Why semilocal functionals work: Accuracy of the on-top pair density and importance of system averaging

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Gradient-corrected density functionals provide a common tool for electronic structure calculations in quantum chemistry and condensed matter physics. This article explains why local and semilocal approximations work for the exchange-correlation energy. We demonstrate the high accuracy of the local spin-density (LSD) approximation for the on-top pair density, which provides the missing link between real atoms and molecules and the uniform electron gas. Special attention is devoted to the leading correction to exchange in the high-density (or weakly correlated) limit. We give an improved analytic expression for the on-top pair density in the uniform electron gas, calculating its spin-polarization dependence exactly in the high-density limit. We find the exact form of the gradient expansion for the on-top pair density, using Levy's scaling of the interacting wave function. We also discuss the importance of system averaging, which unweights spatial regions where the density varies most rapidly. We show how the depth of the on-top hole correlates with the degree of locality of the exchange-correlation energy. Finally, we discuss how well fully nonlocal approximations (weighted-density, self-interaction correction, and hybrid-exchange) reproduce the on-top hole. © *1998 American Institute of Physics.* [S0021-9606(98)30534-6]

I. INTRODUCTION

A fundamental aim of electronic structure theory is to find the ground-state energy E of N electrons in an external potential. Traditional quantum chemical methods directly approximate the wave function.[1] Kohn–Sham spin-density functional theory provides an alternative language,[2,3] in which a self-consistent solution of a one-electron Schrödinger equation yields both E and the electron spin-densities, $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$. Kohn–Sham theory is exact in principle,[4] but in practice the exchange-correlation energy as a functional of the spin densities $E_{XC}[n_\uparrow,n_\downarrow]$ must be approximated. For many years, the local spin-density (LSD) approximation[4,5] has been popular with solid-state physicists,[6] but not with quantum chemists. This nonempirical theory achieves a remarkable moderate accuracy for almost all systems,[6] but that level of accuracy is insufficient for the reliable prediction of atomization energies and heats of reaction.[7,8] Recent semilocal functionals (also called generalized gradient approximations, GGA's)[9–23] have sufficiently improved this accuracy to make Kohn–Sham theory popular in quantum chemistry as a reliable, inexpensive alternative to traditional methods. Simple physical explanations[22] have been given for the character, origins, and consequences of GGA nonlocality. In this paper, we explain why LSD is so reliable, and how this reliability carries over to more accurate functionals such as GGA's.

The local spin-density (LSD) approximation to E_{xc} is

$$E_{XC}^{\mathrm{LSD}}[n_\uparrow,n_\downarrow]=\int d^3r\, n(\mathbf{r})\,\epsilon_{XC}^{\mathrm{unif}}[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})], \tag{1}$$

where $\epsilon_{XC}^{\mathrm{unif}}(n_\uparrow,n_\downarrow)$ is the accurately known[24–26] exchange-correlation energy per electron of the uniform electron gas. LSD is exact for an electron gas of uniform spin densities and is highly accurate for systems of slowly varying densities. LSD may be considered the zeroth order term in an expansion in gradients of the density, and much effort has been expended in the calculation of the leading gradient corrections.[27–30] Inclusion of these corrections yields the gradient expansion approximation (GEA),

$$E_{XC}^{\mathrm{GEA}}[n_\uparrow,n_\downarrow]=E_{XC}^{\mathrm{LSD}}[n_\uparrow,n_\downarrow]+\sum_{\sigma\sigma'}\int d^3r \times C_{\sigma\sigma'}[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})]\,\frac{\nabla n_\sigma}{n_\sigma^{2/3}}\cdot\frac{\nabla n_{\sigma'}}{n_{\sigma'}^{2/3}}, \tag{2}$$

Unfortunately, the GEA typically worsens results for real systems relative to LSD, because real atoms and molecules have rapidly varying densities. The reliability of LSD is not due to its accuracy for slowly varying densities, and so must be due to other considerations.

On the other hand, generalized gradient approximations (GGA's)[9–23]

$$E_{XC}^{\mathrm{GGA}}[n_\uparrow,n_\downarrow]=\int d^3r f[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r}),\nabla n_\uparrow,\nabla n_\downarrow], \tag{3}$$

have reduced the LSD atomization energy errors by about a factor of 5, and so have made density functional theory competitive with the traditional methods of quantum chemistry. For very small systems, the latter methods still provide a benchmark of accuracy, but the favorable size-scaling of density functionals is a great practical advantage.[31] Hybrids of GGA's with exact Kohn–Sham exchange energies[32–34]

can further reduce errors. Unfortunately, the GGA integrand f of Eq. (3) is not so well-defined as the LSD integrand of Eq. (1). The Perdew–Wang 1991 (PW91) GGA,[15] its simplified Perdew–Burke–Ernzerhof (PBE) form,[17,22] and certain hybrids[34] were derived without semiempirical parameters. But there are several semiempirical GGA's,[13,14] and hybrids of these with other methods,[32,33] which are also widely used.[8] Some of these are not exact for the uniform gas (e.g., Refs. 14 and 33, see Table II of Ref. 35). Those GGA's for which Eq. (3) reduces to Eq. (1) when the gradient arguments are set to zero have two powerful advantages: (1) They are exact in the limit in which the restricted GGA form can be exact, and (2) they implicitly include the highly accurate LSD approximation to the on-top hole, which makes them reliable for a broad range of real systems.

The aim of this article is to summarize our current understanding of why local (LSD) or semilocal (GGA) density functionals work for real systems. We discuss only those reasons that we believe are of practical importance, and focus on results new to this work. This article is addressed first to the discriminating users of density functionals, who want to understand the rationale and limitations of the method and to make an informed choice among the functionals available. But it is also addressed to the developers of density functionals, in the belief that a deeper understanding of existing functionals can lead to new ones of greater accuracy and reliability. With another factor of 5 improvement, activation barriers and chemical reaction rates could yield to reliable electronic structure calculations.

Note that, while the next evolution in density functionals[36] may go beyond the semilocal form of Eq. (3), we would still advocate performing and reporting the same calculation at several levels—local, semilocal, and fully nonlocal—for the sake of the insight this can provide toward the continuing development of the theory.

II. BACKGROUND AND SUMMARY OF CONCLUSIONS

In this section, we review the current understanding of why LSD is reliable. We define several exact quantities which are standard in spin-density functional theory, and introduce our notation. We use atomic units ($e^2=\hbar=m=1$) throughout.

Following Levy,[37] the ground-state N-electron wave function may be defined as that wave function which yields the exact ground-state spin densities and minimizes the expectation of $\hat{T}+\hat{V}_{ee}$, where $\hat{T}$ is the kinetic-energy operator and $\hat{V}_{ee}$ is the interelectronic repulsion. This definition may be usefully generalized to $\Psi_\lambda[n_\uparrow,n_\downarrow]$, defined as the wave function which yields $n_\uparrow$ and $n_\downarrow$ and minimizes $\hat{T}+\lambda\hat{V}_{ee}$. The coupling-constant λ continuously connects the physical system ($\lambda=1$) with the Kohn–Sham noninteracting system ($\lambda=0$), so that, e.g., $\Psi_{\lambda=0}[n_\uparrow,n_\downarrow]$ is the Kohn–Sham wave function. The pair density at coupling constant λ is

$$P_\lambda(\mathbf{r},\mathbf{r}')=N(N-1)\sum_{\sigma_1\ldots,\sigma_N}\int d^3r_3\cdots\int d^3r_N \times|\Psi_\lambda(\mathbf{r},\sigma_1,\mathbf{r}',\sigma_2\ldots,\mathbf{r}_N,\sigma_N)|^2. \quad (4)$$

For a discussion of the N-representability [Eq. (4)] of model pair densities, see Ref. 38. The exchange-correlation hole density at $\mathbf{r}'$ around an electron at $\mathbf{r}$ for coupling strength λ, $n_{XC,\lambda}(\mathbf{r},\mathbf{r}')$, is defined by

$$P_\lambda(\mathbf{r},\mathbf{r}')=n(\mathbf{r})[n(\mathbf{r}')+n_{XC,\lambda}(\mathbf{r},\mathbf{r}')], \quad (5)$$

where $n(\mathbf{r})$ is the density at $\mathbf{r}$. The exchange-correlation energy is simply $\frac{1}{2}$ the Coulomb attraction between the λ-averaged hole density and the density of the electron it surrounds, i.e.,

$$E_{XC}=\int_0^1 d\lambda E_{XC,\lambda}=\int d^3r\int d^3u\,\frac{n(\mathbf{r})n_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})}{2u}, \quad (6)$$

where $n_{XC}=\int_0^1 d\lambda n_{XC,\lambda}$. This coupling-constant average is needed to include the kinetic contribution to the exchange-correlation energy. LSD may be considered as an ansatz for the hole

$$n_{XC,\lambda}^{\mathrm{LSD}}(\mathbf{r},\mathbf{r}+\mathbf{u})=n_{XC,\lambda}^{\mathrm{unif}}(r_s(\mathbf{r}),\zeta(\mathbf{r});u), \quad (7)$$

where $n_{XC,\lambda}^{\mathrm{unif}}(r_s,\zeta;u)$ is the λ-dependent exchange-correlation hole of a uniform gas of density $n=3/(4\pi r_s^3)$ and relative spin polarization $\zeta=(n_\uparrow-n_\downarrow)/n$, as a function of separation u. [Insertion of Eq. (7) into Eq. (6) yields Eq. (1).]

