# Validity of the extended electron-electron cusp condition

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The extended cusp condition asserts that $h(u) - a_0 \, dh(u)/du \geq 0$, where $a_0$ is the Bohr radius, $u$ is the interelectronic spacing, and $h(u)$ is the angle-averaged pair density in the ground state. We prove that this inequality is obeyed by Hooke's atom for any value of the spring constant. However, we also show that this condition is violated by the uniform electron gas of high density. We explain the qualitative difference between these two systems by subtracting a long-range contribution from $h(u)$, leaving a short-range contribution which is amenable to a local density approximation. Thus the extended cusp condition is *not* a universal property of the ground state of inhomogeneous electronic systems.

## I. INTRODUCTION

The problem of finding the ground state of $N(> 1)$ electrons, interacting via Coulomb repulsion in a given external potential, is crucial to the study of atoms, molecules, clusters, surfaces, and bulk solids [1]. In most cases of interest, exact solutions are impractical, and many approximate treatments of this problem have been devised [2]. Unfortunately, the errors made by such treatments are usually difficult to estimate in an ab initio fashion.

However, if the exact solution is known to obey some condition, then how well an approximate solution obeys this condition can be a guide to how good such a solution is. Indeed, such properties often suggest improvements on approximate schemes. For example, the total electron number of the exchange-correlation hole is $-1$, both exactly and in the local-spin-density (LSD) approximation of density-functional theory, and many improvements on the LSD are designed to retain this property [3].

Another important example is the electron-electron cusp condition. To state this condition precisely, we define the electron pair (or intracule) density in terms of the many-particle wave function by

$$I(\mathbf{u}) = \frac{N \, (N-1)}{2} \sum_{\sigma_1, \ldots, \sigma_N} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N$$

$$\times \left| \Psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N) \right|^2 \delta(\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{u}), \qquad (1)$$

where $\mathbf{r}_i\sigma_i$ are the spatial and spin coordinates of the $i$th electron and $\mathbf{u}$ is the interelectronic separation. For simplicity, we work with the angle average of the pair density

$$h(u) = \frac{1}{4\pi} \int d\Omega_u I(\mathbf{u}). \qquad (2)$$

We observe that

$$\int_0^\infty du \, 4\pi u^2 h(u) = \frac{N(N-1)}{2} \qquad (3)$$

is the number of distinct electron pairs, and that $4\pi u^2 h(u) \, du$ is the average number of pairs having interelectronic separation between $u$ and $u + du$. Manifestly, $h(u) \geq 0$. Figure 1 displays $h(u)$ for the ground state of $H^-$. The radial intracule density $4\pi u^2 h(u)$ has recently proven useful in a study of the first-row hydrides [4].

In terms of $h(u)$, and using atomic units ($e = \hbar = m = 1$), the cusp condition is written as

$$h(0) = h'(0), \qquad (4)$$

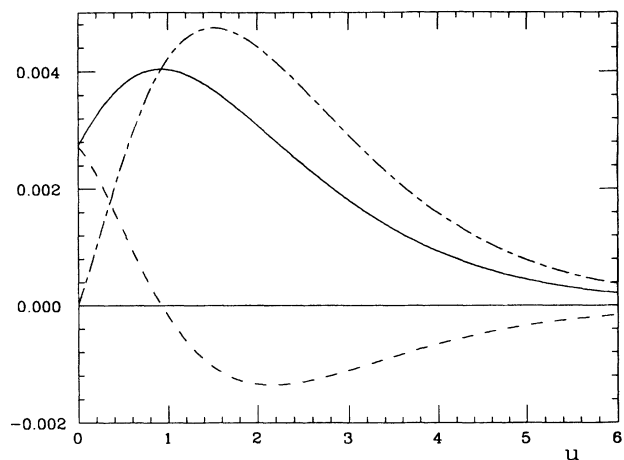where $h'(u) \equiv dh(u)/du$. This condition is true for all



FIG. 1. The solid line is $h(u)$, the dashed line $h'(u)$, and the dotted-dashed line $h(u) - h'(u)$ for $H^-$, calculated using a 204-term Hylleraas-type wave function, as described in Ref. [9].

