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### Exchange holes in inhomogeneous systems: A coordinate-space model

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We present a new coordinate-space model of spherically averaged exchange-hole functions in inhomogeneous systems that depends on local values of the density and its gradient and Laplacian, and also the kinetic energy density. Our model is completely nonempirical, incorporates the uniform-density electron gas and hydrogenic atom limits, and yields the proper  $1/r$  asymptotic exchange potential in finite systems. Comparisons of model exchange energies, holes, and potentials with exact Hartree-Fock results in selected atoms are very encouraging.

#### I. INTRODUCTION

The Hartree-Fock approximation is the foundation of theoretical atomic, molecular, and solid-state physics. Unfortunately, its most interesting feature, the Hartree-Fock exchange energy, is rather unwieldy from a computational point of view. Consequently, a long history of simple approximations to the Hartree-Fock exchange energy has developed, beginning with the early work of Dirac<sup>1</sup> and Slater,<sup>2</sup> and progressing to current efforts (see, for example, Ref. 3 and references therein) in the framework of the so-called "density-functional" theory.<sup>4</sup>

Reasonably accurate exchange approximations depending only on local properties of a system are desirable, and the simplest such approximation is the well-known and popular "local-density" (or, more precisely, local spin-density) approximation, hereafter referred to as the LDA. The LDA is based on a model of the exchange or Fermi "hole" function inspired by the uniform-density electron gas. Though the LDA works surprisingly well overall, it has recently been emphasized by Sahni *et al.*<sup>5</sup> and by Ziegler and Tschinke<sup>6</sup> that the uniform gas model fails to reproduce, even qualitatively, important features of exact spherically averaged exchange holes in atomic systems.

Corrections to the uniform gas model have been proposed by the present author,<sup>7</sup> by Perdew,<sup>8</sup> and most recently by Ziegler and Tschinke.<sup>6</sup> Each of these models suffers inadequacies, however, which are eliminated in the present work. Our own earlier model of Ref. 7, for instance, incorrectly allows negative exchange-hole values, while, on the other hand, the models of Perdew<sup>8</sup> and of Ziegler and Tschinke<sup>6</sup> are analytically discontinuous.

In the present work we introduce a new, analytically continuous exchange-hole model that satisfies all (we think) currently known constraints on exchange-hole

functions, including non-negativity, short-range behavior, and normalization constraints. Our model also gives exact results for both the uniform electron gas and hydrogenic atom limits, and yields the correct  $1/r$  asymptotic dependence of the exchange potential in finite systems. Moreover, our model is completely nonempirical and yet generates exchange energies in very good agreement with exact Hartree-Fock results in typical atomic systems.

In Sec. II we define the so-called exchange or Fermi hole function on which Hartree-Fock theory is based and then summarize its properties. Much of this discussion recalls previously published work<sup>7</sup> but is repeated here for convenience. In Sec. III we consider the special case of the hydrogenic atom and derive an explicit expression for the spherically averaged exchange-hole function in this simple but interesting case. The resulting hydrogenic expression is then used as a model for hole functions in arbitrary inhomogeneous systems. Unfortunately, we do not quite attain the correct uniform gas limit, but a simple adjustment of our model described in Sec. IV satisfactorily resolves this problem. In Sec. V model exchange holes are compared with their exact spherically averaged counterparts for atoms Ne and Ar at reference points reflecting a wide spectrum of qualitative behavior. Also, plots of exchange potentials for atoms He, Ne, and Ar are presented. Finally, in Sec. VI, we conclude with comments on advantages and disadvantages of the present model. Note that atomic units are employed throughout this paper.

#### II. EXCHANGE ENERGIES, HOLES, AND POTENTIALS

The material in this section is well known and has been discussed previously in Ref. 7. For convenience, however, the salient properties of Hartree-Fock exchange ener-

gies, holes, and potentials are reviewed in the following paragraphs.

