Total-energy differences: Sources of error in local-density approximations

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A detailed comparison of local-spin-density (LSD), $X\alpha$ (exchange-only), and Hartree-Fock calculations with experimental data shows that errors in density-functional calculations using the LSD approximation often arise from an unsatisfactory description of the exchange energy. The exchange energy depends sensitively on the angular characteristics and nodal structure of the orbitals, and these features are not properly incorporated into local-density calculations. Examples of the consequences are provided by errors in the sp and sd transfer energies in first-row and $3d$ atoms, respectively, since LSD calculations do not distinguish properly between s, p, and d electrons. We identify the main sources of error in these cases. For atoms and small molecules, we show that there is a "natural" occupancy of orbitals for which local-density approximations give a satisfactory description of the exchange energy. For other occupancies the relative errors are usually large. The consequences for extended systems and for the development of nonlocal functions are discussed.

I. INTRODUCTION

The density-functional formalism[1,2] shows that ground-state properties of a system of interacting electrons can be expressed as functionals of the density $n(\mathbf{r})$. In the case of the total energy E, an analogy with a fictitious system of noninteracting particles allows the problem to be reduced formally to the self-consistent solution of an independent particle wave equation. Exchange and correlation effects are described by a functional of the density $E_{xc}[n]$. Although it is generally assumed that an exact functional exists, most calculations rely on approximations where E_{xc} depends on the density in a simple way. The reduction of the many-particle problem to the solution of single-particle equations has obvious numerical advantages, but the reliability of these approximations remains a central question.

In spin-polarized systems it is common to describe E_{xc} by the local-spin-density (LSD) approximation,[2−4]

$$E_{xc}^{LSD} = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] \,, \qquad (1.1)$$

where $\varepsilon_{xc}[n_\uparrow, n_\downarrow]$ is the exchange-correlation energy per electron of a homogeneous electron gas with spin densities $n_\uparrow$ and $n_\downarrow$. The $X\alpha$ approximation[5] has also been widely used,

$$E_{xc}[n_\uparrow, n_\downarrow] \simeq E_x^{X\alpha} = \tfrac{3}{2}\alpha \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_x[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})]$$
$$= -\tfrac{3}{2}\alpha C \int d\mathbf{r}\{[n_\uparrow(\mathbf{r})]^{4/3}$$
$$+ [n_\downarrow(\mathbf{r})]^{4/3}\} \,, \qquad (1.2)$$

where $\varepsilon_x(n_\uparrow, n_\downarrow)$ is the exchange energy per electron and $C = 3(3/4\pi)^{1/3}$. The prefactor $3\alpha/2$ has historical origins[5] and in the present work we consider only the value $\alpha = \tfrac{2}{3}$, i.e., the special case of Eq. (1.1) where correlation effects have been neglected.

The LSD and $X\alpha$ approximations have been applied to a wide range of problems in solid-state and molecular physics,[6] with remarkably good results for ground-state geometries and vibration frequencies. In the case of total-energy differences, however, approximations (1.1) and (1.2) can lead to significant discrepancies from each other and from experiment. In atoms and ions, for example, local-density approximations underestimate the energy required to transfer an s electron to a d shell, and sp transfer energies if the p shell is more than half-full.[7−10] The binding energies in sp-bonded molecules are usually overestimated by both LSD and $X\alpha$ calculations,[11−12] but there are substantial differences between the two approximations if molecule information involves spin flips, e.g., in C_2 and N_2. Furthermore, the overestimates obtained using the LSD approximation are greater for bonds involving atoms with more than half-filled shells. Examples are O_2 and O_3, where bond strengths are ~ 2 eV greater than experimental values,[13] compared with overestimates ~ 1 eV in C_2 and C_3.[14] Calculated cohesive energies in solids involving sp and sd bonds also exceed the measured values.[15] It is natural to speculate that these deficiencies might be related,[7,8] and that a detailed understanding of the errors in atoms and molecules would lead to estimates of errors in extended systems and to improved approximations. An aim of this paper is then to identify sources of the discrepancies between LSD results and experiment for small systems.

In a study of the multiplet structure of atoms and ions, Wood[16] made the interesting observation that the LSD approximation generally reproduced experimental energy splittings well, while the $X\alpha$ approximation (for all conventional choices of α) gives splittings close to those of the Hartree-Fock (HF) method, where correlation effects are neglected. Since there is an explicit expression for the exchange energy in the HF approximation, it should be

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possible to determine the reason for discrepancies between HF and $X\alpha$ energy differences, and to obtain insight into the differences between LSD results and experiment.

If $\Phi_i(\mathbf{r})$ and $\Phi_j(\mathbf{r})$ are Hartree-Fock orbitals, the exchange energy can be expressed in terms of exchange integrals[17]

$$I_{ij} = e^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{\Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})\Phi_i(\mathbf{r}')\Phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} . \qquad (1.3)$$

These integrals depend strongly on the nodal structure of Φ_i and Φ_j. If, for example, the orbitals have different l and m quantum numbers, the integrand oscillates and I_{ij} is reduced. Since approximations (1.1) and (1.2) do not take such details into account, they cannot be expected to describe the effects of different nodal structures in a precise way. In fact, the value of α required to reproduce the contributions to atomic HF exchange energies shows significant variations for different orbitals,[18] examples being the $2s$ and $2p$ orbitals in first-row atoms, and the $3s$ and $3d$ orbitals in atoms where the latter are occupied. Since the transfer of electrons between subshells involves changes in the angular nature of the orbitals, they provide a sensitive test of local-density approximations.

As an example of the striking variations which can result from using different approximations, we consider the sp transfer from the ground state of the fluorine atom,

$$1s^2 2s_\uparrow 2p_\uparrow^3 2s_\downarrow 2p_\downarrow^2 \rightarrow 1s^2 2s_\uparrow 2p_\uparrow^3 2p_\downarrow^3 . \qquad (1.4)$$
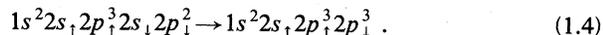
The change in the exchange interaction between the valence electrons when a $s_\downarrow$ electron is transferred to a $p_\downarrow$ orbital is[17]

$$\Delta I = -\tfrac{9}{25} G^2(2p,2p) + \tfrac{2}{3} G^1(2p,2s) , \qquad (1.5)$$

where the Slater integrals G^k are defined by

$$G^k(i,j) = 2 \int_0^\infty dr\, r^2 \int_0^\infty dr'\, (r')^2 \frac{r_<^k}{r_>^{k+1}}$$

$$\times \phi_i(r)\phi_j(r)\phi_i(r')\phi_j(r') . \qquad (1.6)$$

Here $r_>$ $(r_<)$ is the larger (smaller) of r and r', and $\phi_i(r)$ is the radial part of $\Phi_i(r)$. The first term in (1.5) is the exchange interaction between a p electron with $m=-1$ and two p electrons with $m=1$ and 0. The second term is the exchange interaction between an s electron and two p electrons. Inserting realistic values for the Slater integrals yields an estimate of $\Delta I \sim 6$ eV. On the other hand, density-functional calculations for the ground state of fluorine (Fig. 1) show that the radial structures of the $2s$ and $2p$ orbitals are very similar. If we assume that they are *identical* and neglect nonspherical corrections, the $X\alpha$ estimate of the exchange energy is unchanged by sp transfer. It is therefore not surprising that the $X\alpha$ prediction of the transition (1.4) differs from the HF result by about 6 eV.[19] The LSD and $X\alpha$ approximations give very similar results for the total sp transfer energy. The deviation between the LSD result and experiment is, however, reduced to 2.6 eV, since the large change in the exchange energy is compensated by a change in the correlation energy of opposite sign.
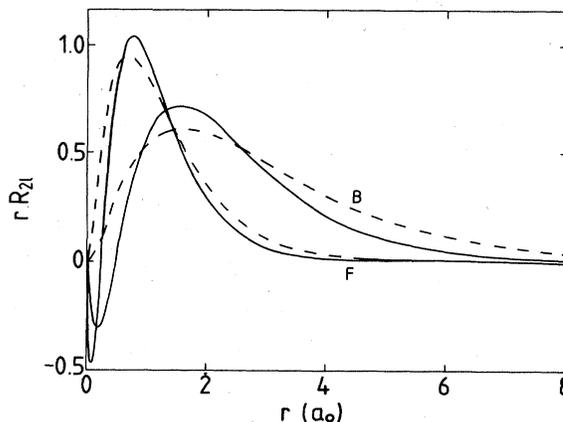

FIG. 1. Valence orbitals from density-functional calculations for B and F. The solid curves represent the $2s$ orbitals, the dashed curves the $2p$ orbitals.

