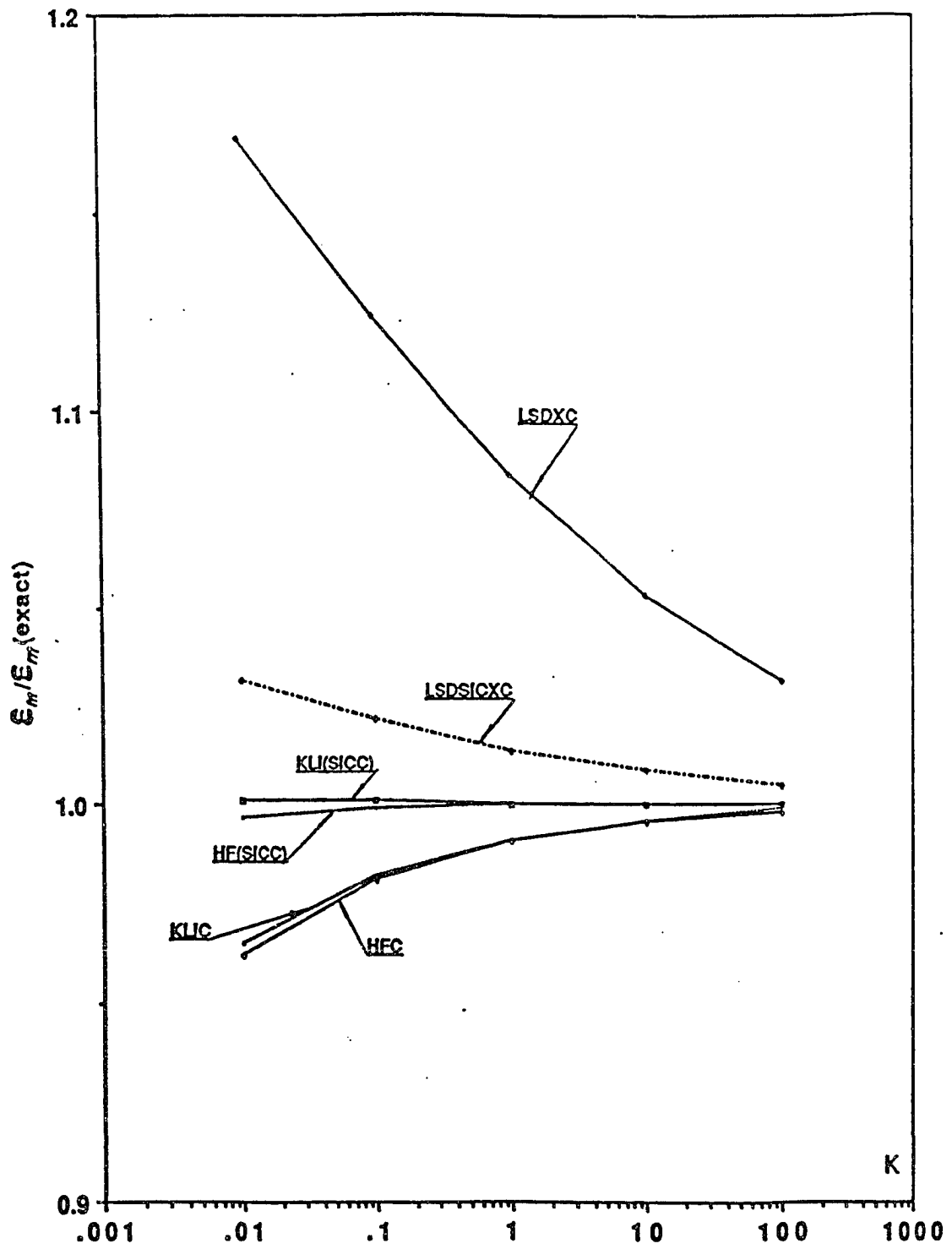


Fig. 4.11 Highest Occupied Energy Eigenvalues(exchange and correlation)

