

DIGGING INTO THE EXCHANGE-CORRELATION ENERGY: THE EXCHANGE-CORRELATION HOLE

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INTRODUCTION

In this chapter, I summarize much of what is known about the exchange-correlation hole in density functional theory. The aim of this summary is to introduce the non-expert to key concepts in electronic density functional theory. For a much broader introduction, see the book by Parr and Yang [1]. For more detail, see the book by Dreizler and Gross [2], and other chapters in the current volume. Most of the references in this chapter are either classic papers in which a fundamental result has been established (and so are well worth reading), or are references to illustrative figures in my own work. I conclude with some simple exercises. Solutions are provided to the odd-numbered problems, while true experts will make short work of the even-numbered ones.

DEFINITIONS AND PHYSICAL INTERPRETATION

Consider the ground state of N electrons, interacting with each other via the Coulomb potential, in some external potential. The Hamiltonian is, in atomic units ($e^2 = \hbar = m = 1$):

$$\hat{H} = \hat{T} + \hat{V}_{ec} + \hat{V}_{ext} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{ext}(\mathbf{r}_i). \quad (1)$$

where \hat{T} is the kinetic energy operator, \hat{V}_{ec} is the (two-body) interelectronic Coulomb repulsion, and \hat{V}_{ext} is the external (one-body) potential. The exact density of the system is

$$n(\mathbf{r}) = N \int d^3r_2 \dots d^3r_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2, \quad (2)$$

where Ψ is the ground-state wavefunction, normalized to unity. Thus $n(\mathbf{r})d^3r$ is the probability of finding an electron in a neighborhood d^3r of \mathbf{r} . By construction the density is everywhere non-negative, and normalized to N . Because the external potential

is a one-body operator, we can then write

$$\langle \Psi | \hat{V}_{ext} | \Psi \rangle = \int d^3r n(\mathbf{r}) v_{ext}(\mathbf{r}). \quad (3)$$

Similarly, the pair density is defined to be

$$P(\mathbf{r}, \mathbf{r}') = N(N-1) \int d^3r_3 \dots d^3r_N |\Psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2, \quad (4)$$

and $P(\mathbf{r}, \mathbf{r}')d^3r d^3r'$ is the probability of finding an electron in d^3r at \mathbf{r} and a second electron in d^3r' around \mathbf{r}' . The pair density is symmetric, non-negative, and is normalized to the number of indistinct pairs of electrons in the system:

$$\int d^3r \int d^3r' P(\mathbf{r}, \mathbf{r}') = N(N-1). \quad (5)$$

Because the interaction between the electrons is two-body, the pair density determines the value of the electron-electron repulsion:

$$\langle \Psi | \hat{V}_{ec} | \Psi \rangle = \frac{1}{2} \int d^3r \int d^3r' \frac{P(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (6)$$

The density can be extracted by integration of the pair density:

$$n(\mathbf{r}) = \frac{1}{N-1} \int d^3r' P(\mathbf{r}, \mathbf{r}'), \quad (7)$$

which determines the expectation value of the external potential. Thus the value of two of the three operators in Eq. (1) are determined by the pair density alone.

ADIABATIC CONNECTION

To relate the pair density to the exchange-correlation hole, we need to vary the strength of the Coulomb repulsion. The constrained search definition [3, 4] of the universal functional of Hohenberg and Kohn [5] is

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ec} | \Psi \rangle, \quad (8)$$

where the minimization is over all wavefunctions yielding the given density $n(\mathbf{r})$. This may be generalized to:

$$F_\lambda[n] = \min_{\Psi_\lambda \rightarrow n} \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{ec} | \Psi_\lambda \rangle, \quad (9)$$