In this work we study energy differences in a variety of systems. As in the above example, many of the known deficiencies of local-density approximations[7-15,20] can be understood in terms of their inability to incorporate correctly the angular character (the "nodality") of the wave function. This is shown clearly in Sec. II, where we compare HF and $X\alpha$ exchange energies for a model system in which the orbitals have identical radial dependences but different l values. In Sec. III we consider sp transfer and ionization energies in first-row atoms, and in Sec. IV the sd transfer energies in iron-series atoms and ions. Applications to molecules and the effect of correlation are considered in Secs. V and VI, respectively. Our final remarks (Sec. VII) include a discussion of the consequences for the development of nonlocal approximations for E_{xc}, including the recent suggestions of Harrison.[21]

II. EXCHANGE ENERGY DEPENDENCE ON ELECTRON NUMBER AND l VALUE

The l dependence of exchange energies is a well-known feature of atomic physics. As the atomic number increases and p and d orbitals become occupied, however, there is an l-dependent variation in the radial extent of the orbitals. If this is treated realistically, as in the atomic exchange energy calculations of Lindgren and Schwarz,[18] it is difficult to isolate the effects of the angular variation of the orbitals. In order to do this, we study here a model system where the radial parts of the s, p, and d orbitals are identical. In this case, the Slater integrals $G^k(i,j)$ [Eq. (1.6)] depend only on k. From calculated values for the $3s$ orbitals in iron-series atoms, we find that

$$G^0 = G^1/0.680 = G^2/0.516 = G^3/0.414 = G^4/0.344 . \qquad (2.1)$$

For the same orbitals, the exchange energy is reproduced very well by

$$C \int d\mathbf{r}\, n^{4/3}(\mathbf{r}) = 0.451 G^0 , \qquad (2.2)$$

where $n(\mathbf{r})$ is the density due to one electron. The cancel-

lation of the unphysical interaction of an electron with it-self, $-G^0/2$, is reproduced to within 10%. If we fill the spin-up states alone, the exchange energy of N electrons in the $X\alpha$ approximation is

$$E_x^{X\alpha}(N) = -0.451G^0N^{4/3} . \tag{2.3}$$

In the Hartree-Fock (HF) approximation, the exchange energy is

$$E_x^{HF}(N) = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} I_{ij} , \tag{2.4}$$

where the exchange integrals I_{ij} can be expressed in terms of the $G^k(i,j)$. If we define an average exchange integral $\bar{I}_{ij}$ by

$$E_x^{HF}(N) = \frac{1}{2}N^2\bar{I}_{ij}(N) , \tag{2.5}$$

it is clear that the $X\alpha$ and HF approximations show different N dependences unless $\bar{I}_{ij}$ decreases as $N^{-2/3}$. In Fig. 2(a) we compare $E_x^{X\alpha}(N)$ and $E_x^{HF}(N)$, where in the HF case we fill the shells in the order s,p,d and within each shell the states in the order $m, m-1, \ldots, -m+1, -m$. The trends are remarkably similar, the smaller $X\alpha$ values being consistent with the values of α needed to reproduce the HF exchange energies (typically about 10% greater than $\alpha = \frac{2}{3}$).[18] It is particularly interesting to study the *interelectronic* exchange energy,

$$E_{x,int}^{HF}(N) = -\frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} I_{ij} , \tag{2.6}$$

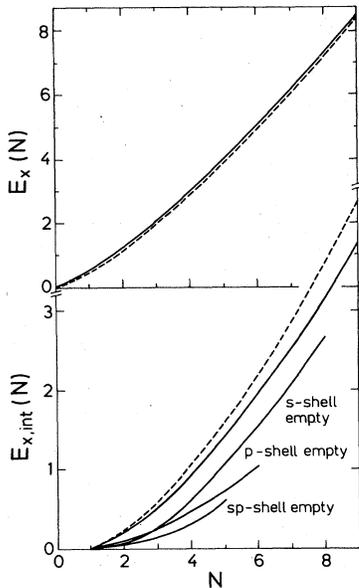$$E_{x,int}^{X\alpha}(N) = -0.451G^0(N^{4/3}-1) , \tag{2.7}$$

FIG. 2. (a) $E_x^{X\alpha}$ (dashed curve) and E_x^{HF} as a function of total occupation number N (in units of G_0). (b) Interelectronic exchange interation $E_{x,int}$ for $X\alpha$ (dashed) and HF (solid curve) approximations. In the HF approximation we show the dependency for different schemes of occupying the orbitals.

where the self-interaction has been subtracted. $E_{x,int}$ focuses on the $X\alpha$ description of the exchange interaction between states with different nodal structures and is plotted in Fig. 2(b). The $X\alpha$ and HF approximations again give similar results. As in the case of realistic l-dependent atomic orbitals,[18] the $X\alpha$ approximation overestimates the strength of the interaction, and we shall discuss other systems where this occurs.

The change in the average exchange integral $\bar{I}$ as N increases is related to the order in which we fill the shells, i.e., $s \rightarrow p \rightarrow d$. While the s state has no node in the valence region, the p and d states have one and two nodes, respectively. (Here and in the following we refer to an orbital as having a nodel plane even if the real and imaginary parts change sign at different planes.) This means, for example, that the sd interaction is weaker than the sp interaction, and $\bar{I}$ decreases with increasing N (Fig. 2). Since $X\alpha$ calculations produce a similar reduction, it is apparent that nodal formation is incorporated into these calculations to some extent. To understand this, we consider an exact sum rule[4] which holds for both the HF and $X\alpha$ approximations.

The exact exchange energy can be written as

$$E_x = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} , \tag{2.8}$$

where

$$n_x(\mathbf{r},\mathbf{r}') \equiv n(\mathbf{r})\int_0^1 d\lambda[g_{HF}(\mathbf{r},\mathbf{r}';\lambda)-1] \tag{2.9}$$

is the exchange hole, defined in terms of the HF pair correlation function and the coupling constant λ. For orthogonal HF orbitals,

$$n_x(\mathbf{r},\mathbf{r}') = -\frac{1}{n(\mathbf{r})}\sum_{i,j}\Phi_i^*(\mathbf{r})\Phi_j(\mathbf{r})\Phi_i(\mathbf{r}')\Phi_j^*(\mathbf{r}')\delta_{\sigma_i\sigma_j} ,$$

$$\tag{2.10}$$

where σ_i is the spin quantum number corresponding to Φ_i. Using the orthogonality of the orbitals we can derive the sum rule

$$\int d\mathbf{r}\, n_x(\mathbf{r},\mathbf{r}') = -1 , \tag{2.11}$$

i.e., for all values of $\mathbf{r}'$ the exchange hole must contain unit charge. By analogy to (2.8), the $X\alpha$ and LSD approximations can be expressed in terms of approximate holes which also satisfy the sum rule (2.11). The use of orthogonal orbitals to derive (2.11) means that schemes such as $X\alpha$ and LSD incorporate aspects of orthogonality and therefore node formation. However, the orthogonality condition is not *sufficient* to guarantee a good description. If the s orbital is occupied, for example, an additional electron placed in either a p or a d orbital would also satisfy the sum rule. The weakness of the sd interaction relative to the sp interaction is evident in Fig. 2(b), where the curve denoted "p-shell empty" shows that the $X\alpha$ approximation gives an unsatisfactory description of the interelectron exchange energy. The same is true if the s or sp shells remain unoccupied.

In the model discussed here, the $X\alpha$ exchange energy depends only on N and it can describe at most one of the

curves in Fig. 2(b). It is natural to ask why the particular filling "$s \rightarrow p \rightarrow d$" is described so much better than the others. To address this question, we have considered a system with N spin-up electrons where the orbitals are solutions to the potential

$$v(r) = \begin{cases} 0, & |r| \leq R_{WS} \\ \infty, & |r| > R_{WS} \ . \end{cases} \quad (2.12)$$

The three lowest solutions of this potential have s, p, and d character, respectively. Apart from the region near $r=0$, they are similar to $3s$, $3p$, and $3d$ atomic orbitals. If the orbitals of (2.12) are occupied according to the order of eigenvalues, there is good agreement between the $X\alpha$ and HF exchange energies. For $R_{WS} = 6$, for example, the magnitude of the former is 5—10% too small for N between 1 and 9. If we use the spd occupancy and let R_{WS} tend to infinity, we would obtain the ground state of a homogeneous electron gas. Since the $X\alpha$ exchange energy is exact in this case, the small error in the result for R_{WS} may not be surprising. However, for a different orbital occupancy, i.e., for an excited state, the discrepancy between the $X\alpha$ and HF exchange energies is large and of the same type as in Fig. 2(b). Since the $X\alpha$ exchange approximation is obtained from the *ground* state of the homogeneous electron gas, good results cannot be expected for these excited states.

These simple examples illustrate two main conclusions of this paper. (i) If we occupy orbitals with the minimum number of nodal planes consistent with the sum rule (2.11), the trends in the interelectronic exchange energy are reproduced rather well by the $X\alpha$ approximation, the absolute value being overestimated in the systems we have considered. (ii) Energy transfer from such a state to one with additional nodal planes is often underestimated by the local-density approximation. The magnitude of the underestimate depends on the system in question, but it can be large, as in the sp transfer energy in F (Sec. I).

III. FIRST-ROW ATOMS AND IONS

A. sp transfer energies

The sp transfer energy of fluorine has been discussed above. In general, we calculate the energy differences

$$\Delta_{sp}^a = E(1s^2 2s \, 2p^{n-1}) - E(1s^2 2s^2 2p^{n-2}) \quad (3.1)$$

in the neutral atoms, and

$$\Delta_{sp}^i = E(1s^2 2s \, 2p^{n-2}) - E(1s^2 2s^2 2p^{n-3}) \quad (3.2)$$

for the ions. These transitions are illustrated in Fig. 3. For each configuration, we consider the lowest-lying term. If relativistic effects are neglected, the theory should give a degeneracy with respect to the z components of the total angular and spin quantum numbers, M_L and M_S. The approximations [Eqs. (1.1) and (1.2)] break this degeneracy, however, and the M_L and M_S values need to be specified. Ziegler *et al.*[22] showed that states which can be represented by a single determinant should be described best by a local-density approximation for exchange, and we have chosen the values of M_L and M_S which correspond to such states. In the LSD calculations we use the
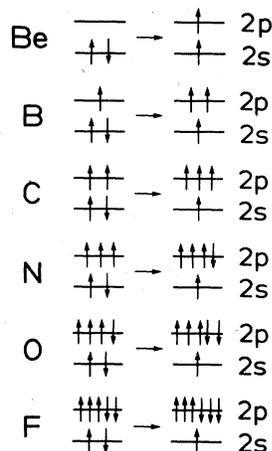

FIG. 3. Occupancies of different spin orbitals for first-row atoms and ions.

electron gas parametrization for ε_{xc} of Vosko *et al.*[25] Nonspherical corrections have been found to be very small for first-row atoms.

