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Local-density theory of multiplet structure

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In order to obtain multiplet energies and therefore energies of excited states of atoms and molecules, the local-density theory of Hohenberg, Kohn, and Sham has recently been extended to give the lowest energy of a specified angular momentum and spin symmetry. It is explained why this method does not work if the exchange correlation functional is taken to be symmetry independent. Instead it is shown how the local-density theory can be used to estimate the energies of states of mixed symmetry and how the multiplet splittings are obtained from these estimates. The new method is tested on light atoms and the local-density theory with exchange only reproduces the Hartree-Fock results within 0.1 eV. With correlation included, the error in the local-density approach is typically a factor of 3 less than in the Hartree-Fock approach.

I. INTRODUCTION

The traditional approach for calculating multiplet energies of atoms and molecules is the Hartree-Fock method[1] and for better accuracy one has turned to multiconfiguration Hartree-Fock calculations[2] or effective-operator techniques.[3] Due to the large computational effort involved, all these methods are, however, limited to systems with a small number of electrons. In recent years, there has been a growing interest in large molecules[4] and atoms and molecules[4] adsorbed on surfaces.[5] For these systems the methods mentioned are quite unmanageable and different local-density schemes have been used, i.e., the Hohenberg-Kohn-Sham scheme[6] and the $X\alpha$ method.[7] The original Hohenberg-Kohn-Sham scheme could only give the ground-state energy but was recently generalized by Gunnarsson and Lundqvist[8] so as to give the energy of the lowest state of a specified angular momentum and spin symmetry. In principle, the exchange-correlation functional $E_{xc}[\rho]$ appearing in this theory should depend on the symmetry of the state under consideration, e.g., it should depend on the usual angular momentum (L) and spin (S) quantum numbers in the case of light atoms. No prescription of how to incorporate this symmetry dependence was, however, offered by Gunnarsson and Lundqvist, and in actual calculations[5] the usual local-density approximation based on electron-gas data is used for E_{xc}. Thus, the symmetry dependence of the energy of a state only enters via the prescription for constructing the charge and spin densities for that state. The inadequacy of this procedure is evident for the p^2 configuration of the carbon atom, for example. The p^2 configuration gives rise to the three terms ^3P, ^1D, and ^1S. The states belonging to ^1D and ^1S are singlets and therefore have no spin density. Furthermore the ^1S state has a spherical charge density and it is possible to form a linear combination of the five states of the ^1D that, according to the procedure by Gunnarsson *et al.*, also has a spherical charge density. Since the ^1D states are all degenerate in the absence of spin-orbit interaction, the above procedure would predict the same energy for the ^1S and ^1D states, which clearly does not make sense. In Sec. II this point is illustrated by numerical results and the excited $1s2s$ configuration of helium is also discussed. A different approach was taken by Ziegler *et al.*[9] within the $X\alpha$ method. Since this method is designed as an approximation to the Hartree-Fock method, they claimed it should be used to evaluate the energies of single-determinantal wave functions. Again invoking Hartree-Fock theory, the multiplet splittings were obtained from these energies and the splittings were in reasonable agreement with experiment. In Sec. III we explain the reason for the success of this method as well as the failure of the method mentioned previously. In Sec. IV we develop a rigorous theory of multiplet splittings within the framework of Hohenberg-Kohn-Sham theory and in Sec. V the method is applied to a number of light atoms (He, C, N, and Si). Section VI contains conclusions.

II. LOCAL-DENSITY ENERGIES OF STATES OF PURE SYMMETRY

In this section we will apply the prescription of Gunnarsson *et al.*[8] to calculate the energies of the ^3P, ^1D, and ^1S states of carbon and the ^1S and ^3S states of the excited configuration $1s2s$ of helium.

The problem of finding the energy of the lowest state, of a specified symmetry, of the interacting many-body system is reduced to the corresponding problem for a noninteracting system, but in an effective potential that incorporates the effects of exchange and correlation. As a consequence, the density matrix of the interacting system is constructed from the same linear combination of Slater determinants that constitutes the solution to the effective noninteracting problem. This is the only way in which the symmetry dependence enters, since the exchange-correlation potential is symmetry independent.

In the present paper, light atoms will be our test cases, although we certainly believe our conclusions to be valid both for heavier atoms as well as for small and large molecules. We will therefore neglect spin-orbit interaction and take the set H, $\vec{L}^2$, $\vec{S}^2$, L_z, S_z in obvious notation, as a complete set of operators for atoms. For not too heavy atoms spin-orbit interaction can easily be included in the way described by Gunnarsson *et al.*[8] We will only consider the lowest energy state of each symmetry and we will label them by $|L, S; M_L, M_S\rangle$. In order to construct the density matrix we need the linear combination of Slater determinants that corresponds in the noninteracting case to the state $|L,S;M_L,M_S\rangle$. It is given in Ref. 1. In Table I we list the states with non-negative M_L and M_S, together with the spin-up and spin-down densities to which they give rise (the density matrix turns out to be diagonal in all cases). $D(m\sigma, m'\sigma')$ is of course the Slater determinant constructed from the one-particle orbitals $R_{2p}(r)Y_1^m(\hat{r})X_\sigma(\xi)$ and $R_{2p}(r)Y_1^{m'}(\hat{r})X_{\sigma'}(\xi)$, and $n(r)$ is just $R_{2p}^2(r)/(4\pi)$.

Now to get the local-density estimate of one of the states in Table I we should really minimize the energy expression[10]

$$E[\rho_{\alpha\beta}] = T_0[\rho_{\alpha\beta}] + W[\rho_{\alpha\beta}] + U[\rho_{\alpha\beta}] + E_{\text{xc}}[\rho_{\alpha\beta}], \tag{1}$$

with $\rho_{\alpha\beta}(\vec{r})$ constrained to be of the form given in Table I. T_0, W, U, and E_{xc} are defined according to

$T_0[\rho_{\alpha\beta}]$ = kinetic energy of noninteracting system with density matrix $\rho_{\alpha\beta}(\vec{r})$,

$$W[\rho_{\alpha\beta}] = -Z\int \rho(\vec{r})\cdot v(\vec{r})\, d^3r\,, \tag{2}$$

$$U[\rho_{\alpha\beta}] = \frac{1}{2}\int \rho(\vec{r})\cdot v(\vec{r}-\vec{r}\,')\cdot\rho(\vec{r}\,')\, d^3r\, d^3r'\,, \tag{3}$$

$$E_{\text{xc}}[\rho_{\alpha\rho}] = \int \rho(\vec{r})\cdot\epsilon_{\text{xc}}(\rho_\uparrow(\vec{r}), \rho_\downarrow(\vec{r}))\, d^3r\,, \tag{4}$$