Gunnarsson and Lundqvist[39,40] long ago pointed out that the exact exchange and correlation holes satisfy sum rules and that, because LSD replaces the exact hole by that of another physical system, it likewise satisfies these relations. They also demonstrated that the complete six-dimensional exchange hole of an atom is not reproduced in detail by its LSD approximation. For example, the LSD hole is spherically symmetric about its electron, while the exact hole is highly asymmetric. However, the energy depends only on the spherical average

$$n_{XC}(\mathbf{r},u)=\int\frac{d\Omega_{\mathbf{u}}}{4\pi}\,n_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u}), \quad (8)$$

which is well-approximated in LSD.

Ziegler, Rauk, and Baerends[41] noted that the exchange hole at $u=0$ is a function of the local spin densities at $\mathbf{r}$ (when the Kohn–Sham wave function is a single Slater determinant), and is, therefore, exact in LSD. This sets the scale for the overall depth of the hole, while the normalization sum rule makes its shape well-approximated by LSD. This fact also helps to explain why LSD is more accurate than the local-density approximation (LDA), even in the absence of an external magnetic field where only the total density is formally needed. Furthermore, Perdew pointed out that the exchange hole is everywhere negative,[11] a condition also satisfied within LSD.

In the present work, we extend several of these ideas. We demonstrate that, even when correlation is included, the LSD approximation to the on-top hole is extremely good (although not exact). This yields an equally accurate cusp at

$u=0$, since LSD also satisfies the electron–electron cusp condition as $u\to 0$. Thus even LSD has an accurate cusp built into its model for the pair density. The difficulty in calculating the on-top hole (as well as slowness of convergence) in wave function methods employing single-particle bases is often attributed to this electron-electron cusp.[42–45]

The density-gradient expansion for the energy of Eq. (2) follows from the gradient expansion for the hole $n_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ around an electron, which has a characteristic structure:[46,47] When the density $n(\mathbf{r})$ varies sufficiently slowly over space, the addition of each term of higher order in ∇ improves the description of the hole close to the electron $(u\to 0)$, while worsening it far away $(u\to\infty)$. There is no gradient correction to the on-top exchange hole $n_X(\mathbf{r},\mathbf{r})$, and we shall argue that the gradient correction to the on-top correlation hole $n_C(\mathbf{r},\mathbf{r})$ is very small. This correction was neglected in the construction of the PW91 GGA via the real-space cutoff of the spurious large-u contributions to the gradient expansion for the hole density.[15]

We also extend the argument that not all details of the hole are well-described in LSD. Define the system average of a function of $\mathbf{r}$ as

$$\langle f\rangle = \frac{1}{N}\int d^3r\, n(\mathbf{r}) f(\mathbf{r}), \tag{9}$$

where $N=\int d^3r\, n(\mathbf{r})$. Then Eq. (6) contains not only a spherical average over the hole, but also a system average. We show that regions of space where LSD is not so good are given little weight in this system average.

We discuss ''abnormal'' systems, in which the LSD on-top hole is not accurate, and we show how the depth of the on-top hole [on the scale of $n(\mathbf{r})$] correlates with the locality of the functional $E_{XC}[n_\uparrow,n_\downarrow]$. Finally, we discuss the on-top hole in approximations other than LSD or GGA. We note that all our conclusions are consistent with the results of recent quantum Monte Carlo calculations of bulk silicon.[48]

III. ACCURACY OF THE LOCAL APPROXIMATION

A. Exact conditions on the on-top hole

As discussed in Sec. II, LSD contains an approximation for the on-top hole, i.e.,

$$n^{\mathrm{LSD}}_{XC,\lambda}(\mathbf{r},\mathbf{r}) = n^{\mathrm{unif}}_{XC,\lambda}(r_s(\mathbf{r}),\zeta(\mathbf{r});u=0). \tag{10}$$

Until recently, it was suspected that the LSD on-top hole density is exact. That possibility is now disproved,[49] but the LSD on-top hole is still remarkably accurate in ''normal'' systems (see below), where the wave function Ψ_λ tends directly to a single Slater determinant as $\lambda\to 0$. To see why, consider the ratio of the on-top hole density to the local density, which is bounded by

$$-1 \leqslant \frac{n_{XC,\lambda}(\mathbf{r},\mathbf{r})}{n(\mathbf{r})} \leqslant -\frac{1}{2}\left[1+\zeta^2(\mathbf{r})\right]. \tag{11}$$

These inequalities hold both exactly and in LSD. The left-hand inequality follows from the non-negativity of the probability in Eq. (4); the limiting value of -1 is achieved both for a fully spin-polarized system $(|\zeta|=1)$ and in the strong-coupling $(\lambda\to\infty)$ or low-density limits.[50] The right-hand inequality is not universal, but holds in LSD and in all normal electronic systems; the limiting value is achieved in the weakly interacting $(\lambda\to 0)$ or high-density limit.

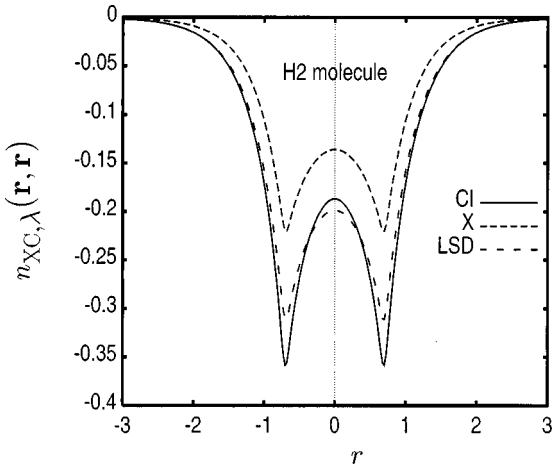

FIG. 1. On-top hole in H_2 molecule $(\lambda=1)$.

Furthermore, the exact interelectronic cusp condition is[42,51,52]

$$\left.\frac{\partial n_{XC,\lambda}(\mathbf{r},u)}{\partial u}\right|_{u=0} = \lambda\left[n(\mathbf{r})+n_{XC,\lambda}(\mathbf{r},\mathbf{r})\right], \tag{12}$$

which is naturally satisfied by the LSD hole. Thus an accurate on-top hole leads to an accurate hole nearby (u close to 0).

B. Importance of being averaged

Given all these bounds and limits, it is possible that $n_{XC,\lambda}(\mathbf{r},\mathbf{r})\approx n^{\mathrm{LSD}}_{XC,\lambda}(\mathbf{r},\mathbf{r})$. Figure 7 of Ref. 35 shows that this is so for the He atom, while Fig. 1 shows that this is also true for the H_2 molecule at equilibrium bond length at $\lambda=1$, except in the region close to the nucleus. It is even true in the classically forbidden tail of the density.

In Fig. 1, the exchange (X) curve is simply $-n(\mathbf{r})/2$, as the system is spin unpolarized. The LSD curve was found using Eqs. (A1) and (A3) of Appendix A for the uniform gas on-top hole. The CI (configuration interaction) curve was constructed from an accurate CI wave function calculation (a modified version of the COLUMBUS program system[53,54] has been used), which recovers 98% of the correlation energy. Given the difficulty of recovering the cusp in such a calculation, we expect that the exact on-top hole is perhaps 10% deeper than found in this CI.

The LSD error in the nuclear region is not as serious as might first appear, as the phase space factor ($4\pi r^2$ for an atom) minimizes its contribution to the system average of Eq. (6). Similarly, inaccuracies at large distances do not contribute heavily, due to the weight factor $n(\mathbf{r})$ in the system average. To illustrate this, we show the He atom radial contribution to the system-averaged on-top hole, $4\pi r^2 n(r) n_{XC,\lambda}(\mathbf{r},\mathbf{r})$, in Fig. 2. The system-averaged quantity is simply the area under this curve, and is underestimated by only 3%.