In this minimization, the density is held constant at its physical value by making the external potential λ -dependent, $v_{ext,\lambda}(\mathbf{r})$. The coupling constant λ may be chosen to have any non-negative value. For $\lambda = 1$, we recover the physical wavefunction and energies, while for $\lambda = 0$ we get the non-interacting Kohn-Sham wavefunction, in which just the kinetic energy is minimized. We can then define the exchange-correlation energy as a function of λ via [6]

$$E_{xc}^\lambda = F_\lambda - T_s - \lambda U, \quad (10)$$

where $U = \int d^3r \int d^3r' n(\mathbf{r}) n(\mathbf{r}')/2|\mathbf{r} - \mathbf{r}'|$ is the Hartree energy. (Note that our definition of E_{xc}^λ differs from that of Ref. 6 by a factor of λ .) Then

$$E_{xc}^{\lambda'} = \int_0^{\lambda'} d\lambda \frac{dE_{xc}^\lambda}{d\lambda} = \int_0^{\lambda'} d\lambda \left(\langle \Psi_\lambda | \hat{V}_{ec} | \Psi_\lambda \rangle - U \right), \quad (11)$$

since the λ -dependence of the wavefunction in Eq. (9) does not contribute to the first derivative, by virtue of the variational principle.

COORDINATE SCALING

There is a conceptually simple way to generalize $E_{xc}[n]$ to $E_{xc}^\lambda[n]$. From dimensional analysis (briefly restoring the fundamental constants),

$$E_{xc}[n] = \frac{e^2}{a_0} f[\alpha_0^3 n(\mathbf{r}/a_0)] \quad (12)$$

where $f[v]$ is a dimensionless functional of a dimensionless density, and $a_0 = \hbar^2/mc^2$ is the Bohr radius. Now consider making the change $V_{ec} \rightarrow \lambda V_{ec}$. In Eq. (12), $e^2 \rightarrow \lambda e^2$, $a_0 \rightarrow a_0/\lambda$, and so the exchange-correlation energy at coupling strength λ is

$$E_{xc}^\lambda[n] = \lambda^2 f[n_{1/\lambda}] = \lambda^2 E_{xc}[n_{1/\lambda}], \quad (13)$$

where $n_{1/\lambda}(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$. Eq. (13) is the fundamental scaling relation for the exchange-correlation energy [6], showing that a change in coupling constant is simply related to a uniform scaling of the density. In practice, this is easy to implement for an approximate density functional, but difficult in an exact calculation, as the interacting problem must be solved for each $v_{\text{ext},\lambda}(\mathbf{r})$.

Levy and Perdew also showed that

$$E_x[n_{\gamma}] = \gamma E_x[n], \quad E_c[n_{\gamma}] > \gamma E_c[n] \quad (\gamma > 1), \quad (14)$$

while Levy [7] has shown that $E_c[n_{\gamma}]$ tends to a negative constant as $\gamma \rightarrow \infty$. E_x is the leading contribution in perturbation theory in powers of λ to E_{xc} (see problem 5), which, from Eq. (13), can be thought of either as small λ or as the limiting behavior as the density is uniformly squeezed toward the high density limit. Since $\Psi_{\lambda=0}$ is just the non-interacting Kohn-Sham wavefunction, which we assume to be a single Slater determinant throughout this article, we have the Fock expression

$$E_x = -\frac{1}{2} \sum_{i \neq j} \int d^3r \int d^3r' \frac{\phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (15)$$

where the ϕ_i are the Kohn-Sham orbitals.

EXCHANGE-CORRELATION HOLE

To construct the exchange-correlation energy from the pair density, we generalize Eq. (4) to

$$P_\lambda(\mathbf{r}, \mathbf{r}') = N(N-1) \int d^3r_3 \dots d^3r_N |\Psi_\lambda(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2, \quad (16)$$

where $\lambda = 1$ corresponds to the physical value, discussed in the definition section. If the distribution of electrons were totally uncorrelated, i.e., if the probability of finding an electron at one location were independent of finding another elsewhere, then

$$P_\lambda^{\text{uncorr}}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) n(\mathbf{r}'). \quad (17)$$