The total Hartree-Fock exchange energy  $E_X$  consists of two distinct parts, one for each spin  $\sigma$ , as follows:

$$E_X = \sum_{\sigma} E_{X\sigma}, \quad (1)$$

where  $E_{X\sigma}$  is expressible in the form

$$E_{X\sigma} = -\frac{1}{2} \int \int \frac{|\rho_{1\sigma}(1,2)|^2}{r_{12}} d1 d2 \quad (2)$$

and  $\rho_{1\sigma}(1,2)$  is the one-body spin-density matrix of the Hartree-Fock determinant:

$$\rho_{1\sigma}(1,2) = \sum_i^{\sigma} \psi_i^*(1) \psi_i(2), \quad (3)$$

with summation over orbitals of  $\sigma$  spin. It is useful for purposes of physical interpretation to rewrite Eq. (2) in the form

$$E_{X\sigma} = -\frac{1}{2} \int \int \frac{\rho_{\sigma}(1) \rho_{X\sigma}(1,2)}{r_{12}} d1 d2, \quad (4)$$

where  $\rho_{\sigma}(1)$  is the total  $\sigma$ -spin density at "reference" point 1, and  $\rho_{X\sigma}(1,2)$  is called the exchange or Fermi hole function. This exchange-hole function is defined by

$$\rho_{X\sigma}(1,2) = \frac{|\rho_{1\sigma}(1,2)|^2}{\rho_{\sigma}(1)} \quad (5)$$

and we note that its value is always *non-negative*.

In addition to non-negativity, further hole properties are easily deduced. From the definitions of Eqs. (3) and (5), its value at the reference point 1 is given by

$$\rho_{X\sigma}(1,1) = \rho_{\sigma}(1) \quad (6)$$

and, from the orthonormality of the Hartree-Fock orbitals, we deduce the following normalization condition:

$$\int \rho_{X\sigma}(1,2) d2 = 1 \quad (7)$$

at any reference point. These simple conditions are, in fact, quite restrictive, accounting for the remarkable success of approximate exchange theories, such as the  $X\alpha$  or Hartree-Fock-Slater theory,<sup>9</sup> which employ them.

The Coulomb potential generated by the exchange hole at its reference point 1,

$$U_{X\sigma}(1) = - \int \frac{\rho_{X\sigma}(1,2)}{r_{12}} d2, \quad (8)$$

is hereafter referred to as the *exchange potential*, and is related to the total exchange energy by

$$E_{X\sigma} = \frac{1}{2} \int \rho_{\sigma} U_{X\sigma} d^3r. \quad (9)$$

Observe that the exchange potential and hence the exchange energy depends only on the spherical average of the exchange hole about the reference point 1, and we shall therefore conveniently and without loss of rigor restrict ourselves to spherically symmetric exchange-hole models.

Notice, also, that the exchange potential  $U_{X\sigma}$  considered in this paper is *not* the variational potential

$$V_{X\sigma} = \frac{\delta E_{X\sigma}}{\delta \rho_{\sigma}} \quad (10)$$

appearing in the single-particle "Kohn-Sham" equation of density-functional theory.<sup>4</sup> We are here concerned with exchange holes and exchange energies only, and will consider variational self-consistency in future work.

The exchange hole in the important special case of the uniform-density or "homogeneous" electron gas is spherically symmetric and reference point independent and is given by

$$\rho_{X\sigma}^{\text{hom}}(s) = 9\rho_{\sigma} \frac{j_1^2(k_F s)}{(k_F s)^2}, \quad (11a)$$

where  $j_1(x)$  is the spherical Bessel function of first order,  $s$  denotes distance from the reference point, and  $k_F$  is the Fermi momentum

$$k_F = (6\pi^2 \rho_{\sigma})^{1/3}. \quad (11b)$$

If the spherically averaged exchange hole at any given reference point  $\mathbf{r}$  in an inhomogeneous system is modeled by the above uniform gas expression, with the local value of  $\rho_{\sigma}(\mathbf{r})$  inserted in Eq. (11), then the following so-called local-density approximation is obtained:

$$U_{X\sigma}^{\text{LDA}} = -3 \left[ \frac{3}{4\pi} \right]^{1/3} \rho_{\sigma}^{1/3}, \quad (12a)$$

$$E_{X\sigma}^{\text{LDA}} = -\frac{3}{2} \left[ \frac{3}{4\pi} \right]^{1/3} \int \rho_{\sigma}^{4/3} d^3r, \quad (12b)$$

which is the basis of the previously mentioned Hartree-Fock-Slater or  $X\alpha$  exchange theory.<sup>9</sup> The LDA gives reasonably good atomic exchange energies. In Table I, for instance, we present total exchange energies of the noble-gas atoms He through Rn and find that the LDA gives a rms deviation from exact Hartree-Fock results (obtained from the orbitals of Clementi and Roetti<sup>10</sup> and McLean and McLean<sup>11</sup>) of only 8%, quite respectable for such a simple theory.