where Z is the atomic number, $v(\vec{r}) = 1/r$ is the Coulomb interaction, $\rho(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r})$ is the total charge density, $\rho_\uparrow(\vec{r})$ and $\rho_\downarrow(\vec{r})$ are the eigenvalues of the density matrix $\rho_{\alpha\beta}(\vec{r})$, and $\epsilon_{\text{xc}}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy of a spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$. This would, however, mean solving a complicated nonspherical self-consistency problem which we are not prepared to do. Instead we will always (if not otherwise stated) take the radial functions from the self-consistent spherical paramagnetic calculation and just evaluate the energy expression (1) for the corresponding density matrix which is not self-consistent but which has the appropriate symmetry. To estimate the error of this procedure we first note that the energy involved in flipping the spin of one electron is much larger than, for example, promoting one of the p electrons from a $m_l = 0$ orbital to a $m_l = 1$ orbital. We will therefore get an upper bound to the error from the difference between the energy of a spherical self-consistent calculation for the configuration $1s\uparrow$, $1s\downarrow$, $2s\uparrow$, $2s\downarrow$, $2p\uparrow^2$ and the energy obtained by evaluating the same energy expression, but with orbitals taken from a spherical self-consistent calculation for the configuration $1s^2$, $2s^2$, $2p^2$. In the case of carbon this amounts to 0.04 eV and is

TABLE I. States of different symmetry, their noninteracting counterparts in terms of Slater determinants, and the corresponding spin-up and spin-down densities for the $2p$ shell of the p^2 configuration. $n(r)$ is the spherical average of the charge density of one $2p$ electron assumed to be the same for both $2p$ electrons. Thus $\int n(r)\, d^3r = 1$. $P_2(t)$ is the second-order Legendre polynomial.

$\lvert LM;M_LM_S\rangle$	Noninteracting counterpart	$\rho_{2p}^{\uparrow}(\vec{r})$	$\rho_{2p}^{\downarrow}(\vec{r})$
$\lvert 11;11\rangle$	$D(1\uparrow,0\uparrow)$	$n(r)\ [2+P_2(\cos\theta)]$	0
$\lvert 11;01\rangle$	$D(1\uparrow,-1\uparrow)$	$n(r)\ [2-2P_2(\cos\theta)]$	0
$\lvert 11;10\rangle$	$1/\sqrt{2}\,[D(1\uparrow,0\downarrow)-D(0\uparrow,1\downarrow)]$	$n(r)\ [1+\frac{1}{2}P_2(\cos\theta)]$	$n(r)\ [1+\frac{1}{2}P_2(\cos\theta)]$
$\lvert 11;00\rangle$	$1/\sqrt{2}\,[D(1\uparrow,-1\downarrow)-D(-1\uparrow,1\downarrow)]$	$n(r)\ [1-P_2(\cos\theta)]$	$n(r)\ [1-P_2(\cos\theta)]$
$\lvert 20;20\rangle$	$D(1\uparrow,1\downarrow)$	$n(r)\ [1-P_2(\cos\theta)]$	$n(r)\ [1-P_2(\cos\theta)]$
$\lvert 20;10\rangle$	$1/\sqrt{2}\,[D(1\uparrow,0\downarrow)+D(0\uparrow,1\downarrow)]$	$n(r)\ [1+\frac{1}{2}P_2(\cos\theta)]$	$n(r)\ [1+\frac{1}{2}P_2(\cos\theta)]$
$\lvert 20;00\rangle$	$1/\sqrt{6}\,[D(1\uparrow,-1\downarrow)+D(-1\uparrow,1\downarrow)+2D(0\uparrow,0\downarrow)]$	$n(r)\ [1+P_2(\cos\theta)]$	$n(r)\ [1+P_2(\cos\theta)]$
$\lvert 00;00\rangle$	$1/\sqrt{3}\,[D(1\uparrow,-1\downarrow)+D(-1\uparrow,1\downarrow)-D(0\uparrow,0\downarrow)]$	$n(r)$	$n(r)$

TABLE II. Change (eV) in different terms of Eq. (1) for states of different symmetry, in the p^2 configuration of the carbon atom relative to the result of a self-consistent spherical paramagnetic calculation.

$\vert LS;M_LM_S\rangle$	ΔU	ΔE_{xc}	ΔE
$\vert 11;11\rangle$	0.13	−1.37	−1.24
$\vert 11;01\rangle$	0.50	−1.75	−1.25
$\vert 11;10\rangle$	0.13	−0.08	0.05
$\vert 11;00\rangle$	0.50	−0.34	0.16
$\vert 20;20\rangle$	0.50	−0.34	0.16
$\vert 20;10\rangle$	0.13	−0.08	0.05
$\vert 20;00\rangle$	0.50	−0.32	0.18
$\vert 00;00\rangle$	0.00	0.00	0.00

negligible compared to the accuracy by which the multiplet splittings can be obtained.

A Gaussian method is used for the angular part of the integrals in Eqs. (1)–(4) and in Table II we give, for each symmetry, the change in the different terms in Eq. (1) relative to their values in the self-consistent spherical paramagnetic calculation. Note that T_0 and W do not depend on symmetry. We only list states with non-negative numbers for M_L and M_S, since the local-density estimates are invariant under a change of sign of M_L and M_S.

Since E_{xc} is taken to be symmetry independent, the only symmetry dependence comes from the construction of the spin densities. It is then immediately clear from Table I that the local-density energies of the states $|11;00\rangle$ and $|20;20\rangle$ will be equal. The same is true for the states $|11;10\rangle$ and $|20;10\rangle$ giving no splitting between the ^3P and ^1D states. Furthermore, the predicted splitting between the ^1D and ^1S states is negligible compared to the experimental splitting which amounts to 1.42 eV.[11] There is also a small unphysical spread in the energies of the ^1D states.[12] This latter effect is not a serious shortcoming and will remain, although reduced in magnitude, in the improved theory that we are about to introduce. More serious is, however, the large splittings (~1.3 eV) predicted between some of the degenerate ^3P states. If, however, we follow the suggestion by Ziegler *et al.*[9] and trust only local-density energies of states, which in the noninteracting case are represented by single Slater determinants, we would say that the splitting between the ^3P and the ^1D states is (0.16 + 1.24) eV = 1.40 eV which is close to the experimental number 1.26 eV.[11] Still there is a small difference between the local-density energies of the two ^3P states $|11;11\rangle$ and $|11;01\rangle$. Since their Coulomb energies (U) are quite different, this difference should be cancelled by a corresponding difference in the exchange-correlation energies E_{xc}. As seen from Table II the cancellation is remarkably accurate (within 0.01 eV) considering the crude local approximation for E_{xc}. The cancellation is certainly much better between these two single-determinantal states than, for example, between the states $|20;10\rangle$ and $|20;00\rangle$.

