PHYSICAL REVIEW A VOLUME 34, NUMBER 6 DECEMBER 1986

Generalized exchange local-spin-density-functional theory: Introduction and theory

S. Manoli and M. A. Whitehead
Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

(Received 18 July 1985; revised manuscript received 23 June 1986)

A local-spin-density-functional (LSD) scheme is developed using the normalization conditions for an electron gas around a nucleus of charge Z. The correlation factor for electrons of parallel spin, the Fermi hole, is decomposed into single-particle correlation factors. This leads to an *orbital-dependent* exchange-only density with *no adjustable parameters* such as the α of the $X\alpha$ theory; the parameters B_1, B_2, and α^{lim} are constant for all atoms once the shape of the Fermi hole is chosen. These parameters are rigorously calculated without assuming an approximate shape for the Fermi-hole correlation factor. The exchange density using this unspecified Fermi-hole correlation factor reduces exactly to the homogeneous free-electron-gas exchange density at the high electron-density limit. The theoretical relationship of this generalized exchange (GX) scheme to the $X\alpha$ and free-electron-gas exchange densities is discussed, and it is found that the $X\alpha$ scheme needs a classical approximation to justify the use of a variable α. These schemes are compared numerically using the total energies and eigenvalues for the atoms helium to krypton, and it is found that the LSD GX scheme gives the most reliable results.

I. INTRODUCTION

The exchange potential in local-spin-density-functional (LSD) theory is derived from free-electron-gas considerations and has a density, $n(\mathbf{r})^{1/3}$, dependence with an α parameter of $\frac{2}{3}$.[1-3] An exchange potential of this form can approximate the exchange potential of an inhomogeneous electron gas, characteristic of the electron gas around a nucleus of charge Z in two ways: (i) the *exact* exchange potential of the free-electron gas can be used, and the inhomogeneity either ignored or treated by various correction terms to the total energy,[4-6] or (ii) the *form* of the free-electron-gas exchange potential can be modified to obey the correct normalization conditions for an electron gas.

An exchange potential will be *derived* that is local in nature, retaining the simplicity of the free-electron-gas exchange potential, and satisfying the correct normalization conditions of the electron gas. This local exchange potential approaches the exact free-electron exchange potential as the electron density around a nucleus gets high, because an inhomogeneous electron gas with a high electron density behaves like a free-electron gas.[3]

The exchange functional is obtained from the exchange density, $U_i^X(\mathbf{r})$, by multiplying it by the corresponding one-electron density, summing over all the electrons and integrating over all space.[7] The exchange potential $V_i^X(\mathbf{r})$ is obtained by minimizing the exchange functional with respect to a variation in the electron density. Hence, the many-electron problem is discussed in terms of a quantity from which is derived the total exchange energy and the one-electron exchange potential. Therefore, the exchange density is the exchange energy *per particle*.

For the free-electron gas and $X\alpha$ exchange densities, the exchange potential is derived directly from[7]

$$V^{X\alpha}(n(\mathbf{r}))=\tfrac{2}{3}U^{X\alpha}(n(\mathbf{r}))\ , \tag{1}$$

where $n(\mathbf{r})$ is the total electron density. These exchange densities are orbital independent and (1) does not apply to orbital-dependent exchange densities. The α parameter is reviewed to simplify the derivation of a new orbital-dependent exchange potential.

II. THE α PARAMETER IN THE $X\alpha$ THEORY

Dirac,[1] Gaspar,[2] and Kohn and Sham[3] derived the exchange density of the free Fermi gas, and obtained the $X\alpha$ exchange density with an α of $\frac{2}{3}$. Therefore, for an inhomogeneous electron gas around a nucleus of charge Z, with the exchange density approximated by an $n(\mathbf{r})^{1/3}$ dependence it can be assumed that an α different from $\frac{2}{3}$ will account, in part, for the inhomogeneity. The degree of inhomogeneity decreases with increasing atomic number, therefore the greater the number of electrons the more they resemble a free-electron gas, and α should be close to $\frac{2}{3}$, implying a unique α for each atom.

In a homogeneous free-electron gas, the $n(\mathbf{r})^{1/3}$ exchange density with an α of $\frac{2}{3}$ correlates the interactions between electrons of parallel spin. The charge variation around each electron over all space is the same for all electrons. For an inhomogeneous electron gas, it is assumed that the charge around each electron varies very slowly and that it is spherically symmetric out to a certain radius. These radii can be averaged to simulate a homogeneous electron gas. This averaged interaction radius will differ from the interaction radius of the true homogeneous free-electron gas, which is infinite, and therefore, the difference between the homogeneous free-electron gas α of $\frac{2}{3}$ and the α of the simulated homogeneous electron gas *must be related to the difference between the corresponding radii of interaction.* These ideas have led to various sets of α values[8-21] being derived for the atoms.

Gopinathan, Whitehead, and Bogdanovic,[17] and Gazquez and Keller[21] derived theoretical α values using the one- and two-particle density matrices of McWeeny[22] and Lowdin[23] and described the electronic interactions in terms of a *correlation factor* $f(\mathbf{r},\mathbf{r}')$,

$$n(\mathbf{r},\mathbf{r}')=n(\mathbf{r})n(\mathbf{r}')+n(\mathbf{r})n(\mathbf{r}')f(\mathbf{r},\mathbf{r}') , \tag{2}$$

$n(\mathbf{r},\mathbf{r}')$ is the pair-probability distribution function and $n(\mathbf{r})$ the total electron density. $n(\mathbf{r},\mathbf{r}')$ accounts for the *Coulomb repulsion* through $n(\mathbf{r})n(\mathbf{r}')$ and the *exchange-correlation* interactions for all the interacting electrons through $f(\mathbf{r},\mathbf{r}')$.

In spin-polarized form (2) becomes[17,21,22]

$$n(\mathbf{r},\mathbf{r}')=n_{ss}(\mathbf{r},\mathbf{r}')+n_{ss'}(\mathbf{r},\mathbf{r}')+n_{s's}(\mathbf{r},\mathbf{r}')+n_{s's'}(\mathbf{r},\mathbf{r}') , \tag{3}$$

where $n_{ss'}(\mathbf{r},\mathbf{r}')$ gives the probability of finding a particle at $\mathbf{r}$ with spin s when another is at $\mathbf{r}'$ with spin s', and $n_s(\mathbf{r})$ and $n_s(\mathbf{r}')$ are the s and s' spin densities, and

$$n_{ss}(\mathbf{r},\mathbf{r}')=n_s(\mathbf{r})n_s(\mathbf{r}')+n_s(\mathbf{r})n_s(\mathbf{r}')f_{ss}(\mathbf{r},\mathbf{r}') \tag{4}$$

and similarly $n_{ss'}(\mathbf{r},\mathbf{r}')$ have correlation factors reflecting the spins of the electrons and therefore $f_{ss}(\mathbf{r},\mathbf{r}')$ and $f_{ss'}(\mathbf{r},\mathbf{r}')$ are *not* the same. Similar equations define $n_{s's}(\mathbf{r},\mathbf{r}')$ and $n_{s's'}(\mathbf{r},\mathbf{r}')$.

The expectation value of the total interelectronic interactions in terms of the two-particle density matrix becomes[17,21]

$$\left\langle \frac{1}{2}\sum_{i,j(\neq i)} 2/|\mathbf{r}_i-\mathbf{r}_j| \right\rangle=\frac{1}{2}\int n(\mathbf{r},\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'d\mathbf{r} . \tag{5}$$

Units are rydbergs. The right-hand side of (5) equals the general form, local or nonlocal, of the spin-density-functional theory total interelectronic interaction, therefore

$$\begin{aligned}\frac{1}{2}\int n(\mathbf{r},\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'d\mathbf{r} &=\frac{1}{2}\int n(\mathbf{r})n(\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'d\mathbf{r}\\ &\quad+\frac{1}{2}\int\sum_i^{s} n_i(\mathbf{r})U_s^{\mathrm{xc}}(\mathbf{r})d\mathbf{r}\\ &\quad+\frac{1}{2}\int\sum_i^{s'} n_i(\mathbf{r})U_s^{\mathrm{xc}}(\mathbf{r})d\mathbf{r} ,\end{aligned} \tag{6}$$

where $n_i(\mathbf{r})$ is equal to $f_i\,|u_i(r)|^2$. The density-functional (DF) terms are in densities for clarity. The exchange-correlation density $U_s^{\mathrm{xc}}(\mathbf{r})$ in (6) is independent of the summation over i and is the exchange-correlation operator defined by Kohn and Sham.[3] This will now be discussed.