TABLE I. Exchange energies of noble-gas atoms (a.u.).

Atom	Exact	LDA <sup>a</sup>	This work $\gamma=1$	This work $\gamma=0.80$
He	-1.026	-0.884	-1.039	-1.039
Ne	-12.11	-11.03	-12.19	-12.33
Ar	-30.19	-27.86	-30.09	-30.55
Kr	-93.89	-88.62	-92.88	-94.77
Xe	-179.2	-170.6	-176.4	-180.3
Rn	-387.5	-373.0	-380.0	-389.2
$\Delta^b$		8.2%	1.3%	1.1%

<sup>a</sup>LDA: local-density approximation.

<sup>b</sup> $\Delta$ : rms relative deviation from exact results.

However, despite the success of the LDA in estimating energies, the uniform gas exchange hole itself fares very poorly in a reference point by reference point comparison with exact spherically averaged hole functions in typical atomic systems (see Sahni *et al.*<sup>5</sup> or Ziegler and Tschinke<sup>6</sup>). In fact, the discrepancies are quite serious, with important qualitative features such as nonlocal maxima at  $s \neq 0$  noticeably absent from the LDA model. Improved models which better reproduce the observed features of exact spherically averaged atomic hole functions are therefore required.

Improved coordinate-space models have indeed been proposed by the present author,<sup>7</sup> by Perdew,<sup>8</sup> and by Ziegler and Tschinke.<sup>6</sup> In particular, our previous model of Ref. 7 is founded on the following Taylor expansion of the exact spherically averaged exchange hole near the reference point:

$$\rho_{X\sigma}(\mathbf{r}, s) = \rho_\sigma + \frac{1}{6}(\nabla^2 \rho_\sigma - 2\gamma D_\sigma)s^2 + \dots, \quad (13a)$$

where the arguments  $(\mathbf{r}, s)$  denote spherical average on a shell of radius  $s$  about the reference point  $\mathbf{r}$  and where

$$D_\sigma = \tau_\sigma - \frac{1}{4} \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma}, \quad (13b)$$

and  $\tau_\sigma$  is the positive definite kinetic energy density defined by

$$\tau_\sigma = \sum_i^\sigma |\nabla \psi_i|^2. \quad (13c)$$

A parameter  $\gamma$  with nominal value  $\gamma=1$  is included in Eq. (13a) for later use (see Sec. IV). The model of the present work relies largely on the second-order term of Eq. (13a), as did its predecessor of Ref. 7, and is described in Sec. III.

### III. THE PRESENT MODEL

Conventional treatments of exchange holes begin with the uniform electron gas as the prototypical system. Here, however, we take a rather different approach and begin with the special case of the hydrogenic atom. The spherically averaged exchange-hole function in this simple one-electron case is given by

$$\rho_X^H(\mathbf{r}, s) = \frac{1}{4\pi} \int \rho_H(\mathbf{r} + \mathbf{s}) d\Omega_s, \quad (14)$$

where  $d\Omega_s$  denotes integration on a spherical shell of radius  $s$  centered at the reference point  $\mathbf{r}$  and  $\rho_H$  is the normalized hydrogenic  $1s$  orbital density,

$$\rho_H(r) = \frac{\alpha^3}{8\pi} e^{-\alpha r}, \quad (15)$$

with  $\alpha$  depending on nuclear charge  $Z$  in a manner that is unimportant in the present work. Evaluation of the spherical average in Eq. (14) is a straightforward exercise with the following result:

$$\rho_X^H(r, s) = \frac{\alpha}{16\pi r s} [(\alpha|r-s|+1)e^{-\alpha|r-s|} - (\alpha|r+s|+1)e^{-\alpha|r+s|}], \quad (16)$$

where  $r$  denotes distance of the reference point from the nucleus (note that its *angular* position is irrelevant),  $s$  denotes distance from the reference point itself, and  $|r-s|$  is the absolute value of their difference.