We have also applied the procedure by Gunnarsson *et al.*[8] to the excited $1s2s$ configuration of helium with the result shown in Table III. Comparing with the experimental energies, also given in Table III, of the triplet and the singlet relative to the ground state of helium, the failure of the method is again obvious. The bad local-density result for the singlet can be improved through arguments similar to those used by Gunnarsson *et al.*[8] for the H_2 molecule. The $1s$ and $2s$ orbitals are sufficiently separated in space for the system to be considered as two weakly interacting ferromagnetic systems with opposite magnetizations. Thus a spin-polarized calculation with one electron in the $1s\uparrow$ and the other electron in the $2s\downarrow$ orbital might be more appropriate since it would give a better cancellation of the self-terms[8] of the individual orbits. Such a self-consistent solution really exists and its energy is 19.56 eV above the local-density ground state of helium. If the energy of the self-consistent solution with both electrons in spin-up orbitals given in Table III is taken as representing the energy of the triplet, we would get a singlet-triplet splitting of 0.5 eV, which is much closer to the experimental result 0.8 eV than the number 1.8 eV suggested by Table III. We point out, however, that the outlined procedure

TABLE III. States of different symmetries, their noninteracting counterparts in terms of Slater determinants, the corresponding spin-up and spin-down densities, and their local-density energies (ΔE in eV), according to Ref. 8 relative to the local-density ground-state for the $1s2s$ excited configuration of helium. ΔE(exp) is the experimental energy in eV from Ref. 11.

$\vert S,M_S\rangle$	Noninteracting counterpart	$\rho^{\uparrow}(\vec{r})$	$\rho^{\downarrow}(\vec{r})$	ΔE	ΔE(exp)
$\vert 1,1\rangle$	$D(\uparrow,\uparrow)$	$\rho(r)$	0	19.08	19.82
$\vert 1,0\rangle$	$1/\sqrt{2}\,[D(\uparrow,\downarrow)+D(\downarrow,\uparrow)]$	$\frac{1}{2}\rho(r)$	$\frac{1}{2}\rho(r)$	21.90	19.82
$\vert 0,0\rangle$	$1/\sqrt{2}\,[D(\uparrow,\downarrow)-D(\downarrow,\uparrow)]$	$\frac{1}{2}\rho(r)$	$\frac{1}{2}\rho(r)$	21.90	20.62

to improve on the local-density results is in conflict with the "clear" rule given by Gunnarsson *et al.*[8], since the spin-polarized state has a net spin density which is incompatible with a singlet state. In Sec. IV we will describe a less *ad hoc* way of getting realistic multiplet splittings from local-density theory.

III. ROLE OF THE PAIR-CORRELATION FUNCTION

In this section we will give an explanation for why the prescription of Gunnarsson *et al.*[8] seems to work in some cases but not in others. The discussion will be based on a comparison between the exchange-correlation part of the electron-electron interaction energy, $E^{\mathrm{xc}}_{\mathrm{int}}$, which is given by

$$E^{\mathrm{xc}}_{\mathrm{int}}[\rho]=\frac{1}{2}\sum_{\sigma\sigma'}\int\int\rho_\sigma(\vec{r})\rho_{\sigma'}(\vec{r}')[g_{\sigma\sigma'}(\vec{r},\vec{r}')-1]\times v(\vec{r}-\vec{r}')\,d^3r\,d^3r' , \qquad (5)$$

and the local-density approximation to the same quantity. In Eq. (5) g is the pair-correlation function and $\rho_\sigma(\vec{r})$ is a diagonal element of the density matrix but, since the latter is always diagonal for an atom without spin-orbit coupling,[14] ρ_σ is either the spin-up or the spin-down density depending on whether σ is $\uparrow$ or $\downarrow$. Now clearly from Table IV the dominant contributions to the multiplet splittings come from exchange. Correlation only gives a 25% reduction of the splittings. We will therefore, concentrate the discussion on the exchange energy and mention correlation later on. The exchange part, E^{X}_{int}, of the interaction energy is obtained from Eq. (5) by replacing the pair-correlation function g by its Hartree-Fock counterpart g^{HF}. Thus we can write

$$E^{X}_{\mathrm{int}}[\rho]=\sum_{\sigma\sigma'}E^{X}_{\sigma\sigma'} , \qquad (6)$$

where

$$E^{X}_{\sigma\sigma'}=\frac{1}{2}\int\rho_\sigma(\vec{r})\rho_{\sigma'}(\vec{r}')[g^{\mathrm{HF}}_{\sigma\sigma'}(\vec{r},\vec{r}')-1]\times v(\vec{r}-\vec{r}')\,d^3r\,d^3r' . \qquad (7)$$

The usual local-density approximation is obtained by replacing $\rho_{\sigma'}(\vec{r}')$ by $\rho_{\sigma'}(\vec{r})$, and $g_{\sigma\sigma'}(\vec{r},\vec{r}')$ by the homogeneous electron-gas pair-correlation function $g^{h}_{\sigma\sigma'}[\vec{r}-\vec{r}';\rho_\uparrow(\vec{r}),\rho_\downarrow(\vec{r})]$ in Eq. (5). The local-density approximation to exchange only, E^{LDX}, is obtained by a similar replacement in Eq. (7) and we have (h = homogeneous)

$$E^{\mathrm{LD}X}_{\sigma\sigma'}=\frac{1}{2}\int\rho_\sigma(\vec{r})\rho_{\sigma'}(\vec{r})[g^{h\mathrm{HF}}_{\sigma\sigma'}(\vec{r}-\vec{r}')-1]\times v(\vec{r}-\vec{r}')\,d^3r\,d^3r' . \qquad (8)$$

But $g^{h\mathrm{HF}}_{\uparrow\downarrow}=g^{h\mathrm{HF}}_{\downarrow\uparrow}=1$, because without correlation there is nothing to keep electrons of different spins apart. Thus

$$E^{\mathrm{LD}X}_{\uparrow\downarrow}=E^{\mathrm{LD}X}_{\downarrow\uparrow}=0 , \qquad (9)$$

which is really the root of the difficulties in the scheme proposed by Gunnarsson *et al.*[8] Consider, for examples, the ^3P state $|11;00\rangle$ for carbon which, according to Table II has an energy that is 1.4 eV too high compared to those ^3P states that supposedly give good multiplet splittings. It is easy to work out the pair-correlation function in the Hartree-Fock approximation to this essentially two-electron state. We can disregard the full 1s and 2s shells since they do not contribute to the multiplet splittings. We then get for the 2p shell

$$\rho_\sigma(\vec{r})\rho_{\sigma'}(\vec{r}')g^{\mathrm{HF}}_{\sigma\sigma'}(\vec{r},\vec{r}')=\tfrac{1}{2}(1-\delta_{\sigma\sigma'})\left|\varphi_1(\vec{r})\varphi_{-1}(\vec{r}')-\varphi_{-1}(\vec{r})\varphi_1(\vec{r}')\right|^2 , \qquad (10)$$

where $\varphi_m(\vec{r})=R_{2p}(r)Y^m_1(\hat{r})$. It is clear from Eq. (10) that $g^{\mathrm{HF}}_{\uparrow\downarrow}$ is not equal to 1 as it would be in the local-density approximation. From Eq. (10) we can also compute the different exchange energies

$$E^{X}_{\uparrow\uparrow}=E^{X}_{\downarrow\downarrow}=-\tfrac{1}{4}U_{2p} , \qquad (11)$$

$$E^{X}_{\uparrow\downarrow}=E^{X}_{\downarrow\uparrow}=-\tfrac{3}{25}F_2(2p,2p) . \qquad (12)$$

TABLE IV. Multiplet splittings in eV for the carbon, silicon, and nitrogen atoms. The configuration is indicated. TDHF is term-dependent Hartree-Fock. HF is Hartree-Fock. LDX is local-density approximation with exchange only. LD is local-density approximation, present theory. exp is spectral data Ref. 11. LDC is local-density correlation, LDX-LD. C is correlation contribution, HF-exp.