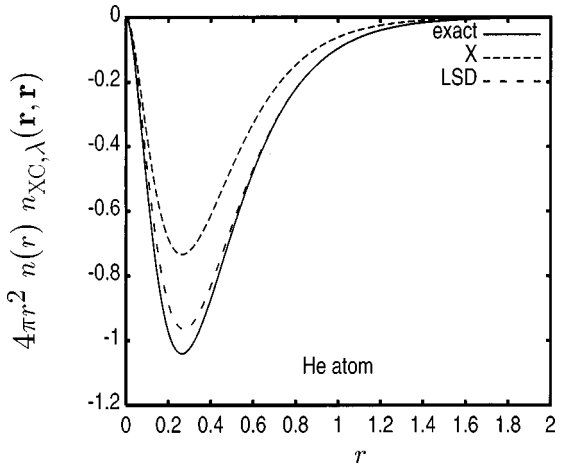

FIG. 2. On-top hole in He atom ($\lambda=1$).

We expect that differences between LSD and exact exchange-correlation holes in other systems[55] will also lessen in the system average.

C. Approximate universal behavior

Multiplying Eq. (11) through by $n^2(\mathbf{r})$ and integrating over all space yields the system average

$$-1\leqslant\langle n_{XC,\lambda}(0)\rangle/\langle n\rangle\leqslant-\tfrac{1}{2}[1+\langle\zeta\rangle^2] \tag{13}$$

where

$$\langle\zeta^2\rangle=\frac{\int d^3r\zeta^2(\mathbf{r})n^2(\mathbf{r})}{\int d^3rn^2(\mathbf{r})}, \tag{14}$$

and the other averages are as in Eq. (9). Figure 3 is an approximate ''universal curve'' for the $\lambda=1$ on-top hole ratio versus the average density parameter[49]

$$\langle r_s\rangle=\frac{\int d^3rr_s(\mathbf{r})n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r})}{\int d^3rn_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r})}, \tag{15}$$

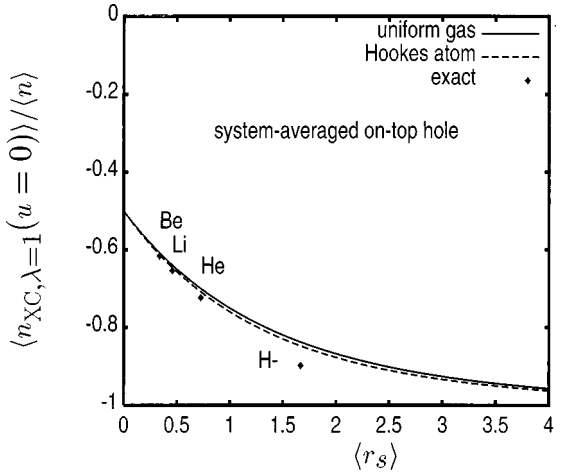

FIG. 3. Approximate universal curve for the system averaged $\lambda=1$ on-top exchange-correlation hole density in spin-unpolarized systems, as a function of the average Seitz radius in the system (see text). The solid curve is for the uniform gas, the dashed curve is for Hooke's atom, while the diamonds indicate essentially exact results from highly accurate wave functions (Ref. 56). The Hartree–Fock or exact exchange value is -0.5.

for $\langle\zeta^2\rangle=0$. The diamonds represent highly accurate quantum Monte Carlo variational calculations[56] for real atoms. The dashed line represents exact analytic results for Hooke's atom, which consists of two electrons bound to a central potential by a spring of frequency ω (see Appendix B). The solid curve in Fig. 3 is the on-top hole ratio for a uniform electron gas. Yasuhara's summation of ladder diagrams gives an expression for this quantity which may be exact at low densities ($r_s\to\infty$), but is slightly in error at high densities ($r_s\to0$). In Appendix A, we give our own analytic expression for this quantity, which corrects Yasuhara's expression at higher densities, and was used to generate the uniform-gas values in Figs. 1, 2, and 3. The accuracy of the LSD approximation for the on-top hole displayed in Fig. 3 shows that this on-top hole density is the missing link between real atoms and molecules and the uniform gas (see below).

Such a curve exists for every value of $\langle\zeta^2\rangle$, becoming lower as $\langle\zeta^2\rangle$ grows, and reducing to a horizontal line along -1 when $\langle\zeta^2\rangle=1$, i.e., the fully spin-polarized case. We have included the value for Li in Fig. 3, because its value of $\langle\zeta^2\rangle=0.03$ is sufficiently close to zero.

D. Leading correction to Kohn–Sham on-top hole

To study the behavior of this approximate universal curve in more detail, we note that, as the high-density limit is approached ($\langle r_s\rangle\to0$), the curve has a finite slope (for normal systems). From the scaling arguments of Appendix C, we can write[49]

$$\frac{\langle n_{XC,\lambda}(0)\rangle}{\langle n\rangle}\to-1+\left(\frac{1-\langle\zeta^2\rangle}{2}\right)(1-\alpha\lambda\langle r_s\rangle), \tag{16}$$

where α is a dimensionless constant, characteristic of the system, which can be calculated from Görling–Levy perturbation theory[57,58] around the $\lambda=0$ limit, keeping the density fixed. A simple expression may be given in terms of the leading (in λ) correction to the pair density[47] of Eq. (4)[49]

$$\alpha=-\frac{\int d^3rP^{(1)}(\mathbf{r},\mathbf{r})}{\int d^3rP_{\lambda=0}(\mathbf{r},\mathbf{r})r_s(\mathbf{r})}, \tag{17}$$

where

$$P_\lambda(\mathbf{r},\mathbf{r}')=P_{\lambda=0}(\mathbf{r},\mathbf{r}')+\lambda P^{(1)}(\mathbf{r},\mathbf{r}')+\cdots. \tag{18}$$

To calculate this from many-body perturbation theory,[3,29] define the exact λ-dependent retarded density–density response function

$$\chi_{\sigma\sigma'\lambda}(\mathbf{r},\mathbf{r}';t-t')=-i\theta(t-t')\langle\Psi_\lambda|[\delta\hat{n}_\sigma(\mathbf{r},t),\delta\hat{n}_{\sigma'}(\mathbf{r}',t')]|\Psi_\lambda\rangle, \tag{19}$$

where $\delta\hat{n}$ is the density-fluctuation operator and Ψ_λ is the ground-state wave function at coupling strength λ.[3] The Fourier transform of Eq. (19) yields the density response $\mathrm{Re}\{\delta n_\sigma(\mathbf{r},\omega)\exp(-i\omega t)\}$ to a time-dependent weak external perturbation $\mathrm{Re}\{\delta v^{\mathrm{ext}}_{\sigma'}(\mathbf{r}',\omega)\exp(-i\omega t')\}$:

$$\delta n_\sigma(\mathbf{r},\omega)=\sum_{\sigma'}\int d^3r'\chi_{\sigma\sigma'\lambda}(\mathbf{r},\mathbf{r}';\omega)\,\delta v^{\mathrm{ext}}_{\sigma'}(\mathbf{r}',\omega). \tag{20}$$

Then

$$P_{\sigma\sigma'\lambda}(\mathbf{r},\mathbf{r}')=n_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r}')-\int_0^\infty \frac{d\omega}{\pi}\,\mathrm{Im}\;\chi_{\sigma\sigma'\lambda}(\mathbf{r},\mathbf{r}';\omega) - \delta_{\sigma\sigma'}n_\sigma(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'). \tag{21}$$

Summation of Eq. (21) over σ and σ' yields a standard expression[29] for the pair density. Equation (21) immediately simplifies when we consider the on-top value, since the Pauli exclusion principle requires

$$P_{\sigma\sigma\lambda}(\mathbf{r},\mathbf{r})=0, \tag{22}$$

i.e., parallel spins do not contribute to the on-top pair density. Furthermore, since at $\mathbf{r}=\mathbf{r}'$ all contributions are symmetric under interchange of σ and σ', we have

$$P_\lambda(\mathbf{r},\mathbf{r})=2\left(n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r})-\int_0^\infty \frac{d\omega}{\pi}\,\mathrm{Im}\;\chi_{\uparrow\downarrow\lambda}(\mathbf{r},\mathbf{r};\omega)\right). \tag{23}$$

Thus only antiparallel contributions to χ contribute, which greatly reduces the number of diagrams needed to be evaluated in perturbation theory.