Though Eq. (16) has physical significance as the exchange hole of a hydrogenic atom, we shall view this expression somewhat more abstractly in the present work. Let us view Eq. (16) as a *purely mathematical* object, namely, as a function of the independent variable  $s$  depending parametrically on two constants  $\alpha$  and  $r$ . To emphasize this purely mathematical interpretation, we write

$$\rho_X^H(a, b; s) = \frac{a}{16\pi b s} [(a|b-s|+1)e^{-a|b-s|} - (a|b+s|+1)e^{-a|b+s|}], \quad (17)$$

where  $a$  and  $b$  are now parameters assumed to have positive value only and not to be accorded any physical significance. The original definition of Eq. (14) ensures non-negativity and also unit normalization in the sense

$$4\pi \int_0^\infty \rho_X^H(a, b; s) s^2 ds = 1 \quad (18)$$

for arbitrary positive  $a$  and  $b$ . Furthermore, as we shall see below, it is possible to force Eq. (17) to reproduce the second-order Taylor expansion of Eq. (13) at *any* reference point in *any* inhomogeneous system by suitable choice of  $a$  and  $b$ . Therefore a very interesting, general purpose exchange model is at hand.

Imposing the condition of Eq. (6), corresponding to the zeroth-order Taylor term, yields the following constraint on  $a$  and  $b$ :

$$a^3 e^{-ab} = 8\pi \rho_\sigma. \quad (19)$$

The second-order term yields the additional constraint

$$a^2 b - 2a = 6b Q_\sigma / \rho_\sigma, \quad (20a)$$

where

$$Q_\sigma = \frac{1}{6}(\nabla^2 \rho_\sigma - 2\gamma D_\sigma). \quad (20b)$$

Then, defining  $x = ab$ , we find after fairly simple algebra that  $x$  satisfies the nonlinear one-dimensional (1D) equation

$$\frac{x e^{-2x/3}}{(x-2)} = \frac{2}{3} \pi^{2/3} \frac{\rho_\sigma^{5/3}}{Q_\sigma}, \quad (21)$$

after solution of which  $b$  is given by

$$b^3 = \frac{x^3 e^{-x}}{8\pi \rho_\sigma} \quad (22)$$

and, of course,  $a$  is given by  $a = x/b$ . Inspection of Eq. (21) reveals that a unique and positive root  $x$  exists under all conditions, though a simple algebraic solution is not possible. Nevertheless, we have implemented a reliable and efficient Newton-Raphson algorithm<sup>12</sup> for automatic solution of Eq. (21) for arbitrary input densities and gradients.

With parameters  $a$  and  $b$  (or, equivalently,  $x$  and  $b$ ) thus suitably fixed at any given reference point, the ex-

change potential of Eq. (8) is given by

$$U_{X\sigma} = -4\pi \int_0^\infty \rho_X^H(a, b; s) s ds \\ = -(1 - e^{-x} - \frac{1}{2} x e^{-x}) / b \quad (23)$$

and the total exchange energy is finally obtained by the integration of Eq. (9) over all reference points. The present model is clearly local in the sense that the exchange potential is completely determined by  $\rho_\sigma$ ,  $\nabla\rho_\sigma$ ,  $\nabla^2\rho_\sigma$ , and  $\tau_\sigma$  at the reference point *only*. Despite this locality, however, it can be shown that for reference points  $r$  very far from a finite system, our theory yields the asymptotic potential

$$\lim_{r \rightarrow \infty} U_{X\sigma} = -\frac{1}{r}, \quad (24)$$

which is *exactly* the expected result (see, for example, Ref. 3). This important feature of the present work will be further discussed in Sec. V.

#### IV. UNIFORM GAS LIMIT

Of some interest, of course, is the limit of the uniform electron gas, obtained by setting  $\nabla\rho_\sigma=0$ ,  $\nabla^2\rho_\sigma=0$ , and

$$\tau_\sigma = \frac{3}{5} (6\pi^2)^{2/3} \rho_\sigma^{5/3}. \quad (25)$$

The present model, given its hydrogenic roots, does *not* yield the exact LDA exchange potential, Eq. (12a), in the homogeneous limit. Rather, the correct  $\rho_\sigma^{1/3}$  functional dependence is attained, but with a coefficient 2.6% too small. The problem is graphically illustrated in Fig. 1(a), where the LDA hole function of Eq. (11) is compared with the homogeneous limit of the present model. We see that our hydrogenic model gives a reasonable first approximation, but obviously cannot regenerate the LDA exactly.

