The density functional formalism, its applications and prospects

R. O. Jones

Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

O. Gunnarsson

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

A scheme that reduces the calculations of ground-state properties of systems of interacting particles *exactly* to the solution of single-particle Hartree-type equations has obvious advantages. It is not surprising, then, that the density functional formalism, which provides a way of doing this, has received much attention in the past two decades. The quality of the energy surfaces calculated using a simple local-density approximation for exchange and correlation exceeds by far the original expectations. In this work, the authors survey the formalism and some of its applications (in particular to atoms and small molecules) and discuss the reasons for the successes and failures of the local-density approximation and some of its modifications.

CONTENTS

I. INTRODUCTION

The description of many-particle systems has been an important goal of physics during this century. Analytic solutions of the Schrödinger equation are possible for a few very simple systems, and numerically exact solutions can be found for a small number of atoms and molecules. However, most cases of interest, such as reaction surfaces in chemistry or electron-electron interactions in solids, require the use of model Hamiltonians or simplified computational schemes. The recent progress in the calculation of the electronic structure of atoms, molecules, and solids has emphasized, perhaps, how far we are from the goal of being able to predict the physical and chemical properties of many-particle systems with reliability and without excessive computation. In theoretical chemistry, for example, "tentative conclusions have been arrived at on the basis of theories which were such a patchwork of approximations that they appeared to have no right to work" (Hoffmann and Woodward, 1968). The development of schemes that provide useful information on real systems continues, and it is the purpose of this paper to describe one of them—the density functional (DF) formalism. We shall point out, in particular, the differences in perspective between this formalism and other methods used to discuss many-particle systems.

If we wish to discuss the properties of an interacting system, such as the electrons in a molecule or solid, it is natural to consider the many-electron wave function, $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, where the $\mathbf{r}_i$ denote the particle coordinates and spins. One of the earliest and most widely used of all approximations for Ψ is due to Hartree (1928), who approximated the many-electron wave function as a product of single-particle functions, i.e.,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots)=\psi_1(\mathbf{r}_1)\cdots\psi_N(\mathbf{r}_N)\ . \tag{1.1}$$

Each of the functions $\psi_i(\mathbf{r}_i)$ satisfies a one-electron Schrödinger equation with a potential term arising from the average field of the other electrons, i.e.,

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{ext}}+\Phi_i\right]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r})\ , \tag{1.2}$$

where the Coulomb potential Φ_i is given by Poisson's equation

$$\nabla^2\Phi_i=4\pi e^2\sum_{j=1,i\neq j}^{N}|\psi_j|^2\ , \tag{1.3}$$

and V_{ext} is the potential due to the nuclei. Fermi statistics can be incorporated into this picture by replacing the product wave function by a single determinantal function (Fock, 1930; Slater, 1930). This so-called Hartree-Fock approximation leads to an additional, nonlocal exchange term in the Schrödinger equation, but the single-particle picture, with the wave function described in terms of orbitals with particular spins and occupation numbers, is unchanged. The inclusion of Fermi statistics ("exchange" effects) improves the total energy calculation, and the Hartree-Fock approximation remains an indispensable benchmark in molecular physics ("We can calculate everything," Clementi, 1972), although extended systems such as solids remain a challenge.

The Hartree-Fock (or "self-consistent-field") calculations, and the very appealing picture that results from them, are so familiar that it is sometimes overlooked that the approximation behind them is not a particularly good one. Coulson (1960) noted that "it is now perfectly clear that a single configuration (Slater determinant) wave function must inevitably lead to a poor energy." The lowest-lying configuration is generally only one of very many with comparable energies, and a better approximation would result from taking a linear combination. Such an approach, where effects beyond the Hartree-Fock approximation ("correlation effects") are included by improving the many-particle wave function, is known as "configuration interaction" (CI). It leads, in principle, to the exact wave function from which most properties of interest can be calculated. This is such an attractive goal that much effort is expended in its pursuit. The explosive increase in the number of configurations with increasing electron number means, however, that only systems with relatively few electrons can be calculated with high accuracy. Furthermore, the complexity of the resulting solutions means that a simple interpretation of the results is often difficult.

A different approach was taken by Thomas (1927) and Fermi (1928), who proposed a scheme based on the density of electrons in the system, $n(\mathbf{r})$. The Thomas-Fermi scheme assumed that the motions of the electrons are uncorrelated and that the corresponding kinetic energy can be described by a local approximation based on the results for free electrons, $[n(\mathbf{r})]^{5/3}$. The potential of the system can be determined by solving Poisson's equation, and the requirement of constant chemical potential leads to the Thomas-Fermi equation for $n(\mathbf{r})$. Although this approach has only limited success in describing real systems, it is a prototype for later DF theories in its focus on the density, i.e., the integrated quantity

$$n(\mathbf{r})=N\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N\Psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\times\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\ ,$$

which may be easier to describe than the precise details of the wave function Ψ. The Thomas-Fermi method also provides a well-defined model whose mathematical properties have received much attention (Lieb, 1981, and references therein).

Shortly after the original work, Dirac (1930) proposed that exchange effects be included by incorporating a term derived from the exchange energy density in a homogeneous system. The use of an approximate exchange potential in addition to the Hartree term in Eq. (1.2) was suggested by Slater (1951a, 1951b) and by Gáspár (1954). Gáspár adopted the Dirac approximation to the exchange energy and derived a slightly different exchange potential by using a variational approach. He found that solutions of the resulting equations for the Cu^+ ion reproduced the Hartree-Fock eigenfunctions and eigenvalues very well. This was an interesting demonstration that an approximation based on results for a homogeneous system could give a satisfactory description even if the density is very far from uniform. Slater used a simple dimensional argument to show that the exchange potential in a system of variable density could be approximated by a term with a local dependence $\sim[n(\mathbf{r})]^{1/3}$ on the density. It is often overlooked that this dependence on the density is a consequence of the concept of the "exchange" or "Fermi" hole, i.e., the region near an electron that is avoided by electrons of the same spin, and not on the exchange potential in a homogeneous system.

All the work mentioned above has been essential to the development of modern density functional theory. As an approximation to the full nonlocal exchange potential, the simple local-density (LD) approximation has provided the basis for much of the work on the electronic structure of solids since the 1950s. The calculation of electronic band structures and quantities related to them is, of course, one of the success stories of modern condensed matter physics. The experience obtained in solving Schrödinger-type equations with local effective potentials and the improvement in numerical methods and computers during the past 30 years have been decisive in carrying out density functional calculations in the last decade or so.

The demonstration that ground-state properties, particularly the total energy E of a system of interacting particles, could be related in a rigorous fashion to the density distribution was given by Hohenberg and Kohn (1964); the proof they gave has been simplified and extended by Levy (1979). The formalism is, in principle, exact, and the Thomas-Fermi equation may be derived from it as an approximation. Its application to the total energy of the interacting system results in a minimum principle, and the determination of the energy of the ground state can be found by the solution of single-particle equations (Kohn and Sham, 1965). In practice, total energy calculations require approximations to be made for the exchange-correlation energy E_{xc}. Kohn and Sham showed that the LD approximation

$$E_{\mathrm{xc}}^{\mathrm{LD}}=\int d\mathbf{r}\; n(\mathbf{r})\varepsilon_{\mathrm{xc}}[n(\mathbf{r})] \;, \tag{1.4}$$

could be applied to the limiting case of a slowly varying density. Here $\varepsilon_{\mathrm{xc}}[n]$ is the exchange and correlation energy per particle of a homogeneous electron gas with density n. The exchange contribution ε_x has the same form as that of Gáspár, and a variety of approximations exists for the correlation term ε_c.

The limiting cases noted above are not realized in atoms, molecules, or solids, and Kohn and Sham (1965) commented that "we do not expect an accurate description of chemical bonding" with the LD approximation. It is perhaps not surprising then that a decade passed before the first attempts were made to test its ability to describe the bonds between atoms. It is remarkable that these attempts showed that the LD approximation could reproduce many measurable quantities satisfactorily. In particular, ground-state geometries, vibration and phonon frequencies, and moments of the density are generally reproduced very well. In the space of the last 15 years, the density functional formalism has become the basis of most of the parameter-free calculations in extended systems and has found growing application to molecules and clusters. Almost all of the calculations performed to date have used the local-density approximation, Eq. (1.4), or approximations related to it.

The practical necessity of approximating E_{xc} leads to an essential difference in perspective between the density functional and the CI approaches. While the CI method seeks an exact numerical solution of the Schrödinger equation, which would yield exact answers for most quantities of interest, even an exact solution of the density functional equations can only reflect the accuracy of the approximation for E_{xc}. We shall therefore pay particular attention to such approximations and to the possibilities available for improving them. The central role played by the electron density in this theory means that it is important to have a clear picture of its nature. We show in Fig. 1 the spherically averaged density in the ground state of the carbon atom. The density falls monotonically from the nucleus and does not show the radial oscillations often expected. The charge density in small molecules also tends to be relatively featureless, with maxima at the nuclei, saddle points along the bonds, and a generally monotonic decay away from both. Furthermore, the electron density in a molecule or solid shows relatively small departures from the overlapped densities of its atomic constituents. Energy differences, such as binding, ionization, and cohesive energies, which form the main focus of this paper, result from subtle changes in relatively featureless density distributions. It is clear that it will not be easy to find a simple prescription for determining such energy differences.

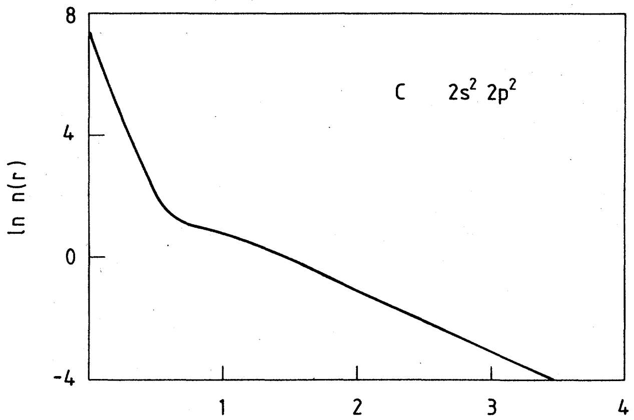

FIG. 1. Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.

In view of the many applications of density functional calculations, it is not surprising that there have been many review articles (see, for example, Rajagopal, 1980; Bamzai and Deb, 1981; Parr, 1983; Callaway and March, 1984; von Barth, 1984a, 1984b) and books (Lundqvist and March, 1983; Dahl and Avery, 1984; Phariseau and Temmerman, 1984; Dreizler and da Providência, 1985; Erdahl and Smith, 1987; March and Deb, 1987) devoted to it. There have also been reviews of closely related fields, such as strongly coupled plasmas (Ichimaru, 1982). These represent a range of viewpoints and emphases, and it is clear that an exhaustive survey of all aspects of density functional theory would be beyond the scope of a single article. It may well be asked what purpose could be served by adding to the present list of reviews. However, density functional theory and some of its applications have formed the basis of much of our own work for more than a decade. Our views on the subject have evolved along with the field, and we believe that it is useful and interesting to discuss our experience and the viewpoint that has resulted. Our focus is on problems that have interested us most—particularly the local-density approximation and its modifications, and their applications to atoms, molecules, and model solids—without implying in the least that these are the only (or necessarily the most important) areas of interest. In spite of our own interests in surfaces and chemisorption, for example, we have said little about them. The past 10–15 years have resulted in density functional calculations for a range of systems and with a reliability anticipated by none. It has been an interesting and surprising story, and we hope to give a feeling for both in this work. In a personal survey of the field, it is natural that our list of references will be selective and far from complete. The above reviews discuss other topics in more detail.

In Sec. II we outline the basic ideas of density functional theory and discuss the Thomas-Fermi approximation as an example. In Sec. III we derive the single-particle equations of Kohn and Sham (1965) and show how the relationship between systems with and without electron-electron interactions leads to an exact equation for E_{xc}. This is useful in discussing the requirements that must be satisfied by the approximations necessary in practical calculations. In Sec. IV we survey the results obtained using the local spin-density (LSD) approximations for a range of inhomogeneous systems—atoms, molecules, and solids. The number of published applications has become so great that we focus on systems that we believe illustrate points of particular importance. In Sec. V we discuss the origins of the errors apparent in LSD calculations and the results obtained using some modifications of this approximation. The important and still controversial question of the applicability of density functional theory to excited states is considered in Sec. VI, and the final section, Sec. VII, presents our perception of the current situation and the future prospects of DF calculations in different areas.

II. THE DENSITY AS BASIC VARIABLE

In this section we show that ground-state (GS) properties of a system can be expressed as functionals of the GS electron density; i.e., they are determined by a knowledge of the density alone. The total energy E can be expressed in terms of such a functional, and we show that $E[n]$ satisfies a variational principle. The Thomas-Fermi (TF) model is a special case of this formalism and is derived as an example. In view of the extensive study of the TF scheme and its well-known deficiencies, we discuss improvements and illustrate the accuracy that can be obtained for atoms, molecules, and simple metals.

A. The density functional formalism

The basic theorems of the density functional formalism were derived by Hohenberg and Kohn (1964). By extending an argument for independent fermions (Percus, 1978), Levy (1979) provided a simpler and more general derivation, which we follow here. We consider N electrons moving in an external potential $V_{\mathrm{ext}}(\mathbf{r})$, i.e., the Hamiltonian is

$$H = T + V_{ee} + \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i) \ , \tag{2.1}$$

where T and V_{ee} are the kinetic and electron-electron interaction operators, respectively. For all "N-representable" densities $n(\mathbf{r})$,[1] i.e., those which can be obtained from some antisymmetric wave function, $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, Levy defined the functional

$$F[n] = \min_{\psi \to n} \langle \psi | T + V_{ee} | \psi \rangle \ , \tag{2.2}$$

where the minimum is taken over all ψ that give the density n. $F[n]$ is universal in the sense that it refers neither to a specific system nor to the external potential $V_{\mathrm{ext}}(\mathbf{r})$. If we denote E_{GS}, ψ_{GS}, and $n_{\mathrm{GS}}(\mathbf{r})$ to be the ground-state energy, wave function, and density, respectively, then the two basic theorems of DF theory are

$$E[n] \equiv \int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + F[n] \geq E_{\mathrm{GS}} \tag{2.3}$$

for all N-representable $n(\mathbf{r})$, and

$$\int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n_{\mathrm{GS}}(\mathbf{r}) + F[n_{\mathrm{GS}}] = E_{\mathrm{GS}} \ . \tag{2.4}$$

To prove the variational principle (2.3) we introduce the notation $\psi^{n}_{\min}(\mathbf{r})$ for a wave function that minimizes (2.2), so that

$$F[n] = \langle \psi^{n}_{\min} | T + V_{ee} | \psi^{n}_{\min} \rangle \ . \tag{2.5}$$

Writing $V = \sum_i V_{\mathrm{ext}}(\mathbf{r}_i)$, we have

$$\int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + F[n] = \langle \psi^{n}_{\min} | V + T + V_{ee} | \psi^{n}_{\min} \rangle \geq E_{\mathrm{GS}} \ , \tag{2.6}$$

according to the minimum property of the GS. This proves the inequality (2.3). Using the minimum property once more we find

$$E_{\mathrm{GS}} = \langle \psi_{\mathrm{GS}} | V + T + V_{ee} | \psi_{\mathrm{GS}} \rangle \leq \langle \psi^{n_{\mathrm{GS}}}_{\min} | V + T + V_{ee} | \psi^{n_{\mathrm{GS}}}_{\min} \rangle \ . \tag{2.7}$$

We subtract the interaction with the external potential and obtain

$$\langle \psi_{\mathrm{GS}} | T + V_{ee} | \psi_{\mathrm{GS}} \rangle \leq \langle \psi^{n_{\mathrm{GS}}}_{\min} | T + V_{ee} | \psi^{n_{\mathrm{GS}}}_{\min} \rangle \ . \tag{2.8}$$

On the other hand, the definition of $\psi^{n_{\mathrm{GS}}}_{\min}$ yields the reverse relation between the two sides of (2.8). This is possible only if

$$\langle \psi_{\mathrm{GS}} | T + V_{ee} | \psi_{\mathrm{GS}} \rangle = \langle \psi^{n_{\mathrm{GS}}}_{\min} | T + V_{ee} | \psi^{n_{\mathrm{GS}}}_{\min} \rangle \ . \tag{2.9}$$

Then we have

$$\begin{aligned} E_{\mathrm{GS}} &= \int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n_{\mathrm{GS}}(\mathbf{r}) + \langle \psi_{\mathrm{GS}} | T + V_{ee} | \psi_{\mathrm{GS}} \rangle \\ &= \int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n_{\mathrm{GS}}(\mathbf{r}) + \langle \psi^{n_{\mathrm{GS}}}_{\min} | T + V_{ee} | \psi^{n_{\mathrm{GS}}}_{\min} \rangle \\ &= \int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r}) n_{\mathrm{GS}}(\mathbf{r}) + F[n_{\mathrm{GS}}] \ . \end{aligned} \tag{2.10}$$

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[1] Hohenberg and Kohn (1964) worked instead in the space of V-representable densities, i.e., those that can be realized for some external potential $V_{\mathrm{ext}}(\mathbf{r})$. This space is a subspace of N-representable densities.

This completes the proof of the basic theorems. An important result also follows from Eq. (2.9). If the ground state is nondegenerate, $\psi_{\min}^{n_{\mathrm{GS}}}=\psi_{\mathrm{GS}}$. If the ground state is degenerate, $\psi_{\min}^{n_{\mathrm{GS}}}$ is equal to one of the GS wave functions, and the others can also be obtained. The GS charge density then determines the GS wave function(s), from which all GS properties can be calculated. These properties are therefore functionals of the density. This theorem is the formal justification for working with the density instead of the wave function.

These theorems provide a general method for calculating GS properties. If an approximation can be found for $F[n]$, we need to minimize $E[n]$ in (2.3) for the potential $V_{\mathrm{ext}}(\mathbf{r})$ of interest. This leads to corresponding approximations for E_{GS} and $n_{\mathrm{GS}}(\mathbf{r})$. If we also have an approximation to the functional $X[n]$ describing some ground-state property X, the same procedure leads to approximations for X.

B. The Thomas-Fermi approximation

1. The Thomas-Fermi equations

In this approximation, the electrons are treated as independent particles, and the electron-electron interaction energy arises solely from the electrostatic energy

$$E_{\mathrm{es}}[n]=\frac{e^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} . \tag{2.11}$$

Furthermore, we assume that the kinetic energy is given by

$$T[n]=\int d\mathbf{r}\, t[n(\mathbf{r})] , \tag{2.12}$$

where $t[n]$ is the kinetic energy density for a system of noninteracting electrons with density n. This should be a good approximation if $n(\mathbf{r})$ varies sufficiently slowly in space that an electron at point $\mathbf{r}$ sees an essentially homogeneous medium with density $n(\mathbf{r})$. We have

$$t[n]=2\frac{1}{(2\pi)^3}\int_{|k|\le k_F} d\mathbf{k}\frac{\hbar^2k^2}{2m} , \tag{2.13}$$

where $2(4\pi/3)k_F^3/(2\pi)^3=n$. This gives

$$T_0[n]=C_k\int d\mathbf{r}[n(\mathbf{r})]^{5/3} , \tag{2.14}$$

where $C_k=3\hbar^2(3\pi^2)^{2/3}/10m$.

We now minimize the functional $E[n]$ under the subsidiary condition that the number of electrons is kept constant:

$$\int d\mathbf{r}\, n(\mathbf{r})=N . \tag{2.15}$$

Using the method of Lagrange multipliers, we require that

$$E[n]+\lambda N=T[n]+E_{\mathrm{es}}[n]+\int d\mathbf{r}\, n(\mathbf{r})[V_{\mathrm{ext}}(\mathbf{r})+\lambda] \tag{2.16}$$

has a minimum. The corresponding Euler equation is the well-known Thomas-Fermi equation

$$\tfrac{5}{3}C_k n(\mathbf{r})^{2/3}+e^2\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{\mathrm{ext}}(\mathbf{r})+\lambda=0 . \tag{2.17}$$

The Thomas-Fermi method has been used frequently in the past. The early work has been reviewed by Gombás (1949) and by March (1957), with a review of applications to atoms and molecules by March (1981). The TF method has been found to give a rough description of, for example, the charge density and the electrostatic potential. A number of theorems have been proved by Lieb and co-workers (Lieb and Simon, 1973; Lieb, 1976, 1981; Lieb and Thirring, 1976). In particular, it was shown that the Thomas-Fermi scheme is exact in the limit of infinite nuclear charge.

There are, however, severe deficiencies in the model. The charge density is infinite at the nucleus, and it does not decay exponentially far from the nucleus of an atom, but as r^{-6}. It has also been shown by Teller (1962), Balázs (1967), and Lieb and Simon (1973) that TF theory does not result in atoms binding to form molecules or solids. Another serious defect is the lack of shell structure in the TF atom, which means that the observed periodic variation of many properties with changing atomic number cannot be reproduced. In fact, the atoms shrink with increasing atomic number Z (as $Z^{-1/3}$; Lieb and Simon, 1973). Work has then focused on properties that are relatively insensitive to these deficiencies (for example, Alonso and Girifalco, 1977b; Jacob *et al.*, 1978; Gross and Dreizler, 1979) or to modifications of the method (e.g., Nordholm, 1987).

2. Modifications and improvements

We now consider improvements to the TF method. In Eqs. (2.11) and (2.12) we introduced two approximations; we consider them in turn. The kinetic energy was obtained by assuming that the density has slow spatial variations. This may be improved (Hohenberg and Kohn, 1964) by considering a system with the density

$$n(\mathbf{r})=n_0+\Delta n(\mathbf{r}) , \tag{2.18}$$

$$\int d\mathbf{r}\, \Delta n(\mathbf{r})=0 . \tag{2.19}$$

To second order in $|\Delta n(\mathbf{r})|/n_0$, the kinetic energy can be written

$$T[n]=T_u+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' K(|\mathbf{r}-\mathbf{r}'|)\Delta n(\mathbf{r})\Delta n(\mathbf{r}') , \tag{2.20}$$

where $T_u=C_k\int d\mathbf{r}[n_0]^{5/3}$. Because of Eq. (2.19), there is no first-order correction to (2.20); since we expand around the result for a homogeneous system, we can assume that $K(\mathbf{r},\mathbf{r}')$ depends only on the distance $|\mathbf{r}-\mathbf{r}'|$. The total energy of a system of noninteracting fermions in the presence of a weak external field $V_{\text{ext}}(\mathbf{r})$ is then

$$E[n]=T_u+\frac{1}{2(2\pi)^3}\int d\mathbf{q}\,K(\mathbf{q})|n(\mathbf{q})|^2+\frac{1}{(2\pi)^3}\int d\mathbf{q}\,V_{\text{ext}}(\mathbf{q})n(\mathbf{q})\ , \tag{2.21}$$

where we have introduced the Fourier transform $n(\mathbf{q})=\int d\mathbf{r}\exp(-i\mathbf{q}\cdot\mathbf{r})\Delta n(\mathbf{r})$. Minimizing the energy we find

$$n(\mathbf{q})=-V_{\text{ext}}(\mathbf{q})K(\mathbf{q})^{-1}\ . \tag{2.22}$$

Thus we can identify $-K(\mathbf{q})^{-1}$ with the response function for noninteracting electrons,

$$-K(\mathbf{q})^{-1}=-\frac{mk_F}{2\pi^2\hbar^2}\left[1+\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right]\ , \tag{2.23}$$

where $\eta=\mathbf{q}/2k_F$ and k_F is the Fermi wave vector of a system with density n. Since it may be difficult to define n_0 in a real system we rewrite (2.20) as

$$T[n]=C_k\int d\mathbf{r}[n(\mathbf{r})]^{5/3}-\tfrac{1}{4}\int d\mathbf{r}\int d\mathbf{R}\,K[\mathbf{r},n(\mathbf{R})]\left[n\left[\mathbf{R}+\frac{\mathbf{r}}{2}\right]-n\left[\mathbf{R}-\frac{\mathbf{r}}{2}\right]\right]^2\ , \tag{2.24}$$

which is identical to (2.20) to second order in $|\Delta n(\mathbf{r})|/n_0$. Although Eq. (2.20) has been derived for weak density variations, it should also be valid for strong variations, provided the variations over the range of K are small.

In Fig. 2 we show a plot of $K(q)$. The rapid increase for large q illustrates the large kinetic energy associated with rapid density variations. Following Jones and Young (1971) we approximate $K(q)$ as

$$K(q)=K(0)\left[\gamma+3\lambda\left[\frac{q}{2k_F}\right]^2\right]\ . \tag{2.25}$$

Using this approximation we can extract a gradient correction from the second term of (2.24):

$$T[n]=C_k\int d\mathbf{r}\{n(\mathbf{r})\}^{5/3}+\frac{\hbar^2\lambda}{16m}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}\ ; \tag{2.26}$$

i.e., Eq. (2.25) leads to a second-order gradient correction for $T[n]$. If we view (2.25) as a power expansion of $K(q)$ around $q=0$, we find $\lambda=\frac{1}{9}$ and $\gamma=1$. This result was obtained by Kompaneets and Pavlovskii (1957) and it is valid for spatially slow variations. On the other hand, we can expand $K(q)$ in the limit of large q (Jones and Young, 1971), giving $\lambda=1$ and $\gamma=-\frac{3}{5}$. This result was obtained by von Weizsäcker (1935); it should be valid for rapid but weak density variations. These two expansions of $K(q)$ are shown in Fig. 2, and it is clear why empirical determinations of λ usually have values between $\frac{1}{9}$ and unity.

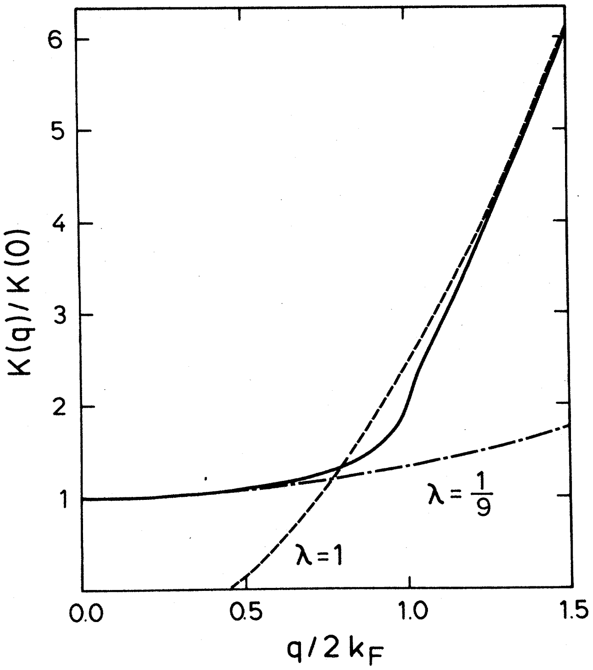

FIG. 2. Function $K(q)$ as a function of $q/2k_F$ (solid curve). The expansion (2.25) is also shown for $\lambda=\frac{1}{9}$ and 1 (dashed curves).

$K(q)$ has a logarithmic singularity at $q=2k_F$, and one should not expect an expansion in powers of q^2 to converge. It should be considered instead as an asymptotic expansion that is valid in the limit of slow density variations. The gradient corrections generated in this way are of second order in the density, and corrections of higher order can be obtained using a method of Kirzhnits (1957; see also Hodges, 1973). Tal and Bader (1978) have shown that such corrections diverge for atoms. The inclusion of the second-order gradient corrections removes several of the defects mentioned above. For example, the charge density is finite at a nucleus and decays exponentially far from an atom. While this modification leads to binding in N_2 (Yonei, 1971), it fails to predict a maximum in the binding energy of first-row dimers (Yonei, 1981). As an example of the accuracy that can result, we show in Table I the results of Wang *et al.* (1976), who calculated the two lowest-order gradient corrections for atomic (Hartree-Fock, hereafter referred to as HF) charge densities and compared the kinetic energies with HF values. The inclusion of the lowest-order correction improves the accuracy by an order of magnitude. The TF kinetic energy is smaller than the HF result in all cases considered. In fact, Lieb and Thirring (1976) proved that the correct kinetic energy is $\geq cT_{\text{TF}}$, where T_{TF} is the Thomas-Fermi kinetic energy and $c=0.277$ (Lieb, 1976). Lieb has conjectured that this inequality is valid for $c=1$, implying that the lowest-order gradient correction always has the correct sign. However, the next correction, T_4,

TABLE I. Kinetic energy of noble-gas atoms. T_{HF} and T_0 are the Hartree-Fock and Thomas-Fermi results, and T_2 and T_4 the lowest-order gradient corrections. T_0, T_2, and T_4 are evaluated for the Hartree-Fock (HF) density, the gradient terms using Eq. (2.26) with $\lambda=\frac{1}{9}$. The numbers in parentheses are the percentage deviations from the HF results (after Wang, *et al.*, 1976).

Atom	T_{HF}	T_0	T_0+T_2	$T_0+T_2+T_4$
He	2.8617	2.5605	2.8785	2.9631
		(−10.5)	(0.59)	(3.54)
Ne	128.55	117.78	127.79	129.72
		(−8.4)	(−0.54)	(0.96)
Ar	526.79	490.62	524.89	531.10
		(−6.9)	(−0.36)	(0.82)
Kr	2752.1	2594.2	2736.1	0.82
		(−5.7)	(−0.58)	(0.29)

sometimes improves and sometimes worsens the agreement. We note that Wang *et al.* (1976) used $\lambda=\frac{1}{9}$ in Eq. (2.26), and that the use of $\lambda=1$ would have led to large errors in Table I.

The gradient expansion has been tested by Ma and Sahni (1977) for a simple model of a metal surface, where the density gradient can be varied continuously. The potential is given by

$$V(z)=\frac{k_F^3}{2y_F}z\Theta(z)\ . \tag{2.27}$$

$\Theta(z)$ is the step function, so that the potential is constant inside the surface, while outside the surface it varies linearly with the distance z from the surface. For large y_F the density gradients are very small; for $y_F=0$ the so-called infinite barrier model is obtained. For this model, Ma and Sahni calculated the change in the kinetic energy when an infinite metal is cleaved into two semi-infinite systems. Their results are shown in Fig. 3. For small density gradients ($y_F \geq 2$), the difference between the exact and the TF values is not large, and the TF value is improved systematically when the T_2 and T_4 corrections are added. For small values of y_F the errors are larger; for y_F close to zero the fourth-order correction was found to be much too large, as was observed for several atoms.

A different approach has been taken by Alonso and Girifalco (1978), who expressed the kinetic energy of noninteracting electrons in terms of the joint density matrix and, for closed systems, derived an exact equation containing the pair correlation function $g(\mathbf{r},\mathbf{r}')$. If the local approximation for $g(\mathbf{r},\mathbf{r}')$ is now introduced, the result of von Weizsäcker (1935) is recovered. Alonso and Girifalco proposed, however, a nonlocal approximation for $g(\mathbf{r},\mathbf{r}')$ similar to the one used for the exchange-correlation energy (Alonso and Girifalco, 1977a; Gunnarsson *et al.*, 1977) and discussed in Sec. V. They showed that this approach improves the TF result for Ne substantially.

We have discussed so far how the treatment of the kinetic energy can be improved. The second major assumption of the TF theory is that the electrons are independent. As noted above, Dirac (1930) proposed the inclusion of an exchange term in the energy of the form

$$E_x^{\mathrm{LD}}=\int d\mathbf{r}\, n(\mathbf{r})\varepsilon_x[n(\mathbf{r})]\ . \tag{2.28}$$

Here $\varepsilon_x[n]$ is the exchange energy per electron of a homogeneous electron gas with density n. This approximation is equivalent to the approximation (2.12) for the kinetic energy. Correlation effects can be included easily in the same way, so that one arrives at formula (1.4). The accuracy of this formula is, of course, one of the main

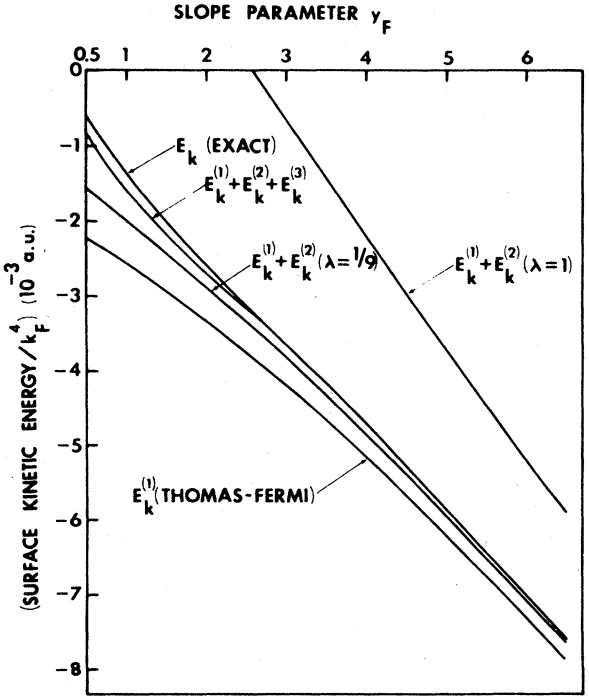

FIG. 3. Surface kinetic energy for the model potential (2.27) as a function of the slope parameter y_F. The exact result [E_k(EXACT)] is compared with the Thomas-Fermi result ($E_k^{(1)}$); with the lowest gradient expansion result ($E_k^{(1)}+E_k^{(2)}$) for both $\lambda=\frac{1}{9}$ and 1; and with the second-order gradient expansion result ($E_k^{(1)}+E_k^{(2)}+E_k^{(3)}$) (Ma and Sahni, 1977).

subjects of this paper. Here we note only that the use of the LD approximations (2.28) or (1.4) with the TF approximation leads to a discontinuous drop to zero of the charge density in the outer regions of an atom. This anomaly disappears if the gradient correction (2.26) is used.

Several modifications have been proposed to correct for the absence of shell structure in the TF model. Perhaps one of the best known is that used by Gordon and Kim (1972; see also Nikulin, 1971; Kim and Gordon, 1974; Clugston, 1978). In this model, the interaction energy between two closed-shell atoms or molecules is estimated by overlapping the HF densities of the free atoms (or molecules) and calculating the energy using the TF approximations (2.11) and (2.12) for the electrostatic and kinetic energy terms and Eq. (1.4) for the exchange-correlation energy. The energies of the constituents are estimated in the same way. In Table II we show that the results obtained for the rare-gas atoms are in remarkably good agreement with experiment.