This cannot be true everywhere, as that would violate the normalization condition, Eq. (5). The probability distribution for the second electron is altered (often reduced) by the finding of the first electron, and we describe this effect by writing:

$$P_\lambda(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r}) [n(\mathbf{r} + \mathbf{u}) + n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})] \quad (18)$$

where $n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ is the (often negative) λ -dependent exchange-correlation hole density at separation \mathbf{u} surrounding an electron at \mathbf{r} . From the normalization condition Eq. (5), we find

$$\int d^3u n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -1, \quad (19)$$

i.e., surrounding every point in space, there is a dearth of probability, integrating up to exactly one missing electron. Now, inserting Eq. (18) into Eqs. (6) and (11),

$$\frac{dE_{xc}^\lambda}{d\lambda} = \int \frac{d^3u}{2u} \int d^3r n(\mathbf{r}) n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \quad (20)$$

is the λ -dependent integrand in the adiabatic connection formula. Thus, if we define the λ -integrated hole as

$$n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = \int_0^1 d\lambda n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (21)$$

then

$$E_{xc} = \int d^3u \frac{1}{2u} \int d^3r n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (22)$$

i.e., the Coulomb energy of the electron density with the exchange-correlation hole surrounding it [8]. Note that, in density functional theory, the exchange-correlation hole n_{xc} incorporates the coupling constant average of Eq. (21).

We illustrate many of the ideas in this chapter using the uniform electron gas hole, as parametrized by Perdew and Wang[9]. In Fig. 1, we plot this hole, divided by the density, as a function of separation for $r_s = 2$, where $r_s = (4\pi n/3)^{1/3}$ is the Wigner-Seitz radius, a useful measure of the mean separation between electrons. Note that, when multiplied by the phase factor $4\pi u^2$, this curve integrates to -1 , satisfying the normalization condition, Eq. (19).

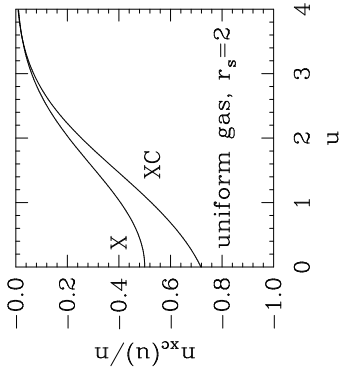


Figure 1. Exchange and exchange-correlation hole densities as a function of separation u for the spin-unpolarized uniform electron gas of $r_s = 2$.

A third way of conveying the same information is the pair distribution function, defined as

$$g_\lambda(\mathbf{r}, \mathbf{r}') = \frac{P_\lambda(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} \quad (23)$$

Thus g is symmetric, everywhere positive, and normalized so that

$$\int d^3r' n(\mathbf{r}') (g_\lambda(\mathbf{r}, \mathbf{r}') - 1) = -1. \quad (24)$$

Because the density is uniform in the case of Fig. 1, this is just a plot of $\bar{g}(u) - 1$, where $\bar{g} = \int_0^1 g_\lambda$.

The pair density (at $\lambda = 1$) is often used in the quantum chemistry literature, because traditional *ab-initio* methods are based on wavefunctions. In that language, $P(\mathbf{r}, \mathbf{r}')$ is the reduced diagonal second-order density matrix. The (λ -averaged) exchange-correlation hole is used in density functional theory, because the definition of the exchange-correlation energy includes a kinetic contribution. The pair distribution function is often used in many-body theory [10] and theory of classical liquids. Via the fluctuation-dissipation theorem, it can be related to the equal-time density-density response function (see Dobson Chapter) which, when frequency decomposed, is proportional to the structure factor probed in scattering experiments. Thus the same basic quantity appears in many guises in several fields.

EXACT CONDITIONS

From its definition in terms of the pair density, we can immediately write down several important conditions the hole satisfies. Since the pair density is symmetric

under interchange of \mathbf{r} and \mathbf{r}' , we find

$$n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n_{xc,\lambda}(\mathbf{r} + \mathbf{u}, \mathbf{r}) \frac{n(\mathbf{r} + \mathbf{u})}{n(\mathbf{r})}. \quad (25)$$

Furthermore, since the pair density is never negative,

$$n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \geq -n(\mathbf{r} + \mathbf{u}), \quad (26)$$

i.e., one cannot dig a hole in the density greater than the density itself. This is reflected by the fact that the curves in Fig. 1 never dip below -1.