Fortunately, a minor adjustment of our theory recovers the exact homogeneous *potential* at least. It is, in fact, for this purpose that parameter  $\gamma$  was introduced previously in Eq. (13a). Though its "proper" value is, of course, unity, we find that the uniform gas exchange potential, Eq. (12a), is precisely recovered by substitution of the slightly smaller value

$$\gamma = 0.80. \quad (26)$$

The corresponding "adjusted" hole function is compared with the LDA in Fig. 1(b), and we note even visually a slight improvement with respect to the original  $\gamma=1$  model of Fig. 1(a). This adjustment of  $\gamma$  in effect compensates for shape deficiencies of our hydrogenic model in the homogeneous limit, while sacrificing some accuracy at short range (i.e., in the Taylor expansion near the reference point). Detailed graphical analyses in Sec. V indicate, however, that a reasonable compromise has been achieved.

Notice, also, that  $\gamma$  adjustment has no effect on *hydrogenic* systems, nor any system locally dominated by the spin-orbital of a single electron (i.e., localized spin pairs), thanks to the fact that the function  $D_\sigma$  of Eq. (13b) vanishes identically in one-electron systems.  $D_\sigma$  vanishes

asymptotically in any finite system as well, and therefore the exact  $1/r$  asymptotic behavior, Eq. (24), of the exchange potential is also unaffected by adjustment of  $\gamma$ . Our  $\gamma$  parametrization has, in fact, been carefully designed to preserve these important properties while regaining the uniform gas potential limit.

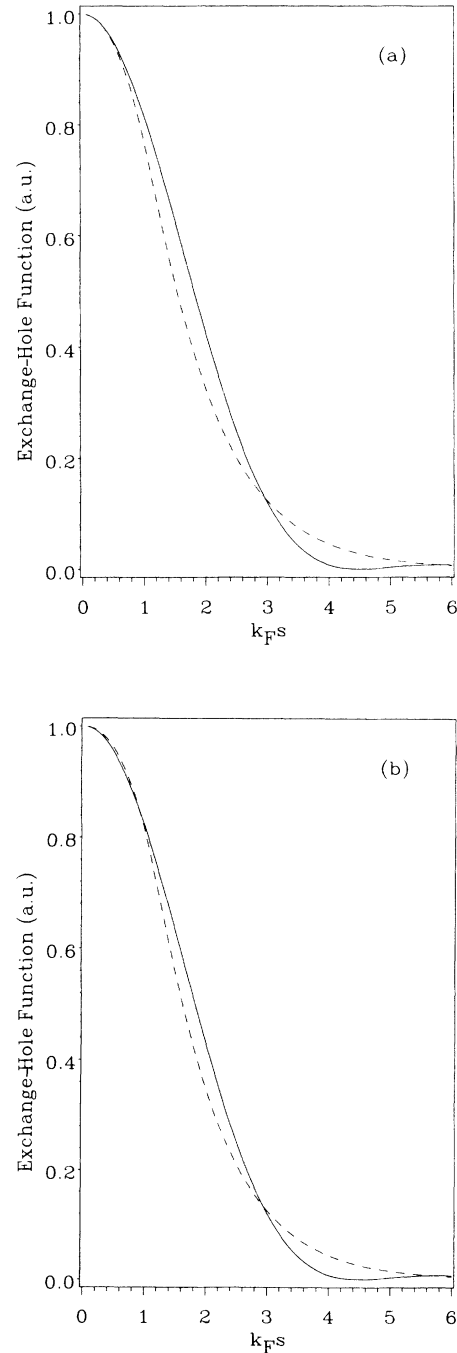


FIG. 1. Uniform electron gas exchange hole ( $\rho_\sigma=1$ ). —, exact; - - -, present model. (a)  $\gamma=1$ . (b)  $\gamma=0.80$ .