Chelikowsky (1980) has introduced a pseudopotential method to treat cohesion in simple metals. In addition to the energy terms (2.11), (2.12), and (2.28), he also included the gradient correction (2.26) for the kinetic energy. Chelikowsky constructed a pseudopotential that, when used with the above functional, reproduces the charge density of a free atom outside the core region. Since the pseudopotential was adjusted to a quantum-mechanical atomic calculation, it contains implicitly some of the shell structure. Finally, the parameter λ in Eq. (2.26) was adjusted to yield the proper quantum-mechanical kinetic energy for the free atom. If the pseudopotential and the functional form are unchanged in the metal, it is straightforward to calculate properties such as the cohesive energy, lattice constant, and bulk moduli. In Table III we compare the results found using this method with experiment and with results of detailed calculations (see Sec. IV). Although some of the trends are not reproduced well, the overall agreement is good. It would be interesting to see how well the method describes systems containing atoms toward the ends of rows of the Periodic Table. A similar approach based on an Ashcroft pseudopotential and a gradient expansion with $\lambda=1$ has been applied to simple metals (Lopez *et al.*, 1980; Lopez and Alonso, 1981) and to simple and alkaline earth metal alloys (Iniguez and Alonso, 1981; Gonzalez and Alonso, 1982).

Various modifications of the TF method have also been applied to the cohesion of some transition and noble metals (Alonso and Santos, 1977), to chemisorption and vacancy formation (Gollisch and Fritsche, 1979), and to charge transfer in alloy formation (Alonso and Girifalco, 1977b). Although these modifications have been quite successful in particular applications, further systematic study is required. We note that the interaction between two open-shell atoms in N_2 (Yonei, 1971) required the use of a self-consistent charge density and the gradient correction for the kinetic energy. On the other hand, Shih (1979) arrived at the opposite conclusion for the Kim-Gordon description of the interaction between rare-gas atoms. He found substantially worse agreement with experiment if one used either a gradient correction or the HF densities of the molecules, not of the overlapped constituents. Some aspects of the gradient expansion have been discussed recently by Pearson and Gordon (1985) and by Perdew *et al.* (1988).

If we reduce the internuclear separation in systems with fixed atomic orbitals, we find striking differences between closed-shell and open-shell systems. The kinetic energy increases in the former, while the formation of bonding molecular orbitals in the latter tends to lower the kinetic energy. Thomas-Fermi theory leads to a kinetic energy increase when the internuclear separation is reduced, while the gradient term tends to lower the kinetic energy because of the reduced density variations in the bonding region. These arguments suggest that it will be difficult to find a modification of the TF method that describes bonding for different classes of systems.

The connection between the Kim-Gordon approach and the density functional scheme has been studied by Harris (1985). For weakly interacting fragments, i.e., for systems where the density is close to the overlapped density of the constituents, it is possible to derive a simple expression for the binding energy for a given geometry,

$$E_R \sim \sum_n a_n \tilde{\varepsilon}_n - \int d\mathbf{r}\, n_f(\mathbf{r})[\tfrac{1}{2}\varphi_f(\mathbf{r}) + V_{\mathrm{xc}}^{n_f}(\mathbf{r})] + E_{\mathrm{xc}}[n_f] + E_N^R \,, \tag{2.29}$$

where n_f is the sum of the densities of the fragments, φ_f and $V_{\mathrm{xc}}^{n_f}$ are the corresponding Coulomb and exchange-correlation potentials, and E_N is the internuclear repulsion. The $\tilde{\varepsilon}_n$ are eigenvalues of the potential

TABLE II. Binding energy ϵ and equilibrium internuclear separation r_m for rare-gas dimers according to Gordon and Kim (1972) and experiment.

	r_m (Å)		ϵ ($\times 10^{-16}$ ergs)	
Molecule	Calc.	Expt.	Calc.	Expt.
Ar—Ar	3.63	3.70	175	195
Ne—Ne	2.99	3.03	56	63
Kr—Kr	3.89	3.95	248	273
He—He	2.49	2.96	62.5	16.5

TABLE III. Cohesive energy of simple metals according to Chelikowsky (1980), C; density functional calculations (Moruzzi *et al.*, 1978), MJW; Vosko and Wilk (1980), VW; and experiment (Gschneidner, 1964).

Metal	C	MJW	VW	Expt.
Li	1.41	1.65	1.74	1.66
Na	1.22	1.12	1.21	1.26
K	1.07	0.90	0.96	0.94
Rb	0.99	0.64	0.76	0.88
Cs	0.94			0.83
Be		3.97		3.33
Mg	1.88	1.69		1.53
Ca	1.72	2.24		1.83
Sr		1.89		1.70
Al	2.98	3.84		3.34

$$\tilde{V}(\mathbf{r})=\varphi_f(\mathbf{r})+V_{\mathrm{xc}}^{n_f}(\mathbf{r})+V_{\mathrm{ext}}(\mathbf{r}) , \tag{2.30}$$

where V_{ext} is the external potential. Aside from small differences arising from differences in the description of exchange and correlation, the expression derived by Harris for the change in the energy has the same form as that of Kim and Gordon. The important difference is that the change in kinetic energy (for the case of bonding between two atoms A and B with potentials V_A and V_B) is

$$\delta T_\epsilon=2\sum_n \delta\tilde{\epsilon}_n-\int d\mathbf{r}\, n(\mathbf{r}_1)[\tilde{V}(\mathbf{r})-V_A(\mathbf{r}_1)] \\ -\int d\mathbf{r}\, n(\mathbf{r}_2)[\tilde{V}(\mathbf{r})-V_B(\mathbf{r}_2)] , \tag{2.31}$$

instead of the corresponding Thomas-Fermi equation.

In the case of He_2, Harris found that the change in kinetic energy was remarkably similar using both these approaches, a result that warrants further study, since the form of Eq. (2.31) does not suggest such a similarity. Harris also applied his approach to Be_2, C_2, N_2, F_2, and Cu_2. The results are in satisfactory agreement with self-consistent DF calculations, showing that the scheme provides a useful alternative for cases in which more detailed calculations would be prohibitive.

A different viewpoint on the deficiencies of the TF description of chemical bonding has been offered by Nordholm (1987). The kinetic energy functional (2.13) assumes that the electron density is able to fill all available phase space up to some energy E_F with equal occupancy of up and down spins, irrespective of whether these parts of phase space are dynamically connected or even accessible. Clear counterexamples are the hydrogen atom, where there is only one type of spin, or widely separated atoms, where the phase spaces for the atoms should not be connected. It has long been known (see, for example, Kauzmann, 1957) that such phase-space arguments have an important effect in determining the stability of molecules. When two atoms are brought together, the phase space for the electrons will initially increase and the kinetic energy will decrease. Such "nonergodic" effects are absent in standard TF theory. Nordholm has provided a prescription for incorporating them into the TF picture, and the initial results for small atoms are encouraging.

The problems with Thomas-Fermi-type approximations have led Herring (1986) to adopt a different starting point in his search for procedures for calculating the minimum kinetic energy consistent with a given particle density. He proposed separating the kinetic energy into a von Weizsäcker term [$\lambda=1$ in Eq. (2.26), but without the Thomas-Fermi term] plus an appropriate correction term. Herring (1986) gave an explicit equation for this correction term in one dimension, and the approach gives promising results (Herring, 1986; Herring and Chopra, 1988). It has not yet been extended to more than one dimension.

Finally, we note that the TF method cannot describe magnetic systems, since it never predicts ferromagnetism (Gunnarsson and Hjelmberg, 1975). Let us assume that the TF energy minimization results in a finite-spin polarization:

$$\zeta(\mathbf{r})=\frac{n_+(\mathbf{r})-n_-(\mathbf{r})}{n_+(\mathbf{r})+n_-(\mathbf{r})} , \tag{2.32}$$

where n_+ (n_-) is the spin-up (-down) density. If we then tried a different solution with $\zeta(\mathbf{r})$ identically zero, but with the total density unchanged, this would change only the kinetic energy (2.14) and the exchange energy (1.4). Electron gas calculations (see, for example, von Barth and Hedin, 1972; Gunnarsson and Lundqvist, 1976) show, however, that such a change would *lower* the total energy, at least for systems with metallic densities. For these systems, therefore, it is not possible to find a TF solution with $n_+(\mathbf{r})\neq n_-(\mathbf{r})$. This conclusion is not affected by the lowest-order gradient correction.

III. DERIVATION OF SINGLE-PARTICLE EQUATIONS

A. Exact single-particle description of a many-particle system

Practical applications of the formalism in the previous section usually rely on approximations related to the Thomas-Fermi approach; many of the drawbacks of this method can be traced to the approximate treatment of the kinetic energy. The task of finding good approximations to the energy functional is greatly simplified by using a different separation introduced by Kohn and Sham (1965),

$$E[n]=T_0[n]+\int d\mathbf{r}\, n(\mathbf{r})[V_{\mathrm{ext}}(\mathbf{r})+\tfrac{1}{2}\Phi(\mathbf{r})] \\ +E_{\mathrm{xc}}[n] ; \tag{3.1}$$

T_0 is the kinetic energy that a system with density n would have if there were no electron-electron interactions, Φ is the classical Coulomb potential for electrons, and E_{xc} may be viewed as a definition of the exchange-correlation energy. Although T_0 is different from the true kinetic energy T, it is of comparable magnitude and is treated *exactly* in this approach. The exact treatment of T_0 removes many of the deficiencies of the Thomas-Fermi approximation, such as the lack of a shell structure of atoms or the absence of chemical bonding in molecules and solids. In Eq. (3.1) all the terms but the exchange-correlation energy E_{xc} can be evaluated exactly, so that the (unavoidable) approximations for E_{xc} play a central role in the following discussion.

The variational principle applied to (3.1) yields

$$\frac{\delta E[n]}{\delta n(\mathbf{r})}=\frac{\delta T_0}{\delta n(\mathbf{r})}+V_{\text{ext}}(\mathbf{r})+\Phi(\mathbf{r})+\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$
$$=\mu\ , \tag{3.2}$$

where μ is the Lagrange multiplier associated with the requirement of constant particle number. If we compare this with the corresponding equation for a system with an effective potential $V(\mathbf{r})$ but *without* electron-electron interactions,

$$\frac{\delta E[n]}{\delta n(\mathbf{r})}=\frac{\delta T_0}{\delta n(\mathbf{r})}+V(\mathbf{r})=\mu\ , \tag{3.3}$$

we see that the mathematical problems are identical, provided that

$$V(\mathbf{r})=V_{\text{ext}}+\Phi(\mathbf{r})+\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\ . \tag{3.4}$$

The solution of (3.4) can be found simply by solving the Schrödinger equation for noninteracting particles,

$$[-\tfrac{1}{2}\nabla^2+V(\mathbf{r})]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r})\ , \tag{3.5}$$

yielding

$$n(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2\ . \tag{3.6}$$

It is necessary to satisfy the condition (3.4), and this can be achieved in a self-consistent procedure.

The solution of this system of equations leads then to the energy and density of the lowest state and to all quantities derivable from them. The formalism has also been generalized to the lowest state with a given set of quantum numbers (Gunnarsson and Lundqvist, 1976).[2] Instead of seeking these quantities by determining the wave function of the system of interacting electrons, the density functional method reduces the problem *exactly* to the solution of a single-particle equation of Hartree form. In contrast to the Hartree-Fock potential,

$$V_{\text{HF}}\psi(\mathbf{r})=\int d\mathbf{r}'V_{\text{HF}}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\ , \tag{3.7}$$

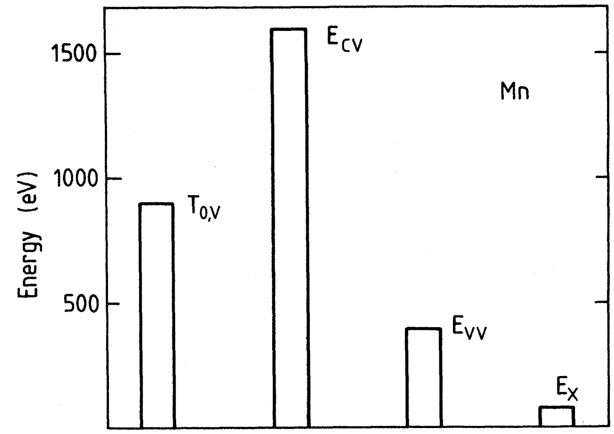

FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

the effective potential $V(\mathbf{r})$ is *local.* With a local approximation to E_{xc}, the equations present no more numerical complications than the solution of Hartree's equations. To illustrate the advantage of Kohn-Sham separation of the energy, we show in Fig. 4 the contributions of the valence electrons to the total energy of the manganese atom. The valence kinetic energy $T_{0,v}$, the electrostatic interaction between core and valence electrons E_{cv}, and the electrostatic interaction between valence electrons E_{vv} are all treated exactly. Only the exchange energy E_x and the even smaller correlation contribution require approximation. This is in marked contrast to the Thomas-Fermi and related methods, where the large kinetic energy term is approximated.

B. Exchange-correlation energy E_{xc}

The numerical advantages of the approach described are obvious. Efficient methods exist for solving single-particle Schrödinger equations with a local effective potential, and there is no restriction to small systems. We have noted, however, that the exchange-correlation energy E_{xc} is defined as the difference between the exact energy and other contributions that may be evaluated numerically exactly. In practice, it is necessary to make approximations for this term. To provide a perspective on such approximations, we now examine E_{xc} in detail.

The crucial simplification in the density functional scheme is the relationship between the interacting system, whose energy and density we seek, and the fictitious, noninteracting system for which we solve Eqs. (3.5) and (3.6). This can be studied by considering the interaction $\lambda/|\mathbf{r}-\mathbf{r}'|$ and varying λ from 0 (noninteracting system) to 1 (physical system). This is done in the presence of an external potential V_λ (Harris and Jones, 1974), such that the ground state of the Hamiltonian

$$H_\lambda=-\tfrac{1}{2}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_\lambda+\lambda V_{ee} \tag{3.8}$$

---

[2] In this case E_{xc} depends on the values of the quantum numbers. In varying the density we must remain inside the space of densities corresponding to the given quantum numbers. Approximate methods for minimizing the energy functional inside this space were discussed by Gunnarsson and Lundqvist (1976). Unfortunately, these authors were misquoted by Kohn and Vashishta (1983) on this point.

has density $n(\mathbf{r})$ for all λ. The exchange-correlation energy of the interacting system can then be expressed *exactly* in terms of an integral over the coupling constant λ (Langreth and Perdew, 1975; Gunnarsson and Lundqvist, 1976; Harris, 1984a),

$$E_{\rm xc}=\tfrac{1}{2}\int d\mathbf{r}\, n(\mathbf{r})\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r}) \;, \tag{3.9}$$

with

$$n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})\equiv n(\mathbf{r}')\int_0^1 d\lambda[g(\mathbf{r},\mathbf{r}',\lambda)-1] \;. \tag{3.10}$$

The function $g(\mathbf{r},\mathbf{r}',\lambda)$ is the pair correlation function of the system with density $n(\mathbf{r})$ and Coulomb interaction λV_{ee}. The exchange-correlation hole $n_{\rm xc}$ describes the effect of the interelectronic repulsions, i.e., the fact that an electron present at point $\mathbf{r}$ reduces the probability of finding one at $\mathbf{r}'$. The exchange-correlation energy may then be viewed as the energy resulting from the interaction between an electron and its exchange-correlation hole.

Three observations should be made here. First, since $g(\mathbf{r},\mathbf{r}')$ tends to unity as $|\mathbf{r}-\mathbf{r}'|\rightarrow\infty$, the above separation into electrostatic and exchange-correlation energies can be viewed as an approximate separation of the consequences of long- and short-range effects, respectively, of the Coulomb interaction. We may then expect that the total interaction energy will be less sensitive to changes in the density, since the long-range part can be calculated exactly.

The second observation (Gunnarsson and Lundqvist, 1976) arises from the isotropic nature of the Coulomb interaction V_{ee} and has important consequences. A variable substitution $\mathbf{R}\equiv\mathbf{r}'-\mathbf{r}$ in Eq. (3.9) yields

$$E_{\rm xc}=\tfrac{1}{2}\int d\mathbf{r}\, n(\mathbf{r})\int_0^\infty dR\, R^2\frac{1}{R}\int d\Omega\, n_{\rm xc}(\mathbf{r},\mathbf{R}) \;. \tag{3.11}$$

Equation (3.11) shows that the exchange-correlation energy depends only on the spherical average of $n_{\rm xc}(\mathbf{r},\mathbf{R})$, so that approximations for $E_{\rm xc}$ can give an *exact* value even if the description of the nonspherical parts of $n_{\rm xc}$ is quite inaccurate. Third, from the definition of the pair correlation function, there is a sum rule that requires that the exchange-correlation hole contain one electron, i.e., for all $\mathbf{r}$,

$$\int d\mathbf{r}' n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})=-1 \;. \tag{3.12}$$

This means that we can consider $-n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})$ as a normalized weight factor and can define locally the radius of the exchange-correlation hole,

$$\left\langle\frac{1}{\mathbf{R}}\right\rangle_{\rm r}=-\int d\mathbf{r}\frac{n_{\rm xc}(\mathbf{r},\mathbf{R})}{|\mathbf{R}|} \;. \tag{3.13}$$

This leads to

$$E_{\rm xc}=-\tfrac{1}{2}\int d\mathbf{r}\, n(\mathbf{r})\left\langle\frac{1}{\mathbf{R}}\right\rangle_{\rm r} \;, \tag{3.14}$$

showing that, provided the sum rule (3.12) is satisfied, the exchange-correlation energy depends only weakly on the details of $n_{\rm xc}$ (Gunnarsson and Lundqvist, 1976). In fact, we can say that it is determined by the first moment of a function whose second moment we know exactly.

C. Some exact results and inequalities for $E_{\rm xc}$ and $V_{\rm xc}$

In systems where the exact wave function is known, it is possible to determine not only the density, but also the correct forms of $E_{\rm xc}$ and $V_{\rm xc}$. Such calculations then provide an additional perspective on both the density functional and the Hartree-Fock approaches to electronic structure calculations. Wave functions of sufficient precision are known only for a few light atoms, but have been analyzed with interesting results (Almbladh *et al.*, 1983; Almbladh and Pedroza, 1984; Almbladh and von Barth, 1985b). A comparison of the exact HF and local densities, for example, showed that the LD results are slightly better than the HF for 2*s* functions and only slightly inferior for the 1*s* shell (Almbladh *et al.*, 1983). The resulting error in the Hartree potential is then rather small.

The exchange-correlation potential $V_{\rm xc}$ can be found from the single-particle equation (3.5). In the case of the He atom, with a single doubly occupied orbital with eigenvalue ϵ_i, the inversion of (3.5) is straightforward, leading to

$$V_{\rm xc}(\mathbf{r})=\frac{\nabla^2\varphi(\mathbf{r})}{2\varphi(\mathbf{r})}-V_{\rm ext}-\Phi(\mathbf{r})-\epsilon_i \;, \tag{3.15}$$

where $\varphi(\mathbf{r})=[n(\mathbf{r})/2]^{1/2}$. In atoms with more than two electrons, $V_{\rm xc}(\mathbf{r})$ may be parametrized and varied until the resulting density agrees with the exact distribution. A similar comparison can be made between the LD exchange-only potential and the HF value. Almbladh and Pedroza (1984) found that, although $E_{\rm xc}[n]$ is described rather accurately by LD approximations (the errors are of the order of 10%), errors in $V_{\rm xc}$ are substantially greater. This is illustrated in Fig. 5, where the LD and exact $V_{\rm xc}$ are shown for He, Li$^+$, and Be^{++}. Although the error in $V_{\rm xc}$ results in a large error in the eigenvalue, a feature in atoms that we discuss below, we see that the deviation of $V_{\rm xc}$ from the exact value is largely independent of the distance from the nucleus and results in small errors in the LD density profile. As numerically accurate densities become available for more systems, such comparisons could be very valuable in understanding deficiencies in particular approximations and in devising improvements.

As noted above, Lieb and collaborators have studied the mathematical structure of the TF method in detail. In an extension of this work, Lieb (1983) has addressed the problems of analysis that arise in discussing Coulomb systems, particularly those using the density functional approach. Lieb noted that there are serious analytical problems with density functional theory as described above ("It is not my intention to present a brief for Hohenberg-Kohn theory."). Some of these appear in the original formulation of the theory (Hohenberg and Kohn, 1964), because it is now known that not every $n(\mathbf{r})$ can be found from the ground state of some external potential $V_{xc}(\mathbf{r})$ (Levy, 1982; Lieb, 1983). This may be less serious, since such densities cannot be obtained for physical systems. The formulation of Levy (1979) furthermore extends the range of definition of the functional F in Eq. (2.2). Such problems are more serious in the Kohn-Sham formulation, since we require that the density $n(\mathbf{r})$ obtained for interacting electrons in the external potential $V_{\text{ext}}(\mathbf{r})$ can also be obtained for noninteracting electrons in some different potential $V'(\mathbf{r})$. If this requirement is not fulfilled, T_0 and E_{xc} cannot be defined. Levy and Perdew (1985b) and Hadjisavvas and Theophilou (1984) have shown, however, that one can solve the Kohn-Sham equations to self-consistency to obtain the ground-state energy of the real system, even if the density is not the noninteracting ground state of some $V(\mathbf{r})$. However, one obtains a hole or holes below the Fermi level in the noninteracting system.

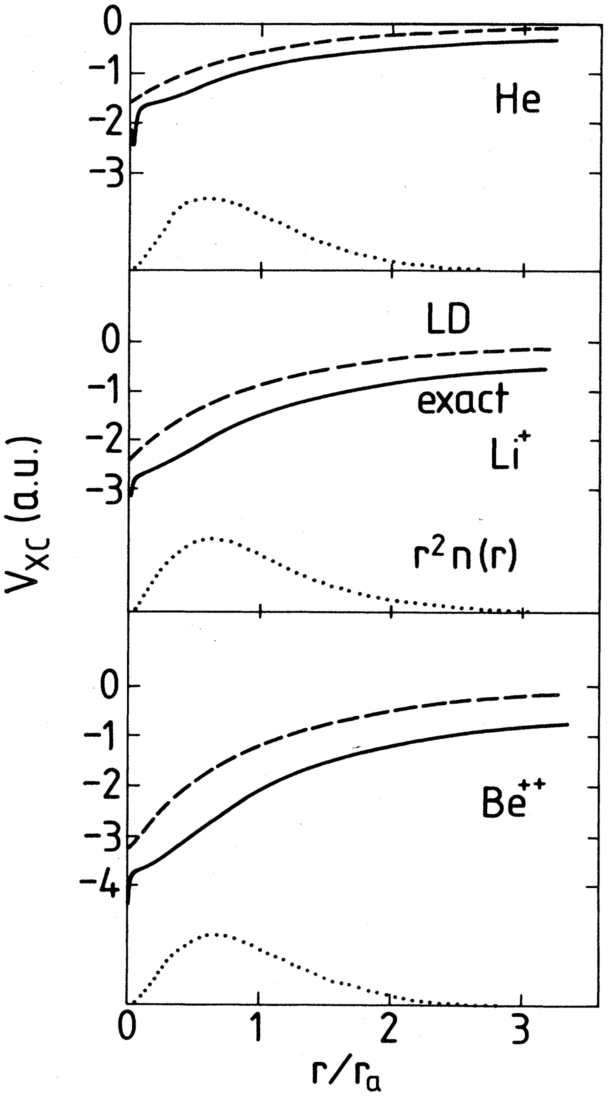

FIG. 5. Exchange-correlation potential V_{xc} (solid curve) and local-density (LD) value (dashed) for He, Li$^+$, and Be^{++}. The lengths are in units of atomic radii r_a (0.929, 0.573, and 0.414, a.u., respectively). The radial density is also shown (dotted curve). After Almbladh and Pedroza (1984).

In addition to pointing out difficulties in the formalism, Lieb and co-workers have studied upper and lower bounds of quantities of interest that may be described in terms of $n(\mathbf{r})$. We noted in Sec. II.B.2 that Lieb and Thirring determined an upper bound on the kinetic energy, and Lieb and Oxford (1981) also found a lower bound for the indirect part, E_ψ, of the repulsive Coulomb energy for the charge density $n_\psi(\mathbf{r})$ belonging to a given state ψ of N particles:

$$E_\psi = \left\langle \psi \left| \sum_{i<j}^{N} \frac{e_i e_j}{|\mathbf{r}_i - \mathbf{r}_j'|} \right| \psi \right\rangle - \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3.16}$$

satisfies

$$|E_\psi| \geq C \int d\mathbf{r}\, n(\mathbf{r})^{4/3} \tag{3.17}$$

with $C = 1.68$. This inequality applies, of course, to the *interaction* energy, but a related inequality applies also to E_{xc}. These inequalities, and possible extensions of them, could be useful in testing and improving approximations to E_{xc}.

D. Extensions to more general systems

The derivation of single-particle equations can be generalized in a straightforward fashion to spin systems, to finite temperatures, and to more complicated external potentials. These cases are reviewed by Rajagopal (1980) and by Kohn and Vashishta (1983), and we restrict our discussion to an outline of the analogies with the above quantities.

The extension to spin systems or an external magnetic field requires the consideration of the spin indices α of the one-electron operators $\psi_\alpha(\mathbf{r})$. In the most general case, this requires the replacement of V_{ext} by a spin-dependent potential $V_{\text{ext}}^{\alpha\beta}(\mathbf{r})$ and the charge density $n(\mathbf{r})$ by the density matrix

$$\rho_{\alpha\beta}(\mathbf{r}) = \langle \Psi | \psi_\beta^+(\mathbf{r}) \psi_\alpha(\mathbf{r}) | \Psi \rangle \ . \tag{3.18}$$

All ground-state properties are functionals of the density matrix $\rho_{\alpha\beta}$, and E is stationary with respect to variations in $\rho_{\alpha\beta}$, provided (von Barth and Hedin, 1972)

$$\sum_\alpha \int d\mathbf{r}\, \rho_{\alpha\alpha} = N \ . \tag{3.19}$$

The application of the variational principle requires that $\rho_{\alpha\beta}$ be N representable, which is guaranteed for all nonnegative, differentiable $\rho_{\alpha\beta}$ that satisfy Eq. (3.19) (see Gilbert, 1975; Harriman, 1981; Lieb, 1983). The effective spin-dependent potential in the single-particle equations is

$$V_{\mathrm{xc}}^{\alpha\beta}=\frac{\delta E_{\mathrm{xc}}}{\delta\rho_{\alpha\beta}(\mathbf{r})} , \tag{3.20}$$

and the analog of the exact equation for E_{xc} [Eqs. (3.9) and (3.10)] is

$$E_{\mathrm{xc}}=\tfrac{1}{2}\sum_{\alpha\beta}\int d\mathbf{r}\, n_{\alpha}(\mathbf{r}) \times\int d\mathbf{r}'\frac{n_{\beta}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\int_{0}^{1}d\lambda[g_{\alpha\beta}(\mathbf{r},\mathbf{r}';\lambda)-1] . \tag{3.21}$$

The generalization to finite temperatures was provided by Mermin (1965), who showed that, in a grand canonical ensemble at a given temperature T and chemical potential μ, the equilibrium density is determined by the external potential V_{ext}. The exact equilibrium density minimizes the grand potential:

$$\Omega\equiv\mathrm{Tr}\rho\left[H-\mu N+\frac{1}{\beta}\ln\rho\right] , \tag{3.22}$$

where ρ is the grand canonical density-matrix operator:

$$\rho\equiv\exp[-\beta(H-\mu N)]/[\mathrm{Tr}\exp-\beta(H-\mu N)] . \tag{3.23}$$

To define the single-particle equations analogous to Eq. (3.5), we can consider a fictitious system of noninteracting particles with kinetic energy T_0 and entropy S_0, both of which can be calculated in a straightforward fashion (Kohn and Vashishta, 1983). The single-particle equations have a potential of the same form as Eqs. (3.20) and (3.21), but with E_{xc} replaced by the exchange-correlation contribution to the free energy.

Spin-dependent systems at finite temperatures can be discussed by combining the above arguments (Gunnarsson and Lundqvist, 1976). A current- and spin-density functional theory for electronic systems in arbitrarily strong magnetic fields has been described by Vignale and Rasolt (1988). Further extensions can be made in the case of nonlocal potentials (Gilbert, 1975), and a discussion of the relativistic formulation of the DF formalism has been given by Rajagopal (1980). There has been much work on time-dependent density functional theory, which is essential for problems such as optical absorption or frequency-dependent polarizabilities. Following the work of Peuckert (1978), there have been a range of developments; these are surveyed by Zangwill (1983) and Bartolotti (1987).

IV. LOCAL SPIN-DENSITY APPROXIMATION AND ITS APPLICATIONS

In the previous section we have shown that the total energy of a system of interacting electrons in an arbitrary external field can be determined, in principle, by the solution of single-particle equations of Hartree-type. The only term that cannot be determined exactly is the exchange-correlation energy E_{xc}. By deriving an exact equation for E_{xc}, we have shown that it is insensitive to many of the details of the interactions in the system. However, it is by no means obvious that E_{xc} can be expressed simply and accurately in terms of the density. To illustrate, we show in Fig. 6 approximate densities for metallic Fe and Cu, obtained by superimposing atomic charge densities. We expect the correlation effects for Fe and Cu to be different, since Fe has a partly filled $3d$ band, while the Cu $3d$ band is full. Thus electron-hole pair excitations within the $3d$ band are possible for Fe but not for Cu. According to the theorem of Hohenberg and Kohn (1964), the exact functional makes this distinction between Fe and Cu. The similarity of the Fe and Cu densities shows, however, that the construction of approximate functionals is a nontrivial problem. A major part of this paper therefore addresses the accuracy of approximate functionals.

The DF formalism shows that it is possible, in principle, to determine the total energy using a functional that depends on the density alone and not the spin densities. The task of finding good approximations to the exchange-correlation energy is, however, greatly simplified if the functional is expressed in terms of the spin densities. This is the simplest way of satisfying the requirement (Hund's rule) that a state with a larger spin tends to be favored energetically. The importance of including this spin dependence in approximate functionals was observed early for the cohesive energy of alkali metals. In the LD approximation the cohesive energy of Na is about 25% too large (Tong, 1972), although one might expect the free-electron-like Na to be an ideal case for the LD approximation. The inclusion of the spin dependence by using the LSD approximation, however, was found to improve the description of the unpaired electron in the Na atom, thereby improving the cohesive energy (4% error) of the solid (Gunnarsson *et al.*, 1974). In this section we focus on the results obtained using such approximations, though it is important to note that they

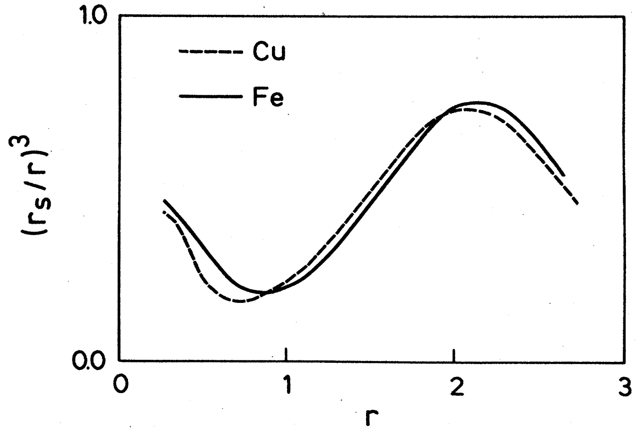

FIG. 6. Density of metallic Fe and Cu as a function of the radius r. The density n is expressed in terms of the parameter r_s, where $n=(4\pi r_s^3/3)^{-1}$.

break rotational invariance in spin space and represent an extension of the DF formalism.

The approximation used most widely in total energy calculations is the local spin-density (LSD) approximation,

$$E_{\rm xc}^{\rm LSD}=\int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{\rm xc}[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})] \ , \qquad (4.1)$$

where $\varepsilon_{\rm xc}[n_\uparrow,n_\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$, respectively. There have been numerous electron gas calculations performed over the years, and parametrizations of $\varepsilon_{\rm xc}[n_\uparrow,n_\downarrow]$ have been given by von Barth and Hedin (1972), Gunnarsson and Lundqvist (1976), Vosko *et al.* (1980), and Perdew and Zunger (1981), among others. Different calculations lead to somewhat different results, but all are free of adjustable parameters. Widely used also is the $X\alpha$ approximation, which is obtained if $\varepsilon_{\rm xc}$ in Eq. (4.1) is replaced by the exchange energy per electron and multiplied by $3\alpha/2$, i.e.,

$$E_x^{X\alpha}=-\tfrac{3}{2}\alpha C\int d\mathbf{r}\{[n_\uparrow(\mathbf{r})]^{4/3}+[n_\downarrow(\mathbf{r})]^{4/3}\} \ , \qquad (4.2)$$

where $C=3(3/4\pi)^{1/3}$. The parameter α has historical origins (Slater, 1974), but the α dependence of energy differences for a given atom or molecule is weak for values near $\frac{2}{3}$, the exchange energy value. Although different electron gas parametrizations lead to similar energy differences, and $X\alpha$ energy differences depend only weakly on α, there are systematic differences between the two sets of calculations. Use of the latter approximation leads to overestimates of the relative stability of states with larger spin densities. This is apparent in excitation energies in atoms and in molecules such as N_2 and CO, where molecular formation is accompanied by spin flips.

A. Atoms

Atoms and ions are particularly useful systems for testing schemes for energy calculations. Not only are the calculations relatively simple to perform, but the experimental information available on excitation energies is reliable and very extensive. The total energies of light atoms and ions can be found from the measured ionization energies. Extensive series of Hartree-Fock calculations can be used for comparison, and accurate CI calculations of the wave functions exist for some light atoms. In extended systems, by contrast, it is only possible to measure the total energy relative to the separated atoms, and exact calculations of the wave functions are presently out of the question. In most of the applications we focus on energy *differences.*

The atomic density distribution shown in Fig. 1 makes it clear that arguments based on small departures from homogeneity cannot be applied. However, we have seen in Sec. III that a partial cancellation of errors can be expected provided that the sum rule (3.12) is satisfied. This is the case in both the LSD and $X\alpha$ approximations, and it is instructive to compare the form of the exchange hole found in LSD calculations with that determined exactly, i.e., in a Hartree-Fock calculation. This is shown in Fig. 7 for two representative values of $\mathbf{r}$ in the nitrogen atom, and we see that the approximate and exact holes are qualitatively different. In particular, the approximate hole is spherically symmetric, while the exact hole is very asymmetric. The spherical average is, however, remarkably similar, and the values of the exchange energy differ by only a few percent. These results demonstrate clearly that the large differences in the exchange holes arise almost completely from the nonspherical components, which contribute nothing to the exchange energy. We can expect that this will also be true if we include correlation effects and if we apply the approximation to other systems with inhomogeneous density distributions.