		TDHF	HF	LDX	LD	exp	LDC	C
C p^2	$E(^1D)-E(^3P)$	1.56	1.56	1.59	1.33	1.26	0.26	0.30
	$E(^1S)-E(^3P)$	3.78	3.90	3.97	3.30	2.68	0.67	1.22
Si p^2	$E(^1D)-E(^3P)$	1.07	1.07	1.09	0.85	0.76	0.24	0.30
	$E(^1S)-D(^3P)$	2.59	2.67	2.71	2.11	1.89	0.60	0.78
N p^3	$E(^2D)-E(^4S)$	···	2.81	2.90	2.46	2.38	0.44	0.42
	$E(^2P)-E(^4S)$	···	4.68	4.83	4.09	3.58	0.74	1.10

Here F_2 is a Slater integral[1] and U_{2p} is the contribution to U [Eq. (3)] from within the $2p$ shell. Thus $E^X_{\uparrow\uparrow}+E^X_{\downarrow\downarrow}$ cancels half the direct Coulomb contribution (the self-term) from the two $2p$ electrons as expected from Hartree-Fock [$g^{\mathrm{HF}}_{\uparrow\uparrow}=0$, Eq. (10)]. We would also expect the local-density approximation to give an accurate cancellation of the self-term.[8] Note that there is an $F_0(2p,2p)$ contribution to U_{2p} which should be cancelled by an exchange contribution, and that the local-density approximation fails to achieve this cancellation by several electron volts.[15] This error is, however, the same for all terms and does not affect the multiplet splittings. These are only affected by a lack of cancellation of those self-contributions to U_{2p}, which are proportional to $F_2(2p,2p)$. In the case we are considering this latter error amounts to 0.07 eV.[16] On the other hand $E^X_{\uparrow\downarrow}+E^X_{\downarrow\uparrow}$ is -1.56 eV, whereas the local-density approximation to this quantity is zero [Eq. (9)]. Thus, in this case the theory is off by an amount equal to the whole Hartree-Fock $^3P-{}^1D$ splitting (1.56 eV from Table IV). One could of course hope that errors in $E^X_{\uparrow\downarrow}$ and $E^X_{\downarrow\uparrow}$ would be compensated by errors in $E^X_{\uparrow\uparrow}$ and $E^X_{\downarrow\downarrow}$. We have shown above that this is not the case for the state $|11;00\rangle$; and there is a general argument against such expectations. According to Gunnarsson and Lundqvist[8] the accuracy of the local-density approximation for total energies can be traced to the sum rules

$$\begin{aligned} n_\uparrow\int[g^h_{\uparrow\uparrow}(\vec{\mathrm{r}})-1]\,d^3r&=n_\downarrow\int[g^h_{\downarrow\downarrow}(\vec{\mathrm{r}})-1]\,d^3r=-1\,, \\ n_\downarrow\int[g^h_{\uparrow\downarrow}(\vec{\mathrm{r}})-1]\,d^3r&=n_\uparrow\int[g^h_{\downarrow\uparrow}(\vec{\mathrm{r}})-1]\,d^3r=0\,. \end{aligned} \tag{13}$$

Consequently, since $E^{\mathrm{XC}}_{\uparrow\uparrow}$ and $E^{\mathrm{XC}}_{\uparrow\downarrow}$ involve exchange-correlation holes that obey different sum rules, we can not expect a large cancellation of errors between them. With correlation included we would of course get a nonzero contribution to $E^{\mathrm{LD}}_{\uparrow\downarrow}$ that would approximate the difference between the exact $E_{\uparrow\downarrow}$ and the Hartree-Fock quantity $E^X_{\uparrow\downarrow}$. Since correlation energies for atoms are a factor of 2 too large[17] in the local-density approximation, one could hope for a misrepresentation of the correlation effect that would partly compensate for the error in the exchange energy. The point is that the correlation energies are much smaller than exchange energies and errors in the former could thus never compensate for the complete loss of a large exchange energy. Furthermore, in Sec. V we will show that the error in the local-density approximation to the correlation contribution to the multiplet splittings is only of the order of 25%. The reduction of the correlation error is due to the fact that the density of the electrons contributing to multiplet structure is much more slowly varying than the density of the deep core electrons which are the main contributors to the total energy.

We end this section with the important observation that any single-determinantal many-body state will have $g_{\uparrow\downarrow}(\vec{\mathrm{r}},\vec{\mathrm{r}}')=g_{\downarrow\uparrow}(\vec{\mathrm{r}},\vec{\mathrm{r}}')=1$. Therefore, any state that, in the noninteracting case, reduces to a single Slater determinant will have $E^X_{\uparrow\downarrow}=E^X_{\downarrow\uparrow}=0$ and consequently this part of its exchange energy is, by virtue of Eq. (9), given exactly by the local-density theory. This is the reason for the nice agreement between the experimental ^3P-^1D splitting (1.26 eV[11]) and the difference (1.41 eV, Table II) between the local-density energies of the states $|20;20\rangle$ and $|11;01\rangle$. A further consequence is the striking agreement between the energies of the states $|11;11\rangle$ and $|11;01\rangle$ in Table II.

IV. DENSITY-FUNCTIONAL THEORY OF MIXED-SYMMETRY STATES

We have seen in Sec. III that, if we insist on using the symmetry-independent approximation to E_{xc} given by Eq. (4), the density-functional theory for states of pure symmetry, as given by Gunnarsson and Lundqvist,[8] only works when the states in the noninteracting case reduce to single Slater determinants. For instance, in the case of the p^2 configuration we can get the energies of the ^3P and ^1D states but not the energy of the ^1S state. One way to proceed would be to try to find an improved approximation to E_{xc} that would reflect its symmetry dependence. In the present paper we will, however, stick to the commonly used approximation for E_{xc} [Eq. (4)], and instead try to construct a Hohenberg-Kohn theory for states of mixed symmetry. We will choose mixtures such that their noninteracting counterparts are single determinants. In the case of the p^2 configuration, for instance, the state $\sqrt{2}/\sqrt{3}\,|20;00\rangle-1/\sqrt{3}\,|00;00\rangle$ reduces to $D(0\uparrow,0\downarrow)$ (Table I). Since a mixed-symmetry state is not an eigenstate of the Hamiltonian, its charge density will oscillate in time, but we will prove that the lowest state of a well-defined mixture of symmetries, i.e., the state with the smallest energy expectation value, is a functional of the density at the time of preparation of the state. For simplicity we will do the proof for the nonmagnetic case, the extension to spin-polarized systems being obvious.[10] Our Hilbert space is spanned by the simultaneous eigenvectors $|S,n\rangle$ of the Hamiltonian $H=H_0+W$ and the symmetry operator $\hat{S}$. W is the external potential which also commutes with $\hat{S}$, $[W,\hat{S}]=0$. Our proof relies critically on the nondegeneracy of the lowest state