### V. APPLICATION TO ATOMIC SYSTEMS

The present model has been applied to the calculation of exchange energies of the noble-gas atoms He through Rn, with the Hartree-Fock orbitals of Clementi and Roetti<sup>10</sup> and McLean and McLean,<sup>11</sup> and results are presented in Table I. Data for both the  $\gamma=1$  and the adjusted model  $\gamma=0.80$  are included. In either case, the present model performs significantly better than the LDA, with rms deviations from exact exchange energies of the order 1% for the present work and 8% for the LDA. However, as a consequence of its incorrect homogeneous limit, the  $\gamma=1$  model underestimates exact Hartree-Fock results in

the case of large  $Z$  (i.e., atomic systems become increasingly "electron-gas-like" as atomic number increases). The  $\gamma=0.80$  model, though it slightly overestimates exchange energies at low  $Z$ , is clearly preferable in the high- $Z$  limit.

In Figures 2(a)–2(e), exchange-hole functions ( $\gamma=0.80$ ) are graphically compared with their exact, spherically averaged Hartree-Fock counterparts at several representative reference points in the Ne atom. These figures display a variety of qualitative features. With reference point  $R$  exactly at the nucleus [ $R=0$ , Fig. 2(a)] the exchange hole has simple exponential appearance with a nuclear cusp at  $s=0$ . Due to the hydro-