The general form of the exchange-correlation energy for electrons of spin s is

$$E_s^{\mathrm{xc}}=\frac{1}{2}\int\sum_j^{s} n_j(\mathbf{r})U_j^{\mathrm{xc}}(\mathbf{r})d\mathbf{r} , \tag{7}$$

where $U_j^{\mathrm{xc}}(\mathbf{r})$ is orbital dependent; it is dependent on the summation over j and will be called the *single-particle* exchange-correlation density. Multiplying and dividing the integrand in (7) by the total density of electrons with spin s,

$$E_s^{\mathrm{xc}}=\frac{1}{2}\int\left[\left[\sum_i^{s} n_i(\mathbf{r})\right]\left[\sum_j^{s} n_j(\mathbf{r})U_j^{\mathrm{xc}}(\mathbf{r})\right]\Big/\left[\sum_i^{s} n_i(\mathbf{r})\right]\right]d\mathbf{r} . \tag{8}$$

Consequently, an orbital-independent exchange-correlation density can be defined

$$U_s^{\mathrm{xc}}(\mathbf{r})=\sum_j^{s} n_j(\mathbf{r})U_j^{\mathrm{xc}}(\mathbf{r})\Big/\sum_i^{s} n_i(\mathbf{r}) . \tag{9}$$

Summation over j shows that this is a total exchange-correlation density averaged over the total electronic density, and will be called the *averaged* exchange-correlation density. Kohn and Sham[3,16] used the Hartree-Fock (HF) exchange potential in (7) and (8) to define the averaged HF exchange density from (9), which enabled them to derive their $n^{1/3}(\mathbf{r})$ exchange potential. Therefore, the exchange-correlation density in (6) is the averaged DF exchange-correlation density.

Equation (5) in terms of the parallel and antiparallel spin-correlation factors[17,21,22] becomes

$$\begin{aligned}U_s^{\mathrm{xc}}(\mathbf{r})=\int &[n_s(\mathbf{r}')f_{ss}(\mathbf{r},\mathbf{r}')+n_{s'}(\mathbf{r}')f_{ss'}(\mathbf{r},\mathbf{r}')]\\ &\times(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' .\end{aligned} \tag{10}$$

Therefore, the complete *exchange-correlation* density depends on the correlation of electrons with *parallel* spins through $f_{ss}(\mathbf{r},\mathbf{r}')$ and *antiparallel* spins through $f_{ss'}(\mathbf{r},\mathbf{r}')$.

The problem is to find the shape of $f_{ss}(\mathbf{r},\mathbf{r}')$, which defines the *Fermi-hole interaction,* and of $f_{ss'}(\mathbf{r},\mathbf{r}')$, which defines the *Coulomb-hole interaction.* Because the exchange and the HF theories include exchange-only interactions, the Coulomb-hole interactions will be neglected and $f_{ss'}(\mathbf{r},\mathbf{r}')$ put equal to zero. These equations will be evaluated using an *unspecified* Fermi-hole correlation factor.

The averaged exchange-only density for spin s electrons from (10) is

$$U_s^{\mathrm{x}}(\mathbf{r})=\int n_s(\mathbf{r}')f_{ss}(\mathbf{r},\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' . \tag{11}$$

Equation (11) will be evaluated using a set of conditions which the Fermi-hole correlation factor must satisfy, derived from the normalization conditions of the one- and two-particle density matrix equations,[21,22,24] (i) the Pauli exclusion principle, the probability of finding 2 electrons at the same position at the same time is zero, hence

$$f_{ss}(\mathbf{r},\mathbf{r})=-1 , \tag{12}$$

when $|\mathbf{r}-\mathbf{r}'|$ equals zero; (ii) at large interelectronic distances, $|\mathbf{r}-\mathbf{r}'|$ approaches infinity, the electrons move independently, and the correlation factor will be constant,

$$f_{ss}^{\text{ind}} = -1/N_s \ , \tag{13}$$

N_s is the number of s spin electrons; and (iii) the *sum rule*

$$\int n_s(\mathbf{r}')f_{ss}(\mathbf{r},\mathbf{r}')d\mathbf{r}' = -1 \ , \tag{14}$$

which shows that the charge density removed *from the vicinity* of the point $\mathbf{r}$ is equal to the negative of the charge density *at* the point $\mathbf{r}$, if they have the same spin; two electrons with spin s cannot exist near one another. This defines the Fermi hole.

In LSD theory, the charge around the point $\mathbf{r}$ is assumed to vary very slowly within a volume defined by a radius r_F. Assuming the Fermi hole spherically symmetric, the sum rule becomes[17,21]

$$4\pi n_s(\mathbf{r}) \int_0^{r_F} f_{ss}(\mathbf{r}')r'^2 d\mathbf{r}' = -1 \ . \tag{15}$$

For a free-electron gas r_F is infinity, therefore using a *finite* radius is an approximation.

The correlation factor can be written to reflect directly the boundary conditions (12) and (13),

$$f_{ss}(r') = (1/N_s - 1)h(r') - 1/N_s \ , \tag{16}$$

where $h(r')$ equals 1 when r' equals zero, and equals zero when r' equals r_F. Using this Fermi hole, the sum rule (14) can be evaluated and solved for r_F,

$$r_F = [4\pi A_2 n_s(\mathbf{r})(1+B_2/N_s)]^{-1/3} \tag{17}$$

with

$$A_2 = \int_{u_F} h(u)u^2 du, \quad u = r'/r_F \tag{18}$$

and

$$B_2 = (\tfrac{1}{3} - A_2)/A_2 \ , \tag{19}$$

where u_F is the reduced Fermi-hole radius; r_F is constant around the point $\mathbf{r}$, and since it depends on N_s it is an averaged radius of the N_s Fermi holes present at the point $\mathbf{r}$.

Using (17), the averaged exchange density (11) is, in the LSD approximation,

$$U^{\text{LSD}}(n_s(\mathbf{r})) = 8\pi n_s(\mathbf{r}) \int_0^{r_F} f_{ss}(r')r'dr' \ , \tag{20}$$

$f_{ss}(r')$ is the general Fermi hole (16). Integrating (20) gives

$$U^{\text{LSD}}(n_s(\mathbf{r})) = -(32\pi)^{1/3}A_1 A_2^{-2/3}(1+B_1/N_s) \times (1+B_2/N_s)^{-2/3} n_s^{1/3}(\mathbf{r}) \tag{21}$$

with

$$A_1 = \int_{u_F} h(u)u\, du, \quad u = r'/r_F \tag{22}$$

and

$$B_1 = (\tfrac{1}{2} - A_1)/A_1 \ . \tag{23}$$

The averaged exchange density has an $n(\mathbf{r})^{1/3}$ dependence. When it is compared to the spin-polarized $X\alpha$ exchange density,

$$\alpha_s = \tfrac{8}{9}(\pi^2/12)^{1/3}A_1 A_2^{-2/3} \times (1+B_1/N_s)(1+B_2/N_s)^{-2/3} \ . \tag{24}$$

Therefore, the α_s depends on N_s and on r_F through the factor $(1+B_2/N_s)^{-2/3}$, and consequently varies with Z, justifying the use of α as a variable parameter.

The α^{HF} values derived by Schwarz[7,15] decrease smoothly with Z, therefore α_s should approach a constant, limiting value as N_s approaches infinity. Differentiated (24) with respect to $1/N_s$, which is then set equal to zero,

$$B_1 = \tfrac{2}{3}B_2 \ . \tag{25}$$

The Fermi-hole function $h(r')$ must satisfy (25) to ensure that the equation for α_s has a single minimum as N_s approaches infinity; the α value of an atom with N electrons must be greater than the α value of another with $N+1$ electrons.