1. Total energies

The total electronic energy of an atom can be determined if all the ionization energies are known. We show in Table IV the experimental total energies, the estimated relativistic contributions to the total energy, the HF energies with relativistic corrections, and the LSD total energies for first-row atoms. The LSD parametrization uses the paramagnetic term of Hedin and Lundqvist (1971) and the spin dependence of Gunnarsson and Lundqvist (1976). There are several points of interest. First, both the HF and the LSD methods lead to departures from experiment that are much greater than would be acceptable for any binding energies of interest. Both methods are dependent on error cancellation for any estimate of ener-

TABLE IV. Total energies in first-row atoms (Ry). Experimental energies $E_{\rm expt}$ and the estimated relativistic corrections $\Delta E^{\rm rel}$ are from Scherr *et al.* (1962); Hartree-Fock (HF) energies with relativistic corrections $E_{\rm HF}^{\rm rel}$ are from Clementi and Roetti (1974).

Atom	$E_{\rm expt}$	$\Delta E^{\rm rel}$	$E_{\rm HF}^{\rm rel}$	$E_{\rm LSD}^{\rm nonrel}$	$E_{\rm expt}-E_{\rm HF}^{\rm rel}$
Li	−14.957	−0.001	−14.866	−14.706	0.091
Be	−29.339	−0.004	−29.150	−28.909	0.188
B	−49.318	−0.011	−49.070	−48.653	0.248
C	−75.715	−0.025	−75.404	−74.958	0.310
N	−109.228	−0.050	−108.856	−108.298	0.373
O	−150.225	−0.090	−149.716	−149.064	0.508
F	−199.618	−0.150	−198.982	−198.336	0.635

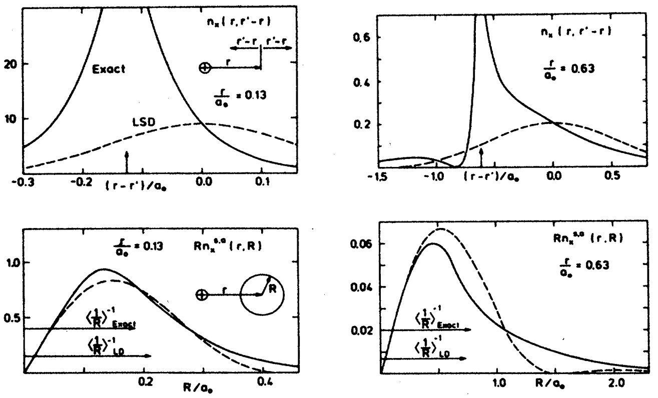

FIG. 7. Exact (solid line) and approximate (dashed line) exchange hole $n_x(\mathbf{r},\mathbf{r}'-\mathbf{r})$ [Eq. (3.10)] for a spin-up electron in a nitrogen atom for $r=0.13$ and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. The arrow indicates the nuclear position and $\mathbf{r}-\mathbf{r}'=0$ gives the electron position. The exact hole has a large weight at the nucleus, while the approximate hole is centered at the electron. The lower figure shows the spherical average of the hole around the electron. The area under the curve is proportional to the exchange energy. The figure also shows the value of $\langle 1/\mathbf{R}\rangle_r$ defined in Eq. (3.13).

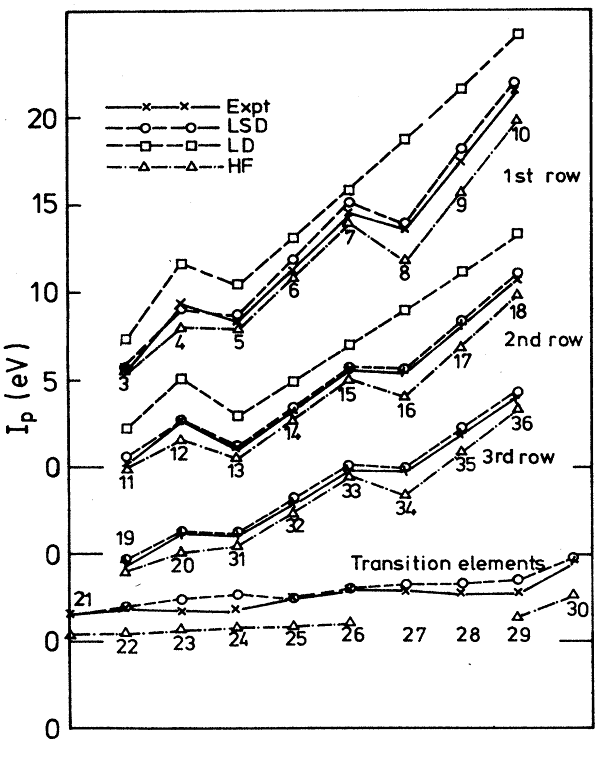

FIG. 8. First ionization energy of atoms in the local-density (LD), local spin-density (LSD), and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. For reasons of clarity, the zero of energy is shifted by 5, 10, and 15 eV for the second row, the third row, and the transition-element row, respectively. The LD results for the first and second rows are increased by an additional 2 eV.

gy differences. Second, the HF total energies are somewhat closer to experiment than are the LSD values. This is also true for the LSD parametrizations of von Barth and Hedin (1972), Gunnarsson and Lundqvist (1976), and Vosko *et al.* (1980).

2. Ionization energies

The energy required to remove a single electron is known accurately for most atoms (Moore, 1949, 1952, 1958). In Fig. 8 we compare the values for some light atoms with HF values and with values calculated using LD and LSD approximations. The calculated values are found from differences between calculations for the ground states of the atom and ion, respectively, $I_p = E_0^{N-1} - E_0^N$. Agreement with experimental trends is significantly better using the LSD approximation than with either the LD functional or the HF method. Cases involving half-filled shells, in particular, are more accurately given. An example is the break between N and O in an otherwise smooth curve. In *N*, the *p* electron removed has its spin parallel to the others ($p_{\uparrow\uparrow\uparrow} \rightarrow p_{\uparrow\uparrow}$), whereas in O it is antiparallel ($p_{\uparrow\uparrow\uparrow\downarrow} \rightarrow p_{\uparrow\uparrow\uparrow}$) and more

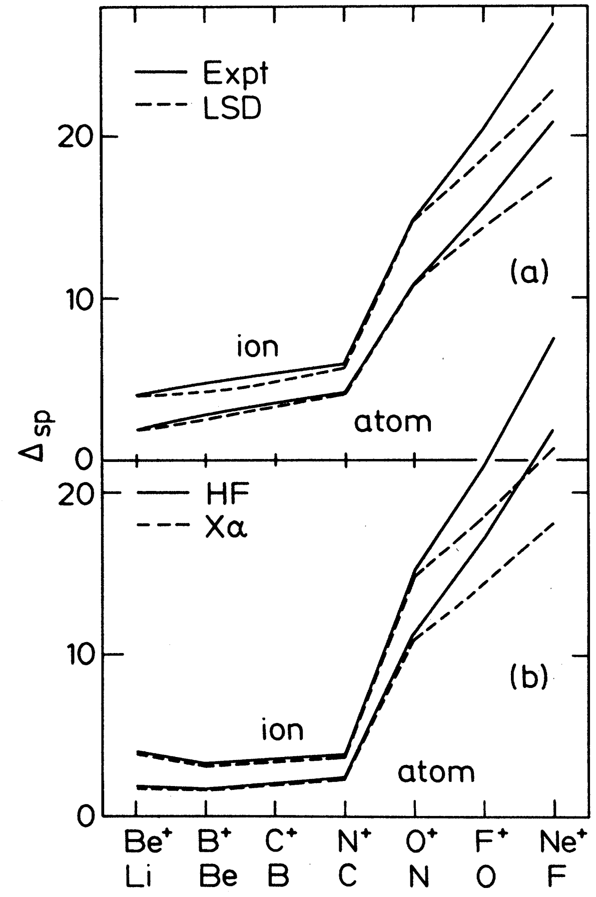

FIG. 9. The *sp* transfer energies Δ_{sp} for the first-row atoms and ions: (a) experimental and local spin-density (LSD) results; (b) Hartree-Fock (HF) and $X\alpha$ results. The energies are in eV.

weakly bound. The HF approximation, which neglects correlations between antiparallel spins, does not describe such energy differences accurately.

3. Transfer energies

When atoms bind to form a molecule or solid, there is generally a change in the relative $s,p,d,\ldots,$ contributions to the wave function. Such energy transfers can be studied directly in atoms by calculating the energy required to change an s electron into a p electron, for example, the $^4S(2s\,^22p^3)$ ground state of N into the $^4P(2s\,^12p^4)$ excited state. Since these are the lowest-lying states of these symmetries, density functional calculations are justified by the extension of Gunnarsson and Lundqvist (1976) to the original formalism.

In Fig. 9 we compare experimental *sp* transfer energies for first-row atoms and ions with the results of LSD calculations (Gunnarsson and Jones, 1985b). For atoms we define

$$\Delta_{sp}=E(1s\,^22s2p^{n-1})-E(1s\,^22s\,^22p^{n-2})\ , \qquad (4.3)$$

with a similar definition for the ions. While the overall trends are given well, the absolute deviations in ΔE_{sp} are of variable quality, with particularly large deviations in the cases of O and N. Shown also are the HF (Verhaegen and Moser, 1970; Fraga *et al.*, 1971) and the $X\alpha$ results. The trends are given fairly well by these calculations; however, there are significant errors, and the comparison with experiment shows differences between the first and second halves of the row.

In Fig. 10 we show corresponding values for *sd* transfer energies in iron-series atoms and ions (Gunnarsson and Jones, 1985b). In this case we write

$$\Delta_{sd}=E([\text{core}]3d^{n-1}4s^1)-E([\text{core}]3d^{n-2}4s^2)\ , \qquad (4.4)$$

with the definition for ions involving one less s electron in each case. The trends are given well, but the LSD approximation overestimates the relative stability of

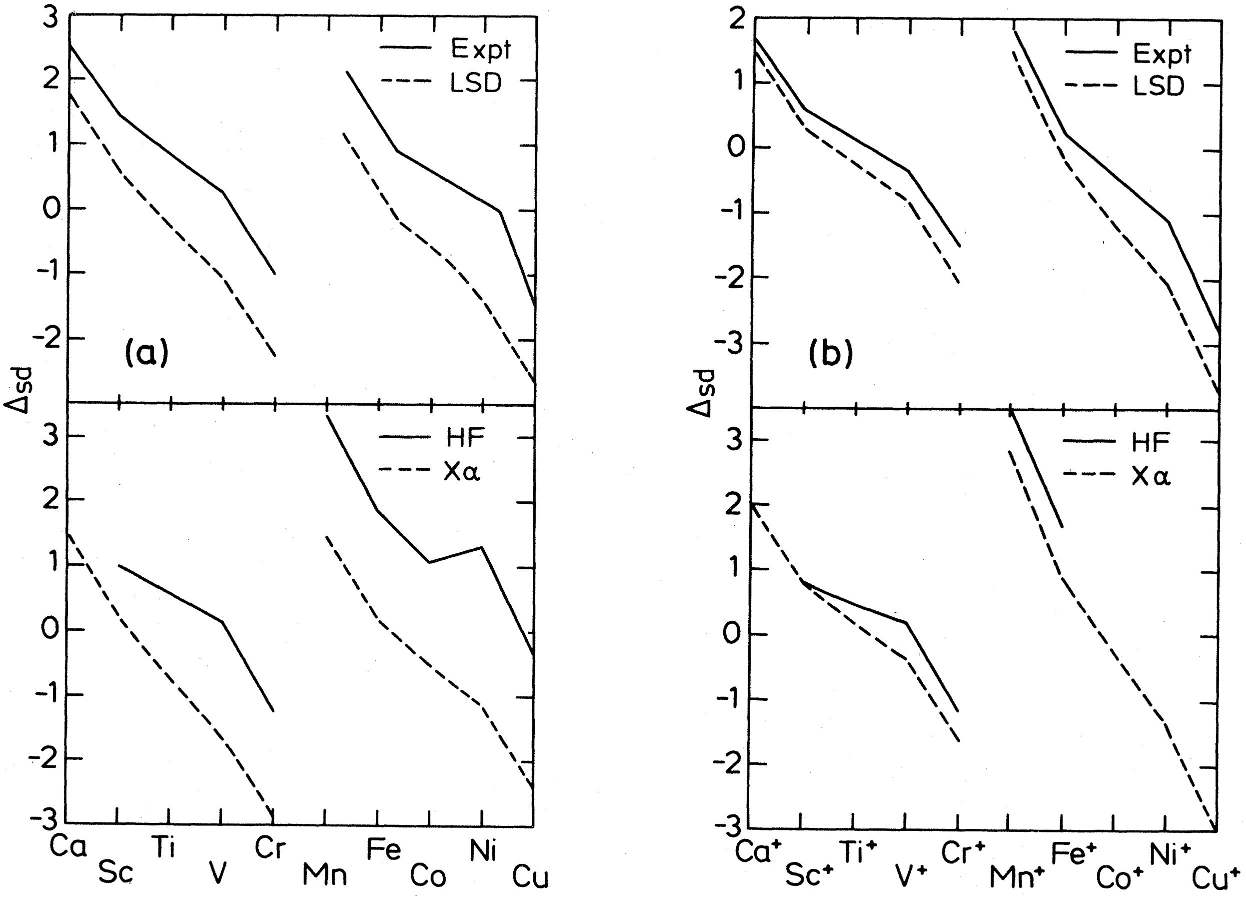

FIG. 10. The *sd* transfer energies Δ_{sd} for (a) $3d$ atoms and (b) $3d$ ions. In the upper panels, local spin-density (LSD) and experiment are compared; in the lower panels, $X\alpha$ and Hartree-Fock (HF) are compared.

configurations with more d electrons by ~ 1 eV in the atoms and by ~ 0.5 eV in the ions. The deviations from experiment are more systematic than for the HF values, particularly for the break in the center of the series. These results do not include relativistic effects. Hartree-Fock calculations by Martin and Hay (1981) show that such effects tend to stabilize configurations with larger s occupancies for the iron-series atoms by $\sim 0.1-0.3$ eV.

Local spin-density calculations have also been performed for other series of atoms (see, e.g., Harris and Jones, 1979b; Jones, 1979; Glötzel, 1980). Although the LSD approximation gives a good description of trends in all cases, there is a consistent tendency to overestimate the stability of p or d occupancy relative to s occupancy, and of f occupancy relative to d occupancy (Glötzel, 1980; see Fig. 11). The large overestimate (~ 2 eV) in the rare earths should caution against overinterpreting the results of LSD calculations on mixed-valent materials, where Δ_{df} is a quantity of interest. Essential to the reproduction of the experimental trends is the use of the *spin*-dependent LSD approximation. Qualitatively inferior results are obtained using the spin-free (LD) approach.

The description of the trends in energy differences given by the HF approximation is not as good as that provided by the LSD approach. As noted in Sec. I, however, the CI method provides a systematic way of improving on the HF wave function and energy by considering more than a single determinant. The present systems demonstrate that such improvements are by no means trivial, as shown by the results of Sasaki and Yoshimine (1974) for first-row atoms. These authors used an extensive basis set (35 orbitals, up to $l=6$, expanded in terms of 47 Slater-type orbitals) and single, double, triple, and quadruple excitations. For first-row atoms, the calculated correlation energies are 3–5 % different from the experimental values, and Δ_{sp} in carbon is ~ 0.1 eV in error. Bauschlicher and Shavitt (1978) have studied the basis-set dependence of both the total energy and the quintet-triplet splittings in carbon. To compute the splitting to within 0.05 eV of the experimental value requires at least a triple-zeta basis with two sets of polarization functions and CI with single and double excitations. Reliable calculations of Δ_{sd} are even more difficult to perform. Bauschlicher *et al.* (1982) found improved results using CI calculations; however, the agreement with experiment is noticeably better in the first half of the iron series, Sc–Cr, where the two states in question have different numbers of paired electrons, than in Mn–Cu.

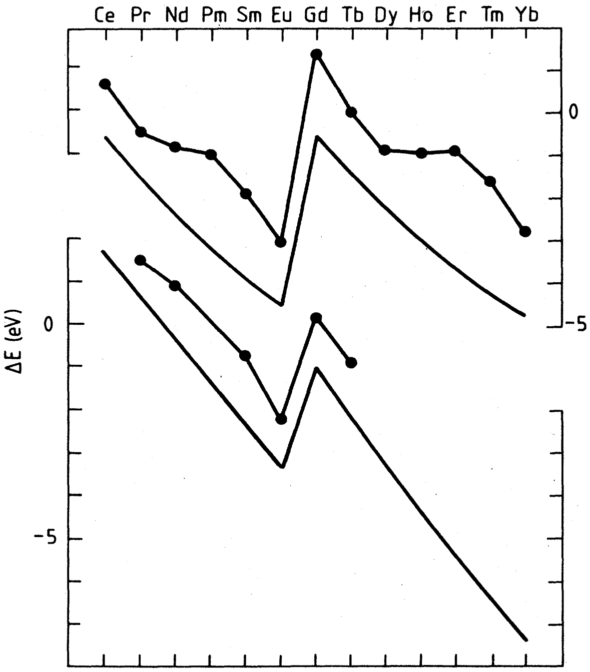

FIG. 11. The df transfer energies $\Delta_{df}[E(f^{n-3}ds^2)-E(f^{n-2}s^2)]$ for rare-earth and actinide atoms (Glötzel, 1980). The calculations (solid lines) are for spherically averaged densities.

4. Multiplet structure

The calculation of multiplet structures using the density functional formalism requires care. In the above discussion of the LSD approximation, the only input required to calculate the energy of the lowest-lying state is the total density and the spin density. It is easy to find cases, however, in which this leads to serious inconsistencies (von Barth, 1979). In the $1s2s$ configuration of He, for example, the $M_S=1$ and $M_S=0$ components of the ^3S state have different spin densities, and the LSD approximation splits the degeneracy by 1.82 eV. Furthermore, the ^1S and the $M_S=0$ component of the ^3S state have identical densities and spin densities, resulting in an artificial degeneracy.

Insight into such problems was provided by Ziegler *et al.* (1977) and by von Barth (1979). Ziegler *et al.* focused on the exchange energy, for which we have an exact equation—analogous to Eq. (3.21)—in terms of the pair correlation functions $g_{\alpha\beta}$. The LSD approximation assumes that $g_{\uparrow\downarrow}$ and $g_{\downarrow\uparrow}$ are both unity. Since this is true for states that can be represented by a single determinant, Ziegler *et al.* suggested that LSD calculations be performed only in such cases. In general, a single determinant is not an eigenstate of $\hat{L}^2$ and $\hat{S}^2$, and a multiplet description requires a linear combination of determinants. The total energy calculated from a single determinant can be represented as a weighted sum of multiplet energies. Provided that the number of determinants with different energies equals the number of multiplets (a situation that by no means always holds), the energies of the latter can be found. The justification of this technique requires a generalization of density functional theory to states of mixed symmetry (von Barth, 1979).

Initial tests of this scheme were encouraging, in that some of the cruder defects of the LSD scheme were removed. It is restricted, however, to those cases described above and cannot be applied in larger systems, where the number of determinants with different energies is usually less than the number of multiplets. Furthermore, Gunnarsson and Jones (1980b) found that the lack of electron-hole symmetry inherent in the LSD approximation in some cases led to significantly greater errors for multiplet splittings in the second half of first-row atoms than for atoms in the first half. We return to this point in Sec. V.A.1.

Atomic multiplet structures also provide an interesting point of comparison with experiment and with other calculations. As noted by Slater (1960a), the HF method leads to energy spreads of multiplets that are substantially greater than experiment. Wood (1980) has carried out multiplet structure calculations for eight light atoms and their ions using the $X\alpha$ and LSD functional forms and compared the results with experiment and with HF values. The $X\alpha$ scheme reproduces the HF splittings well, essentially independent of the value of α used. The LSD results are in good agreement with experiment, as illustrated in Fig. 12 for P and P^+. Wood observed that all of these methods lead to unsatisfactory total energies.

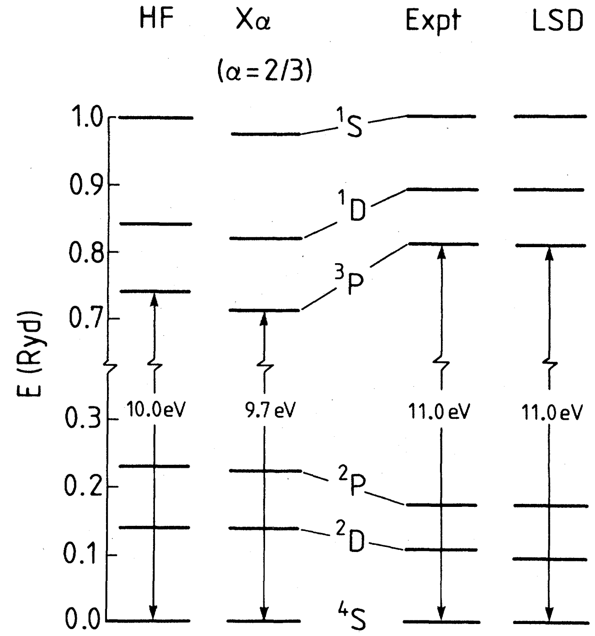

FIG. 12. Multiplet structures for P and P^+ for Hartree-Fock (HF), $X\alpha$ ($\alpha=\frac{2}{3}$), and local spin-density (LSD) calculations, compared with experiment (after Wood, 1980). The lowest levels are set to a common zero.

B. Molecules

The molecular calculations discussed below are a selection of the many that have been performed and serve to illustrate the level of accuracy to be expected from LSD calculations. Of particular interest is the question of whether the single-particle DF method can give satisfactory results in cases where the single-particle HF approximation leads to qualitatively incorrect results.

In discussing the results of calculations using local-density approximations, it is essential to separate the consequences of the LD approximation from those of a numerical nature. An important example is provided by the many calculations of molecular and cluster properties that have used the $X\alpha$ approximation and the scattered wave (Slater, 1974), or Korringa-Kohn-Rostoker, method to solve equations of the form (3.5). In a number of cases, such calculations gave spectacularly incorrect predictions of ground-state geometries, examples being a repulsive energy curve in C_2 (Danese, 1974; experimental well depth 6.3 eV) and a linear geometry for H_2O (Connolly and Sabin, 1972; experimental bond angle 104.5°). These results, and some of the exaggerated claims by protagonists of the method, have not helped density functional methods gain wide acceptance. However, scattered wave calculations use an additional assumption in evaluating the energy, namely, the muffin-tin approximation for the potential $V(\mathbf{r})$ and the density $n(\mathbf{r})$. This assumes that the potential and density are spherically symmetric in spheres centered on the nuclei, and constant elsewhere. It is a poor approximation in open systems such as molecules, and it neglects the buildup of charge density along the bond. On the other hand, accurate LSD calculations for very small molecules, such as H_2 and H_3, showed that the LSD approximation gave very good results for these s-bonded molecules (Gunnarsson *et al.*, 1975; Gunnarsson and Johansson, 1976). There are now several different numerical methods available also for larger molecules that use the full potential (i.e., include non-muffin-tin components) but use different basis sets (Slater-type orbitals: Baerends and Ros, 1978; Gaussian-type orbitals: Dunlap *et al.*, 1979; Painter and Averill, 1982, 1983; linearized muffin-tin orbitals: Jones, 1982a; plane waves: Hohl *et al.*, 1988). It is encouraging that these methods give similar results for the first-row dimers, so that we may confidently ascribe remaining discrepancies with experiment to the local-density approximation.

The single-particle picture basic to the DF formalism is of particular value in discussing the results obtained. In common with other methods of electronic structure calculations (Mulliken, 1942; Walsh, 1953; Buenker and Peyerimhoff, 1974), it is often possible to obtain insight into bonding mechanisms by studying the variation of the single-particle eigenvalues with changing geometry (Walsh diagrams). If we assume that the atomic core densities are frozen and do not overlap, the total energy E can be separated rigorously into core (E_c) and valence (E_v) contributions (Gunnarsson *et al.*, 1977a, 1977b). The large contribution E_c is geometry independent, and E_v is a functional of n_v alone. It can be written in terms of the valence eigenvalues of Eq. (3.5) as

$$E_v[n_v]=\sum_n^{\text{val}} f_n\varepsilon_n+\int d\mathbf{r}\, n_c(\mathbf{r})\{\varepsilon_{\text{xc}}[n(\mathbf{r})]-\varepsilon_{\text{xc}}[n_c(\mathbf{r})]\}+\int d\mathbf{r}\, n_v(\mathbf{r})[\tfrac{1}{2}\varphi_v(\mathbf{r})+\varphi_c(\mathbf{r})+V_{\text{ext}}(\mathbf{r})-V(\mathbf{r})]+\tfrac{1}{2}\sum_{i\neq j}\frac{Z_{ci}Z_{cj}}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{4.5}$$

Here $Z_{ci}\equiv Z_i-\int d\mathbf{r}\, n_{ci}(\mathbf{r})$ is the net charge on the core of atom i (with atomic number Z_i), and φ_v and φ_c are the Coulomb potentials corresponding to n_v and n_c, respectively. The second term in (4.5) is small and slowly varying. Apart from the eigenvalue sum, the remaining contributions to E_v increase as the atoms approach each other (Gunnarsson *et al.*, 1977a, 1977b). While the sum over the eigenvalues cannot be identified with the total energy, the decreasing value of this term as the atoms approach is essential for a stable bond.

1. First-row dimers

Diatomic molecules of first-row atoms have provided a testing ground for numerous methods of electronic structure calculations, including density functional methods. In Table V we compare measured well-depths (Huber and Herzberg, 1979) for first-row dimers with values calculated using Hartree-Fock (Cade and Wahl, 1974), LSD, and $X\alpha$ (Painter and Averill, 1982) approximations. The HF approximation leads to substantial underestimates of the binding energies, particularly for singlet ground states. The LSD values consistently overestimate the stability of these molecules, although the deviations from experiment are small for H_2 and Li_2. The overestimates are greatest for molecules in the second half of the series. As noted above, the LSD and $X\alpha$ approximations give similar energy differences in cases where the change in spin density on bonding is small.

The equilibrium separations calculated using the LSD and $X\alpha$ approximations are generally in good agreement with experiment, with an overestimate of 1–2% being common (Baerends and Ros, 1978; Dunlap *et al.*, 1979; Jones, 1982a; Painter and Averill, 1982; Becke, 1986). There is a corresponding underestimate in the ground-state vibration frequencies. In cases where it leads to an energy minimum, the HF approximation usually leads to a small underestimate of r_e. We note here that the dipole moment of CO and its variation with internuclear separation are given significantly better by the LSD approximation than by the Hartree-Fock approximation (Gunnarsson *et al.*, 1977a, 1977b).

TABLE V. Experimental and calculated well-depths for the experimental ground states of the first-row dimers. Hartree-Fock (HF) calculations for Be_2 give a purely repulsive energy curve.

Molecule	Expt.[a]	LSD[b]	$X\alpha$[b]	HF[c]
H_2	4.75	4.91	3.59	3.64
Li_2	1.07	1.01	0.21	0.17
Be_2	0.10	0.50	0.43	
B_2	3.09	3.93	3.79	0.89
C_2	6.32	7.19	6.00	0.79
N_2	9.91	11.34	9.09	5.20
O_2	5.22	7.54	7.01	1.28
F_2	1.66	3.32	3.04	−1.37

[a] Huber and Herzberg (1979); Bondybey and English (1984), Be_2.

[b] Painter and Averill (1982).

[c] Total energies for experimental geometry from Cade and Wahl (1974).

2. Alkaline earth dimers

While the LSD and HF approximations generally lead to similar bond lengths in first-row molecules, there is a striking difference in the case of Be_2. Here, as in the other group-IIA dimers (Mg_2,Ca_2,Sr_2,. . .), the lowest-lying state is $^1\Sigma_g^+[1\sigma_g(\uparrow\downarrow)1\sigma_u(\uparrow\downarrow)]$; i.e., there is an equal occupancy of bonding and antibonding orbitals. Hartree-Fock calculations (e.g., Blomberg *et al.*, 1980) lead to repulsive curves, and it has been the general view for many years that binding, if present, must be due to polarization (van der Waals) forces (e.g., Furry and Bartlett, 1931; Bender and Davidson, 1967; Jordan and Simons, 1976; Schaefer *et al.*, 1976; Miller *et al.*, 1977). The bond strengths should then increase in the order $Be_2\rightarrow Mg_2\rightarrow Ca_2,\ldots,$ due to the corresponding increase in atomic polarizabilities (Maeder and Kutzelnigg, 1976). The earliest CI calculations supported this picture, with Be_2 having a very weak bond with an equilibrium separation near 9 a.u. (e.g., Blomberg and Siegbahn, 1978).

The local-density approximation gives qualitatively different bonding trends in this family of molecules (Jones, 1979). The energy curves show minima in all cases, and the equilibrium separations in Mg_2 and Ca_2 agree very well with measured values (7.351 and 8.083 a.u., respectively). The bond length in Be_2 (4.86 a.u.) was found to be much shorter than those of previous calculations. Most striking, however, is the variation in well-depth shown in Fig. 13. The energy minimum in Be_2 is deeper than in Mg_2, and the variation with atomic number parallels the irregular behavior observed in the bulk cohesive energies (Fig. 13; Gschneidner, 1964; Moruzzi *et al.*, 1978). The binding energies in the molecules and solids are overestimated by the local-density approximation in those cases where experimental values are known. The error is significant in Be_2, as we show in Table VI, where we include the results of subsequent LD (Jones, 1982b; Painter and Averill, 1982) and CI (Harrison and Handy, 1983; Lengsfield *et al.*, 1983) calculations, as well as the gas phase experimental results of Bondybey and English (1984). The experimental value of the equilibrium separation is in remarkably good agreement with the density functional result, and the extensive CI calcula-

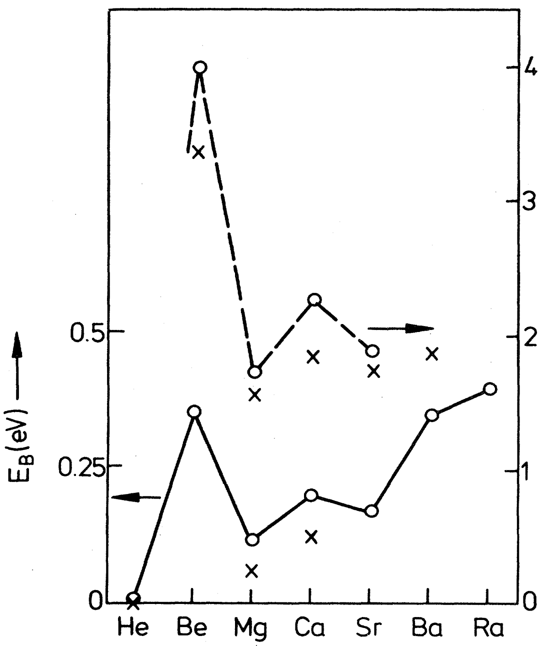

FIG. 13. Well-depths calculated for $^1\Sigma_g^+$ state of group-IIa dimers (solid line, left scale, Jones, 1979) and cohesive energies of bulk materials (dashed line, right scale, Moruzzi *et al.*, 1978). Corresponding experimental values (crosses) are given where known (Gschneidner, 1964; Huber and Herzberg, 1979).

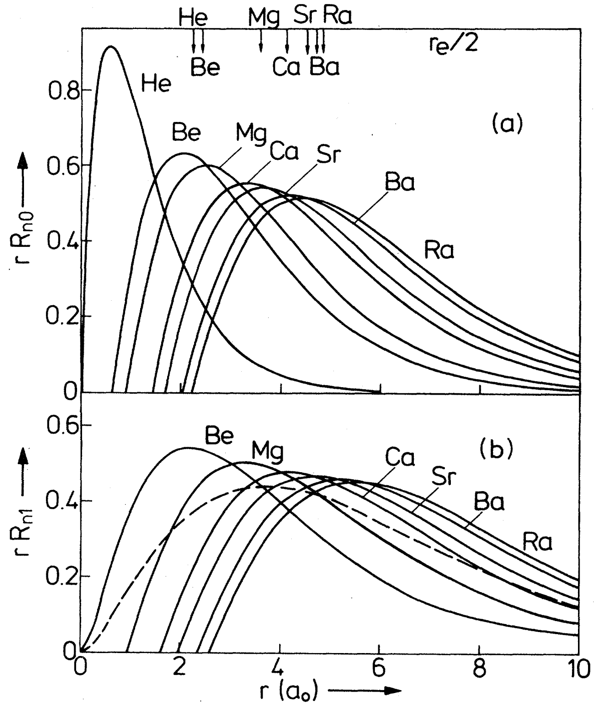

FIG. 14. Tails of valence wave functions for group-IIa atoms: (a) *s* functions for the $^1S(ns^2)$ states; (b) *p* functions for the $^3P(ns^1np^1)$ state. The dashed curve is the $2p$ function of He ($1s2p$). Also shown (arrows) are distances corresponding to half the calculated equilibrium separation in each dimer (Jones, 1979).

tions reproduce both the well-depth and the equilibrium separation satisfactorily. The Be_2 molecule has proved to be a severe test of CI methods, since essentially all of the correlation energy must be found in order to obtain a satisfactory energy curve.

The density functional picture of bonding in this series is very different from that of weakly interacting closed-shell systems bound by polarization forces. The plots of the valence orbitals (Fig. 14) show that, except in He_2, there is a substantial overlap between the densities of the two atoms. This is particularly true in Be_2. It is also interesting that the radial extent of the orbitals does not increase smoothly with increasing core size, but shows what might be termed a "secondary periodicity." In Mg, for example, the $3s$ orbital is relatively compact. The $2p$ functions introduced into the core have no repulsive (orthogonalization) effect on the $3s$ function and are sufficiently extended that the increased core charge is incompletely screened. A similar effect is evident in Sr and Ra, where $3d$ and $4f$ functions are present in the core for the first time. The unoccupied *p* orbitals are generally more extended than the *s* valence functions. Figure 14 shows that Be is an exception. There are no *p* states in the core, and the effective potential experienced by the $2p$ state is more attractive. The similar extent of the $2s$ and $2p$ orbitals suggests that *sp* mixing will be favored.

TABLE VI. Spectroscopic constants of Be_2 ($^1\Sigma_g^+$).

	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
Expt.[a]	4.658	223.4	~0.11
CI[b]	4.73±0.03		0.09±0.01
CI[c]	4.78		0.10(est)
CI[d]	4.9		0.04
LD-LMTO[e]	4.67	360	0.48
LD-LCAO[f]	4.63	362	0.50

[a] Bondybey and English (1984).
[b] Lengsfield *et al.* (1983).
[c] Harrison and Handy (1983).
[d] Blomberg *et al.* (1980).
[e] Jones (1982b).
[f] Painter and Averill (1982).

The importance of *sp* hybridization is also evident in the self-consistent valence eigenvalues ϵ_i for molecules in this series (Jones, 1979). In He_2, the σ_g and σ_u eigenvalues are remarkably symmetrical about the atomic eigenvalue. The wave-function overlap is very small, so that the weak minimum in the energy curve may be considered a van der Waals minimum. The Be_2 eigenvalues show a pronounced asymmetry; i.e., the eigenvalue sum in Eq. (4.5) gives a bonding contribution. The Mg_2 curves are more symmetric, but there is a net bonding in the heavier molecules associated with the increasing importance of *sd* mixing. This picture of bonding in these molecules is very much in accord with the pseudopotential theory of cohesion in the bulk, namely, a stronger *sp* hybridization in Be than in Mg, and the increasing importance of *sd* hybridization with increasing atomic number. Few solid state physicists seem to be surprised by the parallel between cohesion and binding energies shown in Fig. 13.