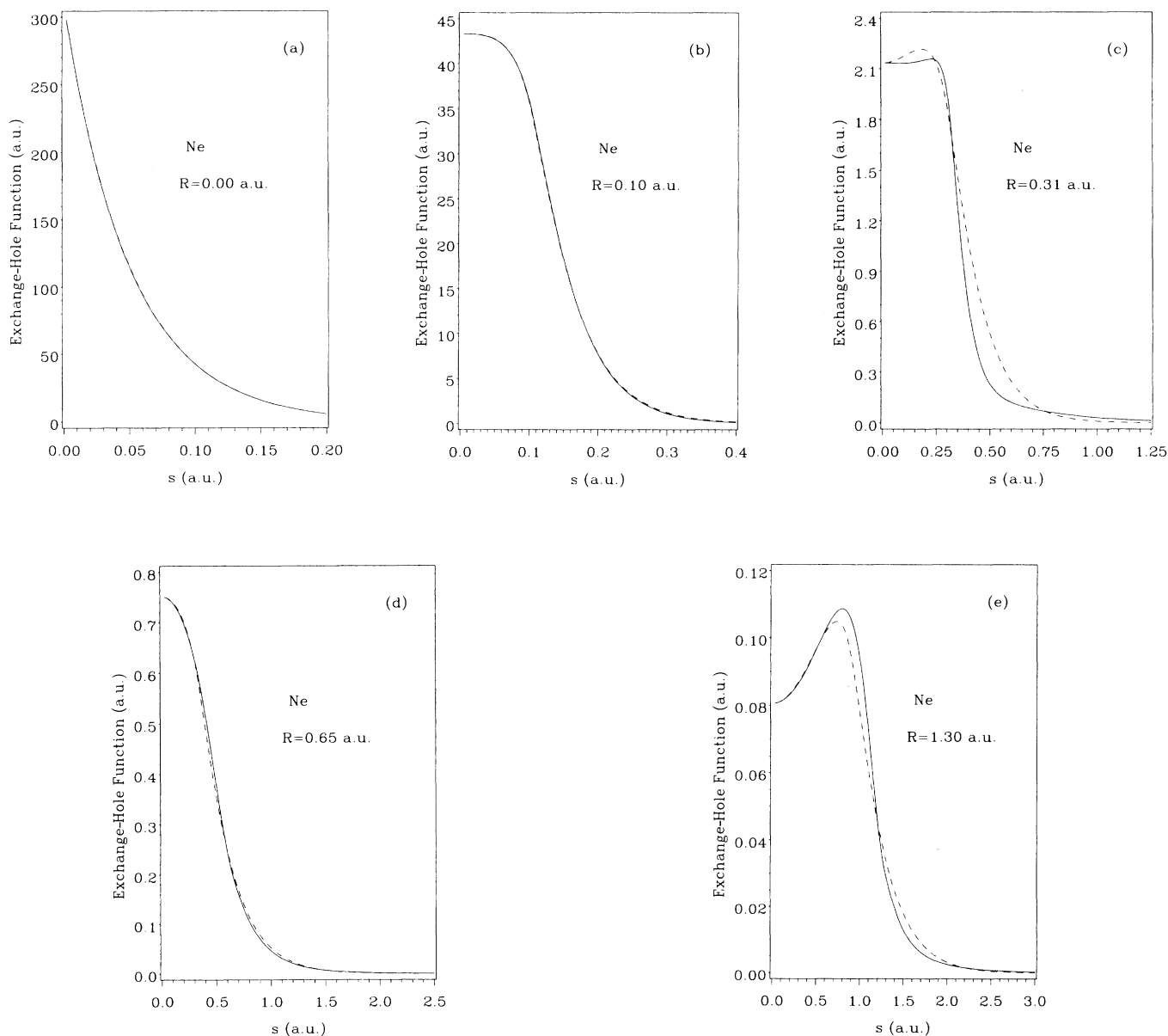


FIG. 2. Exchange hole in neon at various reference points  $R$ : —, exact; ---, present model. (a) At the atomic nucleus  $R=0.00$ ; (b) within the  $1s$  core  $R=0.10$ ; (c) between core and valence shells  $R=0.31$ ; (d) within valence shell  $R=0.65$ ; (e) outer valence region  $R=1.30$ .

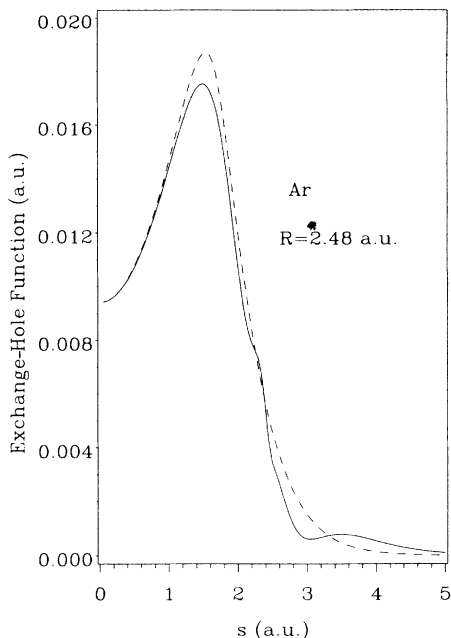


FIG. 3. Exchange hole in argon at  $R=2.48$ . —, exact; ---, present model.

genic nature of the  $1s$  core orbitals, the model and exact holes are virtually indistinguishable. Within the  $1s$  shell [ $R=0.10$ , Fig. 2(b)] the exchange hole assumes a Gaussian-like appearance, and, again, our model hole matches the exact hole extremely well. In the region between core and valence shells [ $R=0.31$ , Fig. 2(c)] a new feature which *cannot* be emulated by the LDA appears, namely, a nonlocal maximum at  $s \neq 0$ . The present model

reproduces this nonlocal maximum reasonably well. Within the valence shell [ $R=0.65$ , Fig. 2(d)] Gaussian-like behavior reappears, but, in the asymptotic region [ $R=1.30$ , Fig. 2(e)], holes with a nonlocal maximum ultimately prevail.

Also, we plot in Fig. 3 the exchange hole at reference point  $R=2.48$  in Ar to further illustrate the typical appearance of exchange-hole functions in asymptotic regions. Figure 3 is dominated by a characteristic nonlocal maximum attributable to the fact that the Fermi hole in a finite system remains "attached" to the system as the reference point is far removed (hence the  $1/r$  behavior of the asymptotic exchange potential). Generalization of this interpretation to individual atomic shells accounts for the nonlocal maximum in Fig. 2(c) as well. Also notable in Fig. 3 is considerable structure near the position of the nucleus (i.e.,  $s=2.48$ ) which, though of minor importance, can obviously not be reproduced by the present model.

Finally, exchange potentials  $U_{X\sigma}$  are plotted in Figs. 4(a)–4(c) for the atoms He, Ne, and Ar, respectively. Agreement between the potentials of the present model ( $\gamma=0.80$ ) and exact potentials (obtained by numerical integration) is very good, even with respect to detailed shell structure. Observe also that the correct  $1/r$  asymptotic limit of the present model is verified in these figures.