$|S,0\rangle$ of each symmetry S. This assumption is invalid for most atoms and molecules and the proof of the Hohenberg-Kohn theorem[6] suffers from the same deficiency. We will ignore this by referring to the usual argument, that any degeneracy can be lifted by a small external field without affecting the quantitative predictions of the theory. The mixed symmetry states will be assumed to have the form

$$|\Psi\rangle = \alpha_1|S_1,0\rangle + \alpha_2|S_2,0\rangle\,, \tag{14}$$

with different symmetries S_1 and S_2 and fixed coefficients α_1 and α_2 obeying $\alpha_1^2+\alpha_2^2=1$. In order to obtain a contradiction we assume that there exists a different state

$$|\Psi\rangle' = \alpha_1|S_1,0\rangle' + \alpha_2|S_2,0\rangle' \tag{15}$$

that has the same density as $|\Psi\rangle$. The state $|S,n\rangle'$ is obtained from the Hamiltonian $H'=H_0+W'$ with a different external potential W' which again commutes with $\hat{S}$. From the variational principle and the assumed nondegeneracy of the states $|S,0\rangle$ we get

$$\begin{aligned}\langle\Psi|H|\Psi\rangle &= \alpha_1^2\langle S_1,0|H|S_1,0\rangle + \alpha_2^2\langle S_2,0|H|S_2,0\rangle\\ &< \alpha_1^2\,{}'\langle S_1,0|H|S_1,0\rangle' + \alpha_2^2\,{}'\langle S_2,0|H|S_2,0\rangle'\\ &= \langle\Psi'|H|\Psi'\rangle\\ &= \langle\Psi'|H'|\Psi'\rangle + \langle\Psi'|W-W'|\Psi'\rangle\\ &= \langle\Psi'|H'|\Psi'\rangle + \int [w(\vec{r})-w'(\vec{r})]n'(\vec{r})d^3r\,.\end{aligned} \tag{16}$$

We note that no cross terms will appear in the above derivation because H_0, W, and W' all commute with $\hat{S}$ and because $S_1\neq S_2$. Interchanging primed and unprimed quantities in the usual way[6,10] leads to

$$\langle\Psi'|H'|\Psi'\rangle < \langle\Psi|H|\Psi\rangle + \int [w'(\vec{r})-w(\vec{r})]n(\vec{r})\,d^3r\,. \tag{17}$$

Adding Eqs. (16) and (17) gives the desired contradiction when $n(\vec{r})=n'(\vec{r})$. Thus the state $|\Psi\rangle$ is a functional of its density $n(\vec{r})$ and so is the energy E given by

$$E[n(\vec{r})] = \alpha_1^2E_0(S_1) + \alpha_2^2E_0(S_2)\,, \tag{18}$$

where $E_n(S)$ is the energy of the state $|S,n\rangle$. Furthermore, the functional $E[n]$ is easily shown to have a minimum at the true density $n(\vec{r})$. It will of course depend on the symmetries S_1 and S_2 and on the coefficients α_1 and α_2. Only for a particular choice of α_1 and α_2 is the functional $E[n]$ reasonably well approximated by the expressions (1)–(4). As mentioned previously, we ought to choose α_1 and α_2 so that $|\Psi\rangle$ reduces to a single determinant in the noninteracting case.

If a state $|\Psi\rangle$ is prepared according to Eq. (14) at some time $t=0$, it will evolve to the state $|\Psi_t\rangle$ at some later time t, and

$$|\Psi_t\rangle = \alpha_1 e^{-iE_0(S_1)t}|S_1,0\rangle + \alpha_2 e^{-iE_0(S_2)t}|S_2,0\rangle\,. \tag{19}$$

The corresponding density $n_t(\vec{r})$ will in general be different from the density $n_{t=0}(\vec{r})$, because $\langle S_1,0|\hat{\rho}(\vec{r})|S_2,0\rangle\neq 0$ [$\hat{\rho}(\vec{r})$ is the density operator]. By using the same technique as above we could just as well have proven that the state $|\Psi\rangle$ is a functional of the density $n_t(\vec{r})$. This follows from the time independence of quantities like $\langle\Psi_t|H|\Psi_t\rangle$, $\langle\Psi_t'|H'|\Psi_t'\rangle$, or $\langle\Psi_t'|H|\Psi_t'\rangle$, which in turn follows from the fact that H_0, W, and W' all commute with $\hat{S}$. For example,

$$0=\langle S_1|W|S_2\rangle = \int w(\vec{r})\langle S_1|\hat{\rho}(\vec{r})|S_2\rangle\,d^3r\,.$$

This new functional $E_t[n]$ will in general be different from $E[n]$ since E_t will be minimized by n_t. Using the approximations (1)–(4) for both $E[n]$ and $E_t[n_t]$ would, however, give $n(\vec{r})=n_t(\vec{r})$, which is clearly wrong. The question then arises as to which of E and E_t is best approximated by Eqs. (1)–(4). The answer is $E[n]$ because α_1 and α_2 were chosen so that $|\Psi\rangle$ reduces to a single determinant in the noninteracting case. This is in general not true for $|\Psi_t\rangle$. We have thus shown that no ambiguity arises from the time dependence of the charge density of the mixed-symmetry states.

V. APPLICATION TO ATOMS AND DISCUSSION

In this section we will apply the method developed in Sec. IV to the p^2 configurations of the carbon and silicon atoms to the p^3 configuration of the nitrogen atom and to the excited $1s2s$ configuration of the helium atom. In order to make our proposed method fully clear and easy to use we will go through the carbon case in great detail but just quote results for the other cases.