The energy differences Δ_{sp}^a and Δ_{sp}^i are shown in Figs. 4(a) and 4(b), respectively. A spin-flip occurs for the neutral atoms $_4$Be to $_6$C (and the ions $_5$B$^+$ to $_7$N$^+$) and the stronger spin dependence in the $X\alpha$ approximation means that Δ_{sp} is substantially smaller than the LSD values. In $_7$N to $_9$F ($_8$O$^+$ to $_{10}$Ne$^+$), the spin is transferred and not flipped, and the two approximations give similar results. The $X\alpha$ and HF results are remarkably similar in the first part of the row ($_3$Li to $_7$N and $_4$Be$^+$ to $_8$O$^+$), as are the LSD results and experiment. In the second part ($_8$O to $_9$F and $_9$F$^+$ to $_{10}$Ne$^+$), both comparisons show large deviations.
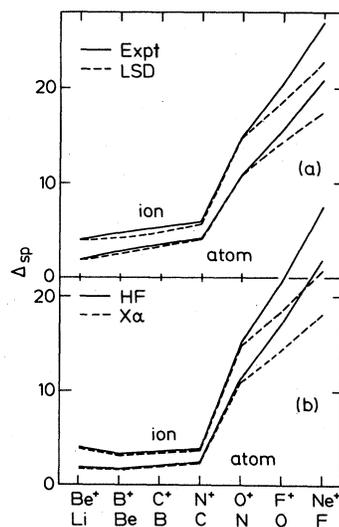

FIG. 4. Transfer energies Δ_{sp} in first-row atoms and ions. (a) Experimental and LSD values. (b) Hartree-Fock and $X\alpha$ values. Energies here and in the following are in eV.

B. Comparison of HF and $X\alpha$ results for Δ_{sp}

As noted above, the comparison between HF and $X\alpha$ results should provide insight into the deficiencies of the local-density approximations. We now present a detailed discussion of the results for Δ_{sp}, distinguishing between a particularly simple case where the transferred electron does not interact with other valence electrons from more general cases, both with and without a spin flip.

1. $_3Li$ and $_7N$ ($_4Be^+$ and $_8O^+$)

In these systems there is no exchange interaction between the transferred electron and other valence electrons. Since core-valence exchange effects are small in first-row atoms,[24] the main remaining source of error is the imperfect cancellation between exchange energy and the unphysical Coulomb self-interaction (SI) in the $X\alpha$ approximation.[25] This cancellation is numerically good [see Eq. (2.2)], and the SI errors for the $2s$ and $2p$ electrons largely cancel, so that there is good agreement between the $X\alpha$ and HF approximations.

2. Systems with spin flip

In $_4Be$-$_6C$ ($_5B^+$-$_7N^+$), sp transfer is accompanied by a spin flip. Since the radial functions for the s and p states in first-row atoms are very similar (Fig. 1) and the core-valence exchange is small, we may apply the arguments of Sec. II. If there are m valence electrons, the interelectronic exchange energy is given by

$$E_{x,int}(N=1)+E_{x,int}(N=m-1) \qquad (3.3)$$

in the initial state, and by

$$E_{x,int}(N=m) \qquad (3.4)$$

in the final state. The discussion in Sec. II shows that the contributions to the energy difference should be reproduced satisfactorily by the $X\alpha$ approximation, and this is confirmed by the results for $_4Be$-$_6C$ ($_5B^+$-$_7N^+$).

3. Systems without spin flip

In $_7N$-$_9E$ ($_8O^+$-$_{10}Ne^+$), a $2s_\downarrow$ electron is transferred to a $2p_\downarrow$ state. The interelectronic exchange energy difference in this case is

$$E_{x,int}(N=m-4)$$
$$-E_{x,int}(N=m-4, \text{ with } s \text{ shell empty}) . \qquad (3.5)$$

This vanishes if $m=5$, i.e., in N or O^+. As noted previously, the agreement between HF and $X\alpha$ is very good for these cases. For $_8O$ ($_9F^+$) with $m=6$, the error in Eq. (3.5) is $0.165G^0$, which is 3.31 eV (4.19 eV) compared with the calculated error of 2.71 eV (3.22 eV). For $_9F$ ($_{10}Ne^+$) with $m=7$, the error in Eq. (3.5) is $0.267G^0$, i.e., 6.16 eV (7.60 eV) compared with the calculated discrepancy of 5.72 eV (6.79 eV). These results provide further confirmation that the $X\alpha$ approximation can give rise to large errors when the electron transfer is associated with a net change in nodality.

The above discussion shows that the dramatic variation

in the sp transfer energy across the row is due to the different types of configurations involved for different electron numbers, and not to intrinsic differences between the atoms. We have seen, for example, that the agreement between $X\alpha$ and HF calculations for the ground state of $_6C^+$ is very good. For $_6C^+$ ($2s_\uparrow 2p_\uparrow^2 \rightarrow 2p_\uparrow^3$), on the other hand, there is a discrepancy of 4 eV between the $X\alpha$ and HF results.

C. Ionization energies

The ionization energies, I_p, of first-row atoms are shown in Fig. 5. For $_3Li$ and $_4Be$, ionization results in the removal of a $2s$ electron, for which there is an exchange interaction only with the $1s^2$ core. Figure 5 shows that the $X\alpha$ approximation for the core-valence exchange and the self-interaction does not lead to large errors in these atoms. For $_5B$ to $_7N$, a spin-up p electron is removed, and the difference in interelectronic exchange energy is

$$E_{x,int}(N=m-1)-E_{x,int}(N=m-2) . \qquad (3.6)$$

In the ionization of $_8O$ and $_9F$, a spin-down p electron is removed and the corresponding difference is

$$E_{x,int}(N=m-4)-E_{x,int}(N=m-5) . \qquad (3.7)$$

The discussion in Sec. II shows that we may expect the $X\alpha$ approximation to describe both (3.6) and (3.7) well, confirmation for which is found in Fig. 5.

D. Electron-hole symmetry

In the HF approximation, configurations such as $2s^1 2p^1$ and $2s^1 2p^5$ have the same multiplet structure, with splittings given by the same linear combinations of exchange integrals of the same type. In this sense, the approximation exhibits "electron-hole symmetry." In earlier work,[10] we showed that this symmetry is absent in both LSD and $X\alpha$ approximations, although an ad hoc incorporation of electron-hole symmetry reduced the errors for configurations such as $2s^1 2p^5$ to the same order as those for $2s^1 2p^1$.

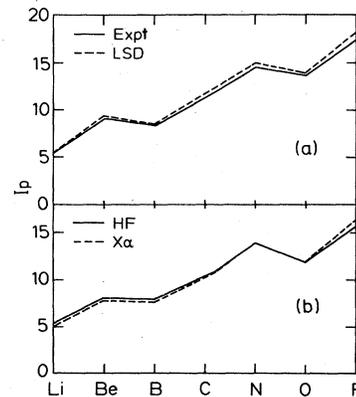The model of Sec. II provides a convenient framework

FIG. 5. Ionization potentials for first-row atoms (eV). (a) Experimental and LSD values. (b) Hartree-Fock and $X\alpha$ values.

for discussing this problem. In Ref. 10, for example, we discussed the energy differences

$$\Delta_{11} \equiv E(2s_\uparrow 2p_\uparrow) - E(2s_\uparrow 2p_\downarrow) \tag{3.8}$$

for a $2s^1 2p^1$ configuration, and

$$\Delta_{15} \equiv E(2s_\uparrow 2p_\uparrow^3 2p_\downarrow^2) - E(2s_\uparrow 2p_\uparrow^2 2p_\downarrow^3) \tag{3.9}$$

for a $2s^1 2p^5$ configuration. These quantities determine the ^3P-^1P splittings in the respective cases and, in the model of Sec. II, are given by

$$\Delta_{11} = E_x(2) - E_x(1) - E_x(1, \text{ with } s \text{ shell empty}) , \tag{3.10}$$

$$\Delta_{15} = E_x(4) + E_x(2, \text{ with } s \text{ shell empty})$$

$$- E_x(3) - E_x(3, \text{ with } s \text{ shell empty}) . \tag{3.11}$$

In the $X\alpha$ and HF approximations we obtain $0.234 G^0$ and $0.226 G^0$, respectively, for the $2s^1 2p^1$ configuration, and $0.097 G^0$ and $0.226 G^0$ for the $2s^1 2p^5$ case. These results are in semiquantitative agreement with the LSD and experimental results quoted in Ref. 10. In particular, the deviation between the $X\alpha$ and HF results are small for the $2s^1 2p^1$ configuration, but large for $2s^1 2p^5$.

A similar analysis can be performed for other other cases discussed in Ref. 10. It is striking that a $2s$ level is empty in all cases where the lack of electron-hole symmetry gives particularly large errors, in agreement with the discussion of Sec. II. In Eq. (3.11), for example, we need the energy difference between a two-electron system and a three-electron system with an empty $2s$ level, and Fig. 2(b) associates this with a large error. On the other hand, $E_x(1, \text{ with } s \text{ shell empty})$ in (3.10) contains only the self-interaction of a single p electron and causes no problems.

IV. IRON SERIES ATOMS AND IONS

A. sd transfer energies

The sd transfer energies are defined as

$$\Delta_{sd}^a = E([\text{core}]3d^{n-1}4s^1) - E([\text{core}]3d^{n-2}4s^2) \tag{4.1}$$

for atoms, and

$$\Delta_{sd}^i = E([\text{core}]3d^{n-1}) - E([\text{core}]3d^{n-2}4s^1) \tag{4.2}$$

for ions. The transitions involved are shown schematically in Fig. 6. In the calculations for these systems, we have included nonspherical corrections to the energies.[26] As in Sec. III, we compare LSD and experimental energy differences, and $X\alpha$ and HF values in Fig. 7. For the neutral atoms [Fig. 7(a)], both LSD and $X\alpha$ approximations overestimate the stability of the configuration with one additional d electron. A similar effect is present in the ions [Fig. 7(b)], with an overestimate of the stability of the $3d^{n-1}$ configuration, but the differences between LSD and experiment, and between HF and $X\alpha$ are smaller in this case.