## VI. CONCLUSIONS

We have introduced in this paper a new, local exchange-hole model with significant advantages over previous coordinate-space models.<sup>6–8</sup> Well-known conditions on value at the reference point, normalization, and non-negativity are all satisfied. Also, we obtain by design both exact hydrogenic atom and exact uniform

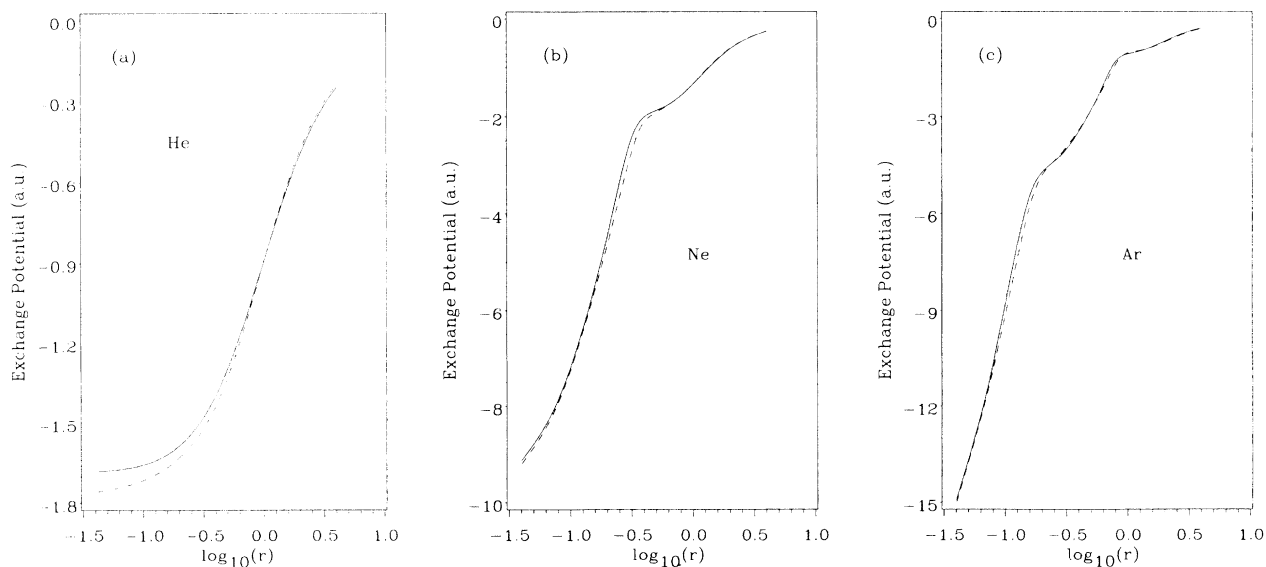


FIG. 4. Atomic exchange potentials. —, exact; ---, present model. (a) He, (b) Ne, (c) Ar.

electron gas exchange potentials in the case  $\gamma=0.80$ . Short-range quadratic behavior of the exact spherically averaged exchange-hole function is also reproduced (only approximately, however, in the case  $\gamma=0.80$ ) and thus our model nicely simulates the various qualitative features observed in Figs. 2 and 3. Finally, the proper  $1/r$  asymptotic limit of the exchange potential in any finite system is guaranteed.

A disadvantage of the present model is the role of the kinetic energy density  $\tau_\sigma$  which enters through the Taylor expansion of Eq. (13). Therefore our theory is not explicitly a pure density-functional theory, and derivation of the associated Kohn-Sham variational potential, to be undertaken in future work, will be somewhat complicated. Furthermore, our theory is not expressible in simple algebraic form since Eq. (21) has no elementary solution. Nevertheless, our automatic Newton-Raphson solution algorithm alleviates this problem. Finally, we note that

the present exchange energies of Table I are not as accurate as obtained by recent semiempirical fits (see, for example, Ref. 3). However, the present results are based on a sound, completely nonempirical exchange-hole model, and are therefore very satisfying from a theoretical perspective.

We hope that this work, along with analogous recent work on coordinate-space correlation models,<sup>13</sup> will inspire further efforts to elucidate the nature of exchange-correlation hole functions in inhomogeneous systems.

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