As $1/N_s$ approaches zero, α_s becomes

$$\alpha^{\lim} = \tfrac{8}{9}(\alpha^2/12)^{1/3}A_1 A_2^{-2/3} \ , \tag{26}$$

which should equal $\frac{2}{3}$, the value derived by Dirac,[1] Gaspar[2] and Kohn and Sham[3] for the homogeneous, free-electron gas.

The approximate Fermi-hole correlation factors[16,17,21] can be expressed using these formulas once the Fermi-hole function $h(r')$ in (16) is defined.

Slater[16] assumed the charge density uniform, i.e., *homogeneous*, hence

$$h^H(r') = 1, \quad 0 \le r' < r_F \ . \tag{27}$$

The electron gas around a nucleus of charge Z is actually *inhomogeneous* and the charge density in the Fermi hole varies, albeit slowly, for the LSD approximation to be effective. Gopinathan, Whitehead, and Bogdonovic[17] (GWB) assumed a linear variation,

$$h^{\text{GWB}}(r') = 1 - r'/r_F, \quad 0 \le r' \le r_F \ . \tag{28}$$

Gazquez and Keller[21] modified an expression derived by Wigner *et al.*[25,26] for the correlation factor of electrons in a metal,

$$h^W(r') = \exp(-br'/r_F)[1 + br'/r_F + b(r'/r_F)^2] \ , \tag{29}$$

b is a constant determined by (25).

These Fermi-hole functions can be used to evaluate the A_1 and A_2 integrals (22) and (18). The reduced Fermi-hole radius in the Fermi-hole function (29) is defined as br'/r_F and the integration limits of (22) and (18) are zero to $-b$. Subsequently, the B_1 and B_2, and hence the theoretical values of α are calculated using (24).

Table I gives A_1, A_2, B_1, B_2, and $\alpha^{\lim}$, defined by (26). The homogeneous Fermi-hole function H *does not give variable* theoretical values of α; α is constant at its limiting value of 0.866173 because both B_1 and B_2 are zero. This value of α was derived by Slater[16] who concluded that, since it was derived from a rough estimate of the shape of the Fermi hole and lay between his original value of 1 and the free-electron value of $\frac{2}{3}$, a variable α parameter was justified. However, the constant α value of

TABLE I. The A_1, A_2, B_1, B_2, and α^{lim} values calculated using the homogeneous, H, GWB, Wigner, and the free-electron limit (FEL) Fermi holes.

	H	GWB	Wigner[a]	FEL
A_1	0.500 000	0.166 667	0.142 256	0.119 647
A_2	0.333 333	0.083 333	0.069 849	0.057 785
B_1	0.0	2.0	2.514 776	3.178 952
B_2	0.0	3.0	3.772 147	4.768 428
α^{lim}	0.866 173	0.727 539	0.698 526	0.666 667

[a]The b value was determined to be 5.029 05 (Ref. 21).

0.866173 means that the homogeneous Fermi hole is *not suitable* for systems with a large number of electrons and *does not fit* the general physical description of the α parameter; it does *not* vary with atomic number. The GWB and the Wigner Fermi holes give variable theoretical α values, and the latter gives a limiting α value closer to $\frac{2}{3}$.

Theoretical α values can be derived, without using a specific Fermi-hole shape, which have the correct free-electron limiting value of $\frac{2}{3}$. The α^{lim} expression (26) is set equal to $\frac{2}{3}$,

$$A_1A_2^{-2/3}=\tfrac{3}{4}(\pi^2/12)^{1/3}\,. \tag{30}$$

The condition (25) can be expressed in terms of A_1 and A_2 using the definitions of B_1 and B_2, (23) and (19),

$$(\tfrac{1}{2}-A_1)/A_1=\tfrac{2}{3}(\tfrac{1}{3}-A_2)/A_2\,. \tag{31}$$

Equations (30) and (31) are solved for A_1 and A_2. These values, and the B_1 and B_2 values, are given in Table I under the heading FEL, the *free-electron limit* Fermi hole.

The theoretical α_s and $\alpha_{s'}$ values for the GWB, Wigner and FEL Fermi holes can be spin averaged,

$$\alpha_{\text{av}}=(N_s\alpha_s+N_{s'}\alpha_{s'})/(N_s+N_{s'})\,. \tag{32}$$

The results are in Table II along with the $\alpha_{\text{sp}}^{\text{HF}}$ of Manoli and Whitehead,[19,20] which are very close to those calculat-

TABLE II. The $\alpha_{\text{sp}}^{\text{HF}}$, $\alpha_{\text{av}}^{\text{GWB}}$, α_{av}^{W}, $\alpha_{\text{av}}^{\text{FEL}}$ values for the atoms helium to krypton.

Z	Atom	$\alpha_{\text{sp}}^{\text{HF}}$ [a]	$\alpha_{\text{av}}^{\text{GWB}}$ [b]	α_{av}^{W} [c]	$\alpha_{\text{av}}^{\text{FEL}}$
2	He	0.772 981	0.866 173	0.866 173	0.866 173
3	Li	0.771 659	0.815 349	0.807 316	0.799 297
4	Be	0.768 230	0.789 938	0.777 888	0.765 859
5	B	0.762 058	0.774 296	0.758 872	0.743 240
6	C	0.753 272	0.764 305	0.746 387	0.727 977
7	N	0.745 217	0.757 531	0.737 771	0.717 248
8	O	0.741 199	0.751 805	0.730 901	0.709 188
9	F	0.735 871	0.747 644	0.725 685	0.702 796
10	Ne	0.730 811	0.744 568	0.721 724	0.697 803
11	Na	0.730 205	0.742 233	0.718 661	0.693 866
12	Mg	0.729 132	0.740 288	0.716 108	0.690 584
13	Al	0.728 109	0.738 760	0.714 073	0.687 925
14	Si	0.726 738	0.737 534	0.712 422	0.685 742
15	P	0.725 440	0.736 533	0.711 062	0.683 926
16	S	0.724 314	0.735 526	0.709 724	0.682 182
17	Cl	0.722 968	0.734 707	0.708 620	0.680 722
18	Ar	0.721 771	0.734 030	0.707 698	0.679 488
19	K	0.720 853	0.733 462	0.706 918	0.678 434
20	Ca	0.719 832	0.732 952	0.706 217	0.677 486
21	Sc	0.718 241	0.732 517	0.705 615	0.676 666
22	Ti	0.716 977	0.732 143	0.705 095	0.675 953
23	V	0.715 498	0.731 819	0.704 642	0.675 327
24	Cr	0.712 793	0.731 620	0.704 349	0.674 901
25	Mn	0.712 646	0.731 285	0.703 890	0.674 284
26	Fe	0.711 298	0.730 998	0.703 495	0.673 745
27	Co	0.710 314	0.730 750	0.703 149	0.673 272
28	Ni	0.709 097	0.730 533	0.702 846	0.672 853
29	Cu	0.706 806	0.730 342	0.702 578	0.672 482
30	Zn	0.706 735	0.730 174	0.702 340	0.672 149
31	Ga	0.706 797	0.730 023	0.702 127	0.671 850
32	Ge	0.706 673	0.729 889	0.701 935	0.671 580
33	As	0.706 515	0.729 767	0.701 761	0.671 335
34	Se	0.706 275	0.729 642	0.701 584	0.671 086
35	Br	0.705 985	0.729 530	0.701 424	0.670 861
36	Kr	0.705 740	0.729 428	0.701 279	0.670 657

[a]References 19 and 20, see also Ref. 27.

[b]Reference 17.

[c]Reference 21.