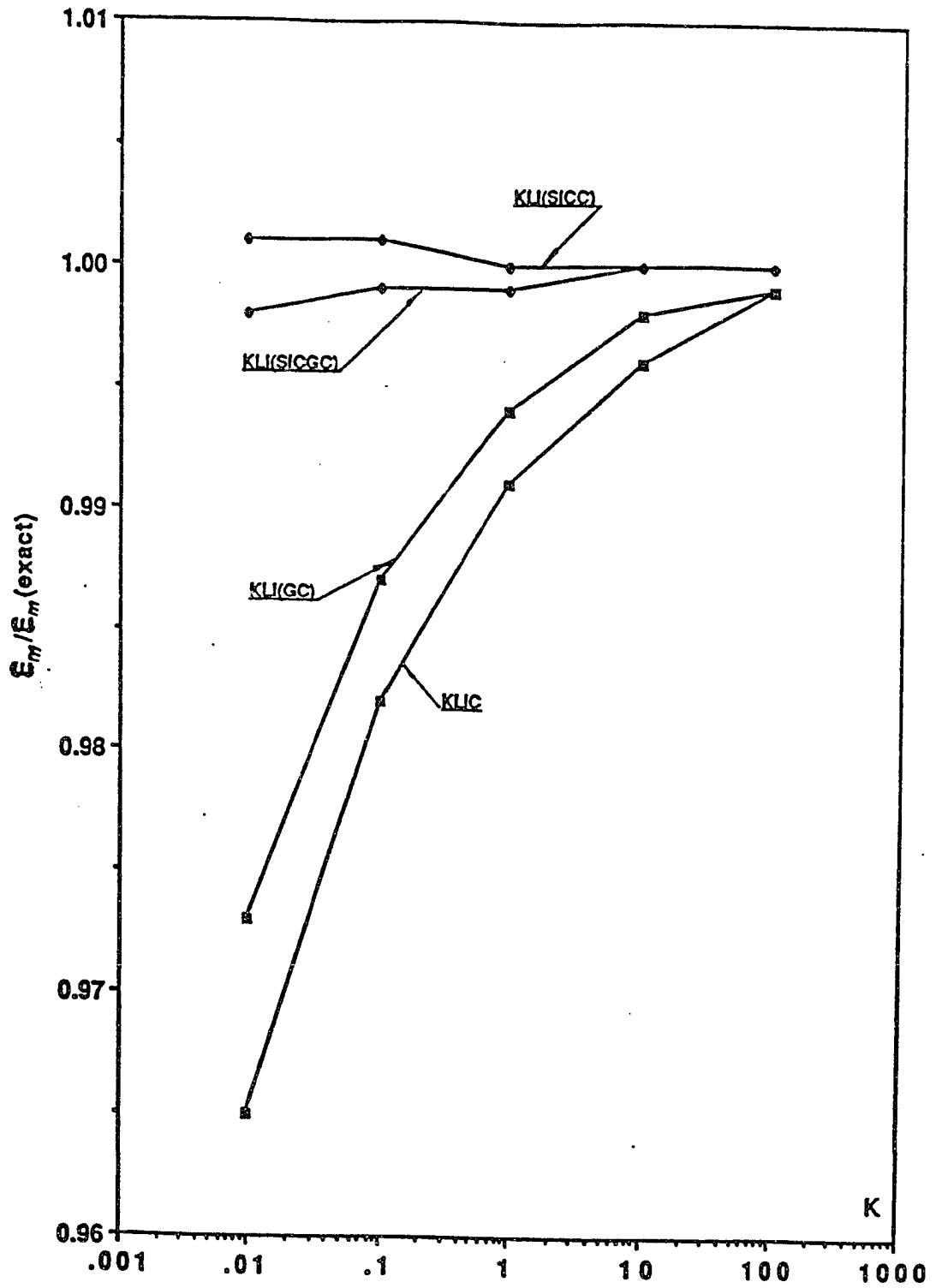


Fig. 4.12 Highest Occupied Energy Eigenvalues (KLI With Correlation)