B. Comparison of HF and $X\alpha$ results for Δ_{sd}

In discussing the HF and $X\alpha$ results for iron-series atoms, we again distinguish between a simple but instruc-

FIG. 6. Occupancies of different spin orbitals for iron-series atoms and ions.

tive case (the Mn atom) and more general trends across the series.

1. sd transfer in the Mn atom

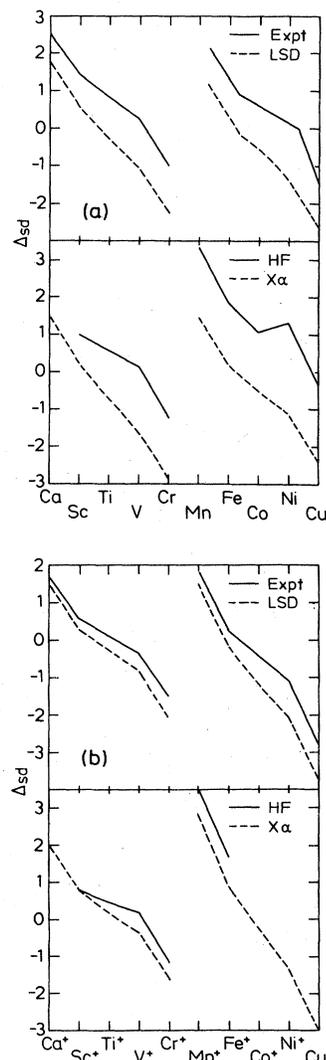In this case, the sd transfer is

FIG. 7. Comparisons of sd transfer energies, experiment against LSD (upper frames) and HF against $X\alpha$ (lower frames). (a) $3d$ atoms. (b) $3d$ ions.

$([core]3d_\uparrow^5 4s_\uparrow 4s_\downarrow) \rightarrow ([core]3d_\uparrow^5 3d_\downarrow 4s_\uparrow)$.   (4.3)

In both $X\alpha$ and HF approximations, the spin-down $4s$ electron does not interact with the other valence electrons, which are all spin up. Nevertheless, the HF and $X\alpha$ results differ by 1.9 eV, a discrepancy which cannot be attributed to the self-interaction corrections, which increase

Δ_{sd} by only 0.16 eV.

To study the effect of core-valence exchange, we have used the orbitals of the $X\alpha$ calculation for the $3d^5 4s^2$ configuration to calculate the change in the exchange energy when a single $3d$ electron interacts with a $1s^2 2s^2 2p^6 3s^2 p^6$ core. In the HF approximation, this energy difference is

$$E_x^{HF}([core]3d) - E_x^{HF}(core) - E_x^{HF}(3d) = -\frac{1}{5}[G^2(3d,1s) + G^2(3d,2s) + G^2(3d,3s)]$$
$$-\frac{6}{15}[G^1(3d,2p) + G^1(3d,3p)] - \frac{63}{245}[G^3(3d,2p) + G^3(3d,3p)] ,   (4.4)$$

which has the value 12.4 eV. The corresponding $X\alpha$ result is 14.1 eV. The same calculation can be performed for the exchange interaction between the $4s$ electron and the core. The $4s$ orbital is more extended than the $3d$ and this interaction is substantially smaller, being 1.8 and 1.3 eV in the $X\alpha$ and HF approximations, respectively. Most of the discrepancy between the $X\alpha$ and HF estimates of Δ_{sd} in Mn can then be attributed to $3d$ core exchange.

2. Trends across the 3d series

In systems other than the Mn atom, it is necessary to study the change in the exchange interaction when a $3d$ electron interacts with a $3d^n$ configuration. In these cases, one can carry out the same analysis as in Sec. III. For the Mn $3d$ orbitals, we find

$$G^0 = G^1/0.624 = G^2/0.434 = G^3/0.330 = G^4/0.265$$
(4.5)

and the numerical equality

$$C \int dr\, n^{4/3}(\mathbf{r}) = 0.432 G^0(3d,3d) .   (4.6)$$

The change in the interelectronic exchange energy is

$$\Delta E_{x,int}(n) = E_{x,int}(3s_\downarrow 3p_\downarrow^3 3d_\downarrow^{n+1}) - E_{x,int}(3s_\downarrow 3p_\downarrow^3 3d_\downarrow^n)$$
$$- E_{x,int}(3d_\downarrow) .   (4.7)$$

The prefactors of G^0 for the $X\alpha$ and HF approximations as a function of n are shown in Table I. The deviations increase with increasing n and are slightly larger than those in Fig. 2(b), since the coefficients used in Eq. (4.5) are different. The value of $G^0(3d,3d)$ also increases with atomic number, enhancing the deviation still further.

A further contribution to Δ_{sd} arises from the $4s$-$3d$ exchange interaction. To study this, we calculate

$$I_1 = E([core]3d_\uparrow^5 4s_\uparrow) - E([core]3d_\uparrow^5 4s_\uparrow 4s_\downarrow)   (4.8)$$

and

$$I_2 = E([core]3d_\uparrow^5 3d_\downarrow) - E([core]3d_\uparrow^5 3d_\downarrow 4s_\uparrow) .   (4.9)$$

In the first case, the added $4s$ electron has an exchange interaction only with the core, and the $X\alpha$ and HF approximations give very similar results (5.85 and 5.91 eV, respectively). This shows that the errors in the self-interaction energy of the $4s$ electron and the $4s$ core exchange approximately cancel.

In (4.9), the $4s$ electron also has an exchange interaction with a $3d^5$ configuration. The $X\alpha$ and HF calculations give 7.16 and 6.06 eV, respectively, so that the $X\alpha$ approximation overestimates the $4s$-$3d^5$ exchange energy for $_{25}$Mn, in agreement with our earlier work.[7] This is confirmed by comparing

$$\Delta E_x^{ds} \equiv E_x(3d^n 4s) - E_x(3d^n) - E_x(4s)   (4.10)$$

in the $X\alpha$ and HF approximations. Using $X\alpha$ orbitals for the $[core]3d^5 4s^2$ configuration, we obtain the results in Table II. They predict an error in the $4s$-$3d^5$ interaction of 1.6 eV, in fair agreement with the discrepancy quoted above. If the $_{25}$Mn orbitals are replaced by those from the $_{21}$Sc $3d^1 4s^2$, we obtain $X\alpha$ and HF results for $\Delta E_x^{sd}(m=1)$ of 1.11 and 0.31 eV, respectively, very close to the values obtained with Mn orbitals.

We now discuss the sd transfer in terms of the $X\alpha$ description of both $3d$-$[core]3d^n$ and $4s$-$3d^n$ interactions. For the neutral atoms $_{20}$Ca to $_{24}$Cr, a spin-down $4s$ electron is transferred to a spin-up $3d$ state. The dominant error in these systems arises from the $3d$-$[core]3d^n$ interaction. In the case of $_{21}$Sc, we estimate from Table I that this error is 1.4 eV, in fair agreement with the error (~ 1.2 eV) estimated using $_{21}$Sc $3d^1 4s^2$ $X\alpha$ orbitals and

TABLE I. Exchange interaction ΔE_x between a $3d$ electron and the system $3s\,3p^3 3d^n$ according to $X\alpha$ and HF approximations.

	$\Delta E_x(n)/G^0(3d,3d)$	
n	$X\alpha$	HF
0	0.52	0.42
1	0.58	0.48
2	0.64	0.49
3	0.70	0.54
4	0.74	0.58

TABLE II. Exchange interaction $\Delta E_x^{sd}(m)$ [Eq. (3.10)] between a $4s$ electron and a $3d^m$ configuration in $X\alpha$ and HF approximations. Energies (in eV) were calculated using $_{25}$Mn $3d^5 4s^2$ $X\alpha$ orbitals.

	ΔE_x^{sd} (eV)	
m	$X\alpha$	HF
1	1.11	0.26
2	1.70	0.52
3	2.15	0.78
4	2.53	1.04
5	2.86	1.30

including the inner core. The error is reduced somewhat by an error of ~ 0.4 eV in the 4s-[core] interaction. As we proceed from $_{20}$Ca and $_{24}$Cr, the increasing error in the $3d$-[core]$3d^n$ interaction (Table I) is reflected in an increasing error in the $3d$-[core]$3d^n$ interaction (Table I) is reflected in an increasing error in Δ_{sd}. In the first half of the ion series ($_{20}$Ca$^+$—$_{24}$Cr$^+$), the transferred 4s electron has an exchange interaction with the $3d$ electrons in the initial state. The resultant error in the $4s$-$3d^n$ interaction (Table II) largely cancels the error in the $3d$-[core]$3d^n$ interaction. For $_{21}$Sc$^+$, the error in Δ_{sd} is about 0.8 eV less than in the neutral atom.

In the second half of the atom series, a $4s_\downarrow$ electron is transferred into a $3d_\downarrow$ state. Except in $_{25}$Mn, these atoms also have a $4d$-$3d^n$ exchange interaction in the initial state. The trend with increasing atomic number is similar to the first half of the *ion* series, except that the increased contraction of the $3d$ orbitals leads to a less complete cancellation between the errors in the $4s$-$3d^n$ and $3d$-[core]$3d^n$ interactions. In the second half of the ion series ($_{25}$Mn$^+$—$_{29}$Cu$^+$), a $4s_\uparrow$ electron is transferred into a $3d_\downarrow$ state, so that there is a $4s$-$3d^5$ exchange interaction in the initial state. The compensation of the error due to the *final* state $3d$-[core]$3d^n$ interaction by the $4s$-$3d$ exchange is then more complete than in the corresponding atoms, particularly at the beginning of the second half of the series.