The p^2 configuration gives rise to 15 different states $|LS,M_LM_S\rangle$ and from these we can form 15 linear combinations, i.e., mixed-symmetry states $|D_i\rangle$, $i=1,2,\ldots,15$, that in the noninteracting case reduce to single determinants D_i. Note the distinction between states $|D_i\rangle$ and determinants D_i. The states $|D_i\rangle$ will all have energies of the form

$$E(D_i) = a_iE(^3P) + b_iE(^1D) + c_iE(^1S) \tag{20}$$

in obvious notation (see Sec. I). The coefficients a_i, b_i, and c_i can easily be obtained from Table I. We will estimate $E(D_i)$ by minimizing the functional (1) with the local-density approximation (4) to $E_{\rm xc}$. From the trick used by Kohn and Sham[6,10] we know that the density matrix for the state $|D_i\rangle$ is built from the resulting one-particle orbitals in the same way as the density matrix for the determinant D_i. For each D_i the minimization requires a self-consistent calculation but, as mentioned in Sec. II, we will only do a self-consistent calculation for the spherical paramagnetic case and use the radial parts of the resulting orbitals in the spin densities corresponding to the different states $|D_i\rangle$. The functional defined by the Eqs. (1)–(4) is then evaluated for each of these spin densities. As discussed in Sec. II this procedure should be perfectly adequate. Note that, due to the variational principle, errors in the energies are second order in the spin-density errors. In the case of helium, however, we are dealing with a spherical problem and the quoted results are therefore fully self-consistent. Quantities given relative to their corresponding values in the spherical self-consistent calculation will be preceded by the symbol Δ. For instance,

$$\begin{aligned}\Delta\rho_\uparrow(\vec{r}) &= n(r)[a + b_\uparrow P_2(\cos\theta)]\,,\\ \Delta\rho_\downarrow(\vec{r}) &= n(r)[-a + b_\downarrow P_2(\cos\theta)]\,,\end{aligned} \tag{21}$$

where $n(r)$ is the spherical average of one of the two $2p$ electrons, assumed to be the same for both electrons. $P_2(t)$ is the second-order Legendre polynomial. In Table V we give for each state $|D_i\rangle$ the local-density estimate of the Coulomb energy ΔU, the exchange-correlation energy ΔE_{xc} and the total energy ΔE relative to the corresponding energies in the spherical paramagnetic calculation. The parameters a, $b_\uparrow$, and $b_\downarrow$ that, according to Eq. (21), determine the spin densities are also given in Table V as well as the coefficients a_i, b_i, and c_i that, according to Eq. (20), give the energy of the state $|D_i\rangle$ in terms of the multiplet energies $E(^3P)$, $E(^1D)$, and $E(^1S)$. For comparison with Hartree-Fock theory, Table V shows the coefficient f_i in front of $\frac{1}{25}F_2(2p,2p)$ in the energy of the determininat D_i. There are only six states listed in Table V. However, for reasons of symmetry between $m_l = +1$ and $m_l = -1$, and $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ the remaining nine states have energies and spin densities identical to those already listed.

From Table V we have local-density estimates of six linear combinations of the three term values $E(^3P)$, $E(^1D)$, and $E(^1S)$, i.e., six linear equations in only three unknowns. Consistency then requires the existence of linear relations between the local-density estimates, e.g., $-0.50 = \frac{1}{2}(-1.24 + 0.16)$, which are only approximately satisfied. This minor deficiency of our theory reflects the fact that the local-density approximation [Eq. (4)] does not work equally well for all the states $|D_i\rangle$. To avoid a discussion as to which state $|D_i\rangle$ the approximation (4) is best suited[18], we solve our six linear equations by a min-max procedure. Note that a least-square procedure would not be appropriate because errors in percentage of ΔE's are irrelevant quantities. If E_0 is the total energy of the spherical paramagnetic calculation ($E_0 = -37.4403$ Hartree for carbon) we get

$$\begin{aligned}&E(^3P) = E_0 - 1.20, \quad E(^1D) = E_0 + 0.12,\\ &E(^1S) = E_0 + 2.10\,,\end{aligned} \tag{22}$$

from which the multiplet splittings in Table IV are deduced. The maximum error in this min-max fit is as small as 0.04 eV, thus demonstrating the internal consistency of our method. The origin of this consistency is revealed by perturbation theory. It is readily shown that, to second order in a, $b_\uparrow$, and $b_\downarrow$, ΔE is given by

$$\Delta E = \tfrac{1}{4}(\alpha+\beta)(b_\uparrow + b_\downarrow)^2 + \gamma\,[5a^2 + \tfrac{1}{4}(b_\uparrow - b_\downarrow)^2]\,, \tag{23}$$

where

$$\begin{aligned}\alpha &= \tfrac{2}{25}\,F_2(2p,2p),\\ \beta &= \frac{2}{5}\int n^2(r)\,\mu'_{\text{xc}}(\rho(r))\,d^3r,\\ \gamma &= \frac{2}{5}\int n^2(r)[\mu'_x(\rho(r)) + \tfrac{1}{3}\nu_c(\rho(r))/\rho(r)]\,d^3r\,.\end{aligned} \tag{24}$$

TABLE V. Local-density estimates of the Coulomb energy ΔU, the exchange-correlation energy ΔE_{xc}, and total energy ΔE for mixed symmetry states $|D\rangle$ that reduce to single determinants D in the noninteracting case. Δ denotes energy change from a spherical paramagnetic calculation. a, $b_\uparrow$, and $b_\downarrow$ describe the spin-up and spin-down densities according to Eq. (21). f is the coefficient of $F_2/25$ in the energy of the determinant D. $E(D)$ is the exact energy of the state $|D\rangle$. Energies in eV.

D	a	$b_\uparrow$	$b_\downarrow$	f	ΔU	ΔE_{xc}	ΔE	$E(D)$
$D(1\uparrow, 1\downarrow)$	0	−1	−1	1	0.50	−0.34	0.16	$E(^1D)$
$D(1\uparrow, 0\downarrow)$	0	−1	2	−2	0.13	−0.62	−0.50	$\frac{1}{2}E(^3P) + \frac{1}{2}E(^1D)$
$D(1\uparrow, -1\downarrow)$	0	−1	−1	1	0.50	−0.34	0.16	$\frac{1}{2}E(^3P) + \frac{1}{6}E(^1D) + \frac{1}{3}E(^1S)$
$D(0\uparrow, 0\downarrow)$	0	2	2	4	2.00	−1.26	0.74	$\frac{2}{3}E(^1D) + \frac{1}{3}E(^1S)$
$D(1\uparrow, 0\uparrow)$	1	1	0	−5	0.13	−1.37	−1.24	$E(^3P)$
$D(1\uparrow, -1\uparrow)$	1	−2	0	−5	0.50	−1.75	−1.25	$E(^3P)$

TABLE VI. The parameters α, β, γ, and δ [Eqs. (24) and (25)] appearing in the perturbation treatment of the local-density theory of multiplet structure. F_2^{HF} is the Hartree-Fock value of the Slater integral and $\tilde{F}_2$ is its local-density equivalent including correlation [Eq. (28)]. F_2^{exp} is obtained by fitting Hartree-Fock energy expressions to spectral data. Energies in eV.