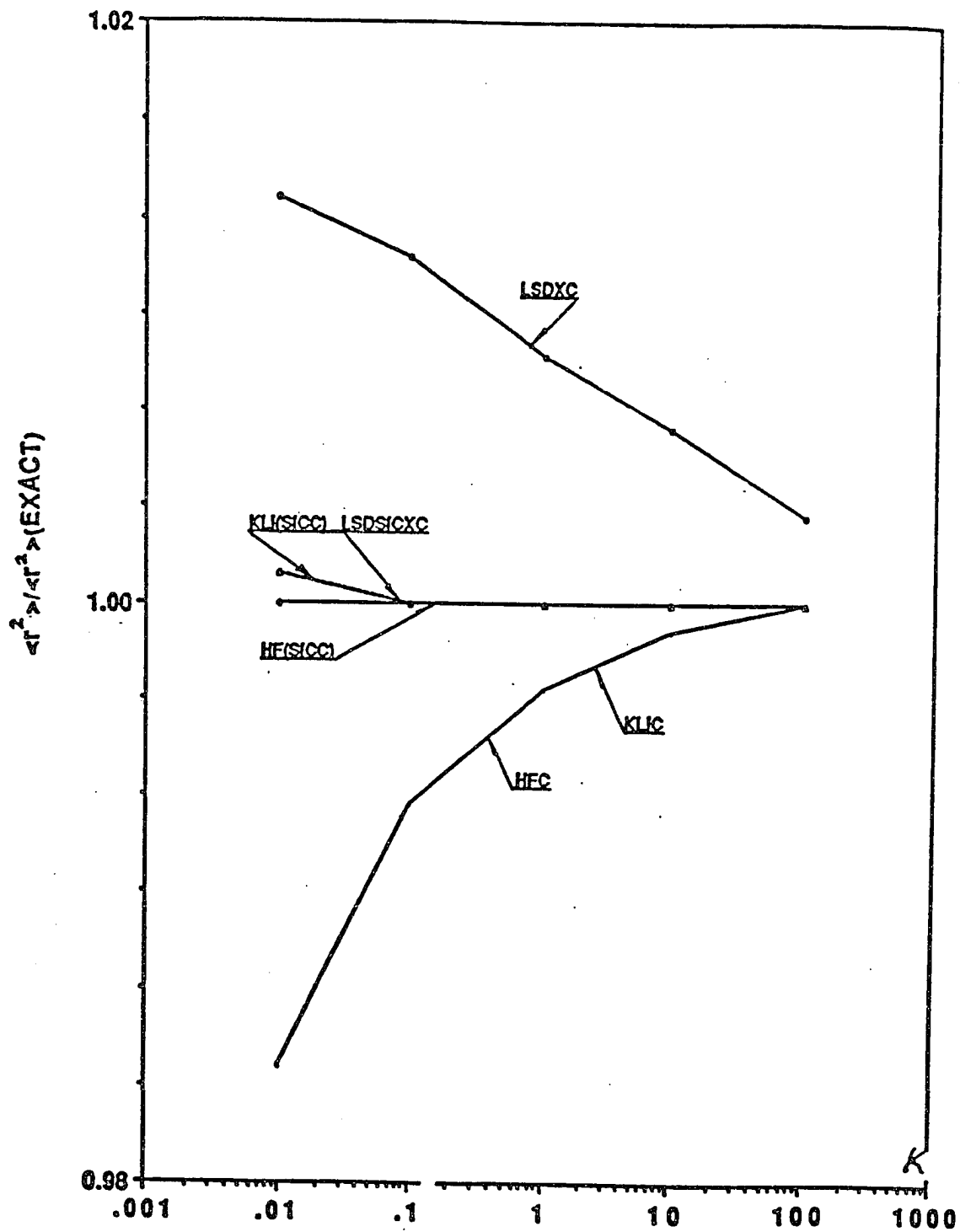


Fig.4.13 Comparison of  $\langle r^2 \rangle$  (Exchange and Correlation)