It is encouraging that the bonding trends predicted by the DF calculations, particularly the relative strength of the bond in Be_2, have been confirmed by both exhaustive CI calculations and experiment. The picture provided of the bond in these molecules is also simple and plausible and has been taken over into the chemical literature by Kutzelnigg (1984). However, there is a substantial overestimate in the calculations of all bond strengths discussed here, as well as in most of the first-row dimers. This is an important point, and we now return to it.

3. Group-IVa molecules C_2, Si_2, C_3, Si_3

The absence of core *p* states and the relatively compact 2*p* valence functions apply to all first-row atoms, not just to beryllium. In fact, these atoms show qualitative differences in their bonding properties from atoms in the remainder of the Periodic Table. An example is given by the group-IVa dimers C_2 Si_2, Ge_2, Sn_2, and Pb_2, where the last four have the same ground state $[{}^3\Sigma_g^-, 2\sigma_g^2(1\pi_u^2)]$, with an excitation energy to the ${}^1\Sigma_g^+$ state $(1\pi_u^4)$ of 1.0–1.5 eV (Harris and Jones, 1978a, 1979a). This is strikingly different from the situation in C_2, where the experimental ground state is ${}^1\Sigma_g^+$ with excitation energies (T_e) to the ${}^3\Pi_u(2\sigma_g\pi_u^3)$ and ${}^3\Sigma_g^-$ states of 0.09 and 0.80 eV, respectively (Huber and Herzberg, 1979). The C—C bond then shows a remarkable ease of $\sigma_g \rightarrow \pi_u$ transfer and substantially stronger π bonds than in the other atoms in this series.

While the pronounced difference between C—C and Si—Si bonds is well known, it is not easy to find a discussion of the reasons in the chemical literature. Density functional calculations for the heavier elements of a group (e.g., Si, Ge, Sn, and Pb in group IVa) are not significantly more difficult than those in the first row (e.g., C), so they provide an ideal means for studying these differences. In Fig. 15 we show the tails of the valence orbitals in the group-IVa atoms. The secondary periodicity noted above in group-IIa atoms is even more apparent here. The *s* and *p* functions in Si are remarkably similar to those in Ge, for example, because the relatively diffuse 3*d* core density in Ge imperfectly screens the additional nuclear charge. This is reflected in the very similar properties, such as ground-state geometries, of these two elements. The special status of the first-row atom (C) is again apparent, in that the maxima of the radial *s* and *p* functions occur at almost the same distance from the nucleus. The behavior of the self-consistent eigenvalues of the ${}^3\Sigma_g^-$ state in C_2, Si_2, and Ge_2 are shown in Fig. 16. As expected from the above discussion, the Si_2 and Ge_2 eigenvalues are very similar.

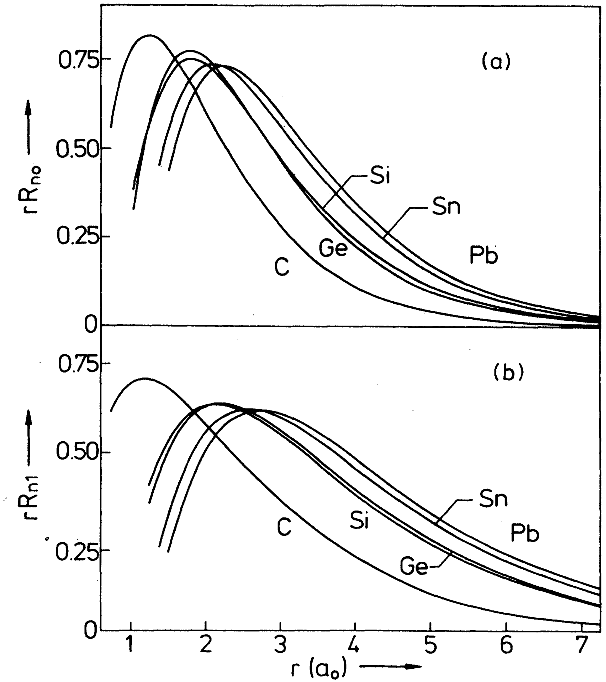

FIG. 15. Radial valence functions for group-IVa atoms: (a) *s* functions; (b) *p* functions.

The qualitative differences between the multiplet structures of C_2 and the other molecules can now be understood. The ${}^1\Sigma_g^+$ state obtained by placing four electrons in the π_u orbital has a very similar energy to the ${}^3\Sigma_g^-$ state obtained by transferring two electrons to the $2\sigma_g$ orbital. The eigenvalues in Fig. 16 show that occupancy of the latter orbital will be favored in the heavier dimers, which is consistent with the relatively compact atomic *p* functions in C and the stronger π bonds that result. The consequences for the formation of simple saturated mole-

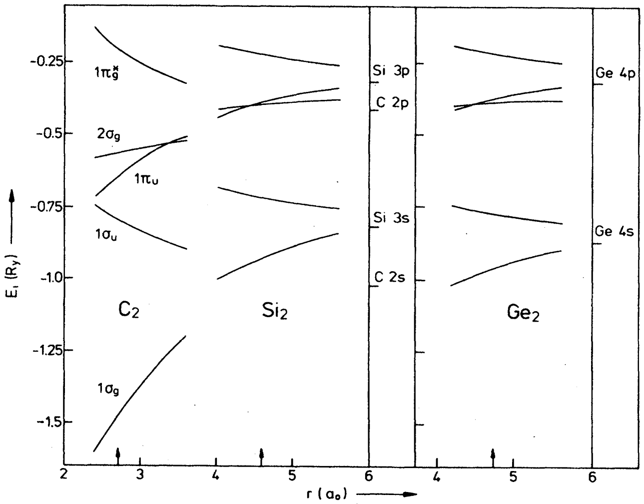

FIG. 16. Self-consistent eigenvalues for ${}^3\Sigma_g^-$ state of C_2, Si_2, and Ge_2. Also shown are the valence eigenvalues for the isolated atoms. The arrows denote the calculated equilibrium separations in each case.

cules has been discussed by Harris and Jones (1979a; see also Harris, 1984b).

The trimers of carbon and silicon are interesting, both individually and in comparison. In agreement with the predictions of Walsh (1953) for triatomic molecules with 12 valence electrons, the ground state of C_3 is linear. However, the bending frequency is remarkably low ($\omega_e = 63$ cm^{-1}, compared with 667 cm^{-1} for CO_2), and it has been a challenge to reproduce this. Hartree-Fock and CI calculations have been performed by Liskow *et al.* (1972), who found a pronounced sensitivity to basis-set choice. The results of the most extensive calculation are shown in Fig. 17. The calculated value of ω_e (69 cm^{-1}) is in good agreement with experiment, but the binding-energy curve has a most unusual form, described by the authors as a square well with a "dimple" for bond angles α between 160° and 180°. This potential is highly anharmonic with very irregular spacings between the vibrational levels. Shown also are the results of multireference double-excitation CI (MRD-CI) calculations of Perić-Radić *et al.* (1977). While these calculations provide a very good description of the stretch vibration frequencies of low-lying states (see also Römelt *et al.*, 1978), the force constant for symmetric bending is an order of magnitude too high. The results of density functional calculations (Jones, 1985a) are also shown in Fig. 17. The energy curve shows no sign of the very unusual structure found by Liskow *et al.*, and the vibration frequency (~ 75 cm^{-1}) is much closer to experiment than the MRD-CI value. The LSD calculations have also been performed for low-lying $^3\Pi_g(^3A_2+^3B_2)$, $^3\Pi_u(^3A_1+^3B_1)$, $^3\Pi_g$, and $^3\Pi_u$ states. The parameters defining the energy surfaces are in reasonable agreement with available experimental information.

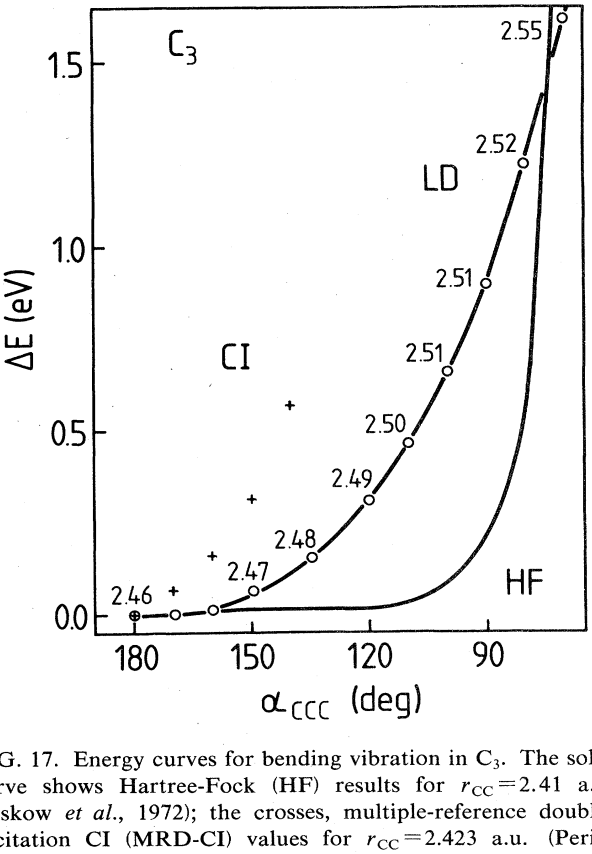

FIG. 17. Energy curves for bending vibration in C_3. The solid curve shows Hartree-Fock (HF) results for $r_{CC}=2.41$ a.u. (Liskow *et al.*, 1972); the crosses, multiple-reference double-excitation CI (MRD-CI) values for $r_{CC}=2.423$ a.u. (Perić-Radić *et al.*, 1977). Local-density (LD) results are given by circles, and the optimum bond length for each bond angle, α_{CCC}, is also shown (Jones, 1985a).

The silicon trimer has received considerable attention recently. The results of density functional calculations (Jones, 1985b) are shown in Fig. 18. The ground-state energy surface is remarkably flat and, in contrast to Walsh's rules, does not have its minimum for a linear geometry. The density functional calculations predict a bond angle of $\sim 85°$, with a bond length of 4.21 a.u. Similar values are found by calculations using Hartree-Fock plus many-body perturbation theory (80.6°, 4.08 a.u., Diercksen *et al.*, 1985; $\sim 78°$, 4.09 a.u., Raghavachari, 1985) and CI calculations (78.1°, 4.08 a.u., Grev and Schaefer, 1985). Several of these calculations, including the DF work, find a second state ($^3A_2', D_{3h}$) with an energy very close to that of the $^1A_1$ minimum. It is reassuring that several independent calculations for this molecule produced such a consistent picture of the ground-state energy surfaces, particularly in the absence of experimental information.

The comparison between the results obtained for C_3 and Si_3 is very interesting. We have noted that the LSD calculations for C_3 reproduce the known features of the energy surfaces of low-lying states satisfactorily. The excitation energies to the $^3\Pi_u$ (1.76 eV) and $^1\Pi_u$ (2.56 eV) are, however, less than the experimental estimates (2.10 and 3.06 eV, respectively), and comparable discrepancies can be expected in similar molecules. It is important to note also that the strengths of *all* the bonds in C_2, Si_2, C_3, and Si_3 are overestimated by ~ 1 eV in the LSD calcula-

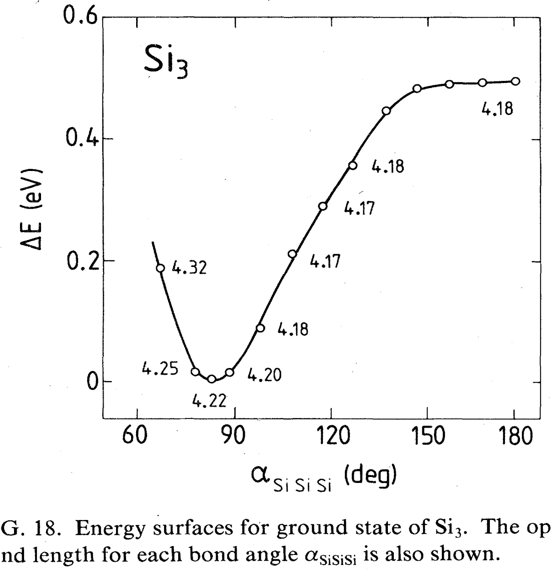

FIG. 18. Energy surfaces for ground state of Si_3. The optimum bond length for each bond angle α_{SiSiSi} is also shown.

tions. It is also noteworthy that Walsh's rules do not predict the correct ground-state geometry for Si_3. In fact, much of the understanding and most of the predictions concerning chemical bonding are based on the extensive experience available from molecules containing first-row atoms. The discussion above shows, however, that the absence of *p* states in the core makes these atoms far from typical for the periodic system as a whole. Heavier atoms, such as Si, also have more important contributions from *d* functions; this contributes to the apparent tendency of Si to favor bent geometries.

4. Iron-series transition-metal dimers

The dimers of iron-series elements K→Cu have provided instructive tests of calculational methods, including density functional methods with the LSD approximation. LSD calculations of low-lying states of all these molecules were described by Harris and Jones (1979b), and this field has been surveyed in extensive reviews by Salahub (1987, transition-metal atoms and dimers) and by Morse (1986, a thorough survey of known information about transition-metal clusters in general). For molecules at the ends of the row—K_2, Ca_2 and Cu_2—the nature of the bond is relatively simple; the vibrational spectra have been measured in detail. It is only recently that detailed information has become available about the other members of the series, and more work remains to be done. The most remarkable feature of the measured binding energies in this row is the pronounced minimum at the center. This is similar to the situation in the cohesive energies of the bulk metals. Griffith (1956) showed that the latter could be understood in terms of a competition between the effects of bonding, spin, and the *sd* promotion energies; Harris and Jones (1979b) used a similar picture for the dimers. "Bonding" in this context means the tendency to occupy levels that are bonding combinations of orbitals on the two atoms, while the "spin" contribution means the preference (Hund's multiplicity rule) to occupy states with high spin degeneracies. The balance between these two effects is particularly important near the center of the row, e.g., Cr_2.

We have seen that LSD calculations give a very good description of the bonding in H_2 and Li_2; this is also true in K_2 and in Cu_2. For the other members of this series, the number of low-lying states is large and all methods of calculation pose problems. We shall illustrate these problems by discussing Cu_2 and Cr_2.

a. Cu_2

The Cu atom has a single 4*s* electron outside the $3d^{10}$ shell (ground state $^2S_{1/2}$) and has obvious similarities to an alkali atom. Although Pauling (1983) has proposed that Cu—Cu is a triple bond based on the configuration $3d^9 4s 4p$ for each atom, most of the evidence indicates a $4s\ \sigma_g^2(^1\Sigma_g^+)$ single bond in the ground state. It has been shown that a carefully constructed pseudopotential incorporating core-valence polarization effects results in an excellent description of the Cu_2 bond (Stoll *et al.*, 1984; Flad *et al.*, 1985, and references therein). The picture of the copper atom with essentially one valence electron means that the extension to larger clusters is straightforward and should lead to reliable results (Flad *et al.*, 1985).

There have been many calculations of the binding-energy curve for Cu_2, and a selection of the results is shown in Table VII. The density functional results show a fairly consistent picture. Improved basis sets lead to somewhat greater bond strengths and slightly shorter bonds. The binding energies found with the $X\alpha$ functional are consistently lower than those found using electron gas functionals and are in better agreement with experiment. The LSD calculations show a clear tendency to overestimate the bond strength, although the overall description of binding is good. Ziegler *et al.* (1981) have shown that relativistic effects in $X\alpha$ calculations result in a reduction of r_e from 4.27 to 4.23 a.u.

The results of *ab initio* calculations for Cu_2 are also shown in Table VII. Regardless of basis set used, Hartree-Fock calculations result in a bond that is sub-

TABLE VII. Spectroscopic constants of Cu_2 ($^1\Sigma_g^+$).

	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
Experiment			
	4.1947[a]	264.55[a]	1.97[b]
Density functional			
LMTO-GL[c]	4.30	280	2.30
LGTO-VWN[d]	4.18	248	2.40
AG-VWN[e]	4.10	330	2.65
AG-$X\alpha$[e]	4.12	290	2.16
num-$X\alpha$[f]	4.20	286	2.10
Ab initio			
HF[g]	4.61	198	0.51
HF[h]	4.578		0.56
CISD[g]	4.37	228	0.15
SD(CI)[i]	4.42	220	1.51
SD(CI)+Q[i]	4.38	219	1.61
POLCI[i]	4.44	227	1.99
CI[j]	4.54	200	2.07
CAS SCF[k]	4.62		1.25
CEPA-1[g]	4.29	242	1.80
CPF[h]	4.23		1.84

[a] Huber and Herzberg (1979).
[b] Hilpert (1979). Mean of second- and third-law values.
[c] Harris and Jones (1979b).
[d] Radzio *et al.* (1986).
[e] Painter and Averill (1983).
[f] Delley *et al.* (1983).
[g] Werner and Martin (1985).
[h] Scharf *et al.* (1985).
[i] Bauschlicher (1983). Q denotes Davidson correction.
[j] Bauschlicher *et al.* (1983).
[k] Shim and Gingerich (1983).

stantially longer than the experimental value and weaker than the measured value by ~ 1 eV. An accurate treatment of Cu_2 requires a large basis set and must allow correlation between all $3d$ and $4s$ electrons. Scharf *et al.* (1985) used a size-consistent coupled pair functional (CPF) method with relativistic corrections and a basis set that included g functions. The agreement with experiment is very good. Relativistic and unlinked cluster contributions were also studied by Werner and Martin (1985). The calculated spectroscopic constants are in good agreement with experiment.

The calculations on the copper dimer produce a remarkably consistent picture of the ${}^1\Sigma_g^+$ ground state. Hartree-Fock calculations underestimate the binding energy by ~ 1 eV and overestimate the bond length by more than 0.3 a.u. Different schemes for including correlation lead to improvements in both quantities; the most extensive calculations give very good binding-energy curves. LSD calculations lead to satisfactory bond lengths and small overestimates in the dissociation energy. As in the case of H_2 and Li_2 (see Table V), the use of the $X\alpha$ approximation for $E_{\rm xc}$ [Eq. (4.2)] leads to lower dissociation energies than those found with electron gas parametrizations [Eq. (4.1)]. In Cu_2 the difference is 0.3–0.5 eV.

b. Cr$_2$

The situation in Cr_2 is very complicated. The ground state of the chromium atom has a high spin degeneracy (${}^7S$, $[3d(\uparrow\uparrow\uparrow\uparrow\uparrow)4s(\uparrow)]$), so that at large separations there is a large spin contribution to the total energy. If the symmetry of the molecule is assumed to be $D_{\infty h}$, there is a relatively simple picture of the main contributions to bonding. The occupancy of levels that are bonding combinations of the atomic orbitals favors a strong bond at relatively short internuclear separation. An example is the ${}^1\Sigma_g^+[7\sigma_g^2 5\sigma_u^2 3\pi_u^4 2\pi_g^4 1\delta_g^4]$, where all the bonding orbitals are occupied. On the other hand, Hund's multiplicity rule notes that states with high-spin degeneracy are favored, an extreme case being the single occupancy of all levels derived from the sd shell (${}^{13}\Sigma_g^+$). In Cr_2, the balance between these two tendencies is particularly delicate, as shown by the LSD calculations of Harris and Jones (1979b). A variety of states has similar energies.

In order for LSD calculations to give a satisfactory description of the ground state, however, it is necessary to lower the symmetry to $C_{\infty v}$, i.e., allowing explicitly the antiferromagnetic ordering of the spins on the two atoms. The results of several groups who incorporated this extension are shown in Table VIII; further discussion is found in Painter (1986). It is apparent that a very good description of both bond length and vibration frequency is possible. The well-depth found in LSD calculations is an overestimate, a situation that is becoming rather familiar. In contrast to the first-row dimers, $X\alpha$ and LSD calculations lead to quite different spectroscopic constants in Cr_2. The $X\alpha$ bond length, in particular, is much greater.

The Cr_2 molecule has proved to be a source of great difficulty for *ab initio* methods of electronic structure calculations, even after the experimental spectroscopic constants became available. Restricted HF calculations for the ${}^1\Sigma_g^+$ state (Wolf and Schmidtke, 1980; Goodgame and Goddard, 1981; Atha and Hillier, 1982) indicate a minimum at a short internuclear separation, but with an energy far (~ 20 eV) above the energy of the separated atoms. Unrestricted HF calculations (Goodgame and Goddard, 1981; McLean and Liu, 1983) lead to improved energies, but give no indication of a minimum in the binding-energy curve. The work of McLean and Liu also showed that the energy is strongly dependent on the choice of basis set, with f and g functions playing an unusually important role. Complete active space self-consistent-field (CASSCF) calculations (Walch *et al.*, 1983, 3088 configurations) also give no minimum; Walch and his colleagues estimated that such calculations would require many millions of configurations to produce reasonable agreement with experiment. It is then not surprising that more modest attempts to calculate correlated wave functions (Table VIII) show no signs of convergence. For example, the generalized valence-bond–van der Waals (GVB–vdW) calculations of Goodgame and Goddard (1981, 26 512 configurations) lead to a very long and weak bond. These authors have proposed a semiempirical extension (Goodgame and Goddard, 1985) in which some atomic Coulomb integrals are adjusted to reproduce the correct atomic electron affinities. This resulted in a second minimum in the binding-energy curve. They also reinterpreted the experimental data of Kant and Strauss (1964) to give a revised value of D_e of 2.0 ± 0.3 eV, so that their calculated value (1.86 eV) is within the error bars. The recent work of Hilpert and Ruthardt (1987) provides a more precise experimental value (1.44 ± 0.02 eV), which seems to question the reliability of the recent modifications. The CI calculations of Kok and Hall (1983, 3250 configurations) give good results for r_e and ω_e, but the absence of proper dissociation in this calculation indicates that the binding energy (not given) would be unreliable.

5. Triatomic group-VI molecules O_3, SO_2, S_3, SOS

As a further example, we study the energy surfaces of a family of triatomic molecules containing oxygen and sulfur, each with 18 valence electrons. The ground states of O_3 and SO_2 are known to have ${}^1A_1(C_{2v})$ symmetry, with similar bond angles (116.8° and 119.4°, respectively). The absorption spectrum of ozone has also been studied in detail, particularly for uv radiation. However, detailed experimental information on the excited-state energy surfaces is not available for any of these molecules, and theory has played an essential role in developing our understanding of them. It is worth noting that the HF approximation gives a qualitatively incorrect ordering of the low-lying states of O_3, since there are two configurations with substantial contributions to the ground-state wave function. These systems then provide ideal tests of schemes for incorporating correlation effects. Attention has been focused in the past on the presence of *two* minima in the $^1A_1$ energy surfaces and on the energy difference between them.

In Fig. 19 we show the energy surfaces for low-lying states of (a) O_3 and (b) SO_2. The ground-state geometries are reproduced very well, and the excitation energy between the two $^1A_1$ minima (1.4 eV) is in reasonable agreement with the most recent CI calculations, which give results between 1.0 and 1.4 eV (Jones, 1985a). In both molecules the bond lengths increase in the order $x\,^1A_1 \rightarrow 1\,^3B_1 \rightarrow 1\,^3B_2 \rightarrow 2\,^1A_1$, and the bond angles in the order $2\,^1A_1 \rightarrow 1\,^3B_2 \rightarrow x\,^1A_1 \rightarrow 1\,^3B_1$. However, there are qualitative differences between the *energy* ordering of the states in O_3 and SO_2. In particular, the excitation energies of the low-lying triplet states are substantially greater in SO_2 than in O_3, and the energy separation between the two $^1A_1$ states (4.1 eV) is almost three times as large.

The bonding trends in these two molecules have been discussed elsewhere (Jones, 1985a), where the qualitative differences are related to the higher-lying valence p eigenvalue in sulfur. The ground state ($x\,^1A_1$) has the valence configuration $1a_2^2 3b_2^2 4a_1^2 2b_1^0$; single excitations give states with symmetries $1\,^3B_1$ ($4a_1 \rightarrow 2b_1$) and $1\,^3B_2$($1a_2 \rightarrow 2b_1$). The $2\,^1A_1$ state corresponds to the excitation ($3b_2^2 \rightarrow 2b_1^2$). The $1a_2$ and $3b_2$ orbitals receive significant contributions only from the outer (oxygen) atoms; the corresponding eigenvalues show similar trends (Jones, 1985a). By contrast, the $4a_1$ and $2b_1$ eigenvalues have a strong contribution from the central atom (O in O_3, S in SO_2). Since these lie highest among the valence eigenvalues mentioned above, it is not surprising that the eigenvalue spread is much larger in SO_2. Assuming that the density distributions are similar in the different states, we can see from Eq. (4.5) that the energy difference between them will be reflected in the difference in the eigenvalue sum. This is consistent with the relative stability of the ground state in SO_2; it also explains the large excitation energy of the $2\,^1A_1$ state in SO_2, since this state corresponds to a double excitation to the high-lying $2b_1$ orbital.

This simple picture can be checked by comparing the S_3 (Jones, 1986a) and the SOS molecules (Jones, 1986b), where the change from trimer to mixed molecule reverses

TABLE VIII. Spectroscopic constants of Cr_2 ($^1\Sigma_g^+$).

	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
Experiment			
	3.17,[a,b] 3.1725[c]	470[c]	1.56±0.3,[d] 1.44±0.02[e]
Density functional			
LSD-BH[f]	3.21	450	1.80
LSD-VWN[g]	3.2	470	2.80
GTO-VWN[h]	3.17	441	2.6
GTO-$X\alpha$[h]	5.10	92	0.4
GTO-$X\alpha$[i]	5.20	110	1.0
Ab inito			
RHF[j]	2.95	750	
RHF[k]	<1.5		
GVB[k]	6.14	70	0.1_3
GVB-vdW[k]	5.78	110	0.3_5
MCSCF[l]	5.93	92	0.14
GMO-CI[m]	3.27	396	
MGVB[n]	3.04		1.86

[a] Efremov *et al.* (1978).
[b] Michalopoulos *et al.* (1982).
[c] Bondybey and English (1983).
[d] Kant and Strauss (1964).
[e] Hilpert and Ruthardt (1987).
[f] Delley *et al.* (1983). Local spin-density parametrization of von Barth and Hedin (1972).
[g] Bernholc and Holzwarth (1983). Pseudopotential calculations.
[h] Baykara *et al.* (1984).
[i] Dunlap (1983). $^1\Sigma^+$, i.e., no inversion symmetry.
[j] Wolf and Schmidtke (1980).
[k] Goodgame and Goddard (1981).
[l] Atha and Hillier (1982).
[m] Kok and Hall (1983).
[n] Goodgame and Goddard (1985). Shorter of two minima.

the order of change in the central atom (S→O). The ground state of S_2O has the asymmetric bent structure S—S—O, with $\alpha_{\mathrm{SSO}}=118.26°$ (Tiemann *et al.*, 1974). Nevertheless, LSD calculations (Jones, 1986b) indicate that the SOS molecule should be bound, and it may be observable as a metastable state. The calculated energy surfaces for low-lying states of S_3 and SOS are shown in Fig. 20. In addition to the states considered in O_3 and SO_2, we include the $1\,^3A_2$ and $2\,^3B_1$ states, which correspond to $(3b_2\rightarrow 2b_1)$ and $(1a_2 3b_2\rightarrow 2b_1^2)$ excitations from the ground state.

The first interesting result is the near degeneracy between the two $^1A_1$ minima in S_3, where the calculations place the ring structure less than 0.1 eV below the open form. The energy separation between the "open" and "ring" structures in this molecule provides a sensitive

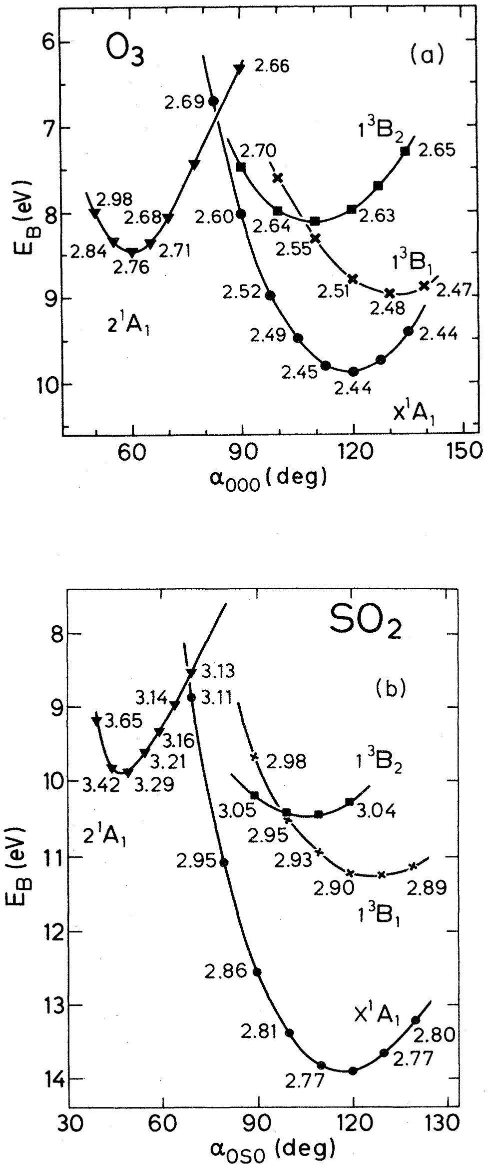

FIG. 19. Energy surfaces for $x\,^1A_1$ (circles), 1^3B_1 (crosses), 1^3B_2 (squares), and 2^1A_1 (triangles) states of (a) O_3 and (b) SO_2. For each bond angle α we show the bond length that optimizes the energy.

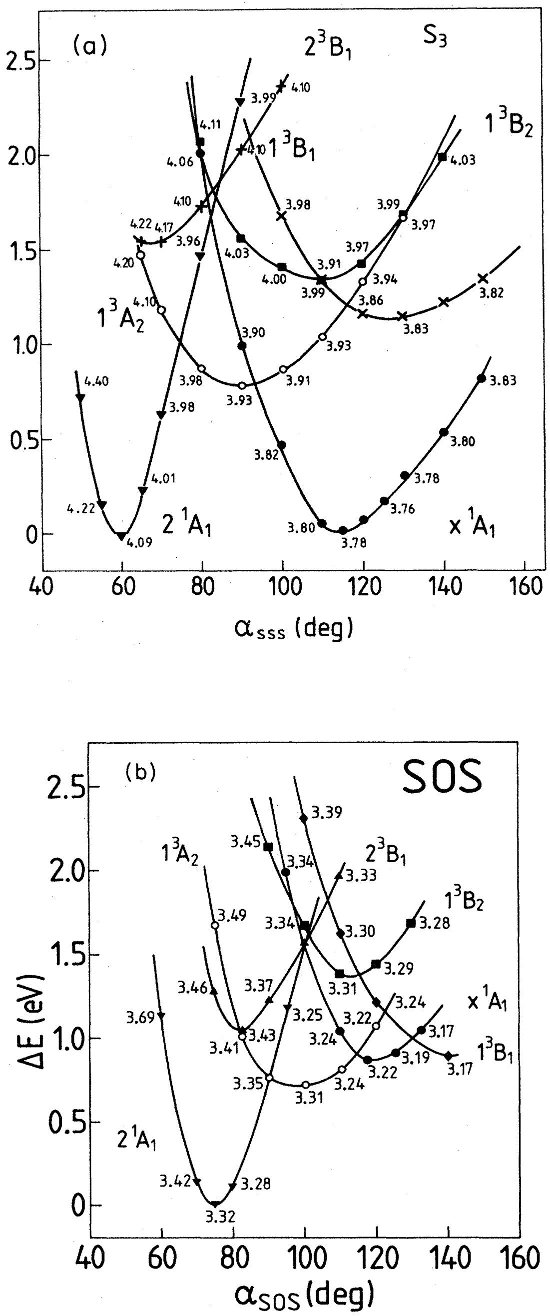

FIG. 20. Energy surfaces for low-lying states of (a) S_3 and (b) SOS. The optimum bond length for each bond angle α is also shown.

test of molecular structure methods. Rice *et al.* (1986) have shown that the D_{3h} state lies lower in both HF and CI single and double excitation (CISD) calculations (by 0.40 and 0.10 eV, respectively), while the relative stability is reversed in CASSCF and multiple reference MR-CISD calculations (0.39 and 0.36 eV, respectively). Similar results have been found by Ahlrichs (1986), who observed different ground states for CISD (D_{3h}) and CPF (C_{2v}) methods. As in the comparison between C_3 and Si_3, the O_3 and S_3 results indicate a tendency of second-row atoms to favor bent geometrics. A contributing factor is the increased importance of *d* functions in this row. The second striking feature is the closed ground state found for the SOS molecule.

In Fig. 21 we show the self-consistent single-particle eigenvalues for the uppermost valence orbitals in S_3 and SOS, calculated for the optimum geometries shown in Fig. 20. As may be expected from the above discussion, the $4a_1$ and $2b_1$ orbitals, which receive an important contribution from the central atom, lie *lower* in SOS than in S_3, so that the triplet states and the ring $^1A_1$ state will be stabilized relative to the open $^1A_1$ state. This is fully consistent with the calculated energy surfaces.

The single-particle picture means that excitation energies between states can often be associated with simple changes in the occupation numbers. This is useful if we calculate the energy surface for one state (e.g., the ground state) and note the geometries where the single-particle eigenvalues are degenerate. The energy surfaces for the ground state and the state corresponding to the change in occupation numbers should then intersect near this geometry. Such arguments must be treated with caution, particularly if electron transfer results in a change in spin degeneracy; however, the results are remarkably consistent with the calculated excited-state surfaces in all molecules discussed in this section. It can be seen that the LSD calculations give a very good description of the energy differences between different states of a given molecule. Nevertheless, the energies required to break all the bonds in this family are overestimated by ~2 eV. The combined molecular dynamics-density functional scheme discussed below (Sec. IV.C.3) has been applied to some molecular systems, and we give some examples there.