The discussion in this section has shown that $3d$-transition series atoms are more complicated than first-row atoms (Sec. III), due to the importance of core-valence exchange effects. The discrepancies in Δ_{sd} are due in large part to errors in describing these, particularly the core-$3d$ exchange energy. This is a further example of point (i) in Sec. II, that the interelectronic exchange energy is overestimated if we fill the orbitals with the minimum number of nodes consistent with the sum rule (2.11). The relative error is not large (14% for Mn), but the absolute discrepancy is important (1.7 eV in Mn).

V. MOLECULES

The accuracy of the local-density methods in bonding situations can best be studied for small molecules. The experimental data are generally more precise than for bulk or interface systems, Hartree-Fock calculations are available in many cases, and numerically exact solutions of the Schrödinger equation in some. The results of Sec. III and IV show that sources of errors in local-density approximations can be identified by comparing the results of different methods of calculation. This is also true in molecules, and further information can be found by studying trends in the binding energies, i.e., the energies required to break specific molecular bonds. In this section we examine both of these aspects.

A. Ground state of H_2 and Li_2

The ground state of H_2 and the alkali-metal-atom dimers is a $^1\Sigma_g^+(\sigma_g^\uparrow\sigma_g^\downarrow)$ bond between the valence s orbitals. This is a well-studied situation and there are not only HF calculations[27,28] and reliable experimental data,[29] but in H_2 (Ref. 30) the energy variation within the Born-

Oppenheimer approximation is known very accurately. The experimental equilibrium internuclear separations are reproduced well by HF and *ab initio* methods, and by LSD and $X\alpha$ calculations.[31] In Table III we compare therefore the well depths calculated with the different methods for the experimental equilibrium internuclear separations in H_2 and Li_2.

The results show that the s-s σ_g bond is a further case where the $X\alpha$ approximation reproduces the HF binding energy well, and there is also satisfactory agreement between the LSD results and experiment. This indicates that the $X\alpha$ approximation gives an adequate description of the change in the self-interaction on formation of a $^1\Sigma_g^+$ bond and that the LSD approximation accounts for the substantial change in correlation energy on bonding. The LSD approximation also gives a satisfactory description of the bond strengths in other alkali-metal-atom dimers[32] and of the cohesive energies of the alkali metals.[33] There is no qualitative change in the nodal structure of the wave function of the H_2 molecule or the alkali-metal-atom dimers when bonding occurs.

B. Occupancy of σ_g and σ_u orbitals: $H_2(^3\Sigma_u^+)$, He_2, Be_2

The first excited state of H_2 is strikingly different from the ground state. Except for a very weak minimum at large separation, the energy curve for the $^3\Sigma_u^+$ state $(1\sigma_g^\uparrow 1\sigma_u^\uparrow)$ is repulsive, and we compare the results of the different methods of calculation with the essentially exact results of Kołos and Wolniewicz[30] at the ground-state equilibrium separation (1.40 a.u.). The difference between the LSD and experimental binding energies is 0.5 eV, i.e., substantially greater than in the ground state. This may at first seem surprising, since the correlation energy is relatively small (0.22 eV compared with 1.10 eV in the ground state)[34] and there is no spin flip on forming the $^3\Sigma_u^+$ state from two ground-state atoms. $X\alpha$ calculations ($\alpha = \frac{2}{3}$) show, however, that there is a comparably large deviation between the $X\alpha$ and HF values.[34] The LSD approximation overestimates the exchange interaction between the $1\sigma_g$ and $1\sigma_u$ orbitals in this state, resulting in an overestimate of the stability of this state relative to the dissociated atoms. The LSD binding-energy curve, for example, has a minimum of ~ 20 meV at a separation of 6.2 a.u., compared with the exact values of 0.5 meV and 7.85 a.u.[30]

To obtain a better understanding of bonding in this state, we study a related model problem. We use the HF

TABLE III. Well depth in $^1\Sigma_g^+$ state of H_2 and Li_2.

	H_2	Li_2
Expt.	4.75[a]	1.03[a]
LSD	4.96[b]	1.01[c]
HF	3.64[d]	0.17[e]
$X\alpha$	3.60[b]	0.21[c]

[a]Reference 29.
[b]Present work.
[c]Reference 12.
[d]Reference 27.
[e]Reference 28 (molecular energy) and Ref. 18 (atomic energy).

orbital $\phi(r)$ for the isolated hydrogen atom to construct molecular orbitals (MO),

$$\Phi_g(r) = \frac{1}{\sqrt{2(1+S)}}[\phi(r-R_a)+\phi(r-R_b)] \,, \qquad (5.1)$$

$$\Phi_u(r) = \frac{1}{\sqrt{2(1+S)}}[\phi(r-R_a)-\phi(r-R_b)] \,, \qquad (5.2)$$

where R_a and R_b are the atomic positions and S is the overlap integral between $\phi(r-R_a)$ and $\phi(r-R_b)$. For small values of the interatomic separation $R \equiv |R_a - R_b|$, these orbitals are more extended than the HF solutions for a helium atom, and would not describe satisfactorily the HF solution for H_2 as $R \rightarrow 0$. For small separations, errors in the SI energy would differ substantially from those near the ground-state equilibrium separation and the errors in the $1\sigma_g$-$1\sigma_u$ exchange interaction would be obscured. Instead of studying the HF solution for the $^3\Sigma_u^+$ state, we therefore use the orbitals [Eqs. (5.1) and (5.2)] to define an instructive *model* problem which focuses on the $1\sigma_g$-$1\sigma_u$ interaction. It is then straightforward to calculate the HF exchange energy in terms of exchange integrals [Eq. (1.3)] and the $X\alpha$ exchange energy from the corresponding density. In Fig. 8 we show the difference between these energies, $\Delta E_x \equiv E_x^{X\alpha}(R) - E_x^{HF}(R)$, as a function of R. The results confirm that the $X\alpha$ approximation overestimates the exchange interaction between σ_g and σ_u orbitals, and the increasing discrepancy as the nuclei become closer is consistent with the discrepancy between the LSD and exact results noted above.

The formation of the bond in H_2 ($^3\Sigma_u^+$) is related to the sp transfer in Be (Sec. III), since in both cases an electron is transferred into a spin-up orbital with a nodal plane. For $R \rightarrow 0$, the $1\sigma_u$ orbital in H_2 approaches a $2p$-like function with the radial part

$$\frac{d}{dt}\phi(r) = \frac{1}{\sqrt{\pi}} \exp(-r) \,. \qquad (5.3)$$

This function differs markedly from the $2p$ solution in the hydrogen atom, but has the same nodel structure.

A similar situation occurs in He_2 and the group IIA dimers (Be_2, Mg_2, ...), for which the LSD calculations give overestimates of the bond strengths.[8] In these sys-

tems, there is a σ_g-σ_u interaction in both spin-up and spin-down systems, and we have repeated the model calculation described above using the HF $2s$ orbitals for a free Be atom. For an internuclear separation of $R=4.7$ a.u., we obtain the difference $\Delta E_x(R=4.7$ a.u.$)$ $-\Delta_x(R=\infty) = -0.3$ eV, smaller in magnitude but of the same sign as the difference between the HF and $X\alpha$ approximations.[35] Inclusion of p and d functions in the basis increases the interaction between the two Be atoms as well as the deviation between the $X\alpha$ and HF energies. For $R \rightarrow 0$, the σ_u state approaches a p-like function with one node in the radial part. This function is, however, quite different from the $3p$ function in Be. The error in the LSD calculation for Be_2 [0.38 eV (Ref. 36)] is smaller than that in the $2s$-$3p$ transfer energy (0.55 eV per Be atom), consistent with the tendency of the error to increase as $R \rightarrow 0$. The overestimate in the interelectronic exchange between σ_g and σ_u orbitals in all these cases is in agreement with the observation (i) at the end of Sec. II.

C. Excited states of H_2 and Li_2

Atomic calculations (Secs. III and IV) have shown that an excitation energy corresponding to the creation of more nodal planes than required to satisfy the sum rule (2.11) is underestimated in the $X\alpha$ approximation. In the $^3\Pi_u$ and $^3\Pi_g$ states of H_2 and Li_2, an electron is excited from the σ_i orbital to the π_u and π_g orbitals, respectively. The π_u orbital has the minimum number of nodes consistent with (2.11), and the above discussion indicates the $X\alpha$ approximation will overestimate the exchange energy. The π_g orbital, however, has *two* nodal planes, and we may expect a greater error in the $^3\Pi_g$ state than in the $^3\Sigma_u^+$ or $^3\Pi_u$ states. In H_2 this is the case, but the $1\sigma_g$ orbital is much more compact than the π orbitals and the exchange integrals are numerically very small.[34] LSD calculations show that the difference between the $^1\Sigma_g^+$ and $^3\Pi_u$ minima is 11.6 eV compared with the experimental value of 12.0 eV.