The dimensional analysis leading to the scaling relation Eq. (13) can also be used to relate the coupling-constant dependence of the hole to its behavior under scaling:

$$n_{xc,\lambda}([n]; \mathbf{r}, \mathbf{r} + \mathbf{u}) = \lambda^3 n_{xc,\lambda=1}([n_1/\lambda]; \lambda\mathbf{r}, \lambda(\mathbf{r} + \mathbf{u})) \quad (27)$$

The exchange (or Fermi) hole is the high-density or weak-coupling limit:

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n_{xc,\lambda=0}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \quad (28)$$

This is the second curve in Fig. 1. The correlation (or Coulomb) hole is then $n_{c,\lambda} = n_{xc,\lambda} - n_x$. Since the exchange contribution satisfies the normalization sum rule

$$\int d^3u n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -1, \quad (29)$$

the correlation hole satisfies

$$\int d^3u n_c(\mathbf{r}, \mathbf{r} + \mathbf{u}) = 0. \quad (30)$$

The exchange hole can be written exactly in terms of the one-particle density matrix. For the spin-unpolarized case, this is simply

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -|n_1(\mathbf{r}, \mathbf{r} + \mathbf{u})|^2 / (2n(\mathbf{r})), \quad (31)$$

where n_1 is the reduced one-matrix. This is never positive:

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) \leq 0 \quad (32)$$

For the uniform gas, this can be written explicitly (see problem 3), and was used to construct the exchange curve in Fig. 1. Note that the correlation hole must contain some positive contributions, so that, e.g., for large u , $n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ is often positive. This occurs for the hole in Fig. 1, but beyond the range of u plotted there. Note also that this figure neglects the Friedel oscillations at large u .

Small separations

The on-top hole, i.e., the hole at zero separation ($u = 0$) from the electron, can be written exactly in special circumstances. The on-top pair density is just $P_{\lambda=0}(\mathbf{r}, \mathbf{r}) = 2n_1(\mathbf{r})n_1(\mathbf{r})$, so that the exchange hole is

$$n_x(\mathbf{r}, \mathbf{r}) = -(n_1^2(\mathbf{r}) + n_1^2(\mathbf{r}))/n(\mathbf{r}) \quad (33)$$

For a spin-unpolarized system, $n_x(\mathbf{r}, \mathbf{r}) = -n(\mathbf{r})/2$, just as shown for the exchange hole in Fig. 1. However, there are two other limits with the interaction turned on where we know the on-top hole. In the strong coupling (or low density) limit, and also in the fully spin-polarized case, the electrons completely avoid each other, so that $P_\lambda(\mathbf{r}, \mathbf{r}) = 0$, or

$$n_{xc,\lambda}(\mathbf{r}, \mathbf{r}) \rightarrow -n(\mathbf{r}) \quad (\lambda \rightarrow \infty \text{ or } \zeta(\mathbf{r}) = 1) \quad (34)$$

where $\zeta = n_1 - n_2$ is the relative spin polarization. One can see that turning on λ in the exchange-correlation hole of Fig. 1 has deepened it relative to $\lambda = 0$. In the low density ($r_s \rightarrow \infty$) limit or if $\zeta = 1$, the curve drops to -1 at $u = 0$.

The on-top hole determines more than just the value of the hole at $u = 0$. As $u \rightarrow 0$, the Coulomb repulsion between electrons dominates their behavior, leading to a cusp in the correlation hole density at $u = 0$. The strength of this cusp is given by a universal condition [11]

$$n'_{xc,\lambda}(\mathbf{r}, 0) = \lambda |n_{xc,\lambda}(\mathbf{r}, 0) + n(\mathbf{r})|, \quad (35)$$

where $n_{xc,\lambda}(\mathbf{r}, u)$ is the spherical average of the hole at \mathbf{r} ,

$$n_{xc,\lambda}(\mathbf{r}, u) = \int \frac{d\Omega_{\mathbf{u}}}{4\pi} n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}), \quad (36)$$

and the prime in Eq. (35) denotes the derivative with respect to u . Thus the on-top hole sets both the scale of the exchange-correlation hole and its leading behavior as $u \rightarrow 0$. This is the origin of the linear behavior of the exchange-correlation curve of Fig. 1, whereas the exchange hole is quadratic in u at small u .