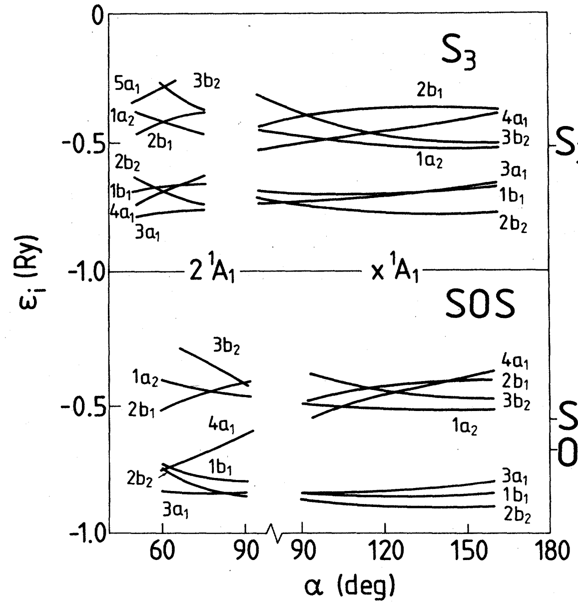

FIG. 21. Self-consistent eigenvalues for the uppermost valence orbitals in S_3 and SOS. For each bond angle α, we show the results for the optimum bond length.

C. Extended systems

In this section we consider some examples of extended systems, paying particular attention to the elements we have considered above—first-row atoms, simple metals (e.g., the alkaline earths), group-IV elements (C, Si, Ge), 3*d* transition elements, and the group-VI elements (S, Se). We focus on the LSD description of the geometry and the cohesive energy of these materials. For the metallic elements with atomic numbers less than 50, nonrelativistic LSD calculations within the muffin-tin approximation have been performed by Moruzzi *et al.* (1978).

1. Crystalline solids

a. Alkali and alkaline earth metals

The cohesive energies calculated by Moruzzi *et al.* (1978) are compared with measured values in Table III. The cohesive energies of the group-IIa elements are also plotted in Fig. 13. In the case of Li, similar results have been found by Callaway *et al.* (1983). Vosko and Wilk (1980) showed that the dependence of the cohesive energy on the choice of the electron gas parametrization was of the order of 10 mRy in the alkali metals; we also show their results in Table III. It is apparent that cohesion in these solids is described very well by the LSD approximation, as are the trends in the alkaline earths. However, the calculations overestimate the strength of the binding in the latter, as we have already seen in the dimers of these elements. The overestimate is greatest in the case of Be. Trends in the lattice constants are described very well. In the case of the alkalis, the LSD calculations underestimate the bond lengths by a small amount.

b. C, Si, Ge

There have been numerous calculations of the cohesive properties of diamond, silicon, and germanium; selected results are compared with experiment in Table IX. Different methods of calculation and different electron gas parametrizations lead to variations in the calculated lattice constants, cohesive energies, and bulk moduli. While there is a tendency for the calculated cohesive en-

TABLE IX. Ground-state properties of diamond, Si, and Ge: lattice constant, a; cohesive energy, E_c; and bulk modulus B.

	a (a.u.)	E_c (eV)	B (Mbar)
	Diamond		
Experiment[a]	6.740	7.37	4.43
ASA-HL[b]	6.67	8.5	4.90
pseud-W[c]	6.807	7.58	4.33
ASA-BH[d]	6.709	8.43	4.64
BH[e]	6.744		4.42
	Silicon		
Experiment[a]	10.26	4.63	0.99
ASA-HL[b]	10.22	4.8	0.98
pseud-W[c]	10.30	4.84	0.98
ASA-BH[d]	10.29	4.94	0.95
pseud-CA[f]	10.20	5.28	0.94
	Germanium		
Experiment[g]	10.68	3.85	0.770
ASA-HL[b]	10.78	3.6	0.660
pseud-W[c]	10.69	4.02	0.730
pseud-CA[f]	10.58	4.67	0.730

[a] Cited by McMahan (1984).
[b] Glötzel *et al.* (1980). Atomic sphere approximation (ASA) with interstitial spheres.
[c] Yin and Cohen (1981). Pseudopotential, local spin-density exchange + Wigner correlation.
[d] McMahan (1984). ASA with interstitial spheres.
[e] Christensen *et al.* (1987).
[f] Hybertsen and Louie (1984). Ceperley-Alder functional.
[g] Cited by Hybertsen and Louie (1984).

ergies to increase as time passes and basis sets improve, the overall trends are unambiguous. Lattice constants and bulk moduli are given remarkably well, and the cohesive energies are overestimated by up to 1.0 eV. Phonon frequencies have also been calculated using the so-called frozen phonon approach, where a static distortion corresponding to the phonon is built into the lattice and the total energy and atomic forces are calculated for the corresponding supercell. In this way phonon frequencies can be obtained for particular points in the Brillouin zone. As an example of the results, we show in Table X some phonon frequencies for Si and Ge. The results of these parameter-free calculations differ from experiment by only a few percent.

c. Transition elements

The ground-state properties of 3*d* and 4*d* transition elements have been studied in detail by a variety of density functional calculations. Moruzzi *et al.* (1978) showed that the calculated lattice constants and bulk moduli are generally in satisfactory agreement with experiment. However, the cohesive energies of the 3*d* transition elements are overestimated substantially, particularly at the center of the series. The inclusion of spin in the LD calculations leads to improved lattice constants and bulk moduli, but does not improve the unsatisfactory description of E_c. In Fe, Co, and Ni, for example, the calculated cohesive energies (6.26, 6.48, and 5.70 eV, respectively)

TABLE X. Comparison of calculated and experimental phonon frequencies (in THz) of Si and Ge at Γ and X. The values for f_E (f_F) were obtained from energy (force) calculations. The deviations from experimental values are given in parentheses. After Yin and Cohen (1982).

	LTO(Γ)	LOA(X)	TO(X)	TA(X)
		Si		
f_E	15.16(−2%)	12.16(−1%)	13.48(−3%)	4.45(−1%)
f_F	15.14(−3%)	11.98(−3%)	13.51(−3%)	4.37(−3%)
f_{expt}	15.53	12.32	13.90	4.49
		Ge		
f_E	8.90(−2%)	7.01(−3%)	7.75(−6%)	2.44(2%)
f_F	8.89(−3%)	6.96(−3%)	7.78(−6%)	2.45(2%)
f_{expt}	9.12	7.21	8.26	2.40

are much greater than the measured values (4.31, 4.41, 4.43 eV). The one-particle-like nature of the Kohn-Sham equations (3.5) makes it possible to derive a Stoner-type theory (Vosko and Perdew, 1975; Gunnarsson, 1976; Poulsen *et al.*, 1976), which includes correlation effects and provides explicit equations for the Stoner parameter. This parameter-free theory predicts correctly the presence or absence of ferromagnetism for systems such as V, Fe, Co, Ni, and Pd; it also gives reasonable magnetic moments (Gunnarsson, 1976). Full-band-structure calculations support such a Stoner theory and give moments in very good agreement with experiment [Callaway and Wang, 1977 (Fe); Wang and Callaway, 1977 (Ni); Moruzzi *et al.*, 1978].

2. Polymers

Polymers, besides having interesting and important properties, are test systems for a whole range of theories, particularly in statistical mechanics. The study of their electronic structure and properties has been the subject of much attention. It is obvious, however, that some of the standard methods are inappropriate. Hartree-Fock methods are known to have serious defects in extended systems, and configuration-interaction calculations are generally impracticable. It is possible to consider the structure and properties of short chains, however, and this has been done with success. On the other hand, the above examples have shown that density functional methods provide a convenient parameter-free scheme for calculations on extended systems and give remarkably good descriptions of trends in atomic properties. Polymers provide a link between these two limits and are ideal candidates for LSD calculations. Springborg and Andersen (1987) have developed a scheme for calculating the electronic structure of infinite chains in a helical structure, which can be used to describe many simple polymers. It has been applied to linear carbon chains (Springborg, 1986a), to polyacetylene (Springborg, 1986b), and to polymeric sulfur and selenium (Springborg and Jones, 1986, 1988). An interesting example is provided by S_∞, which allows comparison with the results of calculations of other sulfur-containing molecules.

As shown in Fig. 22, the helical geometry can be described by the internuclear separation r, the bond angle α, and the torsion or dihedral angle γ. An alternative parameter set is r, the translation along the axis of the helix h, and the rotation angle v. Special cases are the linear chain with $v=2\pi$ and the planar zigzag with $v=\pi$. With a single atom per unit cell, the position of the nth atom in cylindrical coordinates is given by

$$R_n=(x,y,z)=\left[r\cos u_n, r\sin u_n, \frac{h}{v}u_n+z\right] ,$$
$$u_n=nv+\varphi . \tag{4.6}$$

If the solutions of Eq. (1) are written in terms of localized functions, $\psi_{nL}(\mathbf{r})$, where $L\equiv[l,m]$, we may construct Bloch functions:

$$\psi_L^k(\mathbf{r})=\lim_{N\to\infty}\frac{1}{\sqrt{2N+1}}\sum_{n=-N}^{N}e^{iknv}\psi_{nL}(\mathbf{r}) , \tag{4.7}$$

where

$$k\in\left[-\frac{\pi}{v},\frac{\pi}{v}\right] . \tag{4.8}$$

The basis functions, $\psi_{nL}(\mathbf{r})$, are the localized muffin-tin orbital functions used in earlier calculations.

A detailed search of a three-dimensional coordinate space for geometries ranging from linear ($v=2\pi$) to planar zigzag ($v=\gamma_{\text{SSSS}}=\pi$) to spirals with α_{SSS} between 80° and 120° results in the energy surfaces shown in Fig. 23 as a function of α_{SSS}. The energy surface is remarkably

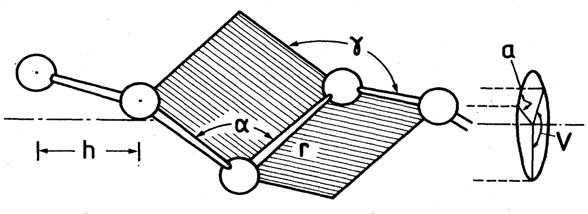

FIG. 22. Structural parameters of a helix with one atom per unit cell.

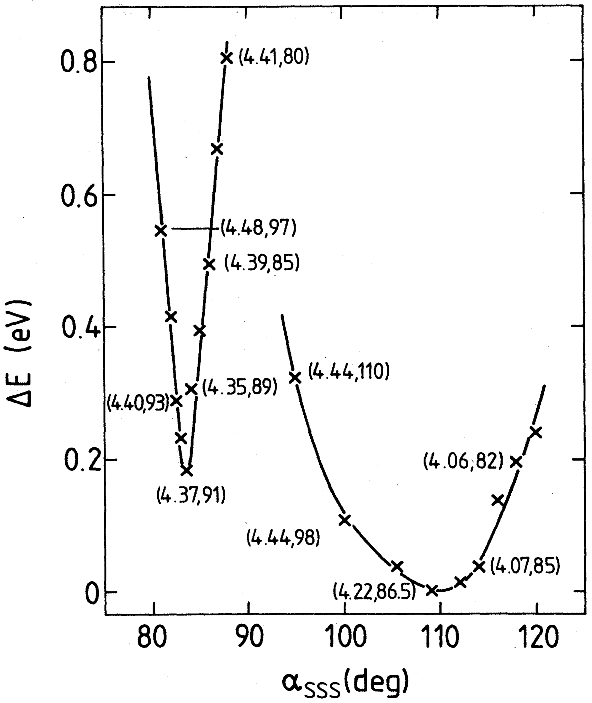

FIG. 23. Total energy surfaces (relative to ground-state minimum) of sulfur helix as a function of bond angle α_{SSS}. Values of $(r_{\text{SS}},\gamma_{\text{SSSS}})$ are also shown.

flat near its minimum ($r_{\mathrm{SS}}=4.22$ a.u., $\alpha_{\mathrm{SSS}}=109°$, $\gamma_{\mathrm{SSSS}}=86.5°$), so that the agreement with experiment ($r_{\mathrm{SS}}=3.90$ a.u., $\alpha_{\mathrm{SSS}}=106.0°$, $\gamma_{\mathrm{SSSS}}=85.3°$, Donohue, 1974) is then satisfactory. The second minimum in Fig. 23 corresponds to the geometry $r_{\mathrm{SS}}=4.37$ a.u., $\alpha_{\mathrm{SSS}}=83.5°$, and $\gamma_{\mathrm{SSSS}}=91°$. This structure has a rotation angle v (124°) that is significantly greater than that of the ground state (107°). The increased compression along the axis is accompanied by an increase in the radius of the helix and a small change in the torsion angle ($\sim 4.5°$). Evidence for the relative compactness of the structure at the second minimum is the reduction in the second- and third-nearest-neighbor distances (5.81 and 7.05 a.u., respectively) compared with the ground-state values (6.88 and 8.87 a.u.). The calculated torsion angles for both minima are similar to the "normal" value for sulfur bonds (100°) predicted by Pauling (1960).

The geometrical structures, the projections along the helical axis, and the calculated energy bands for both minima are shown in Fig. 24. The energy gap between occupied and conduction bands is ~ 2 eV in each case. Since the LSD approximation usually leads to modest underestimates of band gaps, a single sulfur helix in the ground state should be insulating. The calculated dissociation energy per bond in the sulfur helix (~ 2.3 eV) is also greater than the experimental estimates (~ 1.5 eV; see Tobolsky and MacKnight, 1965).

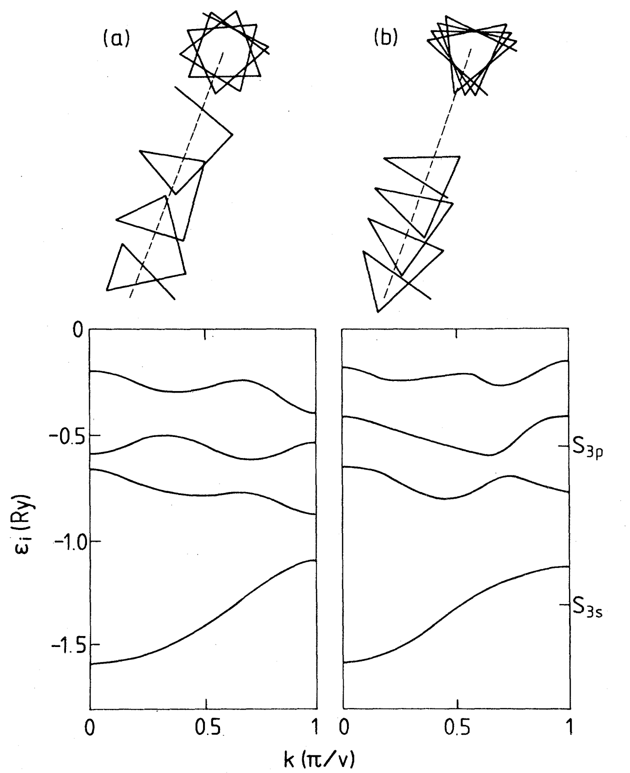

FIG. 24. Geometries (eleven bonds) and electronic band structures of S_∞: (a) calculated ground-state geometry; (b) at second minimum in Fig. 2. The projections along the helical axis and the atomic eigenvalues are also shown.

The planar zigzag and linear structures have energies comparable to the ground state, but both lead to unfilled bands. In the zigzag structure we find a minimum energy for $r_{\mathrm{SS}}=4.27$ a.u. and $\alpha=109.5°$. The bond angle is very similar to that in the ground state, and the energy is only ~ 0.05 eV higher. The energy surface is extremely flat in the neighborhood of the zigzag minimum.

The energy surfaces in Fig. 23 show similarities with the corresponding results for S_3. Bond lengths increase as the bond angle is reduced, and the energy curves near the minima for open structures are flatter than those in the others. There are, however, differences between S_3 and S_∞. Small changes in bond angle in the latter can correspond to large changes in geometry, since γ_{SSSS} can also change, generally increasing with decreasing bond angle. Furthermore, symmetry does not require an energy minimum for a bond angle of 60° in the helix, where a larger bond angle (83.5°) is favored because of the repulsion between next-nearest-neighbor nuclei. The calculated bond lengths are longer than in S_3.

There have been a few calculations for polyacetylene taking the full three-dimensional nature of the system into account, using a plane-wave basis (Vogl *et al.*, 1988; Vogl and Leising, 1988) or the linear augmented plane-wave method (Ashkenazi *et al.*, 1987). These calculations indicate that the dimerization of polyacetylene is substantially underestimated in the local-density approximation (LDA). Furthermore, as for other nonmetallic systems, the band gap is found to be too small.

3. Molecular dynamics—clusters and disordered materials

The calculations of the energy surfaces of polymeric sulfur lead to interesting results. However, they also show that it is difficult to study energy surfaces that are so flat that local minima correspond to quite different and possibly unexpected geometries. The location of the minima in energy surfaces is a general problem, and its complexity is demonstrated in the work of Hoare and McInnes (1983), who studied clusters of up to 13 atoms interacting with pairwise Lennard-Jones forces. As the cluster size grew from $N=6$ to $N=13$, the number of minima increased from 2 to 988, with signs of an exponential increase. In fact, Wille and Vennik (1985a, 1985b) showed that, for clusters of identical particles interacting with a pairwise potential, there is no known algorithm for which the ground-state energy—and hence the structure—can be found with a polynomial time dependence. In the language of the specialists, the problem belongs to the class NP complete (non-deterministic polynomial time complete; see Garey and Johnson, 1979) and may be viewed as "intractable." The determination of ground-state structures by locating and ordering all the local energy minima is then an impracticable proposition for all but the simplest systems. It is certainly sobering to discover that the mathematicians can prove that your basic problem cannot be solved.

In systems where the ground state is unknown or where there are many local minima, it is essential to develop alternative methods for finding solutions that are *near* to optimal. Kirkpatrick *et al.* (1983) noted the connection between statistical physics and the minimization of a function of many variables and suggested "simulated annealing" based on a Monte Carlo sampling as a generally applicable way of finding such solutions. It has been shown recently (Sasaki and Hajek, 1988) that this approach can lead to nearly optimal solutions of special *NP*-complete problems in polynomial average time.

Molecular dynamics (MD) provides an alternative to Monte Carlo methods. Car and Parrinello (1985) showed that it could be combined effectively with the density functional scheme to search large regions of configuration space and locate the deeper energy minima. It allows temperature-dependent effects to be studied by a method that is free of the common assumptions about the nature of the interatomic forces. The DF scheme is well suited to calculations of forces, as shown, for example, by the work Harris *et al.* (1981), Satoko (1984), and Averill and Painter (1986).

In the MD/DF approach, the density functional equation for the energy E is viewed as a function of two interdependent sets of degrees of freedom, the single-particle functions $\{\psi_i\}$ and the ionic coordinates $\{\mathbf{R}_I\}$. The energy minimization is performed by using dynamical simulated annealing techniques to follow the trajectories of $\{\psi_i\}$ and $\{\mathbf{R}_I\}$ given by the Lagrangian:

$$\begin{aligned}\mathcal{L}=&\sum_i \mu_i \int_\Omega d\mathbf{r}|\dot{\psi}_i^*\psi_i|\\&+\sum_I \tfrac{1}{2}M_i\dot{\mathbf{R}}_I^2-E[\{\psi_i\},\{\mathbf{R}_I\}]\\&+\sum_{ij}\Lambda_{ij}\left[\int_\Omega d\mathbf{r}\,\psi_i\psi_j^*-\delta_{ij}\right]\end{aligned} \tag{4.9}$$

and the corresponding equations of motion

$$\begin{aligned}\mu\ddot{\psi}_i(\mathbf{r},t)&=-\frac{\delta E}{\delta\psi^*(\mathbf{r},t)}+\sum_k \Lambda_{ik}\psi_k(\mathbf{r},t)\ ,\\M_I\ddot{\mathbf{R}}_I&=-\nabla_{\mathbf{R}_I}E\ .\end{aligned} \tag{4.10}$$

Here M_I denote the ionic masses, μ_i are fictitious "masses" associated with the electronic degrees of freedom, overdots denote time derivatives, and the Lagrangian multipliers Λ_{ij} are introduced to satisfy the orthonormality constraints on the $\psi_i(\mathbf{r},t)$. From these orbitals and the resultant density $n(\mathbf{r},t)=\sum_i|\psi_i(\mathbf{r},t)|^2$ we determine E, which acts as the classical potential energy in the Lagrangian (4.9). The artificial second-order Newton's dynamics for the electronic degrees of freedom, together with the assumption $\mu_i \ll M_I$, effectively prevent transfer of energy from the classical to the quantum degrees of freedom over long periods of simulation.

One of the first applications of this technique was to the study of liquid and amorphous Si (Car and Parrinello, 1987a, 1988). These authors associated a temperature with the average value of the classical kinetic energy corresponding to the ion motions; the variation of this temperature allowed the study of a variety of thermal treatments, including annealing and quenching. In Fig. 25 we compare the pair correlation functions calculated for liquid and amorphous forms of Si with available experimental results. The differences between the phases are striking, and the agreement between theory and experiment is astonishingly good, when one considers that the only piece of structural information used in the calculations was the volume of the unit cell. The phonon spectra can also be calculated and appear to be at least as good a description of the measured phonons as otherwise available (Car and Parrinello, 1988).

A further example of the usefulness of this technique is provided by the work on small clusters of S and Se by Hohl *et al.* (1987a, 1988). The effect of the cores is represented in this case as well by a pseudopotential; the simulated annealing technique was used to find the structures with the lowest energies. As an example, we show in Fig. 26 the way in which the structure of the Se_5 molecule develops from an almost linear geometry to the stable structure. The time between successive plots corresponds to approximately 500 time steps of 3.4×10^{-16} sec each. It is important to note that there are very many structures that correspond to local energy minima, and the ability to vary the average kinetic energy of the ions enables one to find the structure with the lowest en-

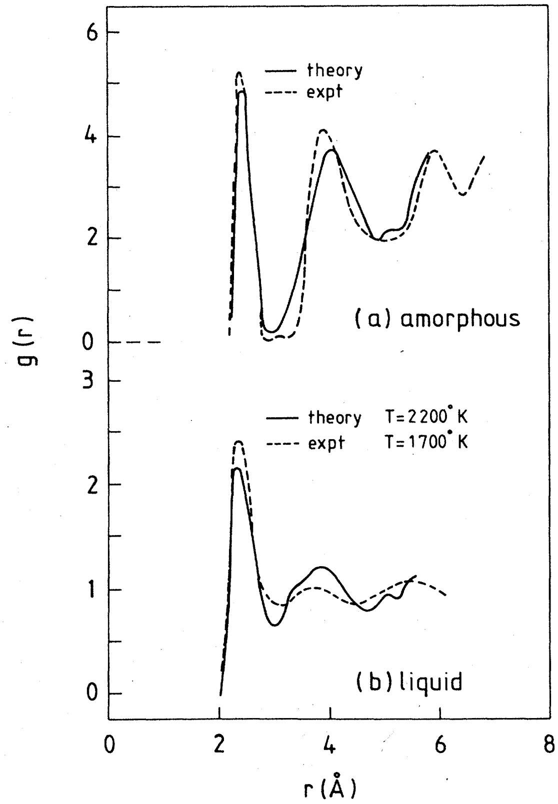

FIG. 25. Pair correlation function $g(r)$ for (a) amorphous and (b) liquid Si (after Car and Parrinello, 1987).

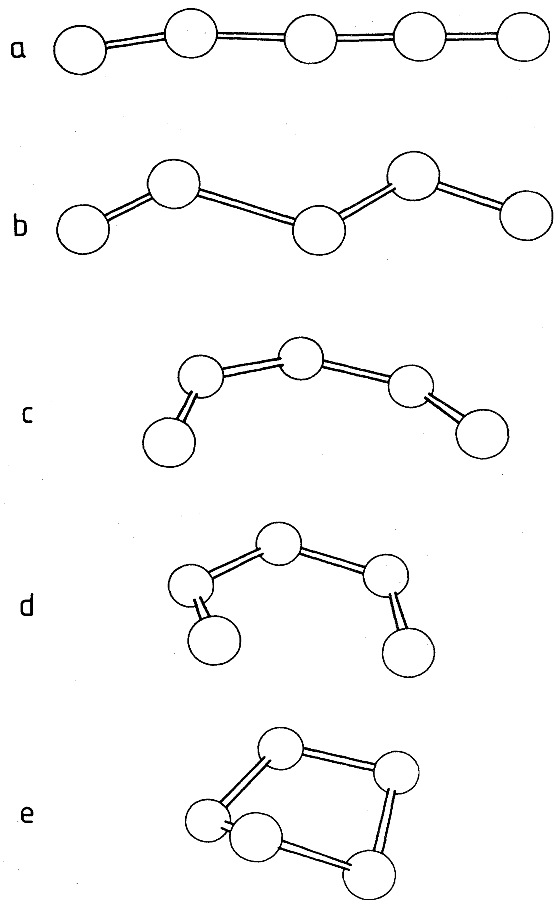

FIG. 26. Deformation of Se_5 linear chain to the calculated ground-state structure (Hohl *et al.*, 1987b).

ergy in a relatively straightforward fashion. Of particular interest are the results obtained for small sulfur clusters, as it is here that the structural information on small clusters is most detailed. Sulfur crystallizes in many more forms than any other element, and most of the structures are ringlike clusters. Known structures are reproduced very well, and the predictions for the unknown structures should be reliable.

A final example is provided by work on the molecule S_7O. This molecule belongs to the family of sulfur ring molecules with an oxygen atom outside and can be prepared in single crystal form. Calculations of Hohl *et al.* (1989) have shown that the cyclic structure, with the oxygen atom in a bridge position, corresponds to a stable minimum in the energy surface. In Fig. 27 we follow the motion of the molecule for 1200 time steps (each of 1.7×10^{-16} sec) at a "temperature" (mean kinetic energy of the ions) of 2000 K. It is remarkable that the oxygen atom moves outside the ring. Further motion and cooling results in the structure shown in Fig. 27(j), the lowest energy structure found in the simulation. The agreement with the experimental structure is very good (Hohl *et al.*, 1989).

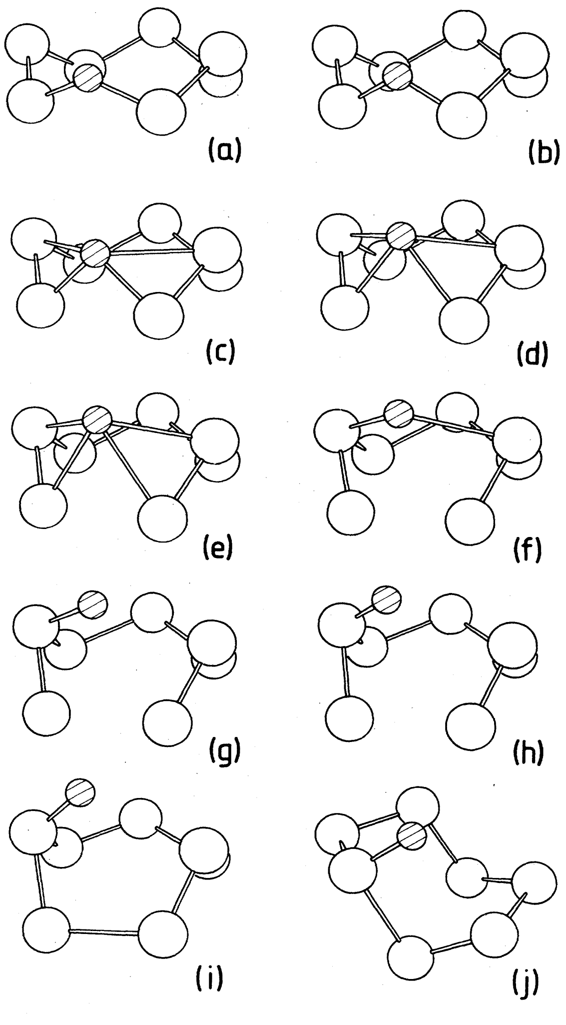

FIG. 27. Structural changes in S_7O at $T=2000$ K. (a)–(i) Evolution of the "ring" structure into the "intermediate" structure (Hohl *et al.*, 1989). The interval between each frame is 150 time steps, each of 1.7×10^{-16} sec. (j) The ground-state structure from the same perspective.

V. LOCAL SPIN-DENSITY CALCULATIONS—SOURCES OF ERROR, MODIFICATIONS

The results of the previous section have demonstrated some persistent, even systematic, errors in LSD calculations of energy differences in a variety of systems. In the present section we shall use the results of a simple model calculation to obtain insight into the sources of these errors and to describe some of the modifications of the LSD approximation that have been developed to overcome them. We have noted that the LSD approximation usually describes the experimental splitting well and that the $X\alpha$ method (with $\alpha=\frac{2}{3}$) gives splittings close to the results of the Hartree-Fock (HF) approximation (von Barth, 1979). We therefore focus on the exchange energy, where the presence of simple explicit formulas greatly simplifies the discussion.

The exchange energy can be expressed in terms of exchange integrals (Slater, 1960a, 1960b),

$$I_{ij}=e^2\int d\mathbf{r}\int d\mathbf{r}'\frac{\Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})\Phi_i(\mathbf{r}')\Phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{5.1}$$

where Φ_i and Φ_j are HF orbitals. Such an integral depends strongly on the nodal structure of Φ_i and Φ_j. For instance, if Φ_i and Φ_j have different l and m quantum numbers, the integrand oscillates and I_{ij} is reduced. Since the LSD and $X\alpha$ approximations are expressed in terms of the charge density, they cannot be expected to include the effects of the nodal structure in a precise way. In fact, the values of α needed to describe the atomic exchange energies show substantial variations for different orbitals (Lindgren and Schwarz, 1972).

As an example, we consider the *sp* transfer in an F atom, where an $s_\downarrow$ electron is transferred to a $p_\downarrow$ orbital (Jones and Gunnarsson, 1985; Gunnarsson and Jones, 1985b):

$$1s^22s(\uparrow\downarrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow)\rightarrow 1s^22s(\uparrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow)\ . \tag{5.2}$$

The change in the exchange energy due to this process is (Slater, 1960b)

$$\Delta E_x=-\tfrac{9}{25}G^2(2p,2p)+\tfrac{2}{3}G^1(2p,2s)\ , \tag{5.3}$$

where the Slater integrals G^k are defined by

$$G^k(i,j)=e^2\int_0^\infty dr\, r^2\int_0^\infty dr'(r')^2\frac{r_<^k}{r_>^{k+1}}\times\varphi_i(r)\varphi_j(r)\varphi_i(r')\varphi_j(r')\ . \tag{5.4}$$

Here $r_<$ ($r_>$) is the smaller (larger) of r and r', and $\varphi_i(r)$ is the radial part of $\Phi_i(\mathbf{r})$. The first term in Eq. (5.3) is the exchange interaction between a p electron with $m=-1$ and two p electrons $m=1$ and 0. The second term is the interaction between an s electron and two p electrons. The integrand of (5.1) corresponding to the *p-p* interaction has two nodal planes as a function of $\mathbf{r}$, while there is only one nodal plane for the *s-p* interaction, which is larger as a result. Using realistic values for the Slater integrals, we find that $\Delta E_x \sim 6$ eV. The $X\alpha$ calculation, however, gives similar radial extents for the s and p orbitals. If the radial parts are identical and we neglect small nonspherical corrections, the $X\alpha$ approximation predicts that the exchange energy is unchanged by the *sp* transfer. It is not surprising then that the $X\alpha$ prediction for the *sp* transition energy differs from the HF result by 6 eV. The $X\alpha$ and the LSD approximations give similar *sp* transfer energies in this case. The deviation between the LSD result and experiment is, however, reduced to 2.6 eV, since the large change in the exchange energy is partly compensated by a change in the correlation energy. Below we discuss several cases in which similar errors occur.

A. A simple model problem

We have performed extensive LSD and $X\alpha$ calculations for atoms and compared the results with HF calculations and experiment (Gunnarsson and Jones, 1985b). The differences between the $X\alpha$ and HF results are reproduced remarkably well by model calculations where we isolate the effects of the l dependence of the orbitals by assuming that the s, p, and d orbitals have the same *radial* dependence. With this assumption G^k depends only on k. For the 3s orbital in Ca we find the numerical relations

$$G^0=\frac{G^1}{0.680}=\frac{G^2}{0.516}=\frac{G^3}{0.414}=\frac{G^4}{0.344} \tag{5.5}$$

and

$$\int d\mathbf{r}\,\varepsilon_x[n(\mathbf{r}),0]=0.451G^0\ , \tag{5.6}$$

where $n(\mathbf{r})$ is the charge density due to a Ca 3s electron. Similar coefficients are obtained for the orbitals of other elements of the iron series. The unphysical self-interaction $-G^0/2$ is canceled to within about 10%. In Fig. 28(a) we compare the $X\alpha$ and HF exchange energies as a function of the number N of spin-up electrons. In the HF case the shells are filled in the order s, p, d, and within each shell in the order $m, m-1, \ldots, -m$. In the $X\alpha$ case the small nonspherical contributions are neglected. The $X\alpha$ and HF results agree remarkably well. The results are consistent with the finding (Schwarz, 1972) that HF exchange energies in atoms are reproduced for values of α slightly larger than $\frac{2}{3}$. Figure 28(b) shows results for the interelectronic exchange energy, for which the self-interaction has been subtracted. With the filling order s, p, d, the $X\alpha$ and HF results are in rather good agreement, with the magnitude of the $X\alpha$ results being somewhat larger. Figure 28(b) also shows results for occupations where a subshell is left empty. This does not influence the $X\alpha$ results in the present model, but it has a strong effect on the HF results. For instance, the curve "s shell empty" is lower than the curve corresponding to the s, p, d filling, since the *p-p* exchange interaction is smaller than the *s-p* interaction. It follows from the orthogonality of the HF orbitals that the exchange hole contains one electron; a similar sum rule is also satisfied by the LSD and the $X\alpha$ approximations (Gunnarsson and Lundqvist, 1976). Aspects of orthogonality and node formation are then included in all these schemes, although Fig. 28(b) shows that the sum rule does not guarantee a good description.

This model problem illustrates two important conclusions: (1) If we occupy the orbitals with the minimum number of nodal planes consistent with the Pauli principle, the trends in the interelectronic exchange energies are reproduced well by the $X\alpha$ approximation. The absolute value is overestimated in all the systems we have considered. (2) The energy for the transfer from such a state to a state with one additional node is often underestimated substantially in the $X\alpha$ approximation.

1. First-row atoms

In Fig. 9 we showed results for Δ_{sp} for first-row atoms and ions. It can be seen that the LSD approximation agrees well with experiment for Li-N and for Be$^+$-O$^+$, while there are large deviations for O, F, F$^+$, and Ne$^+$. A comparison of the $X\alpha$ and HF shows a very similar trend, supporting our focus on the comparison of the $X\alpha$ and HF calculations. The sp transfer in Be-C and B$^+$-N$^+$ involves a spin flip. The weaker spin dependence in the LSD approximation therefore leads in these systems to substantially larger values for Δ_{sp} than in the $X\alpha$ approximation. This effect accounts for the substantial correlation contribution to the sp transfer energy for these systems.