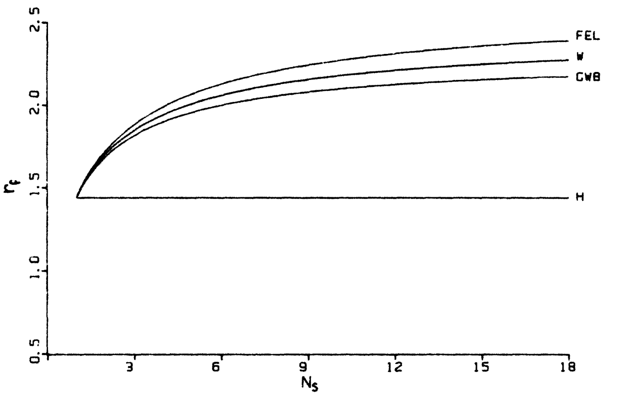

FIG. 1. A plot of the FEL, Wigner, GWB, and H Fermi-hole radii in units of $[4\pi n_s(\mathbf{r})]^{-1/3}$ versus the number of spin s electrons N_s.

ed by Schwarz.[15,27] The $\alpha_{\mathrm{av}}^{\mathrm{GWB}}$ are considerably higher than the $\alpha_{\mathrm{sp}}^{\mathrm{HF}}$ values, and hence the LSD total energy will be too negative with these α values. In contrast, the $\alpha_{\mathrm{av}}^{\mathrm{FEL}}$ values are considerably lower than the $\alpha_{\mathrm{sp}}^{\mathrm{HF}}$ values, and hence the total energy will be higher than the HF total energy. The α_{av}^{W} values reproduce the $\alpha_{\mathrm{sp}}^{\mathrm{HF}}$ trend quite well, especially for the transition metals, in spite of the incorrect limiting α value.

The α values depend on r_F. Figure 1 is a plot of r_F given by (17) for the H, GWB, Wigner and FEL Fermi holes in units of $[4\pi n_s(\mathbf{r})]^{-1/3}$ versus N_s. The r_F^H is constant, as expected for a uniform electron gas distribution, and has the smallest radius for all atoms, while the largest is the r_F^{FEL}. As r_F increases, the α value decreases as does the magnitude of the exchange energy.

III. THE GENERALIZED EXCHANGE LOCAL-SPIN-DENSITY-FUNCTIONAL THEORY

The $X\alpha$ exchange density is orbital independent. The electron gas around each nucleus of charge Z is described in terms of an averaged Fermi-hole correlation factor that depends on N_s. The α parameter is a direct consequence of this averaging process.

A LSD orbital-dependent exchange density will be derived by averaging the Fermi-hole interactions around *one* electron, instead of averaging *all* the Fermi-hole interactions around *all* the electrons, to give an "orbital-dependent α value" which is closer to the exact description of electronic interactions.

The Fermi-hole correlation factor in (4) is written as a sum over one-particle Fermi-hole correlation factors,

$$n_{ss}(\mathbf{r},\mathbf{r}')=n_s(\mathbf{r})n_s(\mathbf{r}')+n_s(\mathbf{r})n_s(\mathbf{r}')\sum_i^s f_{ss}^i(\mathbf{r},\mathbf{r}') . \tag{33}$$

This two-particle density matrix must satisfy the normalization conditions used to derive the boundary conditions of the total Fermi-hole correlation factor, rewritten in terms of one-electron densities. The *single-particle* Fermi-hole correlation must satisfy the following conditions.

(i) As the distance between electrons approaches zero, the pair-probability distribution function approaches zero to satisfy the Pauli exclusion principle,

$$f_{ss}^i(\mathbf{r},\mathbf{r}')=-n_i(\mathbf{r})/n_s(\mathbf{r}) . \tag{34}$$

If (34) is summed over i, this gives (12).

(ii) As the distance between two charge densities at $\mathbf{r}$ and at $\mathbf{r}'$ approaches infinity,

$$f_{ss}^{i,\mathrm{ind}}(\mathbf{r},\mathbf{r}')=-n_i(\mathbf{r})n_i(\mathbf{r}')/n_s(\mathbf{r})n_s(\mathbf{r}') . \tag{35}$$

This is not equal to (13) when summed over i. However, it will be shown to equal the limit of the HF Fermi-hole correlation factor.

(iii) The *sum rule* becomes

$$\int \sum_i^s [n_s(\mathbf{r}')f_{ss}^i(\mathbf{r},\mathbf{r}')+n_i(\mathbf{r}')n_i(\mathbf{r})/n_s(\mathbf{r})]d\mathbf{r}'=0 . \tag{36}$$

A *single-particle sum rule* is obtained by setting each integral to zero,

$$\int n_s(\mathbf{r}')f_{ss}^i(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-n_i(\mathbf{r})/n_s(\mathbf{r}) . \tag{37}$$

Summing over the i gives (14). Therefore, (37) shows that the charge density removed from the vicinity of the charge density at the point $\mathbf{r}$, $n_s(\mathbf{r})$, is the charge density of the ith electron, $n_i(\mathbf{r})$. As $|\mathbf{r}-\mathbf{r}'|$ approaches infinity, the total charge density removed from the Fermi hole in the sum rule (36) equals in magnitude but opposite in sign to the self-interaction charge density. This ensures that a particle does not interact with itself; *self-interaction is removed.* This is why the boundary condition of the single-particle Fermi-hole correlation factor (35) does not equal the corresponding limit of the total Fermi-hole correlation (13) when summed over i.

Writing (34) like (16) to reflect directly the boundary conditions (34) and (35),

$$\begin{aligned} f_{ss}^i(\mathbf{r},\mathbf{r}')=&[n_i(\mathbf{r})n_i(\mathbf{r}')/n_s(\mathbf{r})n_s(\mathbf{r}')-n_i(\mathbf{r})/n_s(\mathbf{r})]h(\mathbf{r},\mathbf{r}')\\ &-n_i(\mathbf{r})n_i(\mathbf{r}')/n_s(\mathbf{r})n_s(\mathbf{r}') , \end{aligned} \tag{38}$$

$h(\mathbf{r},\mathbf{r}')$ approaches 1 as $|\mathbf{r}-\mathbf{r}'|$ approaches zero, and approaches zero as $|\mathbf{r}-\mathbf{r}'|$ approaches infinity. Using (38) in the single-particle sum rule (37) gives

$$\begin{aligned} \int n_s(\mathbf{r}')\{&[n_i(\mathbf{r}')/n_s(\mathbf{r}')-1]h(\mathbf{r},\mathbf{r}')\\ &-n_i(\mathbf{r}')/n_s(\mathbf{r}')\}d\mathbf{r}'=-1 . \end{aligned} \tag{39}$$

The $n_i(\mathbf{r})/n_s(\mathbf{r})$ factors cancel exactly.

The equations developed so far are in principle exact. Now, however, the LSD approximation will be used to simplify evaluating the single-particle sum rule (39). If the total density at the point $\mathbf{r}$ is very slowly varying, the LSD approximation gives

$$n_s(\mathbf{r}')\cong n_s(\mathbf{r}) \tag{40}$$

so that

$$n_i(\mathbf{r}')\cong n_i(\mathbf{r}) . \tag{41}$$

Equation (40) is a direct consequence of the LSD approximation and (41) a natural extension. The Fermi hole is assumed spherically symmetric and localized within a radius r_F. The sum rule (39) is evaluated and solved for r_F,

$$r_F=\{4\pi A_2[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]\}^{-1/3} . \tag{42}$$

The A_2 and B_2 factors are exactly those derived before but *the Fermi-hole radius* $\mathbf{r}_F$ *is now orbital dependent.* Therefore, at every point $\mathbf{r}$, each electron has its own Fermi-hole radius.