Large separations

We can also write down exact asymptotic expressions for the hole as $u \rightarrow \infty$. In any extended system, finding a second electron far from a first electron must be an independent event, so that $g \rightarrow 1$. In jellium, the exchange hole decays as $1/u^4$, but so too does the correlation hole, exactly cancelling the exchange hole at large u , yielding a $1/u^5$ behavior overall. For solids, there should also be a $1/u^3$ contribution which averages to zero over a single unit cell [12].

But consider Ψ when one coordinate is far from the nuclei in a Coulombic system. The wavefunction collapses to a product of the distant orbital times the wavefunction of the $N - 1$ particle ion, assuming it's not degenerate (see problem 3), i.e., when one electron is far away, the remaining $N - 1$ electrons collapse to their ground state, so that

$$\lim_{r \rightarrow \infty} P_\lambda(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n_\lambda^{\text{ion}}(\mathbf{r}'), \quad (37)$$

where $n_\lambda^{\text{ion}}(\mathbf{r})$ is the λ -dependent density of the $N - 1$ particle ground-state wavefunction of $v_{\text{ext},\lambda}(\mathbf{r})$. The asymptotic form of the hole is then

$$n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r} + \mathbf{u}) (n_\lambda^{\text{ion}}(\mathbf{r})/n(\mathbf{r}) - 1) \quad (u \rightarrow \infty). \quad (38)$$

Note that, contrary to expectation [13], this implies that g does not tend to 1 typically in a finite system as $u \rightarrow \infty$ (see Fig. 2 of Ref. [14]). There are even more interesting long-range correlations that occur when the ion's ground state is degenerate (see Figs. 8-10 of Ref. [15]).

APPROXIMATIONS

In this section, we study various approximations to the energy by considering them as ansatz's for the hole. From Eq. (22), it is clear that a good approximation for the 7-dimensional object $n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ implies a good approximation for E_{xc} , but the converse is *not* true. In fact, the underlying shape of the hole cannot be deduced from a given functional approximation for $E_{xc}[n]$. We see below that there are many properties of this 7-dimensional object which standard approximations (e.g., LSD and GGA) screw up, while still yielding 'good' approximations for E_{xc} . The question of which properties of $n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u})$ should be well-approximated to yield a good approximation for E_{xc} is a subtle one.

Local spin density (LSD) approximation

LSD [16] is by far the most successful density functional approximation to date [13]:

$$E_{xc}^{\text{LSD}} = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{\text{unif}}(n_1(\mathbf{r}), n_2(\mathbf{r})), \quad (39)$$

where $\epsilon_{xc}^{\text{unif}}(n_1, n_2)$ is the accurately known exchange-correlation energy per particle of a uniform gas [17]. It has moderate accuracy for most systems of interest, making errors of order 5-10%. Its most remarkable feature is its reliability, making the same kinds of errors on every system it's applied to. It has been the mainstay of solid-state calculations for many years, because many properties of interest do not require such a drastic rearrangement of bonds as to make LSD inaccurate. On the other hand, it was long avoided by the quantum chemistry community, since reaction energies do require such rearrangements [18].

Eq. (39) suggests the interpretation that LSD works because somehow real systems are close enough to uniform. If that were the case, then the logical extension of LSD, the gradient expansion approximation (GEA)[16], which expands the functional in a Taylor series in gradients of the density [19]:

$$E_{xc}^{\text{GEA}}[n_1, n_2] = E_{xc}^{\text{LSD}}[n_1, n_2] + \sum_{\sigma, \sigma'} \int d^3r C_{\sigma\sigma'}(n_1(\mathbf{r}), n_2(\mathbf{r})) \frac{\nabla n_{\sigma'}}{n_{\sigma'}} \cdot \frac{\nabla n_{\sigma'}}{n_{\sigma'}}, \quad (40)$$

would be just as reliable, but more accurate, than LSD for real systems. However, experience has shown that GEA yields worse energies than LSD.