We expand each side of this exact relation to first order in λ. In zeroth order, the Kohn–Sham susceptibility is

$$\chi^{(0)}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega)=\delta_{\sigma\sigma'}\sum_{i,j}\;\frac{(f_{i,\sigma}-f_{j,\sigma})n_i(\mathbf{r},\mathbf{r}')n_j^*(\mathbf{r},\mathbf{r}')}{\epsilon_i-\epsilon_j+\omega+i0_+}, \tag{24}$$

where the sum runs over all Kohn–Sham orbitals, $f_{i,\sigma}$ is the spin-occupation number of the i-th orbital with energy ϵ_i, and

$$n_i(\mathbf{r},\mathbf{r}')=\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}'). \tag{25}$$

Since the zero-order susceptibility is diagonal in spin, it does not contribute to the on-top pair density, so Eq. (23) immediately recovers the exact Kohn–Sham (or exchange or $\lambda=0$) pair density

$$P_{\lambda=0}(\mathbf{r},\mathbf{r})=2n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r}'). \tag{26}$$

In first order, the perturbation consists of both the Coulomb electron–electron repulsion, plus a change in the external potential, chosen so that the density remains fixed, i.e., following the adiabatic connection. This is called Görling–Levy perturbation theory.[57,58] This leads to nine different contributions to $\chi^{(1)}$, but only the direct Coulomb term (as included in the random phase approximation[29]) contains an antiparallel spin contribution. We find

$$\chi^{(1)}_{\uparrow\downarrow}(\mathbf{r},\mathbf{r};\omega)=\int d^3r_2\int d^3r_3\;\frac{\chi^{(0)}_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}_2;\omega)\chi^{(0)}_{\downarrow\downarrow}(\mathbf{r}_3;\mathbf{r};\omega)}{|\mathbf{r}_2-\mathbf{r}_3|}. \tag{27}$$

Insertion of Eq. (27) into Eq. (21), and using Eq. (24), yields, with the help of the identity $1/(x+i0_+)=P(1/x)-i\pi\delta(x)$

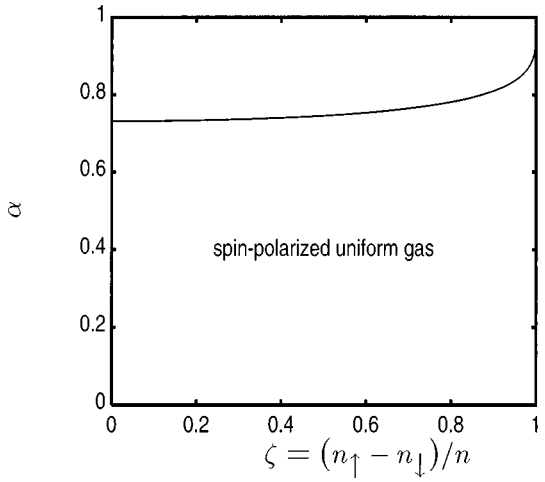

FIG. 4. Coefficient α characterizing leading correction to on-top hole in uniform gas as a function of spin polarization.

$$P^{(1)}(\mathbf{r},\mathbf{r}) = 4\,\mathrm{Re}\left\{\int d^3r'\int d^3r''\;\frac{1}{|\mathbf{r}'-\mathbf{r}''|} \times \sum_{\substack{i\uparrow-\mathrm{occ.}\\ j\uparrow-\mathrm{unocc.}}}\;\sum_{\substack{i'\downarrow-\mathrm{occ.}\\ j'\downarrow-\mathrm{unocc.}}}\frac{n_i(\mathbf{r},\mathbf{r}')n_j(\mathbf{r}',\mathbf{r})n_{i'}(\mathbf{r}'',\mathbf{r})n_{j'}(\mathbf{r},\mathbf{r}'')}{\epsilon_i+\epsilon_{i'}-\epsilon_j-\epsilon_{j'}}\right\}. \tag{28}$$

Equation (28) provides a universal expression for the linear-in-λ correction to the on-top pair density, analogous to similar expressions for the second-order correlation energy. This correction becomes exact in the high-density limit, and yields the high-density limit of the correlation on-top hole. Despite the large number of integrals and sums, it is straightforward to evaluate (easier than second-order perturbation theory for the energy). We evaluate this correction for two extreme situations, the spin-polarized uniform gas and a spin-unpolarized two-electron system, demonstrating its universal applicability. Insertion of Eq. (28) into Eq. (17) yields α entirely in terms of Kohn–Sham quantities.

For the spin-unpolarized uniform gas, α is known analytically:[51,59]

$$\alpha=\left(\frac{4}{9\pi}\right)^{1/3}\frac{2}{5\pi}\,(\pi^2+6\ln 2-3) \approx 0.7317 \quad (\zeta=0\ \text{ uniform gas}). \tag{29}$$

In Appendix D, from Eq. (28), we derive an exact expression $\alpha(\zeta)$, which we evaluate and plot in Fig. 4. We find α changes little with ζ, and

$$\alpha=-\frac{6^{1/3}}{\pi^{4/3}}\left(\frac{\pi^2}{12}+2\ln(3)\ln(2)+\mathrm{dilog}(4)+2\,\mathrm{dilog}(3)\right) \approx 0.9744 \quad (\zeta=1\ \text{ uniform gas}), \tag{30}$$

where $\mathrm{dilog}(x)=\int_1^x dt\;\ln(t)/(1-t)$. Thus the overall polarization dependence of the on-top correlation hole is similar to

that of exchange, as in Eq. (16) and as assumed by Perdew and Wang[60] in their parametrization of the exchange-correlation hole of the uniform gas.

To demonstrate that the on-top hole is not exact in LSD, Burke *et al.*[49] calculated α analytically for the two-electron Hooke's atom in the high-density limit, and found it differed from the uniform gas value

$$\alpha = 2\,\frac{\ln[(2+\sqrt{3})/8(2-\sqrt{3})]5^{3/2}}{(3^{11/6}\pi^{2/3})} \approx 0.7713 \quad \text{(Hooke's atom)}. \tag{31}$$

The result of that calculation was first reported in Ref. 49. In Appendices E and F, we derive that result in detail. We also reported[49] the result of numerical calculations with A. Savin of the on-top pair density in the two-electron ion series as $Z\to\infty$, finding

$$\alpha \approx 0.799 \quad (2-\text{electron ion}). \tag{32}$$

E. Gradient expansion

From the arguments in Appendix C, we can derive the form of the LSD approximation to the system-averaged hole and its leading gradient correction

$$\langle n_{XC,\lambda}(u)\rangle[n,\zeta] = \frac{1}{N}\int d^3r\, n^2(\mathbf{r})[g^{\text{unif}}(\lambda r_s(\mathbf{r}),\zeta(\mathbf{r});u/r_s(\mathbf{r}))-1 + \Gamma(\lambda r_s(\mathbf{r}),\zeta(\mathbf{r});u/r_s(\mathbf{r}))|\nabla n(\mathbf{r})|^2/n^{8/3}(\mathbf{r})+\cdots]. \tag{33}$$

This expression will be accurate for systems of slowly varying density, and for small u should be much better behaved than the corresponding gradient expansion for the energy

$$E_{XC,\lambda} = \int d^3r\left[A_{XC}(\lambda r_s)n^{4/3} + C_{XC}(\lambda r_s)\,\frac{|\nabla n|^2}{n^{4/3}}+\cdots\right], \tag{34}$$

(see next section). The exchange limit is recovered by setting $\lambda=0$. Since $\Gamma(\lambda r_s,\zeta;0)$ vanishes in the $\lambda\to 0$, $\lambda\to\infty$, and $\zeta\to 1$ limits, we anticipate that it is small everywhere.

To evaluate $\Gamma(u=0)$, we would have to calculate the on-top hole for a slowly varying electron gas, a calculation which is beyond the scope of this paper. However, we can get some idea of its magnitude by comparing with the small λ limit of the previous section. We write

$$\Gamma(\lambda r_s,\zeta;u=0) = \lambda r_s\gamma(\zeta)+\cdots. \tag{35}$$

Insertion of Eq. (33) into Eq. (17) then yields

$$\alpha = \alpha^{\text{LSD}} - 2\gamma(0)G \tag{36}$$

where

$$G = \frac{\int d^3r[\gamma(\zeta)/\gamma(0)]|\nabla n|^2/n}{\int d^3r(1-\zeta^2)n^{5/3}}. \tag{37}$$

Thus $\gamma(\zeta)$, a single universal function of ζ, characterizes the gradient expansion for α. For the high-density Hooke's atom, we find $G=(\frac{500}{27})^{1/6}5\pi$, yielding an empirical estimate of $\gamma(0)\approx -7.75\times 10^{-4}$. On the other hand, for the two-electron ion series in the limit $Z\to\infty$, we have $G=(\frac{5}{3})^3(4\pi)^{2/3}$, yielding $\gamma(0)\approx -1.3\times 10^{-3}$. Since this number should be system independent, we can conclude that the gradient expansion for the on-top hole does not apply to both these systems, or that there is numerical error in Eq. (32). We suspect that the Hooke's atom estimate is a reasonably accurate one, since a similar estimate for the noninteracting kinetic energy gives 90% of the correct Kirzhnits[61] gradient coefficient.