The total interelectronic interaction energy of electrons of spins s is expressed using (33) in an equation similar to (5). This gives the sum of the Coulomb repulsion and exchange energies in DF theory,

$$\int \left[n_s(\mathbf{r})n_s(\mathbf{r}')+n_s(\mathbf{r})n_s(\mathbf{r}')\sum_i^s f_{ss}^i(\mathbf{r},\mathbf{r}') \right](2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'d\mathbf{r}$$
$$= \int n_s(\mathbf{r})n_s(\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'d\mathbf{r} + \int \sum_i^s n_i(\mathbf{r})U_{s,i}^X(\mathbf{r})d\mathbf{r} \; . \tag{43}$$

The exchange density $U_{s,i}^X(\mathbf{r})$ is the single-particle, orbital-dependent exchange density (7). This reduces to

$$U_{s,i}^X(\mathbf{r})n_i(\mathbf{r})/n_s(\mathbf{r}) = \int n_s(\mathbf{r}')f_{ss}^i(\mathbf{r},\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' \; . \tag{44}$$

Substituting (38) gives

$$U_i^X(\mathbf{r}) = \int n_s(\mathbf{r}')\{[n_i(\mathbf{r}')/n_s(\mathbf{r}')-1]h(\mathbf{r},\mathbf{r}') - n_i(\mathbf{r}')/n_s(\mathbf{r}')\}(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' \; . \tag{45}$$

As in the sum rule, the $n_i(\mathbf{r})/n_s(\mathbf{r})$ factors cancel. If the LSD approximation is used, and the Fermi hole assumed spherically symmetric, equations (40)—(42) give

$$U_i^X(\mathbf{r}) = -4(\pi/2)^{1/3}A_1A_2^{-2/3}[n_s(\mathbf{r})+B_1n_i(\mathbf{r})] \times [n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3} \; . \tag{46}$$

This $U_i^X(\mathbf{r})$ must approach a $n^{1/3}(\mathbf{r})$ as N_s approaches infinity. It should approach the $X\alpha$ exchange density with α_s equal to $\frac{2}{3}$. Therefore, differentiating $U_i^X(\mathbf{r})$ with respect to $n_i(\mathbf{r})/n_s(\mathbf{r})$ and setting $n_i(\mathbf{r})/n_s(\mathbf{r})$ equal to zero gives exactly the same condition that the total Fermi-hole correlation factor had to satisfy, Eq. (25). Hence, the orbital-dependent, single-particle exchange density $U_i^X(\mathbf{r})$ can be written in terms of the limiting value of (26),

$$U_i^X(\mathbf{r}) = -9c\alpha^{\text{lim}}[n_s(\mathbf{r})+B_1n_i(\mathbf{r})] \times [n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3} \; , \tag{47}$$

where α^{lim}, ideally, should equal $\frac{2}{3}$. The exchange density (47) will be called the *generalized exchange* (GX) *density.*

Any Fermi hole can be used, hence the name generalized exchange. The H, GWB, Wigner, and FEL Fermi holes give specific B_1, B_2, and α^{lim} that are constant; *there are no adjustable parameters* like the α^{HF} of the $X\alpha$ theory. Since the exchange density of large electronic systems should approach the free-electron exchange density, the best Fermi-hole parameters are the FEL.

For the H Fermi hole, the LSD GX exchange energy is

$$E_s^{\text{ex}} = -(9c/2)(0.866\,173) \times \sum_i^s f_i \langle u_i(\mathbf{r}) | n_s^{1/3}(\mathbf{r}) | u_i(\mathbf{r}) \rangle \; , \tag{48}$$

the $X\alpha$ exchange density with an α of 0.866 173. Consequently, the LSD GX theory is a *generalization* of the traditional $X\alpha$ theory based on *single-particle* Fermi-hole interactions.

IV. COMPARISON BETWEEN THE LSD GX AND $X\alpha$ EXCHANGE DENSITIES

The difference between the LSD GX and $X\alpha$ exchange densities is the replacement of $1/N_s$ factor in the theoretical α_s expression (24) by $n_i(\mathbf{r})/n_s(\mathbf{r})$ in the LSD GX exchange density.

A physically correct *total* Fermi-hole correlation factor must satisfy the sum rule (14) and the boundary condition (12). The theoretical α values are derived using these equations and the boundary condition (13). *It is (13) that gives an orbital-independent α value.* Equation (13) was first used by Gopinathan, Whitehead, and Bogdanovic.[17] They used the results of Kutzelnigg, Del Re, and Berthier[24,28] who proposed that for *classical point charges*

$$1/N_s = n_i(\mathbf{r})/n_s(\mathbf{r}) \tag{49}$$

is valid at large interelectronic distances. This shows that *the use of an α varying with atomic number in the $X\alpha$ theory is based on a classical approximation* which makes the expression for α a function of the total number of electrons.

The LSD GX exchange density is derived from the correct *single-particle* Fermi-hole correlation factor which satisfies the sum rule (37), the boundary condition (34), and *the boundary condition (35)* which gives an orbital-dependent exchange density. *There is no classical approximation to the boundary condition (35).*

The $X\alpha$ exchange density with the theoretical α_s expression (24) is obtained when (49) is used as a *classical approximation in the LSD GX expression* for the exchange density and summed over i. When this approximation is used in boundary condition (35) it gives boundary condition (13). Hence, the use of the single-particle correlation factor to describe exchange interactions is *more* accurate than using the total Fermi-hole correlation factor because the classical approximation (49) *is not used.* In addition, the single-particle correlation factor obeys the same boundary conditions as the HF correlation factor, Appendix A. Therefore, the LSD GX exchange density should be closer to the correct exchange density of the electron gas around an atom.

V. THE FREE-ELECTRON-GAS LIMIT

An important limiting case of the LSD GX exchange density is the free-electron (FE) gas limit. This limit is the high electron density limit; the total electron density is much greater than the single-particle electron density, the number of electrons is very large.

Because a free-electron gas is homogeneous, it might seem natural to use the H Fermi-hole correlation factor to derive the FE exchange density. However, this leads to an exchange density which has the *correct form,* a $n_s^{1/3}(\mathbf{r})$ dependence, but with an α value of 0.866 173 and not $\frac{2}{3}$, the correct α value for the FE gas exchange density.[1,3,29,30] Why does the H Fermi-hole give the incorrect FE gas α value?

The H Fermi hole in the present formulism gives a *finite* r_F. In contrast, for the FE gas, the correct r_F is infinite. The assumption of a finite r_f ensures that the exact FE exchange cannot be derived *directly* using the $f_{\mathrm{ss}}^{H}(r)$.[1,3,29,30]

The α value of 0.866 173, obtained from $f_{\mathrm{ss}}^{H}(r)$ and the sum rule, describes an electron gas which is assumed homogeneous *within a finite Fermi-hole radius which obeys the normalization conditions of an electron gas.*

Gunnarsson and Lundqvist[31] and Langreth and Perdew[32–35] concluded that the FE-gas exchange density does obey the sum rule *with an infinite Fermi-hole radius.* This means that the $X\alpha$ and LSD GX schemes attempt to account for the inhomogeneity of the electron gas around a nucleus by using a finite r_F. Therefore, the LSD FE scheme will underestimate the exchange energy of the inhomogeneous electron gas since (Fig. 1) the larger the radius of interaction the smaller the magnitude of the exchange energy.

The FE-gas exchange density can be *indirectly* derived from the LSD GX exchange density; at the high electron-density limit $n_i(\mathbf{r})/n_s(\mathbf{r})$ approaches zero, and the LSD GX exchange density reduces to

$$U^{\mathrm{GX\,FE}}(n_s(\mathbf{r}))=-9c\tfrac{2}{3}n_s^{1/3}(\mathbf{r}) \tag{50}$$

since α^{lim} equals $\frac{2}{3}$ for the FEL Fermi hole. This is exactly the FE-gas exchange density. Therefore, though the LSD GX exchange density was derived within the finite Fermi-hole radius approximation, it has the correct FE-gas limit.

VI. THE ONE-ELECTRON EXCHANGE POTENTIAL

In the Kohn and Sham scheme[3] the total energy is minimized with respect to a variation in the one-electron eigenfunctions $u_i(\mathbf{r})$ which preserves the normalization condition

$$\sum_i^s f_i\langle u_i(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle=\int n_s(\mathbf{r})d\mathbf{r}=N_s\ . \tag{51}$$

This gives

$$\left[f_r+\sum_i f_i\langle u_i(\mathbf{r}')||u_i(\mathbf{r}')\rangle+V^{\mathrm{xc}}k(\mathbf{r})\right]|\,u_k(\mathbf{r})\rangle =\varepsilon_k\,|\,u_k(\mathbf{r})\rangle\ , \tag{52}$$

f_r is the kinetic and nuclear-attraction energy operator $-\nabla_i^2-2Z/|\mathbf{r}|$, and $||$ represents the interelectronic repulsion operator $2/|\mathbf{r}-\mathbf{r}'|$. The one-electron potential $V_k^{\mathrm{xc}}(\mathbf{r})$ is

$$V_k^{\mathrm{xc}}(\mathbf{r})=\tfrac{1}{2}\delta\left[\sum_i^s f_i\langle u_i(\mathbf{r})\,|\,U_i^{\mathrm{xc}}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle\right]\Big/\delta n_k(\mathbf{r})\ . \tag{53}$$

The kth electron has spin s and the $U_i^{\mathrm{xc}}(\mathbf{r})$ is the single-particle exchange-correlation density (7). Expression (52) is the one-electron eigenvalue equation to be solved self-consistently in DF theory; the orbital eigenvalue ϵ_k is the Lagrange multiplier in the minimization procedure.