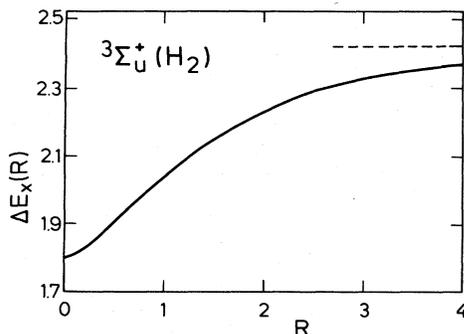Li_2 is a more typical molecule, since the radial extents

FIG. 8. The difference, $\Delta E_x(R)$ (eV), between exchange energies in HF and $X\alpha$ approximations as a function of internuclear separation R for the model problem [Eqs. (5.1) and (5.2)].
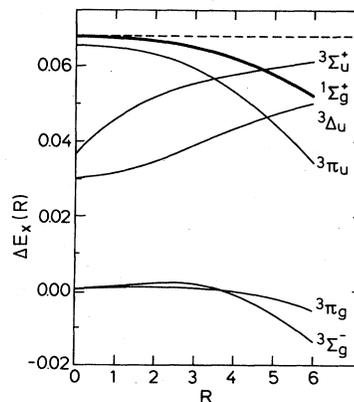
FIG. 9. The difference, $\Delta E_x(R)$, between exchange energies in HF and $X\alpha$ approximations as a function of internuclear separation R for different states of the Li_2 molecule. The equilibrium separation for the ground state is $R=5$ a.u. The dashed curve shows the result for two free Li atoms. Energies in Ry.

of the $2\sigma_g$ and π orbitals are comparable. We have performed the same calculation for Li_2 as described above for Be_2, using Slater orbitals with the exponent 0.65 to describe the valence orbitals. The core states are neglected. In Fig. 9 we show the exchange energies as a function of R for the $^1\Sigma_g^+$, $^3\Sigma_u^-$, $^3\Pi_u$, $^3\Pi_g$, $^3\Delta_u$, and $^3\Sigma_g^-$ states.

For several of these states, the HF and/or $X\alpha$ approximations give incorrect dissociation products, with large deviations as $R \to \infty$. We therefore focus on values of R near or less than the ground-state equilibrium separation, $r_e(\sim 5$ a.u.). The deviation of a given curve from the ground-state ($^1\Sigma_g^+$) curve is a measure of the error in the excitation energy. As expected from the above discussion, there is a marked difference between the states with a single nodal plane ($^3\Sigma_u^+$, $^3\Pi_u$, and $^3\Delta_u$) and those with two ($^3\Pi_g$, $^3\Sigma_g^-$). For $R = 5$ a.u., the corresponding values of the interelectronic exchange energy are 0.099, 0.080, and 0.100 Ry and 0.043 and 0.036 Ry. This difference in nodal structures is not incorporated into the $X\alpha$ approximation. It may be noted that in the $^3\Delta_u$ state $(1\pi_u[m=1]1\pi_g[m=1])$, the $1\pi_g$ and $1\pi_u$ orbitals have one and two nodal planes, respectively. These orbitals have the same azimuthal behavior, however, and the integrand in the appropriate exchange integral changes sign only at one plane. By contrast, both π orbitals in the $^3\Sigma_g^-$ state $(1\pi_u[m=1]1\pi_g[m=-1])$ have a nodal plane, and the error is similar to that in the $^3\Pi_g$ state.

We can make more direct contact with the discussion of the preceding sections by studying the behavior of these states as $R \to 0$. In this limit, the $1\pi_u$, $1\pi_g$, and $2\sigma_u$ orbitals approach $2p$, $3d$, and $3p$ functions, respectively. The error in the excitation energy in the $^3\Pi_u$ ($2\sigma_g 1\pi_u$) state is then given at $R=0$ by the error in the sp transfer energy for a system with two valence electrons. This error is small (see Figs. 2 and 4), in agreement with the result in Fig. 9. In the $^3\Sigma_u^+$ state, the limiting behavior of the $2\sigma_u$ orbital is a $3p$ function with two additional nodal surfaces. For the orbitals used here, they lie in the valence region and lead to an appreciable reduction in the $2s$-$3p$ exchange integrals (see Fig. 9). For large values of R, the nodal surfaces are close to the nuclei and influence the exchange energy little. The zero separation limit of the $^3\Delta_u$ orbitals are $2p$ and $3d$ functions with the same azimuthal behavior, and the exchange energy is weaker than the $2s$-$2p$ interaction. Finally, the behavior of the $^3\Pi_g$ and $^3\Sigma_g^-$

states for small separations is consistent with the substantially larger errors in these cases. The exchange interactions reduce to s-d and p-p interactions, respectively, and Fig. 2(b) shows that large errors are to be expected.

D. Bonding trends in first-row molecules

The above discussion has shown the value of comparing energy differences calculated by different methods. As the number of electrons and the complexity of the calculations increases, however, the quantity and quality of the available data are often insufficient for this purpose. The LSD approximation overestimates bond strengths in first-row molecules, but by amounts which show pronounced changes with increasing atomic number. We study these effects here, using additional information from $X\alpha$ and HF calculations where available and appropriate.

In Table IV we show the atomic and molecular ground-state configurations of the molecules B_2 to F_2, as well as the measured well depths[29] and the corresponding LSD values.[12] Results for the $^3\Sigma_g^-$ and $^3\Pi_u$ states of C_2 are also shown, as we shall discuss them below. The change in nodal structure on dimer formation is shown in Fig. 10, where we correlate the symmetry of the molecular orbitals with those for zero separation. The values shown are for F_2, but qualitatively similar results are obtained in the other cases. For separations near equilibrium, the energy difference between the $2s$- and $2p$-derived orbitals is substantial and justifies a qualitative discussion in terms of these functions separately.

In the molecules B_2 to F_2, the $2s$ atomic orbitals form a closed-shell $2\sigma_g^\uparrow 2\sigma_g^\downarrow 2\sigma_u^\uparrow 2\sigma_u^\downarrow$ configuration. The discussion in Sec. V B indicates that the local-density description of exchange will overestimate the stability of the resulting bond. The effect varies with the localization of the atomic functions and the bond length. The $2p$ orbitals give rise to more pronounced changes in bonding trends. The results of Table IV show that the overestimate of the well depth is particularly large in O_2 and F_2, in the latter case being comparable to the well depth itself. The difference between the results for atoms with $2p$ shells which are more or less than half-full is most clearly shown by comparing the $^3\Sigma_g^-$ states of C_2 and O_2. The atomic ground states also have the same symmetry (^3P) and, as far as the

TABLE IV. Configurations and binding energies of first-row dimers. The $1\sigma_g^\uparrow 1\sigma_g^\downarrow 1\sigma_u^\uparrow 1\sigma_u^\downarrow 2\sigma_g^\uparrow 2\sigma_g^\downarrow 2\sigma_u^\uparrow 2\sigma_u^\downarrow$ configuration is present in each dimer.

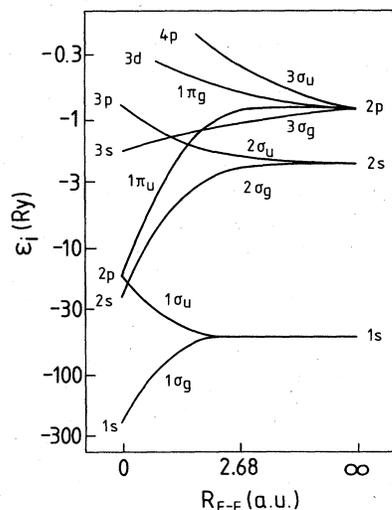| Atom	Dimer	Expt.[a]	LSD[b]
$_5B$ $^2P(2s_\uparrow 2s_\downarrow 2p_\uparrow)$	B_2 $^3\Sigma_g^-[(\pi_u^\uparrow)^2]$	3.09	3.93
$_6C$ $^3(2s_\uparrow 2s_\downarrow 2p_\uparrow^2)$	C_2 $^1\Sigma_g^+[(\pi_u^\uparrow)^2(\pi_u^\downarrow)^2]$	6.37	7.19
	$^3\Pi_u[(\pi_u^\uparrow)^2\pi_u^\downarrow\sigma_g^\uparrow]$	6.28	7.59
	$^3\Sigma_g^-[(\pi_u^\uparrow)^2\sigma_g^\uparrow\sigma_g^\downarrow]$	5.57	6.61
$_7N$ $^4S(2s_\uparrow 2s_\downarrow 2p_\uparrow^3)$	N_2 $^1\Sigma_g^+[\sigma_g^\uparrow\sigma_g^\downarrow(\pi_u^\uparrow)^2(\pi_u^\downarrow)^2]$	9.91	11.34
$_8O$ $^3P(2s_\uparrow 2s_\downarrow 2p_\uparrow^3 2p_\downarrow)$	O_2 $^3\Sigma_g^-[\sigma_g^\uparrow\sigma_g^\downarrow(\pi_u^\uparrow)^2(\pi_u^\downarrow)^2(\pi_g^\uparrow)^2]$	5.21	7.54
$_9F$ $^2P(2s_\uparrow 2s_\downarrow 2p_\uparrow^3 2p_\downarrow^2)$	F_2 $^1\Sigma_g^+[\sigma_g^\uparrow\sigma_g^\downarrow(\pi_u^\uparrow)^2(\pi_u^\downarrow)^2(\pi_g^\uparrow)^2(\pi_g^\downarrow)^2]$	1.66	3.32

[a]Reference 29.

[b]Reference 12.

FIG. 10. Schematic variation of eigenvalues in first-row dimers as a function of separation. The results are shown for F_2 at infinite separation (atomic eigenvalues for F), at the equilibrium separation (2.68 a.u.) and at zero separation (the Ar atom).

FIG. 11. Molecular orbitals of O_2 (left) and O_3 (after Ref. 40), with occupation numbers f_i corresponding to (C_2,O_2) and (C_3,O_3). The other orbitals are doubly occupied.

$2p$-derived molecular orbitals are concerned, bond formation differs only in the replacement of electrons by holes. However, the well-depth overestimate is much greater for O_2 (2.3 eV compared with 1.0 eV in C_2). The oxygen molecule is the first in this series in which the antibonding $1\pi_g$ orbital is occupied. As can be seen from Fig. 10, this has the nodal structure of a $3d$ function at small separations, and we may expect the local-density approximation to overestimate the exchange energy. This is also true for F_2, and the results of Table IV show that the errors in O_2 and F_2 are the largest in the series, both in absolute and relative terms. These results suggest that local-density approximations overestimate the interaction of a π_g orbital with a $2\sigma_g 2\sigma_u 3\sigma_g \pi_u$ shell, in analogy to our earlier observation for the σ_g-σ_u interaction.