The slowly varying gas has been treated within the random phase approximation by Langreth and Perdew,[29] and the high-density limit of the results parametrized by Langreth and Mehl.[10] For $\zeta=0$, this yields (see Ref. 15)

$$n_C^{\text{GEA}}(\mathbf{r},u=0) = n_C^{\text{LSD}}[n(\mathbf{r}),u=0] + \frac{|\nabla n|^2}{72\pi^3 n^2}. \tag{38}$$

Undoing the coupling constant integration and comparing with Eq. (33), we find $\gamma(0)=(4\pi/3)^{1/3}/(36\pi^2)\approx 1.44\times 10^{-3}$. While this value is of the same order as our empirical estimates, the sign is reversed, probably because the simple Langreth–Mehl approximation does not capture the complexity of the hole found in Ref. 29. Thus we give no precise value for $\gamma(\zeta=0)$. The most direct route to this number appears to be either numerical evaluation of Eq. (28) for a gas with a density which is slowly varying in one direction, or extraction from the hole found in Ref. 29.

F. "Abnormal" systems

Under the scaling of Eq. (C3), the on-top hole ratio $\langle n_{XC,\lambda}(u=0)\rangle[n,\zeta]/\langle n\rangle$ remains invariant, as does $\lambda\langle r_s\rangle$. Thus, we can also think of Fig. 3 as a representation of the λ-dependence of the on-top hole density in a spin-unpolarized ($\zeta=0$) normal system: Just relabel the vertical and horizontal axes as $\langle n_{XC,\lambda}(u=0)\rangle/\langle n\rangle$ and $\lambda\langle r_s\rangle$, respectively.

In the noninteracting limit $\lambda=0$, we have the Kohn–Sham wave function $\Psi_{\lambda=0}([n,\zeta];\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)$, which is a single Slater determinant of Kohn–Sham orbitals for a normal system. More generally, $\Psi_{\lambda=0}$ could also be a linear combination of degenerate ground-state determinants for the Hamiltonian $\hat{H}_{\lambda=0}$. For any finite system, we expect to find nonzero overlap $\langle\Psi_{\lambda=0}|\Psi_\lambda\rangle$, and then all λ-dependencies have an analytic perturbation or Taylor expansion, e.g.,

$$\langle n_{XC,\lambda}(u=0)\rangle[n,\zeta]/\langle n\rangle = \sum_{j=0}^{\infty} a_j(\lambda\langle r_s\rangle)^j. \tag{39}$$

The coefficients a_j are functionals of $\zeta(\mathbf{r})$ and of the shape of the electron density $n(\mathbf{r})$, but are invariant under the uniform scaling $n(\mathbf{r})\to\gamma^3 n(\gamma\mathbf{r})$ and $\zeta(\mathbf{r})\to\zeta(\gamma\mathbf{r})$. For example, n_X and E_X are purely of order λ^0, while $n_{C,\lambda}$ and $E_{C,\lambda}$ vary like λ for small λ (in the absence of a strict degeneracy for $\lambda=0$).

These expectations may fail in an infinite system like the uniform electron gas, where $\langle\Psi_{\lambda=0}|\Psi_\lambda\rangle=0$. For example, the on-top hole ratio in the spin-unpolarized gas is[62]

$$\frac{n_{XC,\lambda}^{\text{unif}}(u=0)}{n} = -\frac{1+\alpha\lambda r_s+\beta\lambda^2 r_s^2\ln(\lambda r_s)}{2}+\cdots. \tag{40}$$

The exchange hole has the expected λ^0 dependence, and the correlation hole again starts out like λ, but the next term in the expansion is nonanalytic. In the opposite limit $u\to\infty$, the correlation hole density becomes of order λ^0 in order to cancel the exchange hole, in such a way that $E_{C,\lambda}\sim\lambda\ln\lambda$ for small λ. Capturing this nonanalyticity requires summing the random phase approximation (RPA) or ring-diagrams, which properly account for the long-range part of the Coulomb interaction.

Our model for the uniform gas on-top hole presented in Appendix A is analytic in λ. Thus, the on-top hole ratio in the uniform electron gas has essentially the same kind of λ-dependence as that of a finite normal system, making this quantity more transferable from the uniform gas than $E_{C,\lambda}$ itself.

A system is normal or abnormal to the extent that its system-averaged on-top hole ratio $\langle n_{XC,\lambda}(u=0)\rangle[n,\zeta]/\langle n\rangle$ for each coupling constant λ is or is not close to its LSD or uniform-gas approximation, evaluated using the true ground-state spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ for the system. In other words, a normal system is described approximately by the re-labeled Fig. 3, (or by its generalization to $\zeta\neq 0$). Abnormal systems typically arise in one of two ways: (1) If the Kohn–Sham ($\lambda=0$) system has a ground state which is a linear combination of several determinants (e.g., an atomic triplet state with $S=1$ and $M_s=0$), then the LSD on-top hole ratio can be wrong even at the $\lambda=0$ or exact exchange limit.[63] (2) If the Kohn–Sham or $\lambda=0$ system has a nearly degenerate ground state, then the analytic expansion of Eq. (39) can become irregular, with leading coefficients $|a_j|$ much greater than unity. Examples of abnormal systems will be found in Refs. 35, 63, and 64. The breaking of symmetry which can partially rescue semilocal descriptions of such systems is discussed in Ref. 64.

G. Locality of the energy

In this section, we examine the concept of nonlocality, in the sense of how much error LSD makes. We have seen above that LSD is most accurate near $u=0$, and least accurate at large u. Thus the deeper the hole is at the origin, and therefore, from the sum rule, the shorter its range in u, the better approximated it should be in LSD. We may test this idea by examining the holes and corresponding energies of three different coupling constants: $\lambda=0$ (exchange), $\lambda=1$ (full coupling strength), and averaged over λ (as in the actual E_{XC}). In Fig. 5, we plot these three holes for the spin-unpolarized uniform electron gas[60] at $r_s=3$, a typical valence-electron density. Since the on-top correlation hole is negative, the shallowest of these holes is the exchange hole, followed by the coupling-constant averaged hole, and the deepest is the full coupling-strength hole. These qualitative features will be shared by the system-averaged holes of most inhomogeneous systems. Thus we expect the exchange energy to be the least local, and the full coupling-strength energy the most local, of the three. (This argument, which provides the basis for our hybrid work,[34] is valid at typical core and valence electron densities. It begins to fail for an electron gas of extremely low density, where the exchange-correlation hole develops a strong positive bump at large u.)

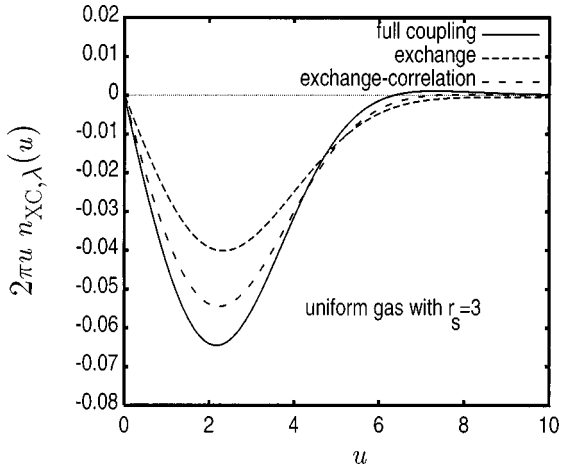

FIG. 5. Exchange-correlation holes in the spin-unpolarized uniform electron gas with $r_s=3$, for differing coupling-constant strengths. Large-u oscillations have been averaged away, following Ref. 60.

We now examine the degree of nonlocality in the PW91 GGA.[15] In the first three columns of Table I, we tabulate the error made by LSD relative to PW91, i.e., $(E^{\mathrm{LSD}}-E^{\mathrm{PW91}})/E^{\mathrm{PW91}}$, as a percentage. Looking across any row, we see that indeed this error is largest for exchange and least for full coupling strength. Looking down any column, we also see that this effect becomes less significant as we approach the high-density limit (in which exchange dominates correlation).