Slater and Wood[36] and Janak[37] proved that ϵ_k is obtained directly by evaluating the derivative of the total energy with respect to *the occupation number* of an orbital at full occupancy. This implies that the total energy is a *continuous function of the occupation numbers,* since the partial derivative can be evaluated for any value of f_k. This concept seems unphysical, but is a powerful tool used to calculate various one-electron energies such as electronegativities.[16,38–40]

Using this approach, the LSD GX one-electron exchange potential is

$$\begin{aligned}V_k^{\mathrm{GX}}(\mathbf{r})=-(9c/2)\alpha^{\mathrm{lim}}\Bigg[&\sum_i^s[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}n_i(\mathbf{r})-\tfrac{2}{3}\sum_i^s[n_s(\mathbf{r})+B_1n_i(\mathbf{r})][n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-5/3}n_i(\mathbf{r})\\&+[n_s(\mathbf{r})+2B_1n_k(\mathbf{r})][n_s(\mathbf{r})+B_2n_k(\mathbf{r})]^{-2/3}-\tfrac{2}{3}B_2[n_s(\mathbf{r})+B_1n_k(\mathbf{r})][n_s(\mathbf{r})+B_2n_k(\mathbf{r})]^{-5/3}n_k(\mathbf{r})\Bigg]\ ,\end{aligned} \tag{54}$$

which is used in (52).

The exchange potential (54) reduces to the $X\alpha$ exchange potential when the H Fermi-hole parameters are used. Setting B_1 and B_2 equal to zero,

$$V^{X\alpha}(n_s(\mathbf{r}))=-6c\alpha^{\mathrm{lim}}n_s^{1/3}(\mathbf{r})\ , \tag{55}$$

where α^{lim} equals 0.866 173. In contrast, using the *classical* approximation (49),

$$V^{X\alpha}(n_s(\mathbf{r}))=-6c\alpha_s n_s^{1/3}(\mathbf{r})\ , \tag{56}$$

where α_s is given by a theoretical expression which is a function of N_s, and depends on the Fermi-hole parameters B_1, B_2, and α^{lim}.

VII. RESULTS AND DISCUSSION

A. Computational notes

Calculations were done on the atoms helium to krypton using (i) the LSD GX scheme with the FEL, Wigner, and GWB Fermi-hole parameters (henceforth called the GX-FEL, GX-W, and GX-GWB, respectively), (ii) the $X\alpha$ scheme with the $\alpha_{\mathrm{sp}}^{\mathrm{HF}}$ of Manoli and Whitehead[19,20,27] and (iii) the LSD FE scheme.

The Herman-Skillman program[18] was extensively modified to permit spin-polarized calculations for all schemes and orthogonalization of orbitals with the same azimuthal quantum number, because the LSD GX exchange potential is orbital dependent.

The units in the calculations were rydbergs; self-consistency was achieved to an accuracy of 10^{-7} for every point in all the eigenfunctions. The results are in eV; the conversion was 1 Ry to 13.605 eV.

B. Total energies

The HF total energies are the basis for comparison between the total energies because the LSD exchange potentials only include Fermi-hole interactions; they do not contain correlation, i.e., Coulomb-hole interactions, and the schemes should be compared to exchange-only calculations.

Table III gives the total energies of atoms helium to krypton in the LSD GX schemes in eV. They are compared to the LSD FE total energies and to the HF total energies given by Clementi and Roetti.[41] The $X\alpha$ total energies are equal to the HF total energies.

The LSD GX total energies are overestimated because the LSD GX exchange density contains too much pure-exchange density.[42] In contrast, the LSD FE total energies are underestimated because the electron gas around a nucleus is inhomogeneous. The GX-FEL total energies are significantly closer to the HF total energies than the LSD FE total energies, because the finite Fermi-hole radius approximation in the GX-FEL scheme attempts to account in part for the inhomogeneity of the electron gas. In addition, the FEL Fermi hole has the correct high electron-density limit, and does not assume a specific, approximate shape of the Fermi hole.

The effect of the different Fermi-hole parameters can be seen in Table IV, which compares the calculated exchange energies. In general, the larger r_F the smaller the

TABLE III. The negative of the total energies in eV of the ground states of the atoms helium to krypton calculated using the LSD GX scheme and the FEL, Wigner, and GWB Fermi holes compared to the HF and LSD FE total energies.

		Negative total energies (eV)				
Z	Atom	FEL	Wigner	GWB	FE	HF[a]
2	He	81.25	81.25	81.25	74.11	77.87
3	Li	207.89	207.94	207.98	195.73	202.24
4	Be	404.74	404.88	405.02	387.02	396.53
5	B	677.59	678.07	678.54	654.77	667.44
6	C	1037.6	1038.7	1039.8	1009.8	1025.5
7	N	1494.0	1496.1	1498.1	1461.4	1480.2
8	O	2051.0	2054.0	2056.8	2013.3	2035.6
9	F	2722.1	2726.2	2730.3	2679.5	2704.9
10	Ne	3516.3	3522.1	3527.7	3469.0	3497.8
11	Na	4424.3	4431.3	4438.0	4371.1	4404.2
12	Mg	5453.7	5461.9	5469.8	5394.4	5431.5
13	Al	6605.1	6614.7	6623.9	6540.1	6581.5
14	Si	7884.8	7895.9	7906.6	7814.2	7859.7
15	P	9297.0	9309.9	9322.4	9221.2	9271.0
16	S	10 843.6	10 858.2	10 872.3	10 762.1	10 816.1
17	Cl	12 531.2	12 547.8	12 563.7	12 444.3	12 502.5
18	Ar	14 364.2	14 383.0	14 401.0	14 272.1	14 334.7
19	K	16 334.6	16 355.2	16 375.0	16 236.5	16 303.3
20	Ca	18 448.0	18 470.6	18 492.2	18 343.9	18 414.6
21	Sc	20 707.5	20 732.5	20 756.4	20 598.2	20 672.4
22	Ti	23 121.4	23 149.0	23 175.4	23 006.9	23 085.1
23	V	25 693.6	25 724.1	25 753.2	25 574.0	26 655.9
24	Cr	28 429.6	28 463.6	29 496.1	28 305.8	28 389.7
25	Mn	31 328.3	31 365.2	31 400.3	31 198.5	31 287.8
26	Fe	34 393.2	34 433.3	34 471.4	34 258.4	34 351.1
27	Co	37 631.3	37 674.8	37 716.1	37 491.6	37 588.3
28	Ni	41 046.4	41 093.5	41 138.2	40 901.8	41 001.9
29	Cu	44 643.4	44 694.9	44 743.7	44 494.9	44 596.2
30	Zn	48 422.5	48 477.6	48 529.7	48 268.1	48 375.2
31	Ga	52 378.6	52 437.3	52 492.9	52 218.6	52 331.9
32	Ge	56 516.8	56 579.3	56 638.3	56 351.4	56 470.5
33	As	60 839.4	60 905.8	60 968.5	60 668.7	60 793.6
34	Se	65 346.3	65 416.5	65 482.7	65 170.0	65 300.3
35	Br	70 042.1	70 116.2	70 186.2	69 860.5	69 996.1
36	Kr	74 929.2	75 007.4	75 081.2	74 742.2	74 883.4

[a] Reference 41.

TABLE IV. The negative of the exchange energies of neon, argon, and krypton calculated using the GX-FEL, GX-W, GX-GWB, and the LSD FE schemes compared to HF exchange energy. All energies are given in eV.