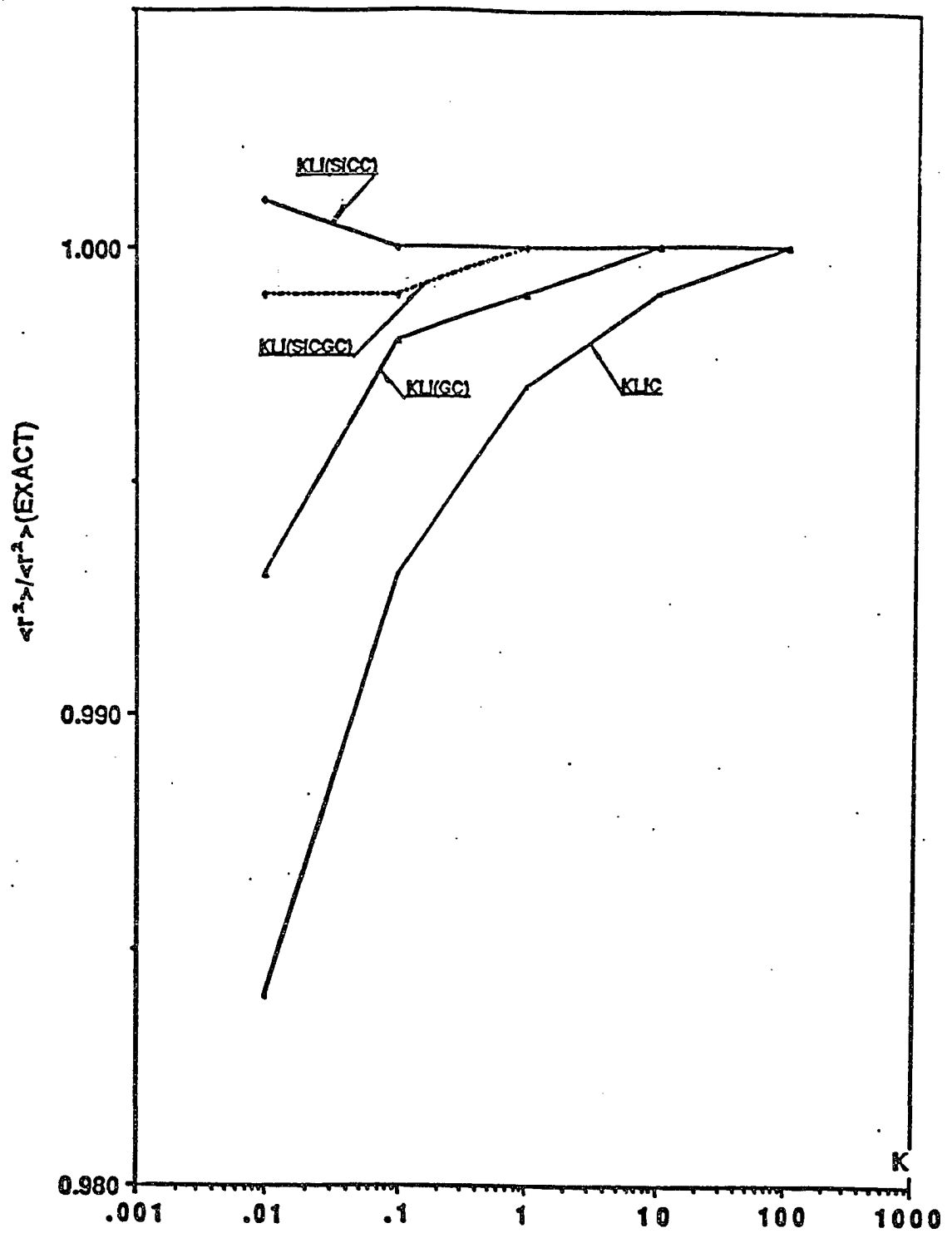


Fig.4.14 Comparison of  $\langle r^2 \rangle$  (KLI With Correlation)