IV. ON-TOP HOLE IN OTHER APPROXIMATIONS

We believe that a correct on-top hole density is an ingredient of every successful first-principles density functional approximation, and that conversely an incorrect on-top density indicates the need for further refinement of an approximation. Here we discuss the on-top hole density in three approximations which attempt to go beyond LSD or GGA. For systems with fixed (integer) electron number, these approximations also satisfy the correct sum rule on the exchange-correlation hole, $\int d^3r' n_{XC}(\mathbf{r},\mathbf{r}')=-1$. The self-interaction correction comes closest[65] to satisfying the generalization of this sum rule to systems with fluctuating (non-integer on average) electron number, and thus can mimic the derivative discontinuity[65,66] of the exact functional.

TABLE I. Errors in LSD energies, relative to PW91, for several atoms (%).

Atom	ΔE_X	ΔE_{XC}	$\Delta E_{XC,\lambda=1}$	ΔE_C
H	−13	−7	−5	236
He	−13	−6	−3	145
Li	−13	−7	−5	162
N	−10	−7	−5	114
Ne	−9	−6	−4	94
Ar	−8	−5	−4	85
Kr	−6	−4	−3	71
Xe	−5	−4	−3	64

A. Weighted-density approximation

Another popular approximation in density functional theory is the weighted density approximation (WDA)[67,68]

$$n_{XC}^{\mathrm{WDA}}(\mathbf{r},\mathbf{r}+\mathbf{u})=n(\mathbf{r}+\mathbf{u})[g^{\mathrm{unif}}(\tilde{n}(\mathbf{r});u)-1], \tag{41}$$

where the weighted density $\tilde{n}(\mathbf{r})$ is chosen to satisfy the sum rules on the exchange and correlation holes, and is a nonlocal functional of $n(\mathbf{r})$. At $u=0$, to the extent that $\tilde{n}(\mathbf{r})$ differs from $n(\mathbf{r})$ [and $n(\mathbf{r})$ is not so large that correlation may be neglected], WDA is apt to be less accurate than LSD, even in a spin-unpolarized system.

We note that a recent variation, which does WDA for only exchange[69] and includes a correction to accommodate the uniform gas, does reproduce the LSD on-top hole.

The on-top hole of the average density approximation (ADA)[67] is incorrect in many of the limits in which that of LSD is correct.

B. Self-interaction correction

The self-interaction correction (SIC) to LSD of Perdew and Zunger[70] is

$$E_{XC}^{\mathrm{SIC}}=E_{XC}^{\mathrm{LSD}}-\sum_{i,\sigma}^{\mathrm{occup.}}\left\{\int d^3r\int d^3r'\,\frac{n_{i,\sigma}(\mathbf{r})n_{i,\sigma}(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|}+\int d^3r n_{i,\sigma}(\mathbf{r})\epsilon_{XC}^{\mathrm{unif}}(n_{i,\sigma}(\mathbf{r}),0)\right\}, \tag{42}$$

where $n_{i,\sigma}(\mathbf{r})=|\psi_{i,\sigma}(\mathbf{r})|^2$ is the contribution to the density from orbital i,σ. The corresponding ansatz for the hole is

$$n_{XC}^{\mathrm{SIC}}(\mathbf{r},\mathbf{r}+\mathbf{u})=n_{XC}^{\mathrm{unif}}(n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r});u)-\sum_{i,\sigma}^{\mathrm{occup.}}\frac{n_{i,\sigma}(\mathbf{r})}{n(\mathbf{r})}[n_{i,\sigma}(\mathbf{r}+\mathbf{u})+n_{XC}^{\mathrm{unif}}(n_{i,\sigma}(\mathbf{r}),0;u)]. \tag{43}$$

At zero separation ($u=0$), the SIC hole density and cusp reduce to those of LSD, since $n_{XC}^{\mathrm{unif}}(n_{i,\sigma},0;u)=-n_{i,\sigma}(\mathbf{r})+\mathrm{O}(u^2)$.

C. Exact exchange mixing

Becke[32] has shown that mixing some exact exchange with GGA in the form

$$E_{XC}^{\mathrm{mix}}=a(E_X-E_X^{\mathrm{GGA}})+E_{XC}^{\mathrm{GGA}}, \tag{44}$$

with $a\approx 0.25$, can lead to significant improvement of atomization energies. It has recently been shown that such exact exchange mixing can be derived without empirical input from very general considerations,[34] and the value of the mixing parameter explained in terms of perturbation theory results.[34] The accompanying hole is

$$n_{XC}^{\mathrm{mix}}(\mathbf{r},\mathbf{r}+\mathbf{u})=a[n_X(\mathbf{r},\mathbf{r}+\mathbf{u})-n_X^{\mathrm{GGA}}(\mathbf{r},\mathbf{r}+\mathbf{u})]+n_{XC}^{\mathrm{GGA}}(\mathbf{r},\mathbf{r}+\mathbf{u}). \tag{45}$$

Since LSD and GGA give the exact on-top exchange hole for normal systems, in these cases the mixing functional reproduces the LSD on-top hole.

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APPENDIX A: INTERPOLATION FORMULA FOR UNIFORM ELECTRON GAS

Consider a spin-unpolarized ($\zeta=0$) electron gas of uniform density $n=3/(4\pi r_s^3)$. The on-top hole density is

$$n_{XC,\lambda}(\mathbf{r},\mathbf{r})=n[g_\lambda(r_s,u=0)-1], \tag{A1}$$

where $g_\lambda(r_s,u)$ is the pair distribution function. From the scaling argument of Appendix C, $g_\lambda(r_s,0)=g_{\lambda=1}(\lambda r_s,0)$. Yasuhara made an approximate summation of ladder diagrams, and found[71]

$$g_{\lambda=1}^{\mathrm{Yasu}}(r_s,0)=\frac{1}{2}\left[\sum_{i=0}^{\infty}\frac{(\kappa^2 r_s)^i}{i!(i+1)!}\right]^{-2}=\frac{1}{2}\frac{\kappa^2 r_s}{I_1^2(2\kappa\sqrt{r_s})}, \tag{A2}$$

where $\kappa=(4/3\pi)(9\pi/4)^{1/3}$ and I_1 is a modified Bessel function of order 1. (This calculation has recently been refined.[72]) The low-density ($r_s\to\infty$) limit of Eq. (A2) can be deduced from the asymptotic behavior of the modified Bessel function [see Eq. (9.7.1) of Ref. 73], yielding $Dr_s^{3/2}e^{-A\sqrt{r_s}}$, where $D=2\pi\kappa^3=32/3\pi=3.3953$ and $A=4\kappa=3.2581$. Its high-density limit is $(1-\alpha r_s)/2$, where $\alpha=(4/\pi\sqrt{3})^{4/3}=0.6634$. An accurate closed-form representation of Eq. (A2) for all r_s is

$$g_{\lambda=1}(r_s,0)=D[(\gamma+r_s)^{3/2}+\beta]e^{-A\sqrt{\gamma+r_s}}, \tag{A3}$$

where $\beta=\exp(A\sqrt{\gamma})/(2D)-\gamma^{3/2}$ makes $g_{\lambda=1}(r_s=0,0)=\frac{1}{2}$ and $\gamma=5.8648$ (and $\beta=379.12$) recovers the Yasuhara value for α.

Geldart[59] and later Kimball[62] evaluated the exact high-density limit for $g_{\lambda=1}(0)$, also finding $(1-\alpha r_s)/2$, but with α given by Eq. (29). We can modify the parameters γ and β of Eq. (A3) to achieve this limit, with the result $\gamma=4.7125$ and $\beta=163.44$. The coupling-constant average is

$$\overline{g}(r_s,0)=\int_0^1 d\lambda\, g_{\lambda=1}(\lambda r_s,0)=\frac{1}{r_s}\int_0^{r_s}dr_s g_{\lambda=1}(r_s,0)=\frac{2D}{A^2 r_s}[F(A\sqrt{\gamma})-F(A\sqrt{\gamma+r_s})] \tag{A4}$$

where

$$F(z)=e^{-z}[(z+1)(\beta+24/A^3)+z^2(z^2+4z+12)/A^3]. \tag{A5}$$

We believe that our interpolation between the low- and high-density ($\alpha=0.7317$) limits provides the most accurate values available for the on-top hole density of the uniform

TABLE II. On-top pair distribution function $g_{\lambda=1}(r_s,0)$ for the uniform electron gas. Comparison of Yasuhara's formula [Eq. (A2)] with two versions of Eq. (A3), and with the results of a Quantum Monte Carlo simulation (Ref. 74). Also shown are the results of the effective potential expansion (EPX) of Ref. 75.

r_s	Eq. (A2)	Eq. (A3) $\alpha=0.6634$	Eq. (A3) $\alpha=0.7317$	QMC	EPX
1	0.266	0.265	0.250	0.272	0.27
3	0.088	0.084	0.074	0.092	0.085
5	0.033	0.031	0.026	0.023	0.027
10	0.004	0.003	0.003	0.002	⋯

gas. These values agree with the results of quantum Monte Carlo simulations,[74] within the accuracy of the latter (Table II).