We now interpret these results using the model calculation described above. For the atoms Be-C, a $2s(\downarrow)$ electron is transferred to a $2p(\uparrow)$ orbital. If the number of valence electrons is m, the change of the interelectronic exchange energy due to the sp transfer is

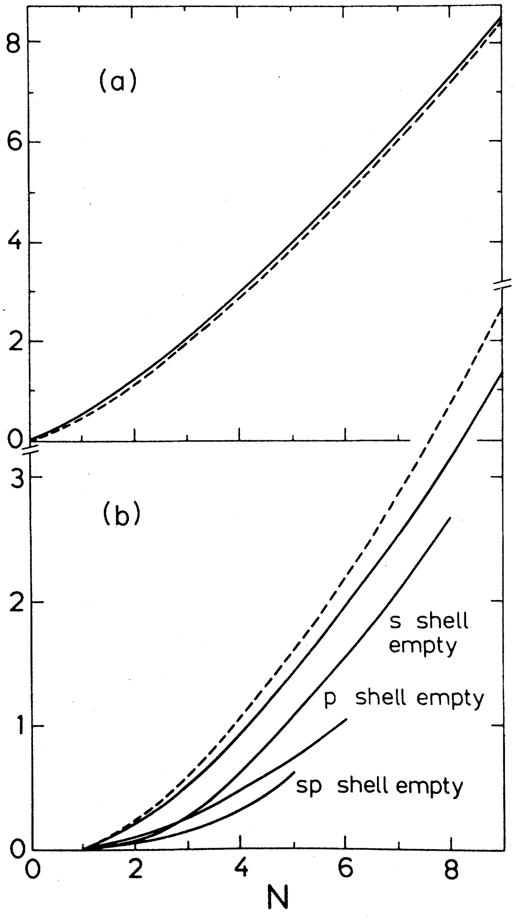

FIG. 28. Exchange energies in model described in text. (a) $E_x^{X\alpha}$ (dashed curve) and E_x^{HF} (solid curve) as a function of the number N of electrons (in units of $-G_0$); (b) the interelectronic exchange $E_{x,\mathrm{int}}$ for the $X\alpha$ and Hartree-Fock (HF) approximations. In the HF approximation we show the dependence for different schemes of occupying the orbitals.

$$\Delta E_{x,\mathrm{int}}=E_{x,\mathrm{int}}(N=1)+E_{x,\mathrm{int}}(N=m-1)$$
$$-E_{x,\mathrm{int}}(N=m)\ . \tag{5.7}$$

In this case all energies refer to the filling order s, p. From Fig. 28(b) we therefore expect the $X\alpha$ approximation to give rather good results, and this is confirmed in Fig. 9(b). For N-F, a $2s(\downarrow)$ electron is transferred to a $2p(\downarrow)$ orbital. The change of the interelectronic exchange energy of the spin-down electron system is

$$\Delta E_{x,\mathrm{int}}=E_{x,\mathrm{int}}(N=m-4)$$
$$-E_{x,\mathrm{int}}(N=m-4,s\text{ shell empty})\ . \tag{5.8}$$

For the nitrogen atom, $N=1$ and Fig. 23(b) predicts an accurate result, while for O and F it predicts large errors, in agreement with the results in Fig. 9(b). Thus Be-C illustrate conclusion (1) and O-F conclusion (2). We note that the large variation in the error across the row is due to the different types of configurations involved and not to intrinsic differences between the atoms.

For the ionization of a first-row atom, we can similarly express the change in the exchange energy in terms of the energies in Fig. 28. This shows that only energies for configurations with the filling s, p are involved, consistent with the good agreement between the $X\alpha$ and HF results and between the LSD results and experiment for the ionization energy.

In the HF approximation, configurations such as $2s^1 2p^1$ and $2s^1 2p^5$ have the same multiplet structure, with the splitting determined by the same linear combinations of Slater integrals. In this sense, these configurations show *electron-hole symmetry.* This is not present in the $X\alpha$ and LSD approximations (Gunnarsson and Jones, 1980b), although an *ad hoc* modification of the LSD approximation leads to similar errors for the $2s^1 2p^1$ and $2s^1 2p^5$ configurations. The errors due to the lack of the electron-hole symmetry can also be analyzed in the above framework. It is interesting that for all cases in which the errors were found to be large, configurations with a filling order other than s, p, d are involved.

2. Iron-series atoms

Figure 10 shows results for Δ_{sd} for the neutral atoms and for the ions. As for the first-row atoms, the deviations between the $X\alpha$ and the HF approximations are similar to the ones between the LSD approximation and experiment. The overall trends are reproduced well by the $X\alpha$ and LSD approximations; the break in the middle of the series, due to the filling of the spin-up d shell, is described well. For the neutral atoms, however, there are substantial differences between LSD-expt and $X\alpha$-HF, which are approximately constant across the series. For the ions this difference is much smaller.

To understand these results, it is helpful to study first the Mn atom, which provides a particularly simple example. In the transition

$$[\text{core}]3d(\uparrow\uparrow\uparrow\uparrow\uparrow)4s(\uparrow\downarrow)\rightarrow[\text{core}]3d(\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow)4s(\uparrow) \tag{5.9}$$

the only spin-down valence electron is transferred from a 4*s* to a 3*d* orbital. Within the $X\alpha$ and HF approximations this electron has no exchange interaction with any other valence electron, and these approximations might be expected to give similar results. Figure 10 shows, however, a difference of about 2 eV, which can be traced to the description of the exchange interaction between the 3*d* spin-down electron and the 3*s*3*p* core. Figure 28(b) shows that this interaction should be described fairly well, and the relative error is only $\sim 13\%$. The absolute error is nevertheless substantial, because the 3*d* electron has a similar spatial extent to the 3*s* and 3*p* electrons and interacts strongly with them. For all the other atoms the $X\alpha$ result is also influenced by interaction with other valence electrons, but the effect is not large and the net error is relatively constant across the series. For the ions, the 4*s* electron removed has spin-up, and its interaction with the 3*d* electrons plays a more important role. The error in the 4*s*-3*d* interaction tends to cancel part of the error in the 3*d* core interaction, thereby explaining the smaller errors for the 3*d* ions (Gunnarsson and Jones, 1985b).

3. Small molecules

The ground state of H_2 and the alkali dimers is a ${}^1\Sigma_g^+[\sigma_g(\uparrow\downarrow)]$ bond between the valence *s* orbitals. The strength of the bonds in H_2 and Li_2 is shown in Table V. This is another case in which the $X\alpha$ approximation reproduces the HF result well and the LSD approximation is in satisfactory agreement with experiment. This shows that the $X\alpha$ approximation gives a good description of the changes in the self-interaction during the formation of this σ bond, and that the LSD approximation accounts for the substantial change in the correlation energy.

The ${}^3\Sigma_u^+[\sigma_g(\uparrow)\sigma_u(\uparrow)]$ state is repulsive, except for a weak minimum at large distance. It may appear that this should be a more favorable case for the LSD approximation than the ${}^1\Sigma_g^+$ state, since the correlation energy is small and there is no spin flip involved in the bond formation. However, the LSD approximation overestimates the binding energy by 0.5 eV. We have studied this question in a model problem and traced the error to the interelectronic interaction (Gunnarsson and Jones, 1985b). For small internuclear separations, the σ_u orbital goes over to a *p* orbital. The σ_g-σ_u interaction therefore shows similarities with the *s*-*p* interaction described above, with a moderate overestimate of the interelectronic exchange energy in both cases. A similar situation occurs in He_2 and for the group-IIa dimers, for which the LSD approximation overestimates the bond strengths (Sec. IV.B.2). These examples also illustrate our conclusion (1).

Figure 29 shows the results of a model calculation for Li_2, using Slater orbitals for the description of the valence orbitals. The figure compares the deviation $\Delta E_x(R)$ of the $X\alpha$ exchange energy from the HF result as a function of the internuclear separation R. The deviation of a given curve from the ground-state curve (${}^1\Sigma_g^+$, thick curve) gives the error in the corresponding excitation energy. The curves fall into two groups. For the states ${}^3\Sigma_u^+$, ${}^1\Sigma_g^+$ ${}^3\Delta_u$, and ${}^3\Pi_u$, the integrand in the relevant exchange integral has one nodal plane. The deviation from the dashed line in Fig. 29, representing the error for separated atoms, shows that the magnitude of the interelectronic exchange energy is moderately overestimated. Since the number of nodes is the minimum consistent with the Pauli principle, this is in agreement with conclusion (1). For the remaining states ${}^3\Pi_g$ and ${}^3\Sigma_g^-$ the integrand of the exchange integral has two nodal planes. As one expects from conclusion (2) in Sec. III, the magnitude of the interelectronic exchange energy is overestimated greatly in these cases. The remaining first-row diatomic molecules were discussed by Gunnarsson and Jones (1985b).

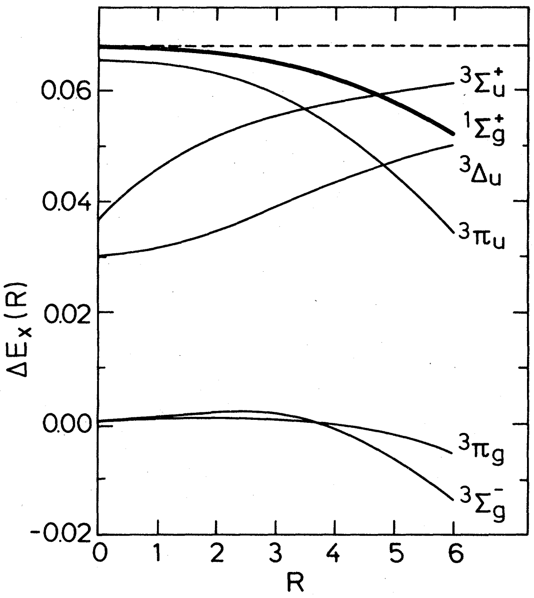

FIG. 29. Difference $\Delta E_x(R)$ between the exchange energies in the $X\alpha$ and Hartree-Fock approximations as a function of the internuclear separation R for different states of the Li_2 molecule. For the ground state the equilibrium separation is $R=5$ a.u. The dashed curve shows the result for two free Li atoms. All energies are in Ry.

It is interesting to ask how the inclusion of correlation influences the discussion, since many of the transitions discussed here involve substantial changes in the correlation energy. When these changes are related to changes in the spin density, the LSD approximation often provides an adequate description, examples being the atoms Li-C in Fig. 9. For cases in which differential correlation effects are not related to large changes in the spin density, however, the LSD approximation can fail badly. An extreme example is the *sp* transfer in F, which involves a change in correlation energy of about 3 eV, which is almost entirely absent in the LSD approximation. An exact HF calculation together with an LSD description of correlation is therefore not a general alternative.

We have demonstrated that the nodal structure of the wave functions can have a great effect on the accuracy of the LSD approximation, and we have identified classes of problems in which the LSD results must be treated with caution. For states with the minimum number of nodal planes consistent with the orthogonality of the orbitals, the LSD approximation usually leads to a moderate overestimate of the exchange-correlation energy. For states with additional nodal planes the exchange-correlation energy is often greatly overestimated. In atoms, the depopulation of *s* orbitals can lead to large errors; similar effects may be expected in bonding situations in which *sp* or *sd* hybridization reduces the *s* occupancy.

A comparison of the results of density functional and Hartree-Fock calculations is the basis of recent work of Cook and Karplus (1987). They noted that some of the most serious errors in HF calculations occur because the single-determinant molecular wave function does not in general allow a molecule to dissociate into neutral atoms. Expanding a single-determinant HF wave function in terms of atomic orbital determinants typically results in high-energy ionic configurations. The HF energy curve then rises too steeply and to an asymptote that is too high. A detailed study of some low-lying states in O_2 showed that much of the error in the HF calculations could be explained in this way. In contrast, the DF formalism focuses on the density, i.e., the square of the wave function; both the "covalent" and the "ionic" contributions produce densities characteristic of neutral atoms. In particular, the LSD approximation can describe the dissociation of a diatomic molecule, if an "antiferromagnetic" spin polarization is allowed.

B. Modifications to local-density approximations

The early work of Hohenberg, Kohn, and Sham introduced the local-density approximation, but it also pointed out the need for modifications in systems where the density is not homogeneous. One modification suggested by Hohenberg and Kohn (1964) was the approximation

$$E_{xc}=E_{xc}^{\mathrm{LSD}}-\tfrac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'K_{xc}\left[\mathbf{r}-\mathbf{r}',n\left[\frac{\mathbf{r}+\mathbf{r}'}{2}\right]\right]\times[n(\mathbf{r})-n(\mathbf{r}')]^2\ , \qquad (5.10)$$

where the kernel K_{xc} is related to the dielectric function of a homogeneous medium. This approximation is exact in the limit of weak density variations

$$n(\mathbf{r})=n_0+\Delta n(\mathbf{r})\ , \qquad (5.11)$$

where $|\Delta n(\mathbf{r})|\ll n_0$, but the results for real systems are not encouraging. For free atoms the energy is infinite (Gunnarsson *et al.*, 1979), indicating that the sum rule (3.12) is not satisfied.

It is natural that there have been many subsequent suggestions for correcting some of the defects of local-density calculations. In the remainder of this section, we discuss representative examples of three types: (1) those based on the exact equation of the exchange-correlation energy [Eq. (3.9)]; (2) those derived from self-interaction corrections; and (3) those developed from a wave-vector analysis of the exchange-correlation energy.

1. Approximations based on an exact equation for E_{xc}

The equation for the exchange-correlation energy [Eq. (3.11)] shows that the differences between the exact and the approximate exchange holes are largely due to the nonspherical components of the hole. Since these do not contribute to E_{xc}, total energies and total energy differences can be remarkably good, even in systems where the density distribution is far from uniform. In the LD approximation we assume that the exchange-correlation hole $n_{xc}(\mathbf{r},\mathbf{r}-\mathbf{r}')$ depends only on the charge density at the electron. It would be more appropriate to assume (Gunnarsson et al., 1976, 1979) that n_{xc} depends on a suitable average $\overline{n(\mathbf{r})}$,

$$n_{xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})=\overline{n(\mathbf{r})}\int d\lambda\{g_h[\mathbf{r}-\mathbf{r}',\lambda,\overline{n(\mathbf{r})}]-1\}\ . \qquad (5.12)$$

It is possible to choose the weight function that determines $\overline{n(\mathbf{r})}$ so that the functional reduces to the exact result in the limit of almost constant density. Approximation (5.12) satisfies the sum rule (3.12). Somewhat different prescriptions for the weight function have been proposed (Gunnarsson *et al.*, 1976, 1979; Alvarellos *et al.*, 1986). The approximation gives improved results for total energies of atoms, but otherwise has not been tested extensively.

An alternative approximation is obtained if we keep the proper prefactor $n(\mathbf{r}')$ in Eq. (3.10), leading to the so-called weighted density (WD) approximation:

$$n_{xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})=n(\mathbf{r}')G[|\mathbf{r}-\mathbf{r}'|,\tilde{n}(\mathbf{r})]\ , \qquad (5.13)$$

where $\tilde{n}(\mathbf{r})$ is chosen to satisfy the sum rule (3.12) (Alonso and Girifalco, 1977a, 1978; Gunnarsson *et al.*, 1977, 1979). Different forms have been proposed for $G(\mathbf{r},\tilde{n})$. We now discuss an analytic form (Gunnarsson and Jones, 1980a), which is computationally simpler and can be chosen to give exact results in certain limits. We assume that

$$G(\mathbf{r},n)=C(n)\{1-\exp[-\lambda(n)/|r|^5]\}\ , \qquad (5.14)$$

where C and λ are parameters to be determined. The functional G behaves as $|\mathbf{r}|^{-5}$ for large distances, which is needed to obtain an image potential. For a homogeneous system with density n, we require that the model functional should both fulfill the sum rule for $\tilde{n}(\mathbf{r})=n$ and give the exact exchange-correlation energy. This leads to two equations,

$$n\int d\mathbf{r}\,G(|\mathbf{r}|,n)=-1\ , \qquad (5.15)$$

$$\frac{e^2}{2}\int d\mathbf{r}\frac{1}{|\mathbf{r}|}G(|\mathbf{r}|,n)=\varepsilon_{\mathrm{xc}}(n)\,, \tag{5.16}$$

which are sufficient to determine the two parameters $C(n)$ and $\lambda(n)$.

This functional is exact in several limiting cases: (1) for a homogeneous system; (2) for one-electron systems, such as the hydrogen atom, where it gives an exact cancellation of the electron self-interaction; (3) for an atom, where it gives the correct behavior of the exchange-correlation energy density far from the nucleus, $\varepsilon_{\mathrm{xc}}(\mathbf{r})=-e^2/2r$; (4) for far outside the surface, where it gives the image potential $\varepsilon_{\mathrm{xc}}(z)=-e^2/(4z)$. The LSD approximation gives qualitatively incorrect answers for cases (3) and (4), and the cancellation in case (2) is only approximate. Since (2) is satisfied, this approximation provides a "self-interaction correction" in the sense that we shall discuss below. In Fig. 30 we show an application of this approximation to the total energy of atoms. The errors in the WD approximation are about an order of magnitude smaller than those in the LSD approximation. However, the *sp* and *sd* transfer energies are disappointingly little improved over LSD results.

The position of the image plane at a surface has been calculated within the WD approximation in two ways: (1) from the asymptotic behavior of the exchange-correlation potential (Ossicini *et al.*, 1986); (2) from the centroid of the image charge (Ossicini *et al.*, 1987). The second calculation appears to be more reliable. Borstel *et al.* (1981) and Przybylski and Borstel (1984a, 1984b) have used variations of the WD approximation in studies of Rh, Cu, and V. For Rh they found that the WD approximation correctly shifts unoccupied bands upward. For Cu they obtained an improved description of the *d* band and the Fermi surface, while for V the errors in the LSD approximation for the Fermi surface were substantially overcorrected. For semiconductors it was found that there is either only little (Si, Hybertsen and Louie, 1984) or no (GaAs, Manghi *et al.*, 1983) improvement over the LSD approximation for the band gap.

The weighted density models provide a link between $\varepsilon_{\mathrm{xc}}$, the density-density correlation function, and the response function of a homogeneous system. By using these equations and the fluctuation-dissipation theorem [which relates the structure factor to the static local-field correction to the random-phase approximation (RPA)], Chacón and Tarazona (1988a) proposed recently a self-consistent scheme for determining properties of the electron liquid. Results for correlation energies are in good agreement with other calculations, and the surface energy values are close to the LD results (Chacón and Tarazona, 1988b).

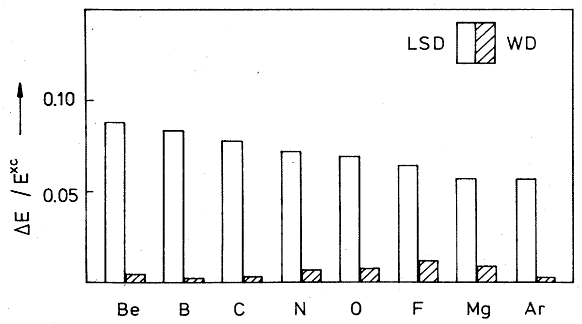

FIG. 30. Error in the total energy of a free atom as a fraction of the exchange-correlation energy in the local spin-density (LSD) and the weighted density (WD) approximations (see Gunnarsson and Jones, 1980a).

Perdew (1985) and Perdew and Yue (1986) have studied the exchange hole using a second-order gradient expansion. The hole has a spurious, undamped, long-range oscillation. Perdew imposed the condition that the exchange hole never be positive and cut it off at a radius where the sum rule (3.12) is satisfied. Integrating this modified exchange hole [see Eq. (3.9)] led to greatly improved exchange energies for atoms.

2. Self-interaction corrected approximations

In the DF formalism each electron interacts with itself via the Coulomb electrostatic energy. This nonphysical interaction would be canceled exactly by a contribution from the exchange-correlation energy in the exact formalism. In the LSD approximation this cancellation is imperfect, but numerically rather good. To illustrate, we consider the H atom (Gunnarsson *et al.*, 1974). For this one-electron system the electron-electron interaction energy should be zero. The electrostatic energy is about 8.5 eV, which in the LSD approximation is canceled to about 95% by the exchange-correlation energy (8.1 eV).

The incorrect treatment of the self-interaction in approximate functionals has led a number of people to consider self-interaction corrected (SIC) functionals. Such a correction was studied in the context of the Thomas-Fermi approximation (Coulson and Sharma, 1962), the Hartree approximation (Cowan, 1967), the Hartree-Slater approximation (Lindgren, 1971), and the LSD approximation (Perdew, 1979; Zunger *et al.*, 1980; Perdew and Zunger, 1981). Within the LSD approximation the SIC functional takes the form

$$E_{\mathrm{SIC}}=E_{\mathrm{LSD}}[\rho\uparrow(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})]-\sum_{i\sigma}\delta_{i\sigma}\,,$$

where E_{LSD} is the LSD energy functional and

$$\delta_{i\sigma}=\frac{e^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho_{i\sigma}(\mathbf{r})\rho_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{xc}}^{\mathrm{LSD}}(\rho_{i\sigma},0) \tag{5.17}$$

is the self-interaction correction (SIC) for the orbital i with spin σ and charge density $\rho_{i\sigma}(\mathbf{r})$. The first term in (5.17) is the self-interaction energy; the second is the LSD approximation to the exchange-correlation energy of a fully spin-polarized system with density $\rho_{i\sigma}(\mathbf{r})$. This functional is exact for a one-electron system. It leads to the equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})+V_{i\sigma}^{\mathrm{SIC}}(\mathbf{r})\right]\varphi_{i\sigma}=\sum_{i}\lambda_{ij}^{\sigma}\varphi_{j\sigma}\ ,$$

where $V(\mathbf{r})$ is the effective potential (3.4) entering in a normal LSD calculation and $V_{i\sigma}^{\mathrm{SIC}}(\mathbf{r})$ is additional potential resulting from the term (5.17). This potential is orbital dependent, and the Lagrange parameters λ_{ij}^{σ} must be introduced to ensure that the solutions $\varphi_i(\mathbf{r})$, sometimes referred to as "local orbitals," are orthogonal. The SIC approximation is not invariant under a unitary transformation of the orbitals, and Harrison (1983) found that the results for atoms depend on whether one uses orbitals in the spherical harmonic set $(s,p_1,p_0,p_{-1},\ldots)$ or in the Cartesian set $(s,p_x,p_y,p_z,\ldots)$. Pederson *et al.* (1984, 1985) and Pederson and Lin (1988) proposed that the local orbitals leading to the lowest total energy should be used. This leads to the requirement (Pederson *et al.*, 1984) that

$$\langle\varphi_{j\sigma}|V_{j\sigma}^{\mathrm{SIC}}-V_{i\sigma}^{\mathrm{SIC}}|\varphi_{i\sigma}\rangle=0\ . \tag{5.18}$$

One can also introduce a set of orbitals satisfying (Pederson *et al.*, 1984, 1985)

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})+\Delta V_{i\sigma}^{\mathrm{SIC}}(\mathbf{r})\right]\psi_{i\sigma}=\sum_{i}\varepsilon_{ij}^{\sigma}\psi_{j\sigma}\ .$$

The potential felt by the orbitals $\psi_{i\sigma}=\sum_j M_{ij}\varphi_{j\sigma}$ is expressed in terms of the local orbitals $\varphi_{j\sigma}$,

$$\Delta V_{i\sigma}^{\mathrm{SIC}}(\mathbf{r})\psi_{i\sigma}=\sum_{j}M_{ij}V_{j\sigma}^{\mathrm{SIC}}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r})\ .$$

From the condition (5.18) it follows that the matrix $\varepsilon_{ij}^{\sigma}$ can be diagonalized. The resulting orbitals are referred to as canonical and correspond to the solutions of the normal LSD equations. The corresponding eigenvalues ε_i satisfy the relation $\partial E/\partial n_i=\varepsilon_i$ [cf. Eq. (6.2) below; Pederson *et al.*, 1985] and they are interpreted as excitation energies. For extended systems these eigenvalues provide a band structure.

We now turn to the application of SIC-LSD calculations to specific systems. Calculations for atoms have been performed by Perdew (1979), Zunger *et al.* (1980), Gunnarsson and Jones (1981), Perdew and Zunger (1981), Harrison (1983), Harrison *et al.* (1983), Heaton *et al.* (1986), and Pederson and Lin (1988). The errors in the total exchange and correlation energies are much less than those obtained with the LSD approximation. For Ne, for instance, the exchange energies are 337.8, 297.6, and 329.5 eV in the SIC-LSD, LSD, and exact calculations, respectively (Perdew and Zunger, 1981). The corresponding correlation energies are 11.4 (SIC), 19.9 (LSD), and 10.0 eV (exact). Unfortunately, ionization and transfer energies of atoms are not generally better in the LSD-SIC approximation, at least if nonspherical corrections are neglected. The improved total energies in SIC calculations can be traced, in fact, to a much better treatment of the innermost core electrons (Gunnarsson and Jones, 1981), which play a relatively minor role in most chemical and physical processes of interest.

The exchange-correlation potential usually becomes more attractive and the eigenvalues are lowered when the SIC is introduced. Lindgren (1971) compared the $X\alpha$ $(\alpha=\frac{2}{3})$, SIC, and HF approximations for atoms and showed that the SIC approximation gave exchange-correlation potentials and eigenvalues in substantially better agreement with the HF results than those obtained with the $X\alpha$ approximation. Similarly, Perdew (1979), Zunger *et al.* (1980), and Perdew and Zunger (1981) showed that the SIC-LSD eigenvalues are in much better agreement with experimental ionization energies than the LSD eigenvalues. Since atomic excitation energies are most reliably calculated from total energy differences, the significance of these observations is not immediately obvious. It is, however, an interesting question how these effects influence the eigenvalues in solids, where the eigenvalues are traditionally interpreted as excitation energies.

In the application of SIC to solids, the choice of orbitals in Eq. (5.17) is an important question. If Bloch orbitals are used, the SIC is zero, while localized orbitals give a finite correction. The requirement that the energy should be minimized with respect to the orbitals φ removes this arbitrariness, but it is difficult to implement for solids. Much of the work for solids has therefore relied on particular forms for φ, e.g., atomic orbitals or some type of Wannier orbitals. Heaton *et al.* (1983) studied Ar and LiCl crystals expressing the SIC in terms of approximate Wannier functions. The band gap was found to be substantially better than that in the LSD approximation. For LiCl the band gap is 10.6 (SIC), 6.0 (LSD), and 9.4–9.9 eV (expt.); for Ar it is 13.5 (SIC), 7.9 $(X\alpha,\alpha=\frac{2}{3})$, and 14.2 eV (expt.) (Heaton *et al.*, 1983; Heaton and Lin, 1984). In these systems the great improvement of the gap is related to an improvement of the eigenvalues for the corresponding free atoms.

A longstanding problem in the DF formalism is the description of localization, for instance, in a Mott insulator or in the α-γ transition in Ce due to the Kondo effect. For systems with a half-filled band the LSD approximation can describe localization effects as a transition to a magnetic state. If the system is completely polarized, the bonding and antibonding orbitals are equally occupied and the contribution of this band to cohesion is lost. The system can then also open up a gap. The Mott transitions in solid H (Kelly *et al.*, 1982; Min *et al.*, 1986), MnO (Andersen *et al.*, 1979), and a phase transition in Am (Skriver *et al.*, 1978) have been described in this way. For a general band filling, however, the LSD approximation cannot describe such localization effects, while this is possible in the SIC approximation (Svane and Gunnarsson, 1988a).

Due to the orbital dependence of the SIC potential, broken-symmetry solutions for the local orbitals can be found where each one-particle solution localizes at a particular site and experiences a more attractive potential at this site. Depending on the strength of the hopping integrals and the Coulomb repulsion on the site, such a solution may or may not remain localized in a self-consistent treatment, as one expects for a system with a Mott transition. These arguments do not assume any particular band filling. The method has been applied to the one-dimensional Hubbard model, for which the exact solution is known (Lieb and Wu, 1968). The band gap, the total energy, the local moment, and the momentum distribution are described substantially better than in the LSD approximation (Svane and Gunnarsson, 1988a). The comparison of SIC, LSD, and exact band gaps in Fig. 31 illustrates the large improvements resulting from the SIC approximation. In these calculations it is essential that the SIC equations are allowed to determine the localization of the one-particle solutions (local orbitals) and that no particular assumption about the extent of the solutions is made.

The tendency to antiferromagnetic moment formation can be underestimated severely by the LSD approximation. One example is the one-dimensional Hubbard model mentioned above, and another is provided by the high-T_c superconductors, where the Stoner parameter I is at least a factor 2–3 too small (Zaanen *et al.*, 1988). Svane and Gunnarsson (1988b) performed calculations for a simple model of La_2CuO_4, which includes the important x^2-y^2 orbital of Cu and the $2p$ orbitals of O, pointing toward the Cu atoms. It was found that the tendency to antiferromagnetism is greatly enhanced in SIC, compared with the LSD approximation, and that the experimental moment may even be overestimated by SIC.

3. Wave-vector analysis

In an early calculation of the correlation energy of an infinite electron gas, Nozières and Pines (1958) demonstrated the advantage of separating contributions from regions with different momentum transfers. This approach has been followed by Langreth, Perdew, and coworkers in the present context. Their starting point is also Eq. (3.9), expressed in reciprocal space (Langreth and Perdew, 1975, 1977):

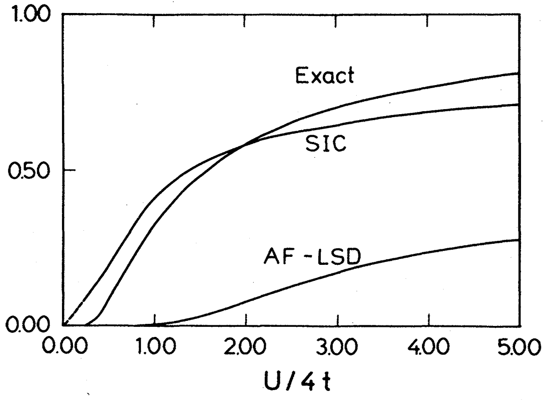

FIG. 31. Band gap E_g for the one-dimensional Hubbard model. The hopping parameter is t and the on-site Coulomb interaction is U. The antiferromagnetic (AF) local spin-density (LSD), the self-interaction corrected (SIC), and the exact results are compared (Svane and Gunnarsson, 1988a).

$$E_{\rm xc}=\frac{1}{2\pi^2}\int_0^\infty E_{\rm xc}(k)k^2dk\ , \tag{5.19}$$

where

$$E_{\rm xc}(k)=N\int\frac{d\Omega_{\mathbf k}}{4\pi}\frac{1}{2}\int_0^{e^2}\frac{d\lambda}{\lambda}\,\frac{4\pi\lambda}{k^2}S_\lambda(\mathbf k) \tag{5.20}$$

and

$$S_\lambda(\mathbf k)=\frac{1}{N}\int d\mathbf r\int d\mathbf r'\langle[\hat n(\mathbf r)-\langle\hat n(\mathbf r)\rangle_\lambda]\times[\hat n(\mathbf r')-\langle\hat n(\mathbf r')\rangle_\lambda]\rangle_\lambda e^{i\mathbf k\cdot(\mathbf r-\mathbf r')}\ . \tag{5.21}$$

As in Eqs. (3.9) and (3.10) there is an integration over the coupling constant λ; an external, λ-dependent potential is introduced to keep the density λ independent. The density operator is given in given by $\hat n(\mathbf r)$, and $\langle\ \rangle_\lambda$ is the expectation value evaluated for the coupling constant λ. The equivalence to Eq. (3.9) follows from the relation between the Fourier transform of $S_\lambda(\mathbf k)$ and $\langle\hat n(\mathbf r)\rangle_\lambda\langle\hat n(\mathbf r')\rangle_\lambda g(\mathbf r,\mathbf r',\lambda)$. Equation (5.19) makes it possible to discuss the contributions to $E_{\rm xc}$ from fluctuations of different wave vectors k. Such an approach was used by Nozières and Pines (1958) for the homogeneous electron gas. It is useful that different approaches can be used for small and large values of k and that exact results can even be found for $k=0$ and $k\rightarrow\infty$ in certain cases. Langreth and Perdew (1975, 1977) applied this approach to the surface energy of some simple model surfaces to discuss the LD approximation. Since this work later developed into a new general approximation (Langreth and Mehl, 1981, 1983; Perdew, 1986), we describe it briefly.

For the infinite barrier model considered by Langreth and Perdew (LP), where the potential is assumed to be constant inside the surface and infinite outside, a many-body calculation within the RPA (Wikborg and Inglesfield, 1975) showed that the contribution $\Delta E_{\rm xc}(k)$ to the surface energy behaves as

$$\Delta E_{\rm xc}(k)\sim\frac{1}{k}(\omega_s-\tfrac{1}{2}\omega_p) \tag{5.22}$$

for small values of k. Here ω_p is the bulk-plasmon frequency and $\omega_s=\omega_p/\sqrt{2}$ is the surface-plasmon frequency. The divergent result (5.22) contrasts with the LD result for small k (a constant), but the effect of this difference is strongly reduced by the volume element k^2 in Eq. (5.19). Since short wavelength fluctuations are insensitive to density variations, the LD approximation gives the exact result for large values of k. In Fig. 32 we show results for

$$\gamma(k)=\frac{1}{2\pi^2}2k_Fk^2\Delta E_{\rm xc}(k) \tag{5.23}$$

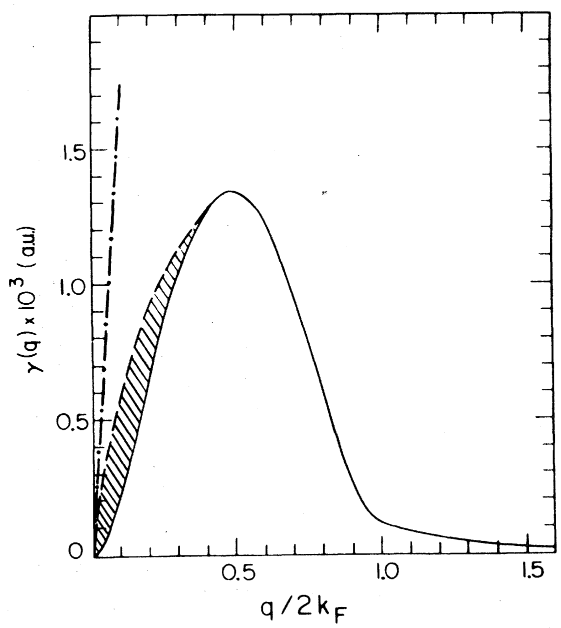

FIG. 32. Wave-vector analysis of the surface energy $\Delta E_{\mathrm{xc}} = \int d(q/2k_F)\gamma(q)$ in the random-phase approximation for the infinite barrier model with $r_s = 2.07$. The local-density result is given by the solid curve, the $k \to 0$ result [Eq. (5.22)] by the dashed-dotted line, and the interpolation by the dashed line. After Langreth and Perdew (1975).

as a function of $k/2k_F$, where k_F is the Fermi wave vector and $\gamma(k)$ has been defined so that the surface energy is the area under $\gamma(k)$. The solid curve shows the LD result, using RPA data for homogeneous electron gas to define the LD approximation. The figure also shows an extrapolation of the exact result (5.22). Langreth and Perdew interpolated between the exact $k=0$ result and the $k \sim k_F$ LD result; the resulting surface energy agreed well with the exact RPA result. The dashed curve is therefore probably a good approximation to the exact $\gamma(k)$ in RPA and suggests that the LD approximation works well for values of k that are not too small. The LD approximation, however, fails qualitatively for small values of k, although the consequences for the surface energy are relatively small. In view of the good result for the interpolation procedure, it would also be interesting to apply an approach of this type to other systems. The method relies, however, on the knowledge of the small-k result (5.22) and on the interpolation method. A more general approach was provided by Langreth and Mehl (LM; 1981, 1983).