Atom	α	β	γ	δ	F_2^{HF}	$\tilde{F}_2$	F_2^{exp}
C	0.499	−0.325	−0.245	−0.070	6.50	5.25	4.73
Si	0.349	−0.214	−0.144	−0.009	4.44	3.49	3.16
N	0.605	−0.340	−0.269	−0.004	7.80	6.66	5.96

Here, $\mu'_{\mathrm{xc}}(\rho)$ is the density derivative of the exchange-correlation contribution to the chemical potential of an electron gas of density ρ, μ'_x is the same quantity without correlation, $\rho(r)$ is the total charge density of the spherical paramagnetic calculation and $\nu_c(\rho)$ is defined in Ref. 10 and vanishes without correlation. Because $\int \Delta\rho\, d^3r = 0$, ΔE does not contain terms linear in a, $b_\uparrow$, and $b_\downarrow$. We have given the parameters α, β and, γ for carbon, silicon and nitrogen in Table VI, and using them in Eq. (23) actually reproduces the numbers for ΔE given in Table V with a maximum error of 0.05 eV. Thus our six local-density estimates (ΔE's) are given in terms of only two parameters, $\alpha+\beta$ and γ. Furthermore, it turns out that our six linear equations can be simultaneously solved if only

$$\delta = \alpha + \beta + \gamma = 0\,. \tag{25}$$

This is because Eq. (23) then reduces to

$$\Delta E = \gamma(5a^2 - b_\uparrow b_\downarrow) = -f\gamma\,, \tag{26}$$

where f is easily identified as the coefficient of $\frac{1}{25}F_2(2p, 2p)$ in the energy of the given determinant (cf. Table V), and the solution becomes

$$E(^3P) = E_0 + 5\gamma, \quad E(^1D) = E_0 - \gamma, \quad E(^1S) = E_0 - 10\gamma\,. \tag{27}$$

Thus, the parameter δ measures the degree of inconsistency. We can carry out a similar analysis for the p^3 configuration (e.g., nitrogen) in which case we find six linear equations for the three unknown term values $E(^4S)$, $E(^2D)$, and $E(^2P)$. The consistency criterion remains the same, Eq. (25). From Table VI we see that δ is relatively small, again indicating the internal consistency of our method.

At this point we would like to draw attention to a limitation of the method. For consistency we require a small δ, but it is clear from the Eqs. (26) and (27) that this imposes Hartree-Fock ratios between the multiplet splittings. The quantity -25γ evidently plays the role of the F_2 integral in Hartree-Fock theory which is also true for the p^3 configuration. In the silicon atom the $3p$ orbitals are rather extended with a radius of 2.8 a.u. and we do not expect the correlations to drastically alter the Hartree-Fock picture. Indeed, from Table IV, $[E(^1S) - E(^3P)]/[E(^1D) - E(^3P)] = 2.48$ which is close to the Hartree-Fock ratio $\frac{5}{2}$. Thus the main correlation effect is a 30% reduction of the F_2 integral (Table VI). In carbon and nitrogen, however, the $2p$ orbitals are more localized (the radii are 1.8 and 1.4 a.u., respectively) leading to a stronger correlation effect. From Table IV we get $[E(^1S) - E(^3P)]/[E(^1D) - E(^3P)] = 2.13$ for carbon and $[E(^2P) - E(^4S)]/[E(^2D) - E(^4S)] = 1.50$ for nitrogen which deviates from the corresponding Hartree-Fock ratios $\frac{5}{2}$ and $\frac{5}{3}$. Thus the multiplet splittings are not accurately given by a single parameter F_2, a situation for which our method is not well suited.

The above discussion suggests a shortcut to obtain the multiplet splittings. From Eq. (27) they only depend on the single parameter γ which is easily calculated from Eq. (24). However, even if this perturbation estimate of γ is accurate to within 10%, it might still produce large errors in the multiplet splittings because these are obtained from γ through multiplication by a factor of order 10. Since we require $\delta = \alpha + \beta + \gamma = 0$ for a simultaneous solution of the linear equations we could equally well use $-\alpha - \beta$ to obtain the splittings. Not knowing which form is most accurate we simply propose to use the average $\gamma_{\mathrm{av}} = \frac{1}{2}(\gamma - \alpha - \beta)$. The corresponding F_2 parameter we call $\tilde{F}_2$. Thus from Eq. (24)

$$\begin{aligned}\tilde{F}_2 &= -25\gamma_{\mathrm{av}} = -25\,\tfrac{1}{2}(\gamma - \alpha - \beta)\\ &= F_2 - 5\int n^2(r)\big[\tfrac{1}{3}\nu_c(\rho(r))/\rho(r)\\ &\qquad - \mu'_c(\rho(r))\big]\,d^3r\,.\end{aligned} \tag{28}$$

Defined in this way and used in Hartree-Fock energy expressions, $\tilde{F}_2$ reproduces all our calculated multiplet splittings in Table IV with an accuracy of a few percent. Thus Eq. (28) represents a shortcut to the splittings. Moreover, it has a very appealing physical interpretation. Equation (28) simply tells us that the local-density treatment of correlations will give us a desired reduction of the F_2 integral from Hartree-Fock theory (compare F_2^{HF}, $\tilde{F}_2$, and F_2^{exp} in Table VI). Finally, Eq. (28) suggests that one could get accurate Hartree-Fock multiplet splittings from local-density theory with only exchange. This is indeed the case as can be seen by comparing the columns marked HF and LDX in Table IV. LDX actually means that we have recomputed the numbers in Table V with ϵ_{xc} replaced by ϵ_x, the exchange energy per particle of the homogeneous electron gas, in the local-density approximation (4). By definition the correlation contribution to the multiplet splittings (marked C in Table IV) is the difference between the Hartree-Fock results (HF) and the experimental results (exp). The local-density approximation to the correlation contribution is marked LDC in Table IV and is obtained as the difference between our full results (LD) and our results with exchange only (LDX). As can be seen by comparing the columns labeled C and LDC in Table IV, the local-density approximation to the correlation contribution is surprisingly accurate. The errors are of the order of 25% which can be compared with errors of the order of 100% involved in the local-density approximation to the total correlation energy of an atom.[17] We conclude that the charge density of those electrons responsible for the multiplet splittings in atoms and molecules is sufficiently slowly varying to allow a meaningful treatment of the correlation effects within local-density theory.

The columns marked TDHF in Table IV and Table VII are results from the term-dependent Hartree-Fock method in which orbitals that minimize the actual energy expression for a specific term are used to calculate the energy of that term. It is evident from Table IV and Table VII that only a small amount of correlation energy is obtainable this way. The local-density treatment is much superior.

Let us now return to the $1s2s$ excited configuration of helium. From the discussion above, it is clear that the energy of the self-consistent calculation, mentioned at the end of Sec. II with one electron in a spin-up orbital and the other electron in a spin-down orbital, is an approximation to the energy of the state $|D(\uparrow\downarrow)\rangle$, i.e., to the energy $\frac{1}{2}\,[E(^1S)+E(^3S)]$ of the state $1/\sqrt{2}(|0,0\rangle + |1,0\rangle)$. It is also clear that the energy of the self-consistent calculation with both electrons in spin-up orbitals is an approximation to the triplet energy $E(^3S)$ and from this we deduce the results of Table VII. It turns out that the Hartree-Fock results for this excited configuration are very bad, giving almost no splitting (0.12 eV) between the singlet and the triplet, whereas the local-density approach is surprisingly reasonable. The singlet-triplet splitting is 0.96 eV compared to 0.80 eV experimentally.