APPENDIX B: NUMERICAL SOLUTION OF HOOKE'S ATOM

To better understand the accuracy of the LSD on-top hole, we performed essentially exact calculations on a simple model system, the Hooke's atom, which consists of two electrons repelling each other via a Coulomb repulsion, but bound to an attractive center by a simple oscillator potential of frequency ω. For certain discrete values of ω, the exact wave function may be written analytically.[76,77] Here, by expanding the wave function in powers of the separation between the electrons,[78] we solve the problem numerically by exact diagonalization for any value of $\omega \gtrsim 10^{-3}$, beyond which numerical instability causes our solution to fail on a machine with 32-digit accuracy. The advantage of this model over the two-electron Coulombic ion series is that there is no cusp in the density at the center, where the rapid variation in the density can cause LSD to become less accurate, as in Fig. 1. Figures 2 and 3 of the first paper in Ref. 64 show that, in all regions of the Hooke's atom in which the on-top hole density is significant, the LSD on-top hole is an excellent approximation. These results for the Hooke's atom system-averaged on-top hole are presented in Fig. 3, and compared with uniform gas values. The LSD hole is an even better approximation in this case than for Coulombic atoms, as can be seen by the proximity of the curves.

APPENDIX C: LEVY SCALING AND THE GRADIENT EXPANSION

The scaling properties of the Kohn–Sham ($\lambda=0$) wave function have been used to derive the forms for the gradient expansions of the noninteracting kinetic and exchange energies.[79] Here we shall use Levy's scaling relation for the interacting wave function to do the same for the exchange-correlation on-top hole.

An external potential $V_{\rm ext}(\mathbf{r})$ acting on a real N-electron system produces a density $n(\mathbf{r})$ and spin-polarization $\zeta(\mathbf{r})$. Associated with $n(\mathbf{r})$ and $\zeta(\mathbf{r})$ for each coupling constant λ (see above) is a wave function $\Psi_\lambda[n,\zeta](\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)$. For any $\gamma>0$, consider the uniform scaling

$$\begin{aligned}&\Psi_\lambda[n,\zeta](\mathbf{r}_1,\sigma_1\ldots,\mathbf{r}_N,\sigma_N)\\&\quad\rightarrow \gamma^{3N/2}\Psi_\lambda[n,\zeta](\gamma\mathbf{r}_1,\sigma_1,\ldots,\gamma\mathbf{r}_N,\sigma_N)\\&\quad=\Psi_{\gamma\lambda}[n_\gamma,\zeta_\gamma](\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)\end{aligned}\tag{C1}$$

where

$$n_\gamma(\mathbf{r})=\gamma^3 n(\gamma\mathbf{r}),\tag{C2}$$

is the scaled density, and $\zeta_\gamma(\mathbf{r})=\zeta(\gamma\mathbf{r})$. The Levy equality of Eq. (C1) asserts that the scaled wave function is associated with the scaled density only if the coupling constant is also scaled. Extracting the hole from the wave function via Eq. (4) yields

$$\begin{aligned}\langle n_{XC,\lambda}(u)\rangle[n,\zeta]&\rightarrow\gamma^3\langle n_{XC,\lambda}(\gamma u)\rangle[n,\zeta]\\&=\langle n_{XC,\gamma\lambda}(u)\rangle[n_\gamma,\zeta_\gamma].\end{aligned}\tag{C3}$$

The important point to note here is that, under coordinate scaling of the wave function, not only is the density scaled, but so too is the coupling constant.

We next use the exact form of Eq. (C3) to deduce the form of the gradient expansion for the hole. The error made by a local approximation may be systematically estimated by treating the local approximation as the zeroth order term in a Taylor series in gradients of the density. This is the gradient expansion. The derivation of the gradient expansion for a quantity is simple in principle: Start with a uniform electron gas, apply an external potential $\delta v(\mathbf{r})$ that is both weak and slowly varying, evaluate the quantity to second order and the density to first order in δv, then eliminate δv to find the quantity as a functional of the density. What often complicates this derivation in practice is that the unperturbed system is an interacting electron gas, with a long range $(1/u)$ interaction. Here, we do not directly calculate the gradient expansion, but take a different approach, using scaling arguments to find the exact form for the gradient expansion.

In an electron gas of slowly varying density, we can expand this hole in powers of the density gradient, and the leading correction to LSD is proportional to $|\nabla n|^2$ by symmetry. The scaling equality of Eq. (C3) constrains this gradient expansion for the on-top hole to be of the form of Eq. (33). The on-top hole density is

$$\begin{aligned}&\langle n_{XC,\lambda}(u=0)\rangle[n,\zeta]\\&\quad=+\frac{1}{N}\int d^3r n^2(\mathbf{r})[g(\lambda r_s(\mathbf{r}),\zeta(\mathbf{r}))-1\\&\qquad+\Gamma(\lambda r_s(\mathbf{r}),\zeta(\mathbf{r}))|\nabla n(\mathbf{r})|^2/n^{8/3}(\mathbf{r})+\cdots].\end{aligned}\tag{C4}$$

The first term here is the uniform gas contribution, discussed at length above. The next term must be very small. We estimate the size of the gradient correction in the text.

APPENDIX D: POLARIZATION DEPENDENCE IN HIGH-DENSITY UNIFORM GAS

Applying Eq. (28) to the case of a uniform gas, the Kohn–Sham orbitals are plane waves, $\phi_i(\mathbf{r})=\exp(i\mathbf{p}_i\cdot\mathbf{r})/\sqrt{V}$, where V is the volume of the system, and $\mathbf{p}_i$ is the

momentum of the ith state, and $\epsilon_i = p_i^2/2$. Transforming to a continuous basis set, so that $\Sigma_i \to V\int^{[(d^3p)]}_{[(2\pi)^3]}$, and using the Fourier transform of the Coulomb potential, we find:

$$P^{(1)}(u=0) = -4\int \frac{d^3k}{(2\pi)^3} \int_{\substack{p\leqslant k_{F,\uparrow} \\ |\mathbf{p}+\mathbf{k}|\geqslant k_{F,\downarrow}}} \frac{d^3p}{(2\pi)^3} \times \int_{\substack{p'\leqslant k_{F,\downarrow} \\ |\mathbf{p}'+\mathbf{k}|\geqslant k_{F,\downarrow}}} \frac{d^3p'}{(2\pi)^3} \frac{4\pi}{k^2(k^2+(\mathbf{p}+\mathbf{p}')\cdot\mathbf{k})}. \tag{D1}$$

This simplifies to

$$P^{(1)}(u=0) = -\frac{k_F^5}{8\pi^7} \int_0^\infty dq I[q;(1+\zeta)^{1/3},(1-\zeta)^{1/3}], \tag{D2}$$

where $I(q;x,y)$ is a dimensionless function given by Eq. (15) of Ref. 80. The denominator in Eq. (17) is easier, leading to $k_F^5(1-\zeta^2)(9\pi/4)^{1/3}/(18\pi^4)$, yielding

$$\alpha(\zeta) = \frac{(9/4\pi^5)^{2/3}}{1-\zeta^2} \int_0^\infty dq I(q;(1+\zeta)^{1/3},(1-\zeta)^{1/3}). \tag{D3}$$

APPENDIX E: HIGH-DENSITY LIMIT OF TWO-ELECTRON SYSTEMS

To illustrate the above results in a simpler fashion, we rederive them for a spin-unpolarized two-electron system using Rayleigh–Schrödinger perturbation theory. Turning on the interelectronic Coulomb repulsion as a perturbation on the Kohn–Sham wave function yields

$$\Psi(\mathbf{r},\mathbf{r}') = \phi_0(\mathbf{r})\phi_0(\mathbf{r}') + \lambda\Psi^{(1)}(\mathbf{r},\mathbf{r}') + \ldots \tag{E1}$$

where

$$\Psi^{(1)}(\mathbf{r},\mathbf{r}') = \sum_{i,j}{}' c_{ij}\phi_i(\mathbf{r})\phi_j(\mathbf{r}'), \tag{E2}$$

with the prime on the sum indicating exclusion of the (0,0) value, and

$$c_{ij} = \int d^3r \int d^3r' \frac{\phi_0(\mathbf{r})\phi_0(\mathbf{r}')\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|(2\epsilon_0-\epsilon_i-\epsilon_j)}. \tag{E3}$$