The above discussion shows that substantial errors in binding energies, or marked changes in binding trends, can be associated with changes in the nodal structure of the orbitals involved. In each case, the local-density estimates of exchange energies are larger in magnitude than the exact values. It is important to note, however, that a *small* error may result from the compensation of several. An example is the excitation energy from the $^2\Pi_g$ ground state of F_2^+ to the $^2\Pi_u$ state, corresponding to the transfer $\pi_u^\downarrow$ to $\pi_g^\downarrow$, i.e., with a change in nodal structure from $2p$ to $3d$. The change in exchange energy is

$$\Delta E_x = E_x(\pi_g,\pi_g) - E_x(\pi_u,\pi_u) + E_x(\pi_g,3\sigma_g)$$
$$- E_x(\pi_u,3\sigma_g) + E_x(\pi_g,2\sigma_u) - E_x(\pi_u,2\sigma_g)$$
$$+ E_x(\pi_g,2\sigma_g) - E_x(\pi_u,2\sigma_g) . \tag{5.4}$$

The sign of the error caused by the local-density approximation is not immediately obvious, and the LSD estimate of the excitation energy (2.95 eV) is a slight overestimate of the experimental value (2.81 eV).
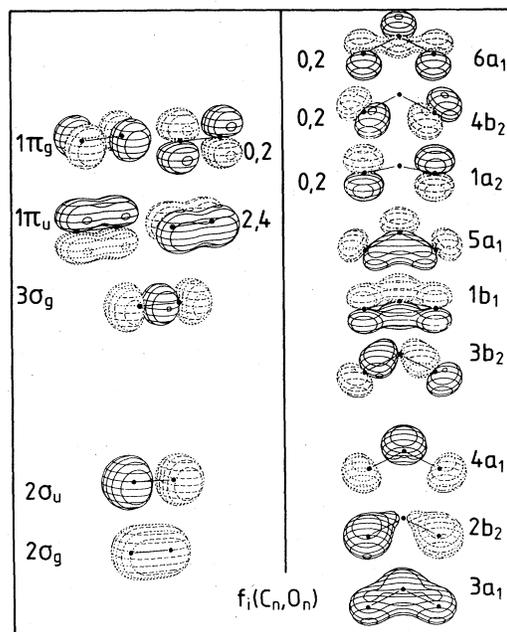
E. Small polyatomic molecules

There are relatively few density-functional calculations on small molecules with more than two atoms. The tendency to overestimate bond strengths is also present in these cases[37] and we discuss this with particular reference to C_3 (Ref. 14) and O_3 (Ref. 13). In C_3 as in C_2, LSD calculations overestimate the well depth by ~ 1 eV, whereas in O_3 (and O_2) the error is much greater (~ 2 eV). This difference can again be correlated with the difference in the nodal structures of the molecular orbitals.

In Fig. 11 we show the orbitals of the ground states of O_2 and O_3,[38] together with the occupation numbers. The C_3 bond is linear, but the orbitals are qualitatively the same and the occupation numbers for C_2 and C_3 are also shown. The formation of the dimer and trimer bonds show definite parallels. In both the $X-X$ and $\dot{X}_2-X$ bonds, the $2s$ orbitals give rise to one bonding and one antibonding orbital, in the latter case with an additional nonbonding $(2b_2)$ orbital. In both cases an additional nodal plane is created, and our experience from σ_g-σ_u bonds suggests that the local-density approximation will overestimate this contribution to the bond.

In O_2 and O_3, the $2p$-derived shells are more than half-occupied and this leads in each case to the occupancy of states with *additional* nodal planes. In view of the discussion of the π_g-$2\sigma_g 2\sigma_u 3\sigma_g \pi_u$ interaction for O_2, it is not surprising that the overestimate of the well depth is larger in O_2 than in C_3. A further observation consistent with this picture comes from the low-lying states of C_3, which have linear geometries and for which the vertical excitation energies are known. The transition from the ground state to the (doubly-degenerate) $^3\Pi_u$ and $^1\Pi_u$ states corresponds to the transfer of a $3\sigma_u$ electron to the $1\pi_g$ orbi-

tals, which have an additional nodal plane. The LSD calculations[14] for the $^3\Pi_u$ and $^1\Pi_u$ excitation energies (1.8 and 2.6 eV, respectively) underestimate the measured values (2.10 and 3.06 eV).

The comparison of HF and $X\alpha$ calculations for the equilibrium geometry of ozone by Salahub et al.[39] is consistent with the above observations. The $X\alpha$ method describes the ground state and the lower ionization potentials better than HF, and the authors queried whether correlation effects might be present in the former. They found that HF and $X\alpha$ orbitals were very similar, so that differences between the results must arise from the different expressions for the exchange energy. Salahub et al. found a particularly small contribution to the exchange energy from the high-lying $1a_2$ orbital, i.e., an orbital with two nodal planes. The $X\alpha$ approximation overestimates the exchange energy, and has therefore a similar effect to configuration mixing of a low-lying MO of the same symmetry,[39] i.e., correlation effects.

VI. CORRELATION EFFECTS

The preceding sections have presented a detailed comparison of energy differences calculated using exact exchange energies and the LSD approximation for exchange. We have noted that the differences which arise are often similar to the differences between experiment and LSD

calculations including correlation. We now discuss the correlation energy E_c the difference between HF energies and experiment.

In Fig. 12 we show the change in correlation energy, ΔE_c, when an sp transfer occurs in first-row atoms. Since correlation in the valence shell is particularly important, it is interesting to compare ΔE_c with the corresponding change in the valence electron exchange energy, ΔE_x^{val}. We find that the two terms have opposite signs. This is not surprising for a transition where the spatial extent of the state changes little, since correlation is usually less important if exchange is efficient. It is interesting, however, that $|\Delta E_c|$ is a substantial fraction of $|\Delta E_x^{\text{val}}|$ for all the first-row systems studied, whether or not ΔE_x arises mainly from a spin flip. For the cases where spin-flip effects are important (Be—N$^+$), the LSD approximation describes ΔE_c well, as shown in Fig. 12(a), The improvement in the LSD results over $X\alpha$ values is due to the weaker spin dependence of E_{xc} in the former case.

The large value of $|\Delta E_c|$ for O—Ne$^+$ arises from the large correlation energy for the $1s^2 2s 2p^{n-1}$ state of these systems,[40] a striking effect for which there appears to be no simple explanation. In these cases there is relatively little change in the spin densities when sp transfer takes place. The LSD and $X\alpha$ results for Δ_{sp} are then very similar, and the small difference between them cannot explain ΔE_c.

In Fig. 12(b) we show the change of the correlation energy on sd transfer. For $_{25}$Mn—$_{29}$Cu and $_{25}$Mn$^+$—$_{26}$Fe$^+$,[41] ΔE_c^{expt} is large and negative. In the final state, the spin of the added d electron is antiparallel to the majority spin direction, and correlation effects are relatively more important. This is particularly true for the ions, where the spin of the transferred $4s$ electron is parallel to the majority spin direction. For the first half of the ion series ($_{21}$Sc$^+$—$_{24}$Cr$^+$), an electron is transferred from a diffuse $4s$ orbital to a relatively compact $3d$ orbital without a spin flip. This increases the importance of correlation. For the first half of the neutral atoms ($_{21}$Sc—$_{24}$Cr), the sd transfer involves a spin fip to final states with all valence spins aligned. Figure 12(b) shows that this reduces the importance of correlation.

Correlation effects are also important in the description of molecules. In diatomic molecules the HF approximation generally leads to substantial underestimates in binding energies. In H_2, for example, the error is over 1 eV (Sec. V A) and the minimum HF energy of F_2 (Ref. 28) is 1.37 eV above the HF energy of the separated atoms.[19] The low-lying states of C_2 provide a particularly interesting case where differential correlation effects are important. In Fig. 13 we show the experimental,[29] LSD,[12] $X\alpha$ ($\alpha = 0.7$),[42] and HF results.[43] The most striking result is the error of nearly 3 eV in the HF estimate of the $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$ energy difference. The $X\alpha$ approximation also overestimates the stability of the triplet states, but is markedly closer to experiment and to the LSD result. The results of Ref. 12 confirm the earlier observation[44] that the $^3\Pi_u$ state is the LSD ground state. The excitation $^1\Sigma_g^+ \rightarrow ^3\Pi_u$ involves the transfer of a $1\pi_u^{\downarrow}$ electron to the $3\sigma_g^{\uparrow}$ orbital. The nodal structure of these orbitals and the spin flip make a prediction of the error difficult.
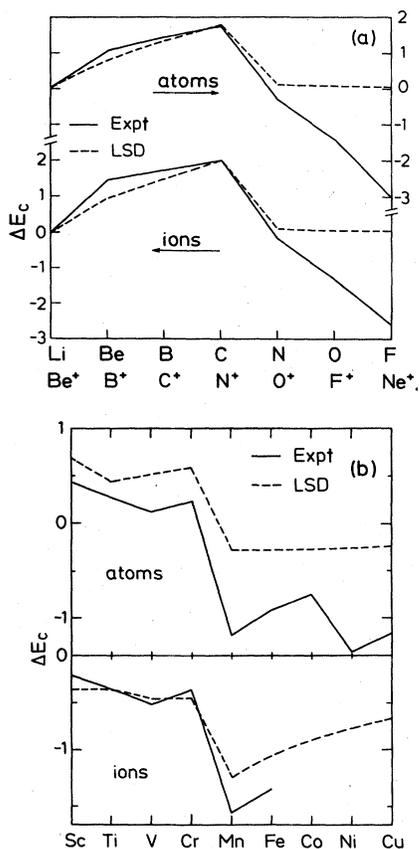
FIG. 12. Change in correlation energy, ΔE_c, for (a) sp transfer in first-row atoms and ions, and (b) sd transfer in iron-series atoms and ions.