Note that the average energy $\frac{1}{4}[E(^1S)+3E(^3S)]$ of the multiplets has the value 19.32 eV in our local-density approximation and that the corresponding experimental number is 20.02 eV. Both these energies are far from the energy 21.90 eV of the spherical paramagnetic calculation. Consequently, such a calculation does not represent the multiplet average as is often stated in the literature. For the p^2 and the p^3 configurations the statement is, however, less inaccurate. In both cases the energy of the spherical paramagnetic calculation lies ~15% of the total span of the multiplets above the multiplet average.

We end this section with a short comment on ionization potentials. These are of course given by the difference between the ground-state energies of the atom and the corresponding ion. Since our method gives a lower ground-state energy as compared to a spherical paramagnetic calculation and since the lowering might be different in the atomic and in the ionic configurations, our method gives ionization potentials different from those obtained from spherical paramagnetic calculations. In Table VIII we compare results from the two methods with the experimental numbers. The theoretical numbers are computed from self-consistent spin-polarized but spherical calculations. Evidently our method does give different ionization potentials but the agreement with the experimental results is not improved. Only the sign of the errors are reversed. We believe this to be due to the fact that, within the local-density approximation, there will be a lack of cancellation of those self-energies which are proportional to F_0-integrals.[15] Errors of this kind

TABLE VII. Energies in eV above the ground state for the $1s2s$ excited configuration of helium. See Table IV for definition of symbols and Table III for comparison.

	TDHF	HF	LD	exp
$E(1s,2s;{}^3S)-E(1s^2;{}^1S)$	18.70	18.71	19.08	19.82
$E(1s,2s;{}^1S)-E(1s^2;{}^1S)$	18.82	18.83	20.04	20.62

TABLE VIII. Ionization potentials in eV for C, Si, and N. SP is the spherical paramagnetic results. LD is the present theory. exp is spectral data from Ref. 11.

	SP	LD	exp
C	11.1	11.9	11.3
Si	7.9	8.4	8.1
N	13.8	15.2	14.5

will come into play when an outer electron is removed, but will not affect the multiplet splittings. Note that in the cases considered here the ground states all reduce to single determinants in the noninteracting case and therefore the method by Gunnarsson and Lundqvist[8] should give the same ionization potentials as our method.

VI. CONCLUSIONS

In recent years interest has focused on realistic total-energy calculations for large molecules and for clusters of atoms simulating molecules and atoms adsorbed on surfaces. One is usually interested in the ground-state energy and perhaps the energy of a few low-lying excited states. Clearly the computational difficulties associated with Hartree-Fock calculations or configuration-interaction calculations on these systems quickly become unmanageable as the number of electrons increases. Consequently, it is highly desirable to develop simplifying techniques that are at least as accurate as the Hartree-Fock method, but hopefully better. For this purpose the local-density scheme by Hohenberg, Kohn, and Sham was recently generalized[8] to give the lowest energy of a specified symmetry. In the present paper we have demonstrated that this straightforward generalization only works in special cases, unless the usual symmetry-independent electron-gas approximation to exchange and correlation is abandoned. We have also shown that the failure of the method is due to the fact that for some states of pure symmetry the exchange-correlation hole is misrepresented by the local-density theory. Stimulated by the empirical success of a procedure proposed by Ziegler *et al.*[9] we have developed a density-functional theory for states of mixed symmetry, which enables us to retain the simple local-density approximation based on electron-gas data. A given configuration is associated with a certain number of Slater determinants. For each determinant we construct a linear combination of states of pure symmetry that reduces to this determinant in the noninteracting case. The energy expectation value of each linear combination is then estimated by the usual local-density approximation and we explain in terms of the pair-correlation function why this should be an adequate procedure. Since the energy expectation value of a linear combination of states of pure symmetry is a linear combination of the energies of the pure states we get as many linear equations as there are Slater determinants to solve for the energies. In general there are more determinants than pure-state energies and, although some of the equations might be identical, we generally get an overdetermined set of equations which we propose to solve by a min-max procedure. It might be possible to argue that the local-density approximation is more accurate for some linear combinations than for others, which would allow us to disregard some of the equations. Because of the small errors involved in the min-max procedure for our test cases, little accuracy is to be gained this way and we have made no attempt in this direction.

We have tested our method on the light atoms carbon, nitrogen, and silicon and on the excited $1s2s$ configuration of helium. In all cases (except for helium, where this was not tried) the local-density theory with exchange only reproduced the Hartree-Fock results with an extraordinary accuracy (~0.1 eV). We have used perturbation theory to explain why this is to be expected. Perturbation theory also shows how a desired reduction of the Slater integrals is achieved by local-density theory when correlations are included. In fact, the errors in the multiplet splittings from Hartree-Fock theory are typically reduced by a factor of three in the full local-density theory. We thus conclude that the charge density of the electrons responsible for the multiplet splittings is sufficiently slowly varying to allow us to treat the correlation between these electrons in the local-density approximation. When, however, the correlations become so strong that they no longer can be described in terms of a reduction of the Slater integrals we do not expect the present theory to apply. Cases where the present form of local-density theory would predict the wrong ordering between levels is conceivable and for such cases some symmetry dependence of the exchange-correlation functional must probably be introduced.

As a byproduct of our investigation we find that the energy of a spherical paramagnetic calculation does not represent the statistical average of the energies of the multiplets.

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[14] Without spin-orbit coupling the ground state of the atom can be chosen to be an eigenstate of the z component of the total spin, and from this it is not difficult to show that the density matrix is diagonal.

[15] The "spherical" part of the Coulomb interaction U_{2p} is $2F_0(2p,2p)$ of which half should be cancelled by a corresponding contribution from exchange. Thus, within the local-density approximation we ought to have

$$F_0(2p,2p)+\int \rho_{3p}(r)\epsilon_x(\rho_{3p}(r))\,d^3r \approx 0\,,$$

where ρ_{3p} is the spherical average of the density of the two $2p$ electrons. In actual fact, this number is 2.05 eV.

[16] The "nonspherical" (F_2 contributions) self-contribution to U_{2p} is $\frac{1}{2}\Delta U_{2p}$, whichis exactly canceled by $\Delta E^{\mathrm{X}}_{\uparrow\uparrow}+\Delta E^{\mathrm{X}}_{\downarrow\downarrow}$. Since $\Delta E^{\mathrm{LDX}}_{\uparrow\downarrow}=\Delta E^{\mathrm{LDX}}_{\downarrow\uparrow}=0$ we ought to have $\frac{1}{2}\Delta U_{2p}+\Delta E_x=0$ in the local-density approximation. From Table II, $\Delta U_{2p}=0.50$ eV and the exchange-only version ΔE_x of ΔE_{xc} is found to be -0.32 eV. Thus $\frac{1}{2}\Delta U_{2p}+\Delta E_x=-0.07$ eV.

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