Insertion of this form into the definition of the pair density produces

$$P^{(1)}_{\rm Coul}(\mathbf{r},\mathbf{r}) = 4\,{\rm Re}\left\{\phi_0^{*2}(\mathbf{r})\sum_{ij}{}' c_{ij}\phi_i(\mathbf{r})\phi_j(\mathbf{r})\right\}. \tag{E4}$$

We denote this result by $P^{(1)}_{\rm Coul}$, as it is not the correct adiabatic connection formula. Turning on the Coulomb repulsion alone causes a change in density, which also alters the on-top hole, via Eq. (26). The density change is easily shown to be

$$n^{(1)}_{\rm Coul}(\mathbf{r}) = 4\,{\rm Re}\sum_{i\neq 0} c_{i0}\phi_0^*(\mathbf{r})\phi_i(\mathbf{r}), \tag{E5}$$

yielding a net change in the on-top pair density of

$$P^{(1)}_{\rm dens}(\mathbf{r},\mathbf{r}) = n(\mathbf{r})n^{(1)}_{\rm Coul}(\mathbf{r}). \tag{E6}$$

This change is included in $P^{(1)}_{\rm Coul}$, but cancelled out of $P^{(1)}$ by the change in the external potential. Thus

$$P^{(1)}(\mathbf{r},\mathbf{r}) = P^{(1)}_{\rm Coul}(\mathbf{r},\mathbf{r}) - P^{(1)}_{\rm dens}(\mathbf{r},\mathbf{r}) = 4\,{\rm Re}[\phi_0^*(\mathbf{r})]^2 \sum_{\substack{i\neq 0 \\ j\neq 0}} c_{ij}\phi_i(\mathbf{r})\phi_j(\mathbf{r}), \tag{E7}$$

i.e., the effect of keeping the density constant is to eliminate all single-particle excitations from the sum. This is precisely the result of applying Eq. (28) to this system.

APPENDIX F: HIGH-DENSITY HOOKE'S ATOM

While Eq. (28) can be evaluated for any normal density by finding the Kohn–Sham potential, orbitals, and energies, and performing the sums and integrals, we show here that the sum can be performed analytically for the high-density limit of Hooke's atom, where the density is simply a Gaussian. The results of this Appendix confirm the initial slope of the dashed curve in Fig. 3, and provide a detailed derivation for the conclusions of Ref. 49. We first calculate $P^{(1)}_{\rm Coul}$, as even in this simple system, Eq. (28) produces a three-dimensional sum. We use center-of-mass $\mathbf{R} = (\mathbf{r}_1+\mathbf{r}_2)/2$ and relative $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$ coordinates, for which the orbitals are denoted $\Phi_{\mathbf{J}}(\mathbf{R})$ and $\phi_{\mathbf{j}}(\mathbf{u})$, respectively. In the center-of-mass motion, the orbitals are those of a three-dimensional oscillator of frequency ω and mass 2, while the relative motion has the same frequency but mass $\frac{1}{2}$. Then

$$P^{(1)}_{\rm Coul}(\mathbf{R},u) = 4\,{\rm Re}\;\Phi_0(\mathbf{R})\phi_0(u)\sum_{\mathbf{Jj}}{}' c_{\mathbf{Jj}}\Phi_{\mathbf{J}}(\mathbf{R})\phi_{\mathbf{j}}(\mathbf{u}) \tag{F1}$$

where

$$c_{\mathbf{Jj}} = -\int d^3R \int d^3u \frac{\Phi_{\mathbf{J}=0}(\mathbf{R})\phi_{\mathbf{j}=0}(\mathbf{u})\Phi_{\mathbf{J}}^*(\mathbf{R})\phi_{\mathbf{j}}^*(\mathbf{u})}{u(\epsilon_{\mathbf{J}}+\epsilon_{\mathbf{j}}-\epsilon_{\mathbf{J}=0}-\epsilon_{\mathbf{j}=0})}. \tag{F2}$$

By orthogonality, $c_{\mathbf{Jj}}$ vanishes, except for $\mathbf{J}=0$, $\mathbf{j}=(j,l=0,m=0)$, yielding a very simple expression

$$P^{(1)}_{\rm Coul}(\mathbf{R},0) = -4\Phi_0^2(\mathbf{R})\phi_0(0)\sum_{j=1}^{\infty} \frac{\left\langle j\left|\frac{1}{u}\right|0\right\rangle}{\epsilon_j-\epsilon_0}\phi_j(0), \tag{F3}$$

where the sum is only over the spherically symmetric eigenstates of the relative motion. These states can be mapped to the odd eigenstates of the one-dimensional harmonic oscillator, given in terms of the odd Hermite polynomials. It is a textbook exercise to show

$$\left\langle j\left|\frac{1}{u}\right|0\right\rangle = \frac{(-1)^j(2j)!}{2^j j!\sqrt{\pi(2j+1)!}}\frac{2}{u_0} \tag{F4}$$

and

$$\phi_j(0)\phi_0(0) = \frac{(-1)^j\sqrt{\pi(2j+1)!}}{u_0^3\pi^2 2^j j!}, \tag{F5}$$

where $u_0 = \sqrt{2/\omega}$. Since $\epsilon_j = (2j+3/2)\omega$, and using the Taylor expansion

$$\ln\left(4\frac{1-\sqrt{1-x}}{x(1+\sqrt{1-x})}\right)=\sum_{j=1}^{\infty}\frac{(2j!)}{j(j!^2)4^j}x^j \tag{F6}$$

we find

$$P_{\mathrm{Coul}}^{(1)}(\mathbf{r},\mathbf{r})=-\frac{2\log(2)\omega}{\pi^2}\Phi_0^2(\mathbf{r}). \tag{F7}$$

To find the density change, we use single-particle orbitals. We need only the spherical component, so only coefficients c_{i0}, where $\mathbf{i}=(i,l=0,m=0)$. Then all functions inside Eq. (E3) are spherically symmetric, and we can write $|\mathbf{r}-\mathbf{r}'|=\max(r,r')$ within the integral without error. This yields

$$c_{i0}=-\frac{4}{\pi r_0 i\omega 2^i\sqrt{(2i+1)!}}(\tilde{b}_i+\tilde{c}_i), \tag{F8}$$

with $r_0=\sqrt{1/\omega}$, and

$$\tilde{b}_i=\int_0^{\infty}dx e^{-x^2}H_{2i+1}(x)\int_0^x dy y^2 e^{-y^2} \tag{F9}$$

and

$$\tilde{c}_i=\int_0^{\infty}dx e^{-x^2}x\int_0^x dy y e^{-y^2}H_{2i+1}(y), \tag{F10}$$

where H_i is the Hermite polynomial of degree i. Using the generating function for Hermite polynomials, we find

$$\tilde{c}_i=\sqrt{\frac{\pi}{2}}\frac{(2i+1)!(-1)^i}{i!2^{i+3}} \tag{F11}$$

and

$$\tilde{b}_i=-\frac{2i-1}{2i+1}\tilde{c}_i. \tag{F12}$$

Inserting these results into Eq. (E6) and integrating over all space, we find

$$\begin{aligned}\int d^3r n(\mathbf{r})n_{\mathrm{Coul}}^{(1)}(\mathbf{r})&=32\pi\int_0^{\infty}dr r^2|\phi_0(r)|^2\sum_{i=1}^{\infty}c_{i0}\phi_i(r)\phi_0^*(r)\\&=\frac{64}{\pi^2 r_0^3}\sum_{i=1}^{\infty}\frac{c_{i0}\tilde{c}_i}{2^{i+1}\sqrt{(2i+1)!}}=-\frac{2\omega}{\pi^2}\ln\frac{16(2-\sqrt{3})}{2+\sqrt{3}},\end{aligned} \tag{F13}$$

where the summation was performed using Eq. (F6), with $x=1$.

Last, to find α, we also need $\langle r_s\rangle$ from Eq. (15). This is a simple Gaussian integral, yielding

$$\langle r_s\rangle=\left(\frac{3^{11}}{5^9\pi^8}\right)^{1/6}\omega. \tag{F14}$$

Combination of Eqs. (17), (E7), (F7), (F13), and (F14) yields Eq. (31) of the main text.

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