We can resolve this paradox by considering the LSD exchange-correlation hole. The LSD approximation to the exchange-correlation hole is

$$n_{xc,\lambda}^{\text{LSD}}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r}) \left(g_\lambda^{\text{unif}}(n_1(\mathbf{r}), n_2(\mathbf{r}); u) - 1 \right) \quad (41)$$

where $g_\lambda^{\text{unif}}(n_1, n_2; u)$ is the pair distribution function of a uniform gas of spin densities n_1 and n_2 . Because LSD approximates the hole by that of another system, it satisfies many exact constraints (see problem 9). Both its exchange and exchange-correlation contributions are correctly normalized, and the exchange hole is never negative. Furthermore, the on-top exchange hole is exact in LSD, the on-top exchange-correlation

hole is very accurate [20], and LSD respects the cusp condition. Thus both the scale and the initial slope of the hole are determined by its on-top value, while its shape is determined by the normalization condition. Since the energy and normalization integrals differ simply by a power of u , the LSD energy is usually close to the exact value.

What about the conditions LSD fails to satisfy, such as symmetry and positivity of the pair density? It was shown long ago that in fact LSD does not reproduce *all* details of the hole correctly[21]. In particular, the uniform gas hole is spherical in u , but the true hole may be highly non-spherical[22]. However, the spherically averaged hole usually does compare well with LSD, and the energy only depends on the spherical average. Thus it is most useful to compare only spherically averaged holes when studying LSD.

This argument can be taken a step further, and applied to the system-average in Eq. (22). For r near a nucleus, the Laplacian of the density becomes large, and LSD does not work so well. However, the phase space factor $4\pi r^2$ unweights such a region in the average (see Figs. 1-3 of Ref. [15]). Also, at large distances from finite systems, in the evanescent tail regions, LSD performs poorly, but now the density weighting ensures this makes little contribution. Similar arguments apply to the large u behavior in finite systems, which LSD misses entirely (see the discussion of exact behavior above). These failings do not show up prominently in E_{xc} . For the system-averaged hole, the symmetry condition becomes trivial, while the positivity condition is not very restrictive. Figures 4 and 5 of Ref. [15] show comparisons between exact system-averaged holes and LSD.

Generalized gradient approximations (GGA's)

The term generalized gradient approximation is used to denote any functional which uses both the density and its gradient [23, 24, 25, 26, 27, 28]:

$$E_{xc}^{GGA}[n_1, n_1] = \int d^3r f(n_1(\mathbf{r}), n_1(\mathbf{r}), \nabla n_1, \nabla n_1), \quad (42)$$

We focus here on those GGA's derived using the exchange-correlation hole. The first modern GGA was that of Langreth and Mehl [29], who introduced the idea of truncating the gradient expansion for the hole. This was refined in a sequence of functionals by Perdew (PW86, PW91, PBE) [28]. The details of the real-space cutoff procedure on the hole, which restores the normalization and negativity conditions on the GEA hole, are given *ad nauseam* in another chapter and in Ref. [30]. System-averaged exchange holes are shown in Figs. 9 and 10 of Ref. [31].

We summarize a few results from that chapter to put the GGA in context. The real-space construction restores those exact conditions which LSD satisfies, and a few more besides. It is designed to have the same qualitative properties as LSD, but be somewhat more accurate. The construction applies only to the system and spherically averaged holes, so that even arguments about contributions from specific values of \mathbf{r} do not apply. The LSD on-top hole is built-in as is, while the asymptotic decay with u is different. The long-range decay is cut off by the real-space cutoff procedure, which improves the asymptotic behavior in finite systems, but does not make it exact.