Differential correlation effects are also apparent in the case of ozone,[13] where the HF ordering of the low-lying states is dramatically different from experiment. As noted above, $X\alpha$ calculations give the correct ground state, and LSD calculation result in a satisfactory description of the relative energies of the low-lying states.

The results in this section show that the LSD approximation often provides a poor description of correlation effects in causes where differential correlation effects are large, but the results are nevertheless closer to experiment than HF results. In general, the errors which result from a local-density description of exchange tend to be compensated when correlation is included. A quantitative comparison of ΔE_c^{expt} with Δ_c^{LSD} shows, however, that the deviations are not negligible (up to ~ 1 eV) and the cancellation between ΔE_x and ΔE_c in these causes is neither complete nor systematic.

VII. DISCUSSION

A main aim of this paper has been to identify sources of error resulting in density-functional calculations using local-density approximations for exchange and correlation. In particular, the local-density description of *exchange* can be studied by comparison with Hartree-Fock calculations, where the nodal structure of the orbitals plays an essential role. Atoms and small molecules are ideal test cases, not only because HF calculations are generally available, but because the extensive experimental literature makes direct comparison with LSD results possible. Insight into the deficiencies of the local-density approximations should aid the development of improved approximations and estimates of the errors to be expected in larger systems. For extended systems, however, the HF approximation leads to unphysical results for properties related to the energy eigenvalue spectrum, e.g., vanishing densities of states at the Fermi level, and substantial overestimates of bandwidths in metals and band gaps in semiconductors and insulators. In these cases, there are large differences between HF and local-density results.

We have focused on the description of the exchange energy in local approximations and the effect of the nodal structure of the orbitals. Our main observations are as follows. (i) For systems where the orbitals have the minimum number of nodal planes consistent with the sum rule (2.11), the $X\alpha$ approximation overestimates the interelectronic exchange energy. Examples are the core-$3d$ and $3d$-$3d$ interactions in iron-series atoms, and the σ_g-σ_u and π_g-$2\sigma_u 2\sigma_g 3\sigma_g \pi_u$ interactions in diatomic molecules. Since molecular binding energies and bulk cohesive energies are usually overestimated, we believe this observation to be more general. (ii) For excitations involving the creation of more nodal planes than required by the sum rule, the $X\alpha$ approximation often underestimates greatly the exchange energy difference, even if the changes in density and spin density are small. Examples are the sp transfer in O, F, F$^+$, and Ne$^+$, and the $^1\Sigma_g^+ \rightarrow {}^3\Pi_g$ and $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ excitations in Li$_2$. An exception is the $^1\Sigma_g^+ \rightarrow {}^3\Delta_u$ transition in Li$_2$, where the nodal structures are such that the relevant exchange integral is not reduced.

In addition to these general observations, our calculations give interesting results in specific cases. (a) For the excitation energies of first-row atoms, the $X\alpha$ values reproduce HF values well, while there is overall agreement between LSD results and experiment. This is *not* true for O, F$^+$, F, and Ne$^+$, where local-density approximations lead to large discrepancies for the sp transfer energies. (b) For iron-series atoms, the systematic overestimate of the core-$3d$ exchange interaction is consistent with the overstability of d occupancies found in LSD calculations. There are smaller errors in both the $4s$-$3d$ and $3d$-$3d$ exchange interactions. Our analysis explains the smaller LSD error in Δ_{sd} for positive ions than for the corresponding atoms. (c) We confirm earlier findings[39,45,46] that the HF and $X\alpha$ orbitals are very similar, i.e., the exchange energies calculated using the two sets of orbitals are remarkably close, within 10 mRy for first-row atoms. Sharp and Horton[47] and Talman and co-workers[46] have shown that a local potential can be found for atoms by minimizing the energy calculated using a Slater determinant constructed from its orbitals. The results are then even closer to the HF values.

In atoms we have found that the depopulation of s orbitals can lead to large errors in local-density descriptions of exchange. In sp-bonded systems, hybridization results in transfer from s orbitals, and similar effects may be expected. The situation in molecules and solids is complex, however, and more work on the effect of such "s-holes" is needed. In transition elements, both LSD and $X\alpha$ calculations overestimate consistently the core-d exchange. A change in d-band occupancy, such as in alloy formation of transition elements, should then lead to an error in formation energy.

There has been much interest recently in developing methods which go beyond the local-density approximation. One modification is to treat the exchange part of the energy exactly and to use the LSD approximation to estimate correlation energies.[48,49] For small systems, the results are sometimes better than those resulting from LSD calculations for exchange *and* correlation. Baroni[49] has found, for example, improved values for Δ_{sd} in iron-series atoms. As noted above, however, the HF method leads to unphysical results in extended systems and the local-density description of correlation alone is often inadequate if differential correlation effects are large, e.g., in C$_2$ and O$_3$. An attractive feature of the HF method is the automatic correction of the unphysical self-interaction, and it is possible to incorporate these corrections into LSD calculations.[50] In LiCl, self-interaction-corrected (SIC) calculations remove most of the large error in the LSD calculation of the band gap.[51] A further possibility is to avoid approximations based on the homogeneous electron gas by parametrizing the pair-correlation function of the system under consideration.[9] Both the SIC and the pair-correlation parametrization methods lead to significantly improved total energies, but to little improvement in excitation energies involving valence electrons.[9,20] It appears that the better total energies are a consequence of the improved treatment of the core.[20]

Recently, Harrison[21] has modified the SIC approach in a way which treats different l orbitals on a different basis.
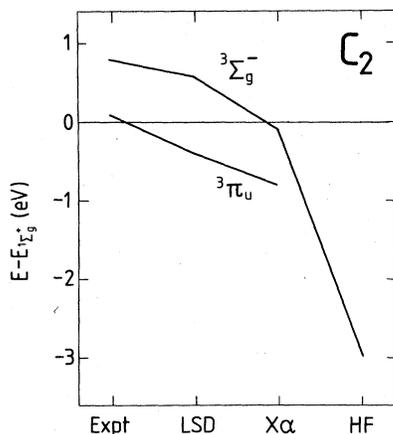
FIG. 13. Comparison of experimental, LSD, $X\alpha$, and HF energies of low-lying states of C_2, relative to the experimental ground state ($^1\Sigma_g^+$).

The correction to the LSD SIC value is given by

$$\Delta E_{\text{SIC}} = - \sum_{k=2}^{2l} \beta_{kl}^c U_k[\bar{n}_l] - \beta_l^x E_{\text{xc}}[\bar{n}_l] , \qquad (7.1)$$

where $\bar{n}_l \equiv n_l(r)/4\pi$, β_{kl}^c and β_l^x are coefficients, and U_k and E_{xc} are integrals which correct the Coulomb and exchange-correlation contributions, respectively. Harrison found that the LSD values for Δ_{sd} in iron-series atoms were improved substantially.

The errors in Δ_{sd} change relatively slowly with increasing atomic number, and a more stringent test is provided by studying Δ_{sp} and I_p in first-row atoms, where the deviations are rather irregular (Figs. 4 and 5). We have evaluated the corrections (7.1) in these cases, and the results for Δ_{sp} and I_p are shown in Figs. 14(a) and 14(b), respectively. While there is some improvement, the changes in Δ_{sp} and I_p vary smoothly with increasing atomic number, and large errors remain in Δ_{sp} for O and F.

Nonlocal modifications to the LSD approximation have led to improved total energies and occasionally to better excitation energies. The present work has shown, however, that changes in the nodal structure of the orbitals lead to exchange energy differences which are not reproduced by local-density approximations. The errors are often compensated but seldom cancelled by errors in the LSD description of the correlation energy (Fig. 12). The sp transfer in O and F, and the sd transfer in Mn provide striking examples of cases where numerically small changes in the density and spin density lead to substantial changes in the exchange energy. These and other examples discussed above indicate the difficulties in finding *simple* modifications of the LSD approximation which will provide accurate energy differences in general. How-
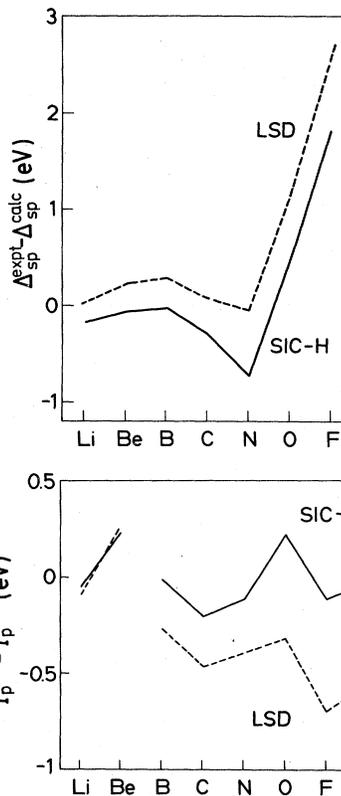

FIG. 14. Deviation from experimental values of (a) Δ_{sp} and (b) I_p for first-row atoms. Dashed curve: LSD results; solid curve: with self-interaction corrections evaluated using the method of Harrison (Ref. 21).

ever, we have identified energy differences associated with a change in wave function nodality as those most prone to error in the local-density description of exchange. High-lying orbitals with nodal planes are precisely those which are most affected by configuration mixing or by schemes which would consider the relative velocities of electrons in particular orbitals. A scheme which *systematically* improves local-density results would be highly desirable. An explicit, if rather impracticable scheme has been suggested by Freed and Levy,[52] and the problem represents a challenge for both solid-state and molecular physicists.

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