	Negative exchange energies (eV)				
Atom	GX-FEL	GX-W	GX-GWB	FE	HF[a]
Ne	346.93	353.45	359.78	297.60	329.5
Ar	849.96	869.96	889.20	755.75	821.3
Kr	2596.4	2677.8	2754.7	2407.5	2561.9

[a]Reference 36.

magnitude of the exchange interaction and since the LSD GX overestimates the pure-exchange interaction, the Fermi hole with the largest r_F gives the smallest exchange energy. The GWB Fermi hole gives the worst exchange energy because it oversimplifies the shape of the hole, and hence has the smallest radius. The Wigner Fermi hole gives better results because it is based on a very good approximation to the correct Fermi hole,[25,26] with a larger radius, but neither are as good as the FEL results, because the GX-FEL exchange density has the largest Fermi-hole radius. The LSD FE exchange energies are underestimated because the electron gas is not homogeneous.

Gunnarsson and Jones[43] have shown that the exchange energy is insensitive to the *shape* of the Fermi hole but very sensitive to the *size* of the hole. Therefore, it is not surprising that, even though the shape of the FEL Fermi hole is not defined, the GX-FEL exchange density gives very good total energies.

C. Eigenvalues

Table V compares the eigenvalues of argon calculated using the GX-FEL, GX-W, and GX-GWB schemes with the HF eigenvalues. Most of the GX-GWB eigenvalues are *negligibly* more negative, and hence closer to the HF eigenvalues than the GX-FEL and GX-W eigenvalues. The GX-FEL 1*s* eigenvalue is negligibly more negative than the GX-W and GX-GWB 1*s* eigenvalues. However, overall there is no significant difference between the LSD GX eigenvalues compared to the HF ones regardless of the Fermi hole used to calculate them. Calculations on all the atoms helium to krypton have been performed and the same trends have been observed.

Table VI compares the eigenvalues of the GX-FEL, LSD FE, and $X\alpha$ schemes with the HF eigenvalues for the krypton atom. The GX-FEL 1*s* eigenvalue is a considerable improvement over the LSD FE and $X\alpha$ 1*s* eigenvalue. Indeed, calculations on the atoms helium to krypton show that the 1*s* eigenvalues of *all* the atoms are improved.

The remaining orbital eigenvalues are very close to each other; there are only slight differences. The LSD FE eigenvalues are only slightly worse than the others and the GX-FEL and $X\alpha$ eigenvalues are generally very close to each other. Calculations on the atoms helium to krypton give the same trends, however the LSD FE eigenvalues for small atoms are significantly different from the GX-FEL and exchange ones. When compared to the HF eigenvalues, *all the LSD schemes give very bad eigenvalues.* The main reason is the lack of self-interaction correction in the LSD exchange densities.[42]

Since the LSD GX exchange potential is orbital dependent, the eigenfunctions will not be orthogonal to each other once self-consistency has been achieved. Table VII compares the eigenvalues for krypton calculated using orthogonal and nonorthogonal eigenfunctions. The effect of orthogonalizing the eigenfunctions is very small, and hence the eigenvalues in Tables V and VI were obtained without orthogonalizing the eigenfunctions. Furthermore, the orthogonalization procedure would not affect the trends in the calculated eigenvalues.

D. Overall trend

The best overall trend in the eigenvalues and total energies is given by the GX-FEL scheme; while other schemes give better numbers in certain cases, the GX-FEL scheme would give the most reliable results if it were used to cal-

TABLE V. Comparison of the eigenvalues of argon calculated using the GX-FEL, GX-W, and GX-GWB schemes and the HF scheme. All energies are given in eV.

	GX-FEL	GX-W	GX-GWB	HF[a]
$-\varepsilon_{1s}$	3139.9	3139.2	3138.4	3227.4
$-\varepsilon_{2s}$	294.04	295.15	296.25	335.29
$-\varepsilon_{2p}$	230.48	231.59	232.68	260.44
$-\varepsilon_{3s}$	23.42	23.72	24.01	34.76
$-\varepsilon_{3p}$	9.59	9.88	10.16	16.08

[a]Reference 41.

TABLE VI. Comparison of the eigenvalues of krypton calculated using the GX-FEL, LSD FE, and $X\alpha$ schemes and the HF scheme. All energies are given in eV.

	FE	$X\alpha$	GX-FEL	HF[a]
$-\varepsilon_{1s}$	13 874.1	13 891.3	13 996.8	13 959.2
$-\varepsilon_{2s}$	1801.7	1806.4	1805.9	1821.5
$-\varepsilon_{2p}$	1631.1	1636.3	1637.1	1652.8
$-\varepsilon_{3s}$	251.76	253.56	252.12	261.00
$-\varepsilon_{3p}$	191.13	192.89	191.49	200.44
$-\varepsilon_{3d}$	81.97	83.52	82.37	90.42
$-\varepsilon_{4s}$	20.99	21.53	21.67	23.46
$-\varepsilon_{4p}$	8.16	8.61	8.63	10.24

[a]Reference 41.

TABLE VII. Comparison of the GX-FEL eigenvalues, $-\varepsilon$ (GX-FEL) in eV, of krypton calculated using orthogonal and nonorthogonal eigenfunctions.

Orbital	$-\varepsilon$ (GX-FEL) (eV) Orthogonal	Nonorthogonal
1s	13 968.6	13 966.8
2s	1806.4	1805.9
2p	1637.8	1637.1
3s	252.20	252.12
3p	191.58	191.49
3d	82.44	82.37
4s	21.67	21.67
4p	8.63	8.63

culate an *unknown system;* the price to be paid for a negligible improvement in the eigenvalues by using the GWB Fermi hole is a gross overestimation of the total energy.

The $X\alpha$ scheme *could not be used* because it requires a HF calculation to determine the α^{HF} value. It must be emphasized that the LSD GX results were obtained *without the use of adjustable parameters* such as the α^{HF}; B_1, B_2, and α^{lim} are *the same for all atoms.*

VIII. CONCLUSIONS

The LSD GX scheme represents a significant improvement over the $X\alpha$ and LSD FE schemes for two reasons.

(i) Theoretically, the LSD GX scheme is based on the correct normalization conditions for an electron gas and this leads to an exchange potential that does not contain any adjustable parameters. In contrast, the LSD FE scheme contains the homogeneous free-electron gas exchange density which is not a good approximation to the exchange potential for an electron gas around a nucleus of charge Z. The $X\alpha$ scheme tries to correct this deficiency by using an adjustable parameter α that is empirically determined, therefore theoretically this scheme is not suitable for calculations on unknown systems. In addition, *the use of a variable α value can only be theoretically justified using classical arguments* [approximation (49)]. Furthermore, the FEL Fermi-hole parameters were derived without assuming a specific shape of the Fermi hole and the GX-FEL exchange density reduces to the correct LSD FE exchange density as the number of electrons approaches infinity. Therefore, the LSD GX scheme with the FEL parameters gives a completely rigorous exchange density, within the LSD approximation.

(ii) Numerically, the GX-FEL scheme gives the best overall trend in the total energies compared to the HF scheme. Only the GX-FEL 1s eigenvalues are significantly better than the LSD FE and $X\alpha$ 1s eigenvalues when compared to the HF eigenvalues. The eigenvalues of the other orbitals are very much the same, and they are all far from the corresponding HF eigenvalues.

Perdew[44] has proposed a gradient expansion of the Fermi hole with a step function to ensure that the sum rule is obeyed. This scheme successfully corrects the deficiencies of the gradient-expansion technique.[45] The results obtained using the LSD-GX scheme, which contains *no gradient correction* since A_1 and A_2 are constants, are very close to those of Perdew. Therefore, it may be possible to improve the LSD GX scheme using Perdew's step-function scheme.

The LSD GX theory can also be improved by correcting the exchange density for self-interaction,[42] and will be presented in a forthcoming paper. Another forthcoming paper will deal with ionization potentials, electronegativities, and electron affinities using both the LSD GX and the self-interaction corrected LSD GX schemes.

ACKNOWLEDGMENTS

This research was supported by NSERC (Canada). The authors wish to thank the McGill University Computing Centre for providing support and facilities.

APPENDIX A: THE BOUNDARY CONDITIONS OF THE HARTREE-FOCK FERMI HOLE CORRELATION FACTOR

Using the HF exchange-only potential in (7) and (8) and comparing with (11) gives

$$f_{ss}^{\text{HF}}(\mathbf{r},\mathbf{r}')=-[1/n_s(\mathbf{r})n_s(\mathbf{r}')]\times\sum_{i,j}^{s}\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}') \tag{A1}$$

showing that the HF total Fermi hole is the sum of orbital-pair exchange interactions, each an orbital-pair Fermi-hole correlation factor; each electron has a Fermi hole.