Following LM (1983) we write

$$E_{\mathrm{xc}}[k_F] = \frac{e^2}{4\pi^3}\int d\mathbf{r}\, k_F^4 \left[-\frac{\varepsilon_{\mathrm{xc}}}{\varepsilon_x} + \delta W[k_F] \right] , \tag{5.24}$$

where the local Fermi wave vector $k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$ is used as the basic variable instead of $n(\mathbf{r})$. The electron gas exchange energy ε_x has been factorized out; the dimensionless quantity in parentheses has a LD contribution $-\varepsilon_{\mathrm{xc}}/\varepsilon_x$, which is of the order 1 for typical densities, and a correction term δW. Langreth and Mehl assumed that, apart from the local Fermi wave vector the system could be characterized by a single inverse length scale q. For a surface, the characteristic length is the healing length of the surface layer; for a tightly bound atomic orbital, it is the size of the orbital. Langreth and Mehl also assumed that

$$\delta W[k_F] = Z(k_F, q)\frac{q^2}{k_F^2} , \tag{5.25}$$

where the quantity q^2/k_F^2 was factorized out to show that the LD approximation becomes exact when $q \to 0$, and defined

$$q(\mathbf{r}) \equiv \frac{1}{2}\frac{|\nabla k_F(\mathbf{r})|}{k_F(\mathbf{r})} = \frac{1}{6}\frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})} . \tag{5.26}$$

For sufficiently slowly varying densities the gradient expansion is correct. Since $q \sim 0$ for such a system, the gradient expansion is recovered by the choice (5.26) of LM if $Z(k_F, q=0)$ is given the appropriate value. To determine the q dependence of $Z(k_F,q)$, LM used a wave-vector analysis of the type described above,

$$Z(k_F,q) = \int_0^\infty z(k_F,q,k)\,dk , \tag{5.27}$$

divided z into an exchange z_x and a correlation z_c contribution, and introduced a simple approximation based on an analysis by Langreth and Perdew (1979, 1980, 1982) for $z(k_F,q,k)$.

Here we follow Langreth and Vosko (LV, 1987), who studied an almost homogeneous electron gas with the density

$$n(\mathbf{r}) = n_0 + \frac{1}{\Omega}\sum \delta n_{\mathbf{Q}} e^{i\mathbf{Q}\cdot\mathbf{r}} , \tag{5.28}$$

where

$$|n(\mathbf{r}) - n_0| \ll n_0 , \tag{5.29}$$

and Ω is the volume of the system. The correction to the LD approximation is given by (Sham and Kohn, 1966)

$$\delta E_{\mathrm{xc}} = \frac{1}{2\Omega}\sum [K_{\mathrm{xc}}(\mathbf{Q}) - K_{\mathrm{xc}}(0)]|\delta n_{\mathbf{Q}}|^2 , \tag{5.30}$$

where K_{xc} is determined from the dielectric function

$$\varepsilon(\mathbf{Q}) = 1 - \frac{4\pi e^2}{\mathbf{Q}^2}\frac{\chi_0(\mathbf{Q})}{1 - K_{\mathrm{xc}}(\mathbf{Q})\chi_0(\mathbf{Q})} , \tag{5.31}$$

where χ_0 is the response function for noninteracting electrons. The function K_{xc} was rewritten as

$$K_{\mathrm{xc}}(\mathbf{Q}) - K_{\mathrm{xc}}(0) \equiv \frac{\pi e^2}{8k_F^4}\tilde{Z}(k_f,\mathbf{Q})\mathbf{Q}^2 . \tag{5.32}$$

It is now clear that for $\mathbf{Q} \sim 0$, the LM formula (5.25) gives the exact result for the density (5.28), if $Z(k_F,0) = \tilde{Z}(k_F,0)$. However, for a density with very weak variations of the type (5.28), the prescription (5.26) for q gives a poor estimate. For finite values of $\mathbf{Q}$ the LM functional is therefore not exact even for densities of the type (5.28) and (5.29). Langreth and Mehl argued that this is irrelevant since the approximation in practice has to be applied to systems with much stronger density variations than (5.29).

Langreth and Vosko calculated the wave-vector decomposition of the correlation part of $\tilde{Z}_c$

$$\tilde{Z}_c(k_F,\mathbf{Q})=\int_0^\infty \tilde{z}_c(k_F,\mathbf{Q},k)dk \tag{5.33}$$

for large densities. The result is shown in Fig. 33. It is striking that $\tilde{z}_c$ becomes very small for $k<\mathbf{Q}$. Langreth and Mehl therefore proposed the simple approximation

$$z_c(k_F,q,k)=\tilde{z}_c(k_F,0,k)\Theta(k-k_c) \ , \tag{5.34}$$

where Θ is the step function and k_c is a cutoff of the order q. They proposed

$$k_c=6fq \ , \tag{5.35}$$

where f is an adjustable parameter of the order $\frac{1}{6}$, which will be fixed to a particular value to be used for all systems. To simplify the use of the approximation, they also introduced an interpolation formula for $\tilde{z}_c$,

$$\tilde{z}_c(k_F,0,k)=\frac{4\sqrt{3}}{k_{\mathrm{TF}}}e^{-2\sqrt{3}k/k_{\mathrm{TF}}} \ , \tag{5.36}$$

where k_{TF} is the Thomas-Fermi wave vector. This interpolation formula is shown by the dashed curve in Fig. 33. The function $\tilde{z}_x(k_f,\mathbf{Q},k)$ grows linearly with k for small k and has a weaker dependence on $\mathbf{Q}$ than does $\mathbf{z}_c$. Langreth and Mehl then used the $\mathbf{Q}=0$ result and integrated Eq. (5.36) to obtain

$$Z(k_f,q)=2e^{-2\sqrt{3}k_c/k_{\mathrm{TF}}}-\frac{7}{9} \ . \tag{5.37}$$

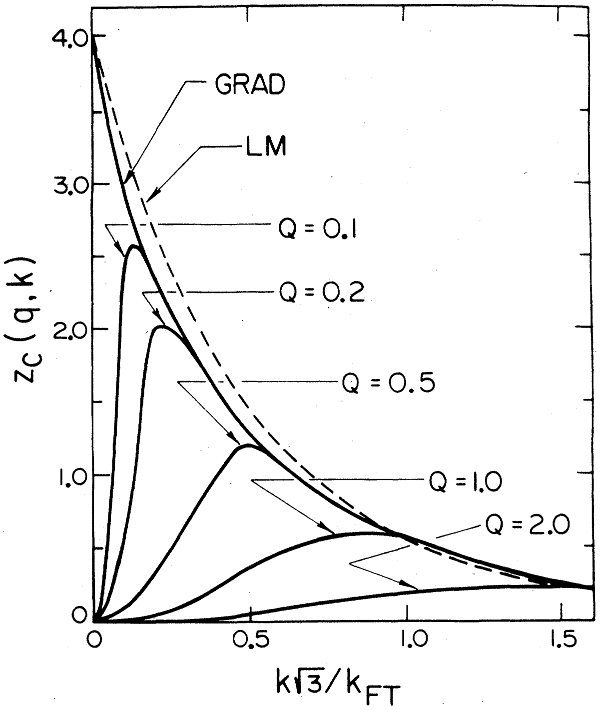

FIG. 33. Wave-vector decomposition of $\tilde{Z}_c(k_F,Q)$ [Eq. (5.33)] for the almost homogeneous density (5.28) and (5.29) for different values of Q. The unit of Q is $k_{FT}/\sqrt{3}$. The curve labeled GRAD shows the corresponding result for the gradient expansion; the dashed curve (LM) shows the result for the interpolation formula (5.37). The LM (Langreth-Mehl) approximation consists of truncating the dashed curve at $k=k_c\sim Q$.

Although LV performed this analysis for the high-density limit, they argued that the curves $\tilde{z}(k_F,\mathbf{Q},k)$ are not very different for metallic densities, except for some rapid variations as a function of k, which give a small numerical contribution. An important question is the extrapolation from the results for weakly varying densities (5.28) and (5.29) to realistic, strongly varying densities. For instance, it has been found that apparently reasonable extrapolations (Kohn and Sham, 1965) of the exact result (5.30) can give infinite results for finite systems such as atoms (Gunnarsson *et al.*, 1979). It is probably significant that LM focused on the suppression of contributions from small k, which also applies to real systems with strong density variations. One example is a metallic surface, as illustrated by the result $\gamma(k)\sim k$ [Eqs. (5.22) and (5.23)]. Langreth and Mehl also showed that for a finite system the corresponding contribution goes as k^2. While the definition (5.20) of q is somewhat arbitrary, q enters the final result for $Z(k_f,q)$ via k_c. Since it is multiplied by f, some of this arbitrariness can be compensated for by an appropriate choice of f.

The value of f was determined by studying small atoms and the linear potential model of a surface (Sahni *et al.*, 1977). Since $f\sim 0.13-0.14$. was the optimum value for a surface and $f\sim 0.15-0.16$ best for atomic total energies, LM proposed the value $f=0.15$. Later, Langreth (1984) argued for $f=0.17$. This work has been extended to spin-polarized systems by Hu and Langreth (1985; see also Rasolt, 1977). A method was also proposed for separating the exchange and correlation energies (Langreth and Mehl, 1983). Perdew (1986) proposed an alternative equation for the correlation energy. This equation is based on an analysis similar to that used in the LM approach, but it uses a different separation of the exchange and correlation energy and attempts to include correlation effects beyond the RPA. The wave-vector analysis of Langreth and Perdew and the LM functional have been criticized by Rasolt and Geldart (1986a, 1986b), who noted that the nonuniform electron gas has an exchange-correlation hole that is both long range and sensitive to the nature of the inhomogeneity. Since the long range is a property of the *macroscopic* system, these authors believe that corrections to the LDA based on electron gas data should be restricted to extended (bulk and surface) systems. For further references and a more detailed discussion of these points, see Rasolt and Geldart (1986a, 1986b, 1988) and Langreth and Vosko (1988). A survey of approximate exchange-correlation functionals is provided by Geldart and Rasolt (1987).

The LD approximation can now be discussed in the light of these results. In Eq. (5.24) the LD contribution is of the order unity, as is the coefficient $Z(k_F,q)$ in the correction term. The correction term is therefore small if

$$\frac{q(r)}{k_F(r)}=\frac{1}{6}\frac{|\nabla n(r)|}{k_F(r)n(r)}\ll 1 , \tag{5.38}$$

a criterion that is a factor 6 smaller than the one normally used for the LD approximation. Langreth and Mehl concluded that the large reduction reflects factors (such as the sum rule and spherical average discussed in Sec. III.B) that make the LD approximation more accurate than was originally expected. The criterion (5.38) is satisfied reasonably well for most systems of interest, in contrast to the criterion where the factor $\frac{1}{6}$ is missing. It is now also possible to discuss the traditional gradient expansion, where $Z(k_F,q)=\tilde{Z}(k_F,0)$. As can be seen from Fig. 33 this is a poor approximation unless $q \ll k_{\mathrm{TF}}$. Langreth and Mehl suggested the criterion

$$\frac{6q(r)}{k_{\mathrm{TF}}}=\frac{|\nabla n(r)|}{k_{\mathrm{TF}}n(r)}\ll 1 , \tag{5.39}$$

which is normally not fulfilled for real systems.

Before turning to applications of this model, it is interesting to note the recent work of Kleinman and Lee (1988), who evaluated $K_x(\mathbf{Q})$ [Eq. (5.32) for exchange only] for a screened interaction $\exp(-\lambda|\mathbf{r}'-\mathbf{r}|)$. They found that the limits $\mathbf{Q}\to 0$ and $\lambda \to 0$ do not commute. This ambiguity may be traced to the spurious undamped oscillation in the gradient expansion for the x hole far from the electron it surrounds. Alternatively, it may be cast (Perdew and Wang, 1988) as a discrepancy (at $\lambda=0$) between the zero temperature limit $(T\to 0)$ and $T=0$. The gradient expansion used above (see also Sham, 1971) is recovered when *either* $T=0$, $\mathbf{Q}\to 0$ is followed by $\lambda\to 0$ *or* $\lambda=0$, $\mathbf{Q}\to 0$ is followed by $T\to 0$. A coefficient $\frac{10}{7}$ as large (Antoniewicz and Kleinman 1985) is recovered when $T=0$, $\lambda\to 0$ is followed by $\mathbf{Q}\to 0$. It is not clear at present which coefficient should be favored in real systems.

We now discuss some of the results found so far with the LM model. Langreth and Mehl (1981, 1983) and Hu and Langreth (1985) showed that the total energy of atoms is much better than in LD results, as found in other nonlocal schemes. Pedroza (1986) compared the density obtained in the LD and the LM approximations with accurate configuration-interaction calculations. The density is already rather well described in the LD approximation, and the LM scheme gives further improvement. Removal energies of valence electrons in atoms were calculated by Langreth and Mehl (1981, 1983) and Hu and Langreth (1985). Again the LSD approximation gives rather accurate results in most cases; further improvements were found in the LM approximation.

In Table XI we show binding energies for some diatomic molecules, calculated by Becke (1986). The LSD approximation generally overestimates the binding energy, and in some cases—e.g., N_2, O_2, and F_2—the overbinding is appreciable. In these cases the LM approximation gives a substantial improvement. Similar results were obtained by Kutzler and Painter (1987), who emphasized the corrections due to the nonspherical density of the free atoms. These corrections are very small for the first-row atoms in the LSD approximation, but nonnegligible in the LM scheme. Kutzler and Painter also showed that the generalized gradient expansion (GGA) of Perdew (1986) and Perdew and Yue (1986) led to improved agreement with experiment, particularly for O_2 (see Table XI). Almbladh and von Barth (1985c) applied the LM functional to the *sp* transfer energy of a fluorine atom. As noted previously, this quantity is very poorly described in the LSD approximation (error ~2.6 eV), and the LM functional gives only a small improvement. This is not surprising, since the large error in the LSD approximation arises from its failure to take properly into account the nodal structure of the orbitals (Gunnarsson and Jones, 1985b). It seems unlikely that a functional with a simple dependence on the density, like the LM functional, can correct for this failure.

TABLE XI. Dissociative energies (eV) for some diatomic molecules in the Langreth-Mehl (LM) and local spin-density (LSD) approximations compared with the experimental values (Becke, 1986). The results (Kutzler and Painter, 1987) using the generalized gradient expansion approximation (GGA) (see Perdew, 1986, and Perdew and Yue, 1986) are also shown.

	Expt.	LSD	LM	GGA
H_2	4.8	4.9	5.0	
Li_2	1.1	1.0	0.6	
Be_2	0.10	0.56	0.36	
B_2	3.0	3.9	3.3	3.2
C_2	6.3	7.3	6.1	6.2
N_2	9.9	11.6	10.2	
O_2	5.2	7.6	6.4	5.9
F_2	1.7	3.4	2.4	2.2

The effect of the LM potential on the band structure of V and Cu has been studied by Norman and Koelling (1983), who found that the 3*d*-like states are shifted upward by the LM potential, so that the Fermi surface is improved in V but not in Cu. The deviation between the band structure and the photoemission results also increased somewhat for Cu. von Barth and Car (1982) calculated the band gap of Si and found that, as in the LD approximation, the band gap is about a factor of 2 too small. It is not clear whether the underestimation of the gap in the LD and LM functionals is due to a discontinuity in the exchange-correlation potential, which would clearly not be described in functionals of the LD and LM types, or to a less satisfactory description of the $\mathbf{r}$ dependence of the exchange-correlation potential. The cohesive properties are improved compared with the LD approximation. The cohesive energy of Si, for instance,

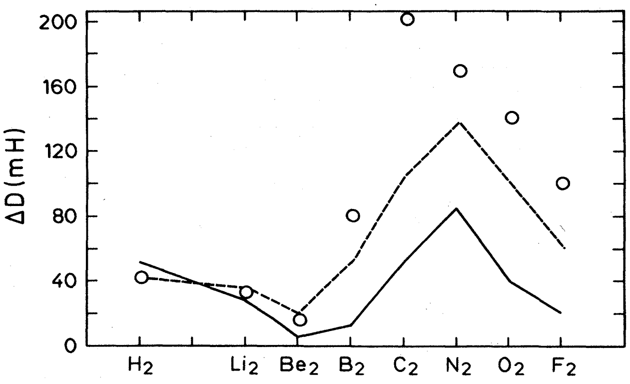

FIG. 34. Correlation energy contribution to the dissociation energy of some dimers. The local spin-density (solid line), the Langreth-Mehl (dashed line), and the empirical (circles) results are shown (after Savin *et al.*, 1986).

is 4.89 eV compared with the experimental result of 4.63 eV and the LD result of 5.19 eV. von Barth and Pedroza (1985) also found an improvement in the cohesive energy of Be. The LM result is 3.20 eV, the experimental result is 3.32 eV, and the LD result is 3.65 eV.

An alternative to the normal treatment of exchange and correlation in the SDF formalism is to treat the numerically large exchange energy exactly and to include correlation via an approximate functional. In the LSD approximation, this approach is questionable, since the correlation energy is overestimated by a factor of 2 or more; a treatment of both exchange and correlation in the LSD approximation is usually preferred. Langreth and Mehl (1983) showed that their separation of exchange and correlation yielded greatly improved results for the total correlation energy of atoms, and Pedroza (1986) obtained very accurate results for the electron density of some small atoms. Savin *et al.* (1984) found that the total correlation energy of many small molecules is greatly improved over the LSD approximation. The correlation contribution to the dissociation energy is of particular interest and is shown in Fig. 34. While the improvement for this correlation energy *difference* is much less pronounced than for the total correlation energy, the results are better than LSD values. The errors remain substantial and are not, in general, smaller than the LM errors in the exchange and correlation contribution to the dissociation energy (see Table XI). In these cases the exact treatment of the exchange energy together with the present partitioning of exchange and correlation does not seem to reduce the error in the dissociation energy.

4. Combination of density functional and configuration-interaction methods

The above discussion has shown that it is unlikely that one can find a simple modification to the local-density description of exchange and correlation that will describe energy differences reliably. The energy difference resulting from the promotion of an s to a p electron in the fluorine atom is an example in which the nature of the wave function plays a central role. It is natural to ask whether a combination of DF and CI methods can lead to a systematic improvement in such cases.

Lie and Clementi (1974a, 1974b) showed that the addition of local-density correlation energy to the results of a CI calculation with a few configurations resulted in a satisfactory description of some small molecules. In the same spirit, Savin (1988a) developed a scheme that has some important advantages and provides, in principle, a systematic method for improving on DF results. We have seen that the arguments of Levy (1979) allow us to determine the exact wave function and other quantities such as the exact first-order density matrix, the natural orbitals (Löwdin, 1955), and the energy. The same arguments can be applied to a trial wave function restricted to a single determinant, resulting in the Hartree-Fock energy and wave function. The difference between the two energies is the correlation energy (Levy, 1987).

In Savin's (1988a) scheme, the correlation energy is split into two parts. One is determined by a CI calculation in the space of all natural orbitals with occupation numbers beyond a given threshold (ν), the remainder from a DF calculation with an appropriate (ν-dependent) equation for $E_{\rm xc}$. In the limit of large ν one would get the combination of HF+DF, while in the other extreme a CI calculation is needed. The approach has been applied successfully to a number of interesting cases, including the sp transfer energy in Ne^+ (Savin, 1988b). In this case, an MCSCF (multiconfiguration SCF) calculation with the sp^6 and s^2p^4d configurations gives, on including the M shell, a correlation energy of 0.320 a.u. for the s^2p^5 state and 0.426 a.u. for the sp^6. The DF contributions are 0.146 and 0.177 a.u., respectively. The calculated transfer energy is then 0.977 a.u., within 0.3 eV of the experimental value. While this method cannot be viewed as a general solution to the problems we have discussed, it does address the "near-degeneracy" problem—cases in which a qualitative description of the wave function requires more than one determinant—while maintaining the advantages of the density functional description of "dynamic" correlations.

VI. EXCITATION ENERGIES

The DF formalism has been designed to give ground-state (GS) properties. In many situations we are, however, interested in the excitations of the system, and it is an important question to what extent these can be obtained within the DF formalism. We now discuss methods for calculating such properties, ranging from those that are rigorously justified within the DF formalism to ones where the justification is essentially empirical.

A. The meaning of the eigenvalues

The eigenvalues of the Kohn-Sham equation (3.5) enter the formalism as Lagrange parameters, due to the requirement that the orbitals $\psi_i(\mathbf{r})$ be orthogonal. The possible physical meaning of the eigenvalues is therefore not immediately obvious. In Hartree-Fock theory the eigenvalues acquire a meaning through Koopman's theorem, which states that

$$\varepsilon_i^{\mathrm{HF}}=E(n_1,\ldots,n_i,\ldots,n_N)-E(n_1,\ldots,n_i-1,\ldots,n_N)\ , \tag{6.1}$$

where $\varepsilon_i^{\mathrm{HF}}$ is a HF eigenvalue and $E(n_1,\ldots,n_N)$ is the total energy of the system with the occupation numbers $n_1,\ldots,n_N$. This theorem requires that the other orbitals do not change when the occupancy n_i is reduced, and it identifies $\varepsilon_i^{\mathrm{HF}}$ with the energy required to remove an electron from the orbital i. The corresponding theorem is not, in general, valid in the DF formalism, where one finds (Slater, 1974; Janak, 1978) that

$$\varepsilon_i(n_1,\ldots,n_N)=\frac{\partial E}{\partial n_i}\ . \tag{6.2}$$

The total energy difference in Eq. (6.1) can then be written as

$$E(n_1,\ldots,n_i,\ldots,n_N)-E(n_1,\ldots,n_i-1,\ldots,n_N)=\int_0^1 dn\,\varepsilon_i(n_1,\ldots,n_i+n-1,\ldots,n_N)\ . \tag{6.3}$$

In contrast to Eq. (6.1), Eq. (6.3) has a formal justification only if the occupation numbers in (6.3) refer to the ground states of the systems with M and $M-1$ particles, where $M=\sum n_i$; i.e., ε_i should refer to the highest occupied eigenstate in the M-electron system. Within the exact DF formalism, Eq. (6.3) can be simplified by using a result for the highest occupied orbital

$$\varepsilon_N(n_1,\ldots,n_N=n)=\varepsilon_N(n_1,\ldots,n_N=1)\ ,\quad 0<n\le 1\ , \tag{6.4}$$

which was derived by Perdew *et al.* (1982) by using the $T\to 0$ limit of the finite T theory. Inserting (6.4) in (6.3) we can see that in the exact DF formalism the highest eigenvalue gives the ionization energy of the system (or work function for a metal; see Perdew *et al.*, 1982; Levy *et al.*, 1984; von Barth, 1984b; Almbladh and von Barth, 1985b). For most approximate functionals, however, Eq. (6.4) is not valid for localized states, and the ionization potential is then not equal to $\varepsilon(n_M=1)$. We also emphasize that the arguments above only give significance to the highest occupied eigenvalue.

B. Two limiting cases

Although the above arguments are well known, it is standard practice, in particular for solids, to interpret all the eigenvalues as excitation energies, since in many situations there is no simple alternative. To obtain an idea of the errors introduced in such an approach, we discuss two limiting cases: the homogeneous electron gas and a free atom. Figure 35 shows results for the homogeneous electron gas (Hedin and Lundqvist, 1969). The exact energy of a quasiparticle with momentum k is given by

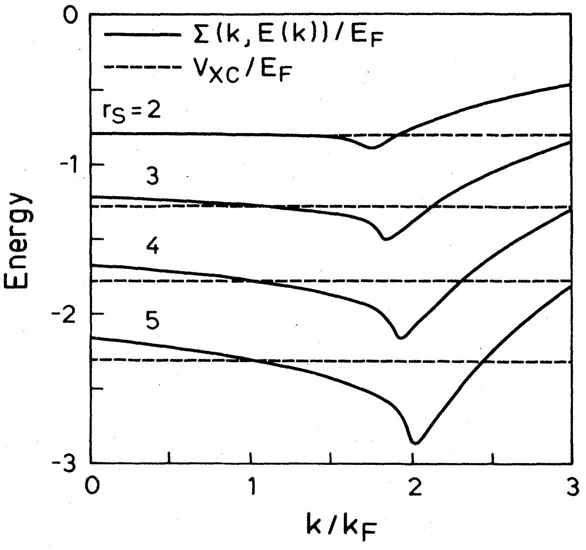

FIG. 35. Self-energy Σ (solid curves) and the exchange-correlation potential V_{xc} (dashed curves) for a quasiparticle with momentum k in a homogeneous system with the density $n=(\frac{4}{3}\pi r_s^3)^{-1}$. The results are expressed in units of the Fermi wave vector k_F and the Fermi energy E_F.

$$E(k)=\frac{\hbar^2k^2}{2m}+\Sigma(k,E(k))\ , \tag{6.5}$$

where $\Sigma(k,\omega)$ is the self-energy. In the LD approximation we associate, for the moment, $E(k)$ with the eigenvalue $\varepsilon(k)$,

$$\varepsilon(k)=\frac{\hbar^2k^2}{2m}+V_{\mathrm{xc}}\ , \tag{6.6}$$

where V_{xc} only depends on the homogeneous density n. Figure 35 shows the self-energy $\Sigma[k,E(k)]$ contribution to the quasiparticle energy according to an accurate calculation (solid curve) and the exchange-correlation potential (dashed curve). Since the LD approximation gives the exact V_{xc} in this case, the dashed curve also represents the exact DF result. The deviations to the self-energy are therefore due to the fact that, in general, the DF eigenvalues are different from excitation energies. The highest occupied eigenvalue $\varepsilon(k_F)$, however, agrees with the exact result. The figure also illustrates that the deviation is not very large for the occupied eigenvalues and for states not very far above the Fermi energy. On the other hand, the exact curve goes to zero for large values of k, in marked contrast to the constant LD result. This is of particular importance in calculations for low-energy electron diffraction (LEED), extended x-ray-absorption fine structure (EXAFS), and inverse photoemission, where these states are sampled.

Another limiting case is a free atom, where the charge-density variations are very large. We have seen in Sec. III that accurate results for V_{xc} have been calculated for small atoms (Smith *et al.*, 1979; von Barth and Car, 1982; Almbladh and Pedroza, 1984) using densities obtained from accurate many-body calculations, e.g., a CI calculation. Using a parametrized form of V_{xc}, the density is calculated and the procedure repeated until the correct density is reproduced. Figure 36 shows the V_{xc} as well as the correlation potential $V_c \equiv V_{xc} - V_x$ obtained by Almbladh and Pedroza (1984). The exact correlation potential shows a pronounced nonmonotonic behavior, and Levy and Perdew (1985a) have shown that V_c *cannot* be monotonic in a tightly bound closed-shell atom. As for the simple case of an H atom (Gunnarsson *et al.*, 1974), the exact potential is more attractive than the LD potential, but the deviation is rather constant over the range where the electron density is large. The LD approximation therefore reproduces the electron density well for Be (Almbladh *et al.*, 1983). The DF eigenvalues calculated (Almbladh and Pedroza, 1984) for the accurate V_{xc} are shown in Table XII for a Be atom. These eigenvalues are compared with the LD and HF eigenvalues as well as with the corresponding excitation energies. The highest occupied (2*s*) DF eigenvalue agrees with the lowest ionization energy, in agreement with the exact result mentioned above. The HF eigenvalue is somewhat too high (0.9 eV) and the LD eigenvalue is almost 4 eV too high, a result that is typical for atoms. The DF 1*s* eigenvalue is about 8 eV higher than the corresponding ionization energy, while the LD 1*s* eigenvalue is about 19 eV higher. In this case the large deviation between the LD 1*s* eigenvalue and the corresponding excitation energy is therefore largely due to the LD approximation itself. Similar conclusions were reached by Perdew and Norman (1982), following a numerical study of atoms in the exchange-only approximation.

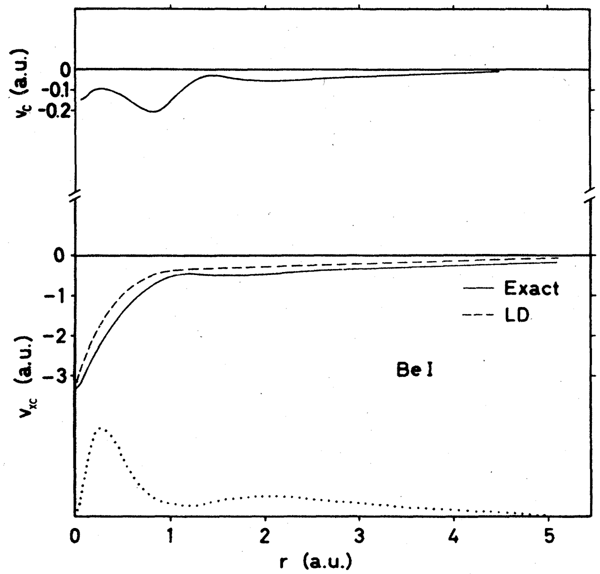

FIG. 36. Accurate exchange-correlation potential V_{xc} compared with the local density (LD) V_{xc} for Be. The dotted line gives the radial density. The upper part of the figure gives the correlation potential (Almbladh and Pedroza, 1984).

TABLE XII. Energy eigenvalues (in eV) compared with excitation energies for a Be atom. The density functional (DF) eigenvalue refers to an accurate calculation of the V_{xc}.

	ε DF	LD	HF	Excitation energy
1*s*	−115.10	−104.94	−128.78	−123.6
2*s*	−9.32	−5.60	−8.42	−9.32
2*p*	−5.7	−2.1		

It is interesting that the unoccupied 2*p* orbital is bound ($\varepsilon_{2p} < 0$), although the negative Be ion does not exist, providing a case in which an unoccupied orbital is too low in energy. Finally, we emphasize that the rather poor results obtained in the LD approximation are due to the association of eigenvalues with excitation energies. For atoms there is no reason to treat the eigenvalues as excitation energies, since we can perform total energy difference or transition-state calculations, as discussed below. We have seen (Sec. IV.A) that the agreement with experiment is generally satisfactory.

C. The ΔSCF

There are basically two classes of methods for calculating excitation energies. In Sec. VI.E we shall discuss calculations based on the Dyson equation and the fact that the self-energy entering this equation is a functional of the density (Sham and Kohn, 1966). Here we focus on another class of methods where the ground-state scheme is applied to both the excited state and the ground state, and the energy difference is calculated. This approach is referred to as the ΔSCF scheme, since it is based on the energy difference between two self-consistent-field (SCF) calculations. The application of the DF formalism to the excited state can be justified if applied to the lowest state for a given set of quantum numbers (Gunnarsson and Lundqvist, 1976). In many cases, however, the scheme is applied to states for which no justification has been given.

As an example we consider the transition 1*s*→2*p* in a hydrogen atom:

$$\Delta E(1s \to 2p) = E(2p) - E(1s) , \tag{6.7}$$

which is of interest in optical absorption. The use of the DF formalism for the excited 2*p* state is justified since this is the lowest state with *P* symmetry. As discussed in Sec. IV.A.3, this approach often gives satisfactory results. For the application to atomic multiplets, the accuracy of the results is usually improved greatly by using the method of Ziegler *et al.* (1977) and von Barth (1979), as discussed in Sec. IV.A.4.

For the practical calculations of energy differences, Slater's transition-state method (Slater, 1974) is useful. This method follows from Eq. (6.3) by replacing the integral by the value of the integrand at the middle of the interval:

$$E(n_1,\ldots,n_i,\ldots,n_N)-E(n_1,\ldots,n_i-1,\ldots,n_N)\approx\varepsilon_i(n_i-0.5)\ . \qquad (6.8)$$

This formula has the advantage that the eigenvalues are often numerically much smaller than the total energy; the numerical accuracy required is therefore lower. If the state i refers to an extended state in an infinite system, the eigenvalues are independent of a change in the occupation numbers of the order 1 for approximate functionals such as the LD functional. In such a case we can use the eigenvalue for the occupation number n_i in Eq. (6.8), which then goes over to Koopman's theorem. The eigenvalues are then directly related to excitation energies and support the common interpretation of band-structure calculations for solids. It should be emphasized, however, that no justification has been given for using the scheme for the excited state(s) involved in most applications of Eq. (6.8). A rigorous justification for the calculation of excited states is given in the method of Theophilou (1979); see also Hadjisavvas and Theophilou (1984, 1985); Theophilou (1987). If one wishes to discuss the M lowest-energy eigenstates for a system of N electrons, it is necessary to consider a subspace S of Fock space spanned by the M-state vectors of lowest energy. If the M lowest eigenstates of H are $\phi_1,\ldots,\phi_M$, then the trace of the Hamiltonian matrix is the sum of the eigenvalues for the exact states in S,

$$\mathrm{tr}_S(\hat{H})=\sum_{i=1}^{M}\langle\phi_i|H|\phi_i\rangle=\sum_{i=1}^{M}E_i\ , \qquad (6.9)$$

where E_i are the energies corresponding to ϕ_i. By separating the external potential V_{ext} from the Hamiltonian $\hat{H}$, one can prove that $\mathrm{tr}_S(\hat{H})$ is a functional of the density operator; we denote this functional $E_S[n]$. Theophilou showed that this functional obtains its minimum value if the subspace on which it is evaluated coincides with the space spanned by the exact eigenstates. As in the case of the formalism described in Sec. III, this minimum principle can be used to find a set of single-particle equations and their eigenfunctions u_i.

The first step then in determining the excited-state energies is to solve for the ground-state energy E_1. We may then consider the density,

$$n(\mathbf{r})=\sum_{i=1}^{N-1}|u_i(\mathbf{r})|^2+\tfrac{1}{2}[|u_N(\mathbf{r})|^2+|u_{N+1}(\mathbf{r})|^2]\ , \qquad (6.10)$$

and determine E_1+E_2 by minimizing the functional $E_S[n]$. This procedure may then be continued for as many excited states as desired. A major drawback here, as in the discussion of Gunnarsson and Lundqvist (1976) for the excited states of a particular symmetry, is that nothing is known about the state dependence of $E_S[n]$. For large systems with very many low-lying states, this method becomes impracticable.