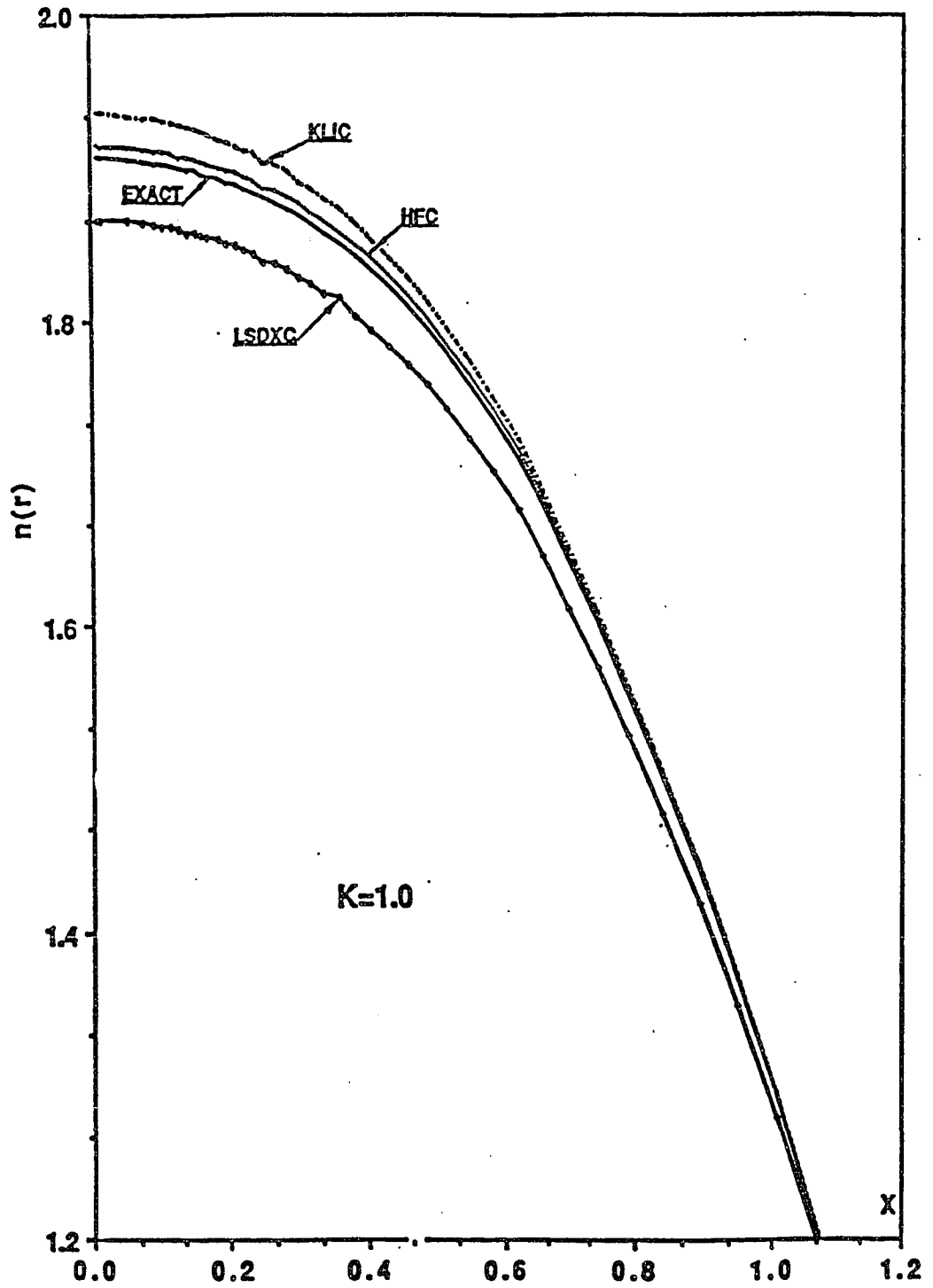


Fig.4.15 Electron Density (With LSD Correlation)