CONCLUSIONS

As we progress in computer power, more sophisticated approximations to the exchange and correlation holes become practical. An early version of a direct construction of these holes is the weighted-density approximation (WDA), which has produced mixed results. The Colle-Salvetti orbital functional is a more successful construction (see SIC chapter), from which the Lee-Yang-Parr (LYP [25]) was derived. A promising way forward to even greater accuracy is to use the exact exchange hole, calculated within, e.g., the KLI approximation[32], as a starting point for modeling the exchange-correlation hole [33]. However, to retain the reliability of what we know (LSD), new approaches should incorporate at least all the known good features of that approximation, as well as some new ones, but not try to get every last detail correct. This philosophy has led to the successful construction of non-empirical GGA's, and may also lead to their successors.

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EXERCISES

1. Calculate explicitly the exchange and correlation holes in a one-electron system.
2. Repeat the previous problem for $N > 1$.
3. Write an explicit expression for the asymptotic behavior of the exchange hole in a finite system as $u \rightarrow \infty$.
4. Develop a functional which incorporates the exact asymptotic exchange-correlation hole.
5. Write down a plausible perturbation expansion for $F_X[\eta]$ as $\lambda \rightarrow 0$.
6. Repeat previous problem for $\lambda \rightarrow \infty$.
7. Construct analytically the exact exchange hole of a uniform gas.
8. Redo previous problem for correlation (see Ref. [9] for an approximation).
9. Prove that the LSD hole satisfies the electron-electron cusp condition.
10. Construct a wavefunction with a cusp using a standard quantum chemical program, i.e., by expanding in single-particle states.

ANSWERS TO ODD-NUMBERED PROBLEMS

1. For a one-electron system, $P(\mathbf{r}, \mathbf{r}') = 0$ everywhere, as there is no chance of finding a second electron. Thus

$$n_{x,c,\lambda}(\mathbf{r}, \mathbf{r}') = -n(\mathbf{r}'). \quad (43)$$

Since the density is held fixed in the coupling constant integration, $n_x(\mathbf{r}, \mathbf{r}') = -n(\mathbf{r}')$ and $n_c(\mathbf{r}, \mathbf{r}') = 0$. Note, however, that local and semi-local functionals which use the density and its gradient at \mathbf{r} to construct the hole, have difficulty reproducing these simple results (see SIC chapter and Ref. [34]).

3. Taking $\lambda = 0$ in Eq. (38), we find

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = n(\mathbf{r} + \mathbf{u}) \left(-|\phi_N(\mathbf{r})|^2/n(\mathbf{r}) \right) \quad (u \rightarrow \infty), \quad (44)$$

where $\phi_N(\mathbf{r})$ is the highest occupied Kohn-Sham orbital.

5. From the same dimensional arguments used to derive Eq. (13), we know $F^\lambda[n] = \lambda^2 F[n_1/\lambda]$. Then, from its definition, we know $T_s[n_\gamma] = \gamma^2 T_s[n]$, we know how E_x scales from Eq. (14), and we can write down a plausible expansion for $E_c[n_\gamma]$ as $\gamma \rightarrow \infty$ consistent with Eq. (14), yielding

$$F^\lambda[n] = T_s[n] + \lambda(T[n] + E_x[n]) + \lambda^2 E_c^{(2)}[n] + \lambda^3 E_c^{(3)}[n] + \dots \quad (45)$$

This expansion is correct for finite systems [35, 36, 37], but logarithmic divergences occur in the uniform gas correlation energy [10].

7. For the uniform gas, the orbitals are simply plane waves, occupied up to the Fermi energy. Evaluation of V_{cc} on this wavefunction, after summing over the occupied states, yields [10] in the spin-unpolarized case

$$n_x^{\text{unif}}(u) = -\frac{9n}{2} \left[\frac{\sin(k_F u) - k_F u \cos(k_F u)}{(k_F u)^3} \right]^2 \quad (46)$$

where n is the density and $k_F = (3\pi^2 n)^{1/3}$ is the Fermi wavevector.

9. Since the uniform gas is a well-defined system, its hole must satisfy the cusp condition Eq. (35) which, in terms of g , is simply

$$g'_\lambda(0) = \lambda g_\lambda(0). \quad (47)$$

Insertion of the LSD hole of Eq. (41) in Eq. (35) and use of the above implies that the LSD hole does satisfy the cusp condition.

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