D. Discontinuity in the exchange-correlation potential

In the previous section we used the fact that in simple approximations, such as the LD approximation, the eigenvalue for an extended state in an infinite system does not change with a change in the number of electrons of the order one. This follows, since the charge density then has a change of the order $1/V$, where V is the volume of the system. As V goes to infinity the change in the Hartree potential goes to zero. The same is true for any exchange-correlation potential with a simple, explicit finite range dependence on the density. It was, however, realized by Perdew and Levy (1983) and by Sham and Schlüter (1983) that this need not apply to the exact potential. Actually, in addition to an $\mathbf{r}$-dependent change of the order $1/V$ of the exchange-correlation potential when one electron is added to the system, there could be a finite change Δ independent of $\mathbf{r}$, since this would be consistent with a change in the density of the order $1/V$. This observation has important consequences for the band gap of a semiconductor or an insulator, as discussed below.

We first relate the band gap to ground-state energies, so that all quantities are well defined within the DF formalism. The band gap E_g is defined in terms of the ionization potential I and the affinity energy A as

$$E_g\equiv I-A$$
$$\equiv[E_1(M-1)-E_1(M)]-[E_1(M)-E_1(M+1)]\ , \qquad (6.11)$$

where $E_1(N)$ is the ground-state energy of the N-electron system. We now use Eq. (6.2) to relate I and A to the eigenvalues:

$$I=-\int_0^1 df\,\varepsilon_M(M-1+f)=-\varepsilon_M(M-\eta)\ , \qquad (6.12)$$

$$A=-\int_0^1 df\,\varepsilon_{M+1}(M+f)=-\varepsilon_{M+1}(M+\eta')\ , \qquad (6.13)$$

where $0<\eta,\eta'<1$. It then follows that (Perdew and Levy, 1983; Shan and Schlüter, 1983)

$$E_g=\varepsilon_{M+1}(M+\eta')-\varepsilon_M(M-\eta)=\Delta\varepsilon+\Delta\ , \qquad (6.14)$$

where

$$\Delta\varepsilon=\varepsilon_{M+1}(M)-\varepsilon_M(M) \qquad (6.15)$$

is the eigenvalue band gap in the calculation for the M-electron system. Here we have used the result (6.4) that the eigenvalues only change when the number of electrons N goes from $M-0$ to $M+0$. Equation (6.14) states that, due to the possible discontinuity Δ in the V_{xc}, the true band gap can be different from the exact DF eigenvalue gap $\Delta\varepsilon$. It is now well established that the LD approximation gives too small band gaps for semiconductors. It is then an interesting question whether the exact DF formalism would give a $\Delta\varepsilon$ substantially closer to E_g, so that the poor band gap in the LD approximation is due to the LD approximation itself (i.e., a poor description of the **r** dependence of the exchange-correlation potential) or to the discontinuity.

The discontinuity can be large for free atoms (Perdew *et al.*, 1982; Almbladh and Pedroza, 1984), as illustrated by Table XII. Since a negative Be ion cannot be formed, the affinity energy of Be is zero. The discontinuity must therefore shift the $2p$ eigenvalue from -5.7 eV to the vacuum level, when one electron is added to the system. The intriguing question is if the discontinuity can also be nonzero for an infinite system. By considering a solid in the limit of a very large lattice parameter, Perdew and Levy (1983) and Almbladh and von Barth (1985a) showed that this is the case. A simple example is the half-filled one-dimensional Hubbard model (Gunnarsson and Schönhammer, 1986), where the occupancies of the spin-up and spin-down s orbitals are 0.5. The exact DF potential is therefore site and spin independent, and the DF eigenvalue spectrum is the same as that for noninteracting electrons. The eigenvalue gap is therefore zero. The half-filled one-dimensional Hubbard model is, however, a Mott insulator for all values of $U/t>0$, where U is the Coulomb integral and t is the hopping integral. In this case the gap is therefore entirely due to the discontinuity, independent of the value of t (or the lattice parameter).

To obtain quantitative results in a general situation, Sham and Schlüter (1983) used the Luttinger-Ward (1960) many-body equation for the grand canonical potential to derive a formula for the discontinuity. This formula gives (incorrectly) zero discontinuity (Gunnarsson and Schönhammer, 1986; Schönhammer and Gunnarsson, 1987). A different equation for the discontinuity was derived by von der Linden and Horsch (1988), but it is hard to use in practice since it requires the exact V_{xc}. Most attempts to determine the discontinuity (Godby *et al.*, 1986; Gunnarsson and Schönhammer, 1986) have used a different approach. First the density is determined from a many-body calculation, the V_{xc} that reproduces this density is then found, and $\Delta\varepsilon$ is determined from the eigenvalue spectrum. A comparison with the gap E_g, determined from a many-body calculation or experiment, gives an estimate of the size of the discontinuity.

Godby *et al.* (1986) used the so-called GW approximation (Hedin, 1965), where the self-energy is approximated to lowest order in the screened interaction. They calculated the self-energy for Si and obtained a gap in good agreement with experiment. The V_{xc} corresponding to the GW self-energy was then calculated approximately and found to give an eigenvalue gap $\Delta\varepsilon$ close to the LD value. Godby *et al.* (1986) concluded that the LD approximation gives an excellent approximation to the V_{xc} of the M-particle system and that the poor gap in the LD approximation is due to the discontinuity.

Gunnarsson and Schönhammer (1986) and Schönhammer and Gunnarsson (1987) considered a simple model consisting of a finite linear chain with two levels per atom. The nearest-neighbor hopping, the on-site, and the nearest-neighbor Coulomb interactions were included. For this model it is also possible to study the influence of the poor gap and the discontinuity on impurities. While it is unclear to what extent the conclusions of this simple model also apply to Si, for example, it has the advantage of being an exactly solvable nontrivial model. For appropriate parameter ranges this model gives a Mott insulator or a charge-density-wave-like ground state. In these cases the discontinuity was found to be quite important. For parameters more appropriate for a semiconductor the discontinuity is, however, very small. Thus this model contains both the limit where the poor band gap in the LD approximation is due to the discontinuity and the limit where it is due to the approximation itself.

This model also shows that an approximate many-body scheme can give an excellent approximation to the band gap, but nevertheless overestimate the discontinuity greatly (Gunnarsson and Schönhammer, 1987a). Furthermore, the LD approximation cannot give a very accurate exchange correlation potential for a number of impurities in semiconductors, since it predicts incorrectly that there is no well-localized state in the gap, so that a qualitatively incorrect spin density must follow (Schönhammer and Gunnarsson, 1987). As an example of the results obtained in this model, we compare in Fig. 37 the eigenvalue spectrum in the exact DF formalism (ε_iDF) and in the LD approximation (ε_iLD) with the corresponding exact excitation energies (Excitations).

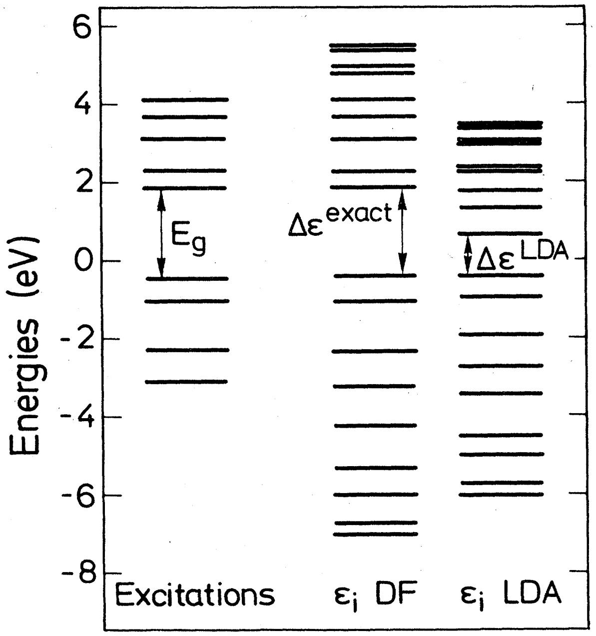

FIG. 37. Eigenvalue spectrum (ε_i) and the corresponding excitation energies for a semiconductor chain with nine atoms. E_g shows the exact band gap (Gunnarsson and Schönhammer, 1986).

The figure illustrates that the eigenvalue gap in the exact DF formalism is almost exactly equal to the exact band gap; i.e., the discontinuity is small in this case. The LD eigenvalue gap is much smaller than the exact DF eigenvalue gap; i.e., the LD approximation itself is rather poor. It is remarkable that the exact DF eigenvalues away from the gap also agree rather well with the corresponding excitation energies, although these eigenvalues have not been shown to have any meaning.

E. The Dyson equation approach

The second class of methods for calculating excitation energies is based on the Dyson equation (Hedin and Lundqvist, 1969):

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right]\phi_k(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_k)\phi_k(\mathbf{r}')=E_k\phi_k(\mathbf{r}) , \quad (6.16)$$

where $V(\mathbf{r})$ is the Hartree potential from the electronic and nuclear charge and $\Sigma(\mathbf{r},\mathbf{r}';E_k)$ is the self-energy operator. The self-energy is a nonlocal, complex, and energy-dependent operator, which in general is very difficult to calculate. However, there have been several recent calculations of Σ, in most cases using the GW approximation (Hedin, 1965), for covalent crystals (Brener, 1975a; Strinati *et al.*, 1980, 1982; Hybertsen and Louie, 1985a; Godby *et al.*, 1986; von der Linden and Horsch, 1987), for simple metals (Northrup *et al.*, 1987), and for ionic crystals (Brener, 1975b; Hybertsen and Louie, 1985b). The agreement with experiment is encouraging and this approach is promising for systems where the calculations are feasible. The direct calculation of the self-energy falls outside the scope of this paper, and we discuss here only the usage of the Dyson equation in the spirit of the DF formalism.

The DF approach to the Dyson equation is based on the observation by Sham and Kohn (1966) that Σ is a ground-state property and can therefore be expressed as a functional of the density. Sham and Kohn (1966) further argued that (1) $\Sigma(\mathbf{r},\mathbf{r}';E)$ has a short range; i.e., that Σ is small if $|\mathbf{r}-\mathbf{r}'|\geq 2\pi/k_F$, where k_F is the Fermi momentum corresponding to the local density, and (2) $\Sigma(\mathbf{r},\mathbf{r}';E-V(\mathbf{r}_0))$ depends only on the density in the neighborhood of $\mathbf{r}_0=(\mathbf{r}+\mathbf{r}')/2$. The Hartree potential $V(\mathbf{r}_0)$ is introduced in the energy argument of Σ to make Σ independent of a constant shift of $V(\mathbf{r})$. Sham and Kohn (1966) argued that, because of property (2) above, one can make a local-density approximation for Σ and relate it to electron gas data,

$$\Sigma(\mathbf{r},\mathbf{r}';E_k)\approx\Sigma_h\{\mathbf{r}-\mathbf{r}',E_k-\mu+\mu_h[n(\mathbf{r}_0)],n(\mathbf{r}_0)\} , \quad (6.17)$$

where Σ_h and μ_h are the self-energy and chemical potential, respectively, of the homogeneous system. There are different ways of choosing the energy argument in Σ_h in Eq. (6.17). The choice used here was recommended by Hedin and Lundqvist (1971), based on an analysis of the vertex function. The approximation (6.17) still leads to a nonlocal potential, and the calculations are nontrivial. To further simplify Eq. (6.17), Sham and Kohn (1966) expressed ϕ_k as

$$\phi_k(\mathbf{r})=A(\mathbf{r})e^{i\mathbf{p}(\mathbf{r})\cdot\mathbf{r}} \quad (6.18)$$

and assumed that $A(\mathbf{r})$ and $\mathbf{p}(\mathbf{r})$ have a weak variation over the range of Σ_h, which is of the order $2\pi/k_F$ according to property (1) above. This assumption yields

$$\int d\mathbf{r}'\,\Sigma_h\{\mathbf{r}-\mathbf{r}',E_k-\mu+\mu_h[n(\mathbf{r}_0)],n(\mathbf{r}_0)\}\phi_k(\mathbf{r}')\approx\Sigma_h\{p(\mathbf{r}),E_k-\mu+\mu_h[n(\mathbf{r})],n(\mathbf{r})\}\phi_k(\mathbf{r}) . \quad (6.19)$$

The magnitude of the local momentum $p(\mathbf{r})$ is determined from

$$E(p,n(\mathbf{r}))=E_k-\mu+\mu[n(\mathbf{r})] , \quad (6.20)$$

where $E(p,n)$ is the energy of a quasiparticle with the momentum p in a homogeneous system with the density n. This way of determining the momentum was advocated by Hedin and Lundqvist (1971), who also provided numerical data for Σ_h. The self-energy has now been simplified to a local but energy-dependent potential, shown by the solid curves in Fig. 35. The energy dependence is weak close to the Fermi energy, where one may simplify the potential further by replacing E_k with μ in the energy argument in Eq. (6.20). Then the potential reduces to

$$\Sigma_h\{\mathbf{p}(\mathbf{r}),E_k-\mu+\mu_h[n(\mathbf{r}_0)],n(\mathbf{r})\}\approx\Sigma_h\{\mathbf{p}(\mathbf{r}),\mu_h[n(\mathbf{r}_0)],n(\mathbf{r})\}\equiv V_{\text{xc}} . \quad (6.21)$$

The ground-state potential V_{xc} and the quasiparticle energies E_k then coincide with the LD potential and eigenvalues in the ground-state scheme, which provides some support for interpreting the eigenvalues as quasiparticle energies. We emphasize, however, that this result is based on several approximations and requires justification in real systems. In particular, it has been shown in Sec. VI.B that the LD eigenvalues in atoms can deviate appreciably from the quasiparticle energies.

At this point a comment amount the Fermi surface (FS) is appropriate, since there are in principle two FS's in the formalism. The solution of the Dyson equation (6.16) leads to the quasiparticle (QP) FS, and the solution of the Kohn-Sham (KS) equation (3.5) leads to a second, which we refer to as the KS-FS. It is a longstanding question whether the two surfaces, obtained using the exact self-energy and the exact exchange-correlation potential, respectively, are identical. We note that the approximation (6.21) is exact for quasiparticles at the Fermi surface, and that the two FS's are identical for the homogeneous electron gas. The latter can be proved by noticing that the approximations (6.17) and (6.19) are exact for the electron gas or by referring to the spherical symmetry of the system and Luttinger's theorem (Luttinger, 1960).

To study the Fermi surface for an inhomogeneous system, Schönhammer and Gunnarsson (1988) studied a two-dimensional Hubbard model, introducing a density functional formalism for this model. Because of the simplicity of the model the exact KS-FS could easily be calculated. The self-energy to second order in the Coulomb interaction U was calculated and the corresponding QP-FS was obtained. In the limit of a small U the self-energy and the QP-FS calculated this way become exact. Figure 38 shows the deviation between the two FS's for a Hubbard model with nearest- ($t_1=-1$) and second-nearest- ($t_2=0.3$) neighbor hopping and a band filling of 0.3 electrons per spin and atom. Although the Fermi surfaces are very similar for this model, they are not identical, showing that the experimentally measurable QP-FS and the KS-FS are not generally the same. Another counterexample has been found be Mearns (1988).

We now discuss the approximations (6.17), (6.19), and (6.21) introduced above and the attempts to avoid some of them. The first approximation is the use of electron gas data for the self-energy in Eq. (6.17), which is equivalent to the LD approximation for the ground-state potential. To be specific, we discuss this approximation in the context of Si, for which there are several different types of calculations. The accuracy of the LD approximation is sometimes discussed in terms of the strength of the density variations. Wang and Pickett (1983) and Pickett and Wang (1984) pointed out, however, that a solid like Si differs from the electron gas not just by being inhomogeneous but also by having a energy gap. To test the effect of the energy gap, they considered a homogeneous model electron gas with an energy gap E_g. Thus they shifted the unoccupied states in the normal electron gas by a constant energy E_g, where E_g was defined as the average direct gap of (in this case) Si. The dielectric function of the model was assumed to be given by the dielectric function of Levine and Louie (1982). This function is related to the Lindhard dielectric function in such a way that the imaginary part is zero for $\omega<\lambda E_F$, where E_F is the Fermi energy of the electron gas. The parameter λ was adjusted to describe the static dielectric function of Si. With these model assumptions the self-energy was calculated in the GW approximation (Hedin, 1965). The approximations (6.17)–(6.20) above were then used with this model self-energy replacing Σ_h in (6.17).

In Fig. 39 their quasiparticle band structure is compared with the LD energy eigenvalues and with some experimentally known energies and energy differences. The figure shows a substantial improvement over the LD results. For the indirect gap, Wang and Pickett (1983) obtained the value 0.93 eV, which is smaller than the experimental result of 1.17 eV but larger than the LD result of 0.56 eV. The main reason for the improvement over the LD result was found to be the energy dependence of the self-energy. As discussed above, the energy dependence of the electron gas self-energy is very weak over the energy range discussed here. The use of Eq. (6.19) with electron gas data therefore gives very similar results to the LD ground-state scheme (Pickett and Wang, 1984). The model electron gas with an energy gap, on the other hand, gives an appreciable energy dependence and raises doubts about the use of the approximation (6.17) together with electron gas data for semiconductors and insulators. von der Linden *et al.* (1986) further emphasized the importance of the different spatial character of the wave functions corresponding to the top of the valence band

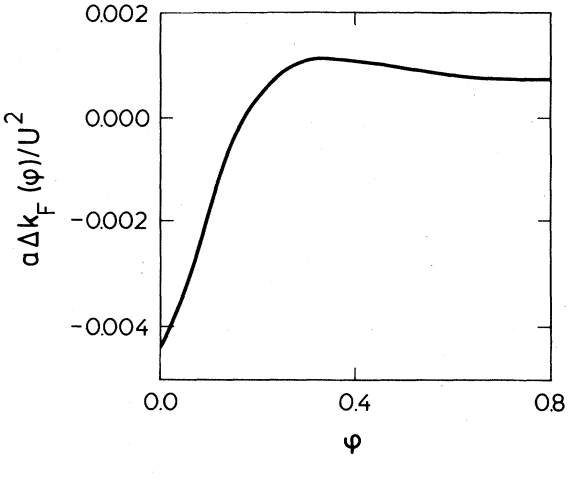

FIG. 38. Deviation $\Delta k_F(\varphi)$ of the Fermi-surface (FS) radius $k_F(\varphi)$ between the quasiparticle FS and Kohn-Sham FS as a function of the angle φ for small values of U, where φ is the angle to the k_x axis. Because of the symmetry of the Fermi surface, results are shown only for $0\le\varphi\le\pi/4$. The lattice parameter is a and the same energy unit has been used for U, t_1, and t_2.

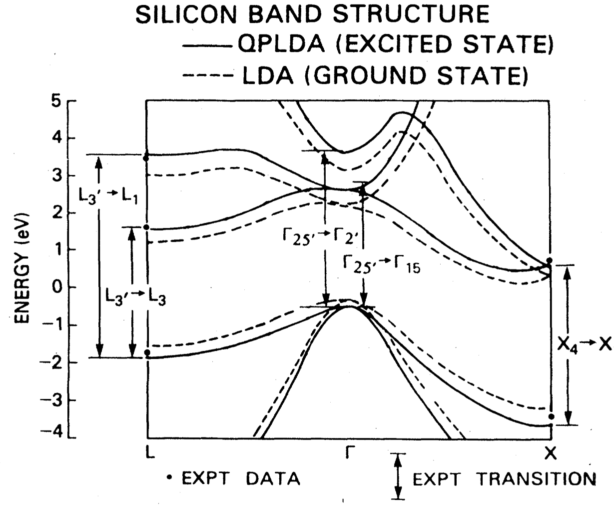

FIG. 39. Quasiparticle (QP) energies of Si (solid lines) according to the calculation of Pickett and Wang (1984) compared with the local-density (LD) energy eigenvalues in the ground-state scheme (dashed lines). Dots and arrows indicate experimental quasiparticle energies and energy differences (Pickett and Wang, 1984).

and the bottom of the conduction band. This influences the self-energy in a way that is not fully included when the approximations (6.17)–(6.20) are made, whether the normal electron gas or the Wang and Pickett (1983) model electron gas is used.

The second approximation is the WKB-type assumption in Eq. (6.19), which converts the nonlocal potential into a local energy-dependent potential (6.19). This approximation has been discussed by Rasolt and Vosko (1974a, 1974b) in the context of the alkali metals. These systems have almost spherical Fermi surfaces. The small deviations from sphericity predicted by the LD ground-state eigenvalues are, nevertheless, as much as a factor of 2 larger than the experimentally measured ones (Rasolt and Vosko, 1974a, 1974b). Rasolt and Vosko argued that this is due to the approximation (6.19). Model calculations (Rasolt and Vosko, 1974a, 1974b; Rasolt *et al.*, 1975; Nickerson and Vosko, 1976) indeed showed that the distortions are reduced when the approximation (6.19) is removed. Realistic calculations for the alkalis have been performed by MacDonald (1980), who calculated the ground-state density in the linearized augmented plane wave (LAPW) method. The wave functions were then expanded in plane waves, and the expectation value of the self-energy (6.17) was evaluated. In this way the deviation between the nonlocal potential (6.17) and the local potential (6.19) was included to lowest order. In Fig. 40 the results for Fermi-surface extremal areas are shown for different high-symmetry planes in Cs. The figure illustrates how the distortions from sphericity in the LD approximation are reduced by about a factor of 2 when the nonlocal potential (6.17) is used. The latter result is in satisfactory agreement with experiment. These results also suggest that the approximation (6.19) should be used with caution.

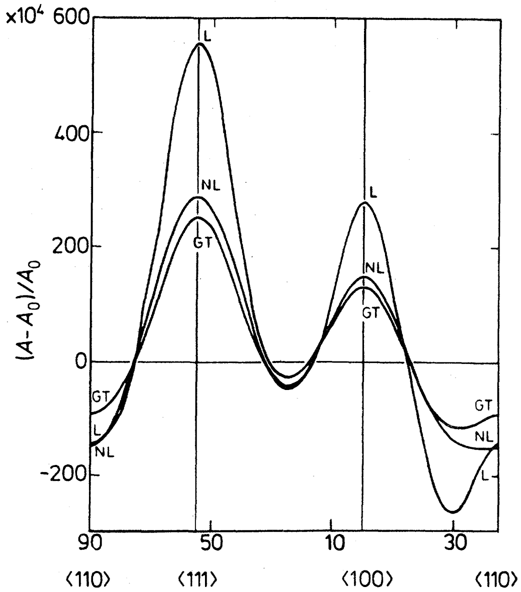

FIG. 40. Extremal Fermi-surface areas for different high-symmetry planes in Cs. The figure compares the local-density eigenvalue results (L), the results using the nonlocal potential (6.17) (NL), and experimental results (GT) (MacDonald, 1980).

F. Comparison of eigenvalues and experimental excitation energies

Above we have discussed the approximations (6.17)–(6.21) leading to the ground-state LD potential V_{xc}. We now take a more empirical approach and compare band-structure calculations based on the LD V_{xc} with experimental excitation energies. One may expect the LD band-structure approach to fail when the correlation effects are very different from the electron gas correlations. For instance, in semiconductors and insulators the correlation effects tend to be weaker than in the electron gas. The self-energy of the unoccupied states therefore tends to be less negative than for the occupied states, leading to too low energies of the unoccupied states in band calculations (see Fig. 39). For metallic systems the correlation effects should be more important than in the electron gas if the system has a narrow, partly filled band. The bandwidth W and the effective Coulomb interaction U are then relevant parameters, and the correlation effects should be very important if $U \gg W$.

It is interesting to consider the $3d$ series, where the $3d$-band width decreases as the atomic number increases. According to band calculations (Andersen and Jepsen, 1977) the d-band width, defined as the square root of the second moment, is 4.6, 4.1, 3.6, and 2.7 eV for Fe, Co, Ni, and Cu, respectively. At the same time the effective $3d$ Coulomb interaction increases along the $3d$ series. According to the interpretation of Auger spectra (Antonides *et al.*, 1977) the value of U is about 8 eV for Cu, 4 eV for Ni, and small for Fe and Co. We would therefore expect the agreement between the LD eigenvalues and the excitation properties to worsen along the $3d$ series. This has been studied by Eastman *et al.* (1980), who compared angle-resolved photoemission data with LD band calculations (Moruzzi *et al.*, 1978) and found that the ratio of the theoretical to experimental width of the occupied $3d$ band is about 1.1, 1.2, 1.45, and 1.1 for Fe, Co, Ni, and Cu, respectively. For the exchange splitting the theoretical to experimental ratio was found to be about 1.0, 1.2, and 2.2 for Fe, Co, and Ni, respectively. Thus the results for Fe, Co, and Ni are in agreement with the qualitative arguments above. Cu is discussed below.

To illustrate further the good results obtained for Fe, we show experimental and theoretical results for some critical points in the Brillouin zone in Table XIII. The calculation of Moruzzi *et al.* (1978) was based on the paramagnetic potential of Hedin and Lundqvist (1971) and a spin dependence based on a RPA scaling. The calculation of Wang and Callaway (1977) used the potential of von Barth and Hedin (1972). For Ni there is substantial disagreement, and it is necessary to use a more detailed many-body treatment (Liebsch, 1979, 1981; Penn, 1979; Treglia *et al.*, 1980). In spite of the relatively large

TABLE XIII. Critical-point energies and exchange splittings Δ_{exc} for Fe. The experimental results (Turner *et al.*, 1984) are compared with local-density calculations by Moruzzi *et al.* (1978) and Wang and Callaway (1977) (WC).

Point	Moruzzi	WC	Expt.
$\Gamma_{1\downarrow\uparrow}$	8.42	8.12	8.15±0.20
$\Gamma_{25'\uparrow}$	2.48	2.25	2.35±0.10
$\Gamma_{12\uparrow}$	0.97	0.86	0.78±0.10
$H_{12\uparrow}$	5.17	4.50	3.80±0.30
$P_{4\uparrow}$	3.50	3.17	3.20±0.10
$P_{3\uparrow}$	0.68	0.53	0.60±0.08
$N_{1\uparrow}$	5.24	4.75	4.50±0.23
$N_{2\uparrow}$	3.65	3.27	3.00±0.15
$N_{4\uparrow}$	0.72	0.69	0.70±0.08
Δ_{exc}			
$\Gamma_{25'}$	2.03	1.82	2.08±0.10
H_{12}	1.46	1.51	1.30±0.30
P_4	1.55	1.34	1.35±0.10
N_2	1.83	1.65	1.60±0.15

U/W ratio for Ni, ground-state properties, such as the cohesive energy, the lattice parameter, the bulk modulus, and the magnetic moment, are described with an accuracy comparable to that for $3d$ elements with smaller values of U/W. For Cu, where the $3d$ band is essentially filled, the bandwidth is in fair agreement with experiment. If a $3d$ electron is removed in a photoemission experiment, the system is left with essentially one $3d$ hole. Therefore many-body effects play a relatively small role for photoemission from Cu, while they are important for Auger processes involving two $3d$ holes. Nickel has $3d$ holes even in the initial state, and final states with two $3d$ holes on the same atom are important in photoemission. For Fe and Co, on the other hand, U/W is too small to give *large* many-body effects on the bandwidth and spin splitting.

Although the many-body effects in photoemission are reduced for systems with a filled $3d$ band, we note that the description of the $3d$-band position becomes gradually worse as the localization of the $3d$ state increases. The state becomes more atomiclike, and we have seen that the LD eigenvalues reproduce atomic ionization energies poorly. As a result, the $3d$ bands of Cu, Zn, and Ga are 0.5 eV (Jepsen *et al.*, 1981), 2 eV (Himpsel *et al.*, 1980), and 3 eV (Moruzzi *et al.*, 1978; Chiang and Eastman, 1980) too high, respectively. This is to be compared with the deviation of 6 eV between the $3d$ eigenvalue and the experimental $3d$ ionization energy for a free Zn atom. Even for Ga, where the calculated bandwidth is very small (~ 0.5 eV), the deviation between the eigenvalue and the measured $3d$ ionization energy is far from the atomic limit. This can be understood in terms of extra-atomic relaxation (Lang and Williams, 1977). Assume that the $3d$ hole created in Ga in photoemission is localized on one atom. Using the transition-state idea, the binding energy is then predicted by the $3d$ eigenvalue calculated with the $3d$ occupancy 9.5 on that atom. The lowering of the $3d$ eigenvalue relative to the band-structure calculation provides an estimate of the error made by using the band-structure eigenvalue to describe the ionization energy of a state that is assumed to be well localized. While this also applies to a free atom, the $3d$ hole in the solid is screened by a $4p$ electron. Thus the lowering of the $3d$ eigenvalue when the occupancy is reduced from 10 to 9.5 is smaller than that for the atom, since for the solid the $4p$ occupancy increases by ≈ 0.5. In this respect the atomic limit is reached when the potential from the screening electron is negligible compared with the $3d$ Coulomb interaction.

A more extreme case is provided by the $4f$ band in Ce. Here the values of U and W are about 6 and 1 eV, respectively, and $U \gg W$ (Gunnarsson and Schönhammer, 1987b). Experimentally the $4f$ spectrum is spread out over about 8 eV, much greater than the 1-eV broad $4f$ band in the LD approximation. Nevertheless, the topology of the LD (exchange only) Fermi surface of $CeSn_3$ is claimed to be in good agreement with experiment, even though the low-T specific heat is wrong by a factor of 7 (Koelling, 1982). The results for the heavy-fermion system UPt_3 are even more remarkable. The heavy fermions are related to the $5f$ band, which in terms of the U/W value should be between the $3d$ and the $4f$ series. Wang *et al.* (1987) found that the LD approximation gives a Fermi surface in fairly good agreement with experiment, although shifts (a few mRy) had to be applied to the different bands. The agreement with experiment was lost if the $5f$ electrons were forced into the core with the occupancy 2 or 3. On the other hand, for the related system UPd_3, agreement with experiment was obtained only when the $5f$ electrons were treated as corelike (Norman *et al.*, 1987). As for $CeSn_3$, the calculated specific heat (factor 30; see Strange and Gyorffy, 1985) and effective masses (factor 20; see Wang *et al.* 1987) are much too small for UPt_3. The reasons for the accuracy of the LDA Fermi surface for UPt_3 have been discussed by Zwicknagl (1988), who concluded that the LDA would not give good Fermi surfaces for systems where the Kondo temperature is smaller than the crystal-field splitting.

G. General remarks on eigenvalue distributions

Although the eigenvalues ε_i of the Kohn-Sham equations (3.4)–(3.6) have no direct physical significance, the above discussion has shown their usefulness. Their sum is also an important contribution to the total energy and has proved valuable in discussing molecular bonding (Sec. IV). We close this section with some remarks on eigenvalue distributions in general.

The eigenvalues of complex systems have been the subject of much discussion during the past 40 years (see, for example, Wigner, 1951, 1967, and Dyson, 1962), and some remarkable results have been found. For a classical Coulomb gas of N unit charges on a ring, for example, Dyson (1962) found that the distribution of the positions of charges at finite temperature T is *identical* to the distribution of eigenvalues of a random matrix. Different forms of randomness (e.g., "orthogonal" or "unitary" ensembles), which might apply to different systems, correspond simply to different values of T. This remarkable result gives a physical feeling for the concept of "repulsion of energy levels."

In the present review we have focused on atoms, molecules, and solids, which are generally quantum, nonintegrable systems for which little theory is available. However, a careful analysis of rare-earth atoms and ions (Camarda and Georgopoulos, 1983) showed that the predictions of the orthogonal ensemble are well satisfied under certain conditions. They found, for example, that the eigenvalue spectra of Tb I for total spin $J=\frac{9}{2}$ and parity $\Pi=-1$ has a particularly simple form, and that there are both long- and short-range correlations. These and other experimental observations on complex atoms and nuclei support the predictions of random-matrix theory that the eigenvalue spectra of real systems (and hence the eigenvalue sum) have features that are both simple and universal.

The local-density approximation, which is exact for a homogeneous system, can give remarkably good results in systems far from homogeneity. This can be understood in terms of the exchange-correlation hole, so that E_{xc} is remarkably insensitive to details of the approximations necessary to evaluate it. The above observations indicate that other contributions to the energy are surprisingly insensitive to the assumption concerning the interactions in the system. They are further evidence against the common argument that the local-density approximation cannot be expected to work for inhomogeneous systems.

VII. CONCLUDING REMARKS

The use of the electron density as a basic variable has a long history in the calculation of electronic properties. We have traced this path from the Thomas-Fermi method through the approximate exchange potentials of Slater and Gáspár-Kohn-Sham to the density functional formalism. Against the initial expectations of Kohn and Sham (1965), the local-density approximation (and its spin analog, the LSD approximation) has been remarkably successful in describing the ground-state properties of a great range of physical systems. Molecular ground-state geometries, in particular, are very well described from the simplest diatomic molecules to infinite chains in polymers. The equilibrium geometries of many extended systems are also reliably treated. This has been a great boon for the solid state theorist. The familiar approximations of the last 30 years (e.g., $n^{1/3}$) not only seem to "work," but they at last have a sound justification in terms of a variational principle involving an (admittedly poorly known) energy functional. It is understandable that many solid state theorists are satisfied with this situation and are somewhat uncritical of the approximations used.

We have seen, however, that the LD and LSD approximations, while giving a very satisfactory description of binding *trends*, can yield an unreliable description of the actual binding energies and their differences. The deviations from experimental values are far from trivial, being ~ 2 eV in the dissociation energies of O_2 and O_3. This sort of error is quite unacceptable, and we have surveyed some of the attempts to understand the origin of these discrepancies and to correct for them. While there are now some indications that a significant part of the error comes from the inability of the LSD approximation to describe (obviously nonlocal) exchange energy differences, it does not seem to us that any simple modification of the LSD form will lead to accurate answers in general. Nevertheless, the forms proposed by Langreth and Mehl and by Perdew have given improved energy differences in a number of cases. In spite of the difficulties, the LSD method is the most practicable parameter-free scheme for studying the electronic structure of complicated systems. It has advantages over some more traditional methods (e.g., configuration interaction) not only because of its numerical efficiency but also because of the absence of problems with size consistency. Other approaches—such as the GW scheme described in Sec. VI.E, the local approach (Stollhoff and Fulde, 1980) or the quantum Monte Carlo method (see, for example, Fahy *et al.* 1988; Hammond *et al.*, 1988; Bachelet *et al.*, 1989)—are promising, but await application to systems of the complexity discussed above.

We noted at the beginning of this review that the DF formalism, with the LSD approximation for exchange and correlation, has exceeded all the expectations of a decade or so ago. Not only have we seen a great range of applications, but some of the early criticism of the formalism has been answered by theoretical developments. The method will doubtless remain a widely used, parameter-free method for electronic structure calculations. It can be expected to give a reliable description of many structures and of *trends* in bonding characteristics, and to complement the more traditional schemes of molecular physics and quantum chemistry. It remains an important challenge to solid state physicists and chemists to seek further for ways to improve on the local-density results. We hope that this article will encourage not only new applications but also further work toward this goal.

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