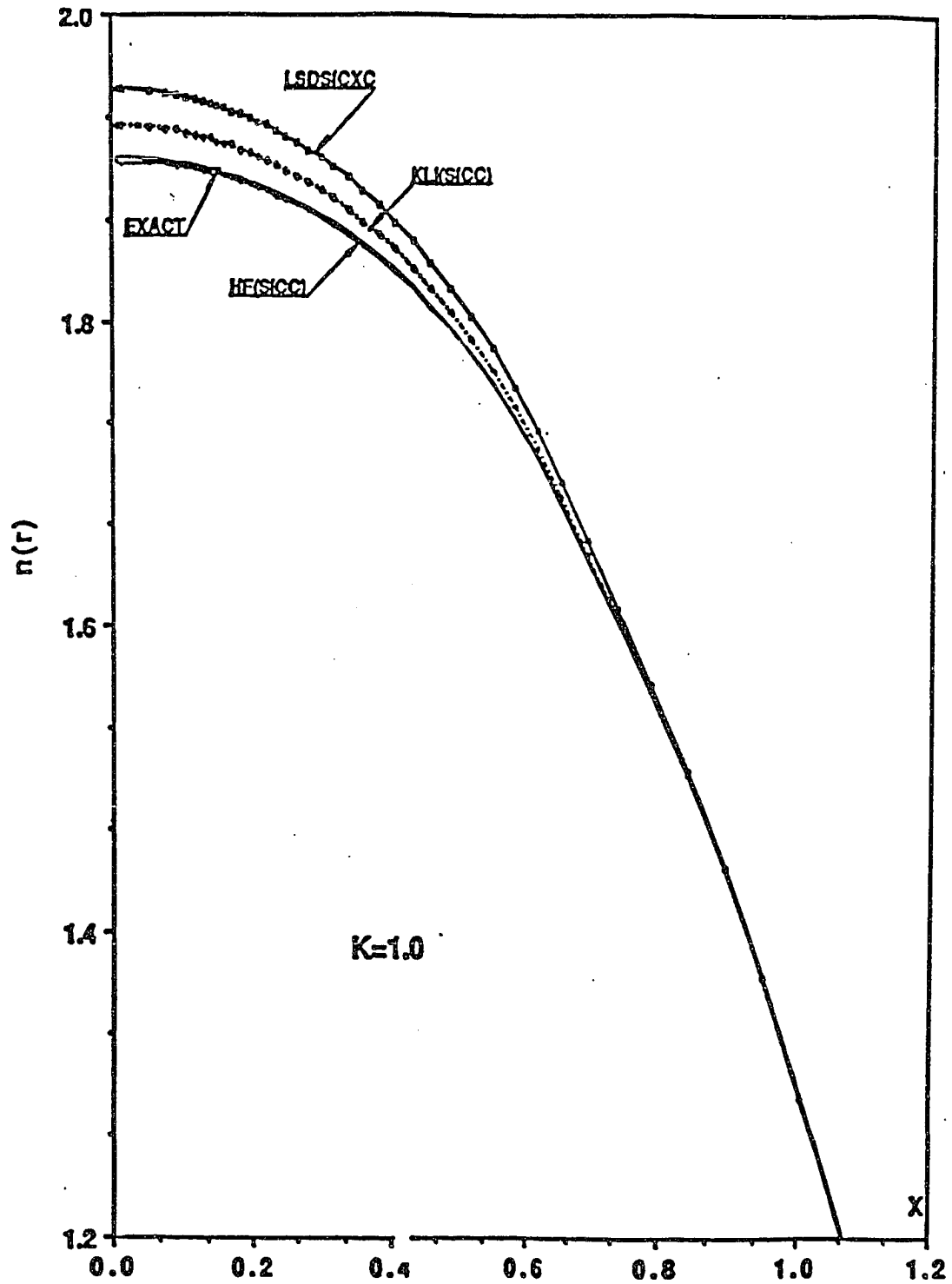


Fig.4.16 Electron Density (With LSDSIC Correlation)