As $|\mathbf{r}-\mathbf{r}'|$ approaches zero,

$$f_{ss}^{\text{HF}}(\mathbf{r},\mathbf{r}')=-[1/n_s(\mathbf{r})n_s(\mathbf{r})]\times\sum_{i,j}^{s}\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r})\phi_j(\mathbf{r})\phi_i(\mathbf{r})\ . \tag{A2}$$

Since the electron density is

$$n_s(\mathbf{r})=\sum_{i}^{s}|\phi_i(\mathbf{r})|^2\ , \tag{A3}$$

summing (A2) over j gives (34) exactly, the boundary condition the unspecified *single-particle* Fermi-hole correlation factor had to satisfy. If (A2) is summed over *both* i and j, this gives (12) exactly, the boundary condition the unspecified *total* Fermi-hole correlation factor had to satisfy.

As $|\mathbf{r}-\mathbf{r}'|$ approaches infinity, the exchange terms in (A1) approach zero; the only nonzero terms are the self-interaction terms. Consequently, at this limit, the HF Fermi-hole correlation factor reduces to

$$f_{ss}^{\text{HF,ind}}(\mathbf{r},\mathbf{r}')=-[1/n_s(\mathbf{r})n_s(\mathbf{r}')]\times\sum_{i}^{s}\phi_i^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_i(\mathbf{r}')\ , \tag{A4}$$

which is rewritten as

$$f_{ss}^{\text{HF,ind}}(\mathbf{r},\mathbf{r}')=-\sum_{i}^{s}n_i(\mathbf{r})n_i(\mathbf{r}')/n_s(\mathbf{r})n_s(\mathbf{r}')\ . \tag{A5}$$

Decomposing (A4) into individual electron boundary conditions gives boundary condition (35) exactly; the boundary condition that the unspecified *single-particle* Fermi correlation factor had to satisfy. The only way to derive the corresponding boundary condition for the *total* Fermi-hole correlation factor is to assume that at large interelectronic distances the electrons act like *classical point charges* and hence approximation (49) can be used. This will give boundary condition (13). Therefore, as in the case of the LSD GX exchange, the HF exchange does *not* include any classical approximations.

Substituting the total HF Fermi-hole correlation factor into the sum rule given by (14) gives

$$[1/n_s(\mathbf{r})]\sum_{i,j}^{s}\int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})d\mathbf{r}'=1\ , \tag{A6}$$

which is rewritten as

$$\sum_{i,j}^{s}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\int \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')d\mathbf{r}'=n_s(\mathbf{r})\ . \tag{A7}$$

The one-electron wave functions can be assumed orthonormal with no loss of generality, and therefore, the only nonzero integrals are the self-interaction ones. Furthermore, these integrate to 1 for singly occupied spin orbitals, leaving

$$\sum_{i}^{s}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})=n_s(\mathbf{r})\ , \tag{A8}$$

which is exactly the definition of the electron density given by (A3). Therefore, the total HF Fermi-hole correlation factor satisfies the sum rule (14). Removing the summations over i from (A7) and (A8) shows that the single-particle HF Fermi-hole correlation factor satisfies the single-particle sum rule (37).

---

[1] P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).

[2] R. Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1954).

[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[4] F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Lett. **72**, 807 (1969).

[5] K. Schwarz and F. Herman, J. Phys. (Paris) Colloq. Suppl. **33**, C3-277 (1972).

[6] F. Herman, I. B. Ortenburger, and J. P. Van Dyke, Int. J. Quantum. Chem. **3S**, 827 (1970).

[7] J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4, Chap. 1.

[8] I. Lindgren, Phys. Rev. Lett. **19**, 382 (1965).

[9] I. Lindgren, Ark. Fys. **31**, 59 (1966).

[10] E. A. Kmetko, Phys. Rev. A **1**, 37 (1970).

[11] J. H. Wood, Int. J. Quantum Chem. **3S**, 747 (1970).

[12] M. Berrondo and O. Goscinski, Phys. Rev. **184**, 10 (1969).

[13] L. J. Sham, Phys. Rev. A **1**, 969 (1970).

[14] J. C. Slater and K. H. Johnson, Phys. Rev. B **5**, 844 (1972).

[15] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[16] J. C. Slater, Ref. 7, Chap. 2.

[17] M. S. Gopinathan, M. A. Whitehead, and R. Bogdanovic, Phys. Rev. A **14**, 1 (1976).

[18] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[19] S. Manoli and M. A. Whitehead, *Local Density Approximations in Quantum Chemistry and Solid State Physics*, edited by J. P. Dahl and J. Avery (Plenum, New York, 1984), p. 805.

[20] W. Lees, S. Manoli, and M. A. Whitehead, J. Comput. Chem. **6**, 56 (1985).

[21] J. L. Gazquez and J. Keller, Phys. Rev. A **16**, 1358 (1977).

[22] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

[23] P. O. Lowdin, Phys. Rev. **97**, 1474 (1955).

[24] W. Kutzelnigg, G. Del Re, and G. Berthier, Phys. Rev. **172**, 49 (1968).

[25] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[26] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[27] The $\alpha_{\rm sp}^{\rm HF}$ of Manoli and Whitehead[19,20] were from making the $X\alpha$ total energy equal the HF ground-state total energy while the $\alpha^{\rm HF}$ of Schwarz[15] were from making the $X\alpha$ total energy equal a HF total energy averaged over multiplet states, the Hyper-Hartree-Fock theory of Mann [see. J. B. Mann, Los Alamos Scientific Laboratory Report No. LA3690, 1967 (unpublished); J. C. Slater, Ref. 16]. These techniques give the same α values for closed-shell atoms and slightly different α values for open-shell atoms. Schwarz used his α values for non-spin-polarized calculations; those of Manoli and Whitehead are more suitable for spin-polarized calculations.

[28] At very large interelectronic distances, if N_s electrons of spin s behave like *classical point charges* with a probability distribution given by $n_s(\mathbf{r})$, the probability density of finding the ith electron at the point $\mathbf{r}$ (where $\mathbf{r}$ is a dummy variable) is (Ref. 24) $n_i(\mathbf{r})=1/N_s n_s(\mathbf{r})$ if the electrons are indistinguishable. Under these conditions, the only interelectronic interactions that need be taken into account are the Coulomb and self-interaction repulsions. Equation (13) removes the self-interaction from the Coulomb term describing the repulsion of *independent*, i.e., classical, electrons. Therefore, the use of (49) is a classical approximation to the correct quantum-mechanical probability densities. The use of electronic wave functions in (49) to construct the probability densities shows clearly that this approximation is *not correct.*

[29] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[30] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. II, Appendix 22.

[31] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[32] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975).

[33] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

[34] D. C. Langreth and J. P. Perdew, Solid State Commun. **31**, 567 (1979).

[35] D. C. Langreth and J. P. Perdew, Phys. Rev. B **21**, 5469 (1980).

[36] J. C. Slater and J. H. Wood, Int. J. Quantum Chem. Suppl. **4**, 3 (1971).

[37] J. F. Janak, Phys. Rev. B **18**, 7105 (1978).

[38] K. Schwarz, J. Phys. B **11**, 1339 (1978).

[39] L. J. Bartolotti, S. R. Gadre, and R. G. Parr, J. Am. Chem. Soc. **102**, 2945 (1980).

[40] S. Manoli and M. A. Whitehead, J. Chem. Phys. **81**, 841 (1984).

[41] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[42] S. Manoli and M. A. Whitehead (unpublished). This is an extension of the present work which will deal with the self-interaction correction to the LSD GX theory. This paper will discuss in detail the role of the self-interaction in the various LSD theories.

[43] O. Gunnarsson and R. O. Jones, *Local Density Approximations in Quantum Chemistry and Solid State Physics,* edited by J. P. Dahl and J. Avery (Plenum, New York, 1984), p. 229.

[44] J. P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985).

[45] J. P. Perdew, D. C. Langreth, and V. Sahni, Phys. Rev. Lett. **38**, 1030 (1977).