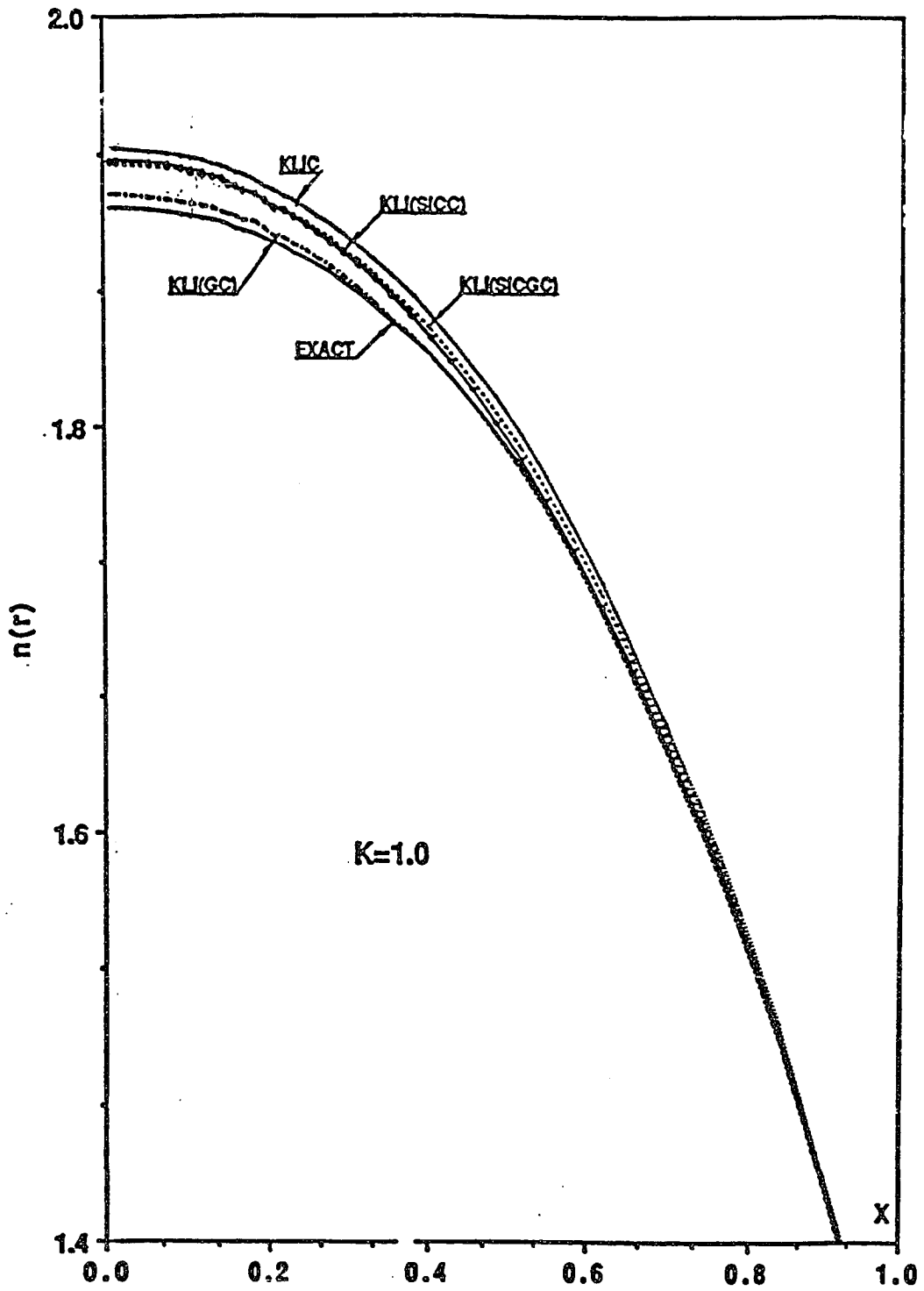


Fig.4.17 Electron Density (KLI With Correlation)

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