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electronic systems, being a consequence of the $u^{-1}$ singularity of the Coulomb interaction between electrons [5,6]. It is *not* obeyed by some popular approximations, e.g., the random phase approximation [7,8].

Recently, an extension of this cusp condition has been found to be true numerically, in a Hylleraas-type framework, for certain two-electron ions [9]. This extended cusp condition is simply stated as

$$h(u) - h'(u) \geq 0 \tag{5}$$

for all values of $u$. The above expression becomes an equality for $u = 0$, which corresponds to the usual cusp condition. This property, along with the unimodality of $h(u)$ [10] (see Sec. II for details), has been used to generate exact bounds [11] on the central pair density $h(0)$, the location $u_{max}$ of the maximum of $h(u)$, and various expectation values $\langle u^\alpha \rangle$ [9,10,12]. Other related results have been obtained by means of variational procedures [13] or from the study of the logarithmic convexity of $h(u)$ [14]. This naturally leads to the question of whether or not $h(u)$ obeys the extended cusp condition for the ground state of all electronic systems, the answer to which is the focus of this paper.

We may also write $h(u)$ in terms of the pair distribution function for the system, $g(\mathbf{r}, \mathbf{r}')$, defined by

$$g(\mathbf{r}, \mathbf{r}') = \frac{\langle \hat{n}(\mathbf{r}) \, \hat{n}(\mathbf{r}') \rangle}{n(\mathbf{r}) \, n(\mathbf{r}')} - \frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})}, \tag{6}$$

where $\hat{n}(\mathbf{r})$ is the density operator at point $\mathbf{r}$, and $n(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle$ [15]. Then

$$h(u) = \frac{1}{2} \int d^3r \, n(\mathbf{r}) \int \frac{d\Omega_u}{4\pi} \, n(\mathbf{r} + \mathbf{u}) \, g(\mathbf{r}, \mathbf{r} + \mathbf{u}). \tag{7}$$

Note that there is no coupling-constant average here, so we are not dealing with the exchange-correlation hole of density-functional theory [16].

However, we can still apply the ideas of density-functional theory to analyze $h(u)$. For large values of $u$, $g(\mathbf{r}, \mathbf{r} + \mathbf{u}) \to 1$, so that $h(u)$ is typically a long-ranged function of $u$. We may separate out a reasonably short-ranged contribution, in the spirit of the LSD approximation. We write

$$h(u) = h_{sr}(u) + h_{lr}(u), \tag{8}$$

where

$$h_{sr}(u) = \frac{1}{2} \int d^3r \, n(\mathbf{r}) \int \frac{d\Omega_u}{4\pi} \, n(\mathbf{r} + \mathbf{u})[g(\mathbf{r}, \mathbf{r} + \mathbf{u}) - 1] \tag{9}$$

and vanishes for large $u$, while

$$h_{lr}(u) = \frac{1}{2} \int d^3r \, n(\mathbf{r}) \int \frac{d\Omega_u}{4\pi} \, n(\mathbf{r} + \mathbf{u}). \tag{10}$$

Note that since $h_{lr}(u) = h_{lr}(0) + O(u^2)$ for small values of $u$, it has no cusp, and integrates to $N^2/2$, while $h_{sr}(u)$ contains the cusp, and integrates to $-N/2$. Now the expectation value of the electron-electron repulsion

operator is

$$\langle \hat{V}_{ee} \rangle = \int_0^\infty du \, 4\pi u^2 \, h(u) \, \frac{1}{u}, \tag{11}$$

where the long-range (lr) part is the "direct classical Coulomb energy," treated exactly in Hartree, Hartree-Fock, and density-functional theories [17], while the short-range (sr) part is amenable to a local-spin-density approximation, like the exchange-correlation energy [17] which is its average over coupling constant [18,19]. [More precisely, the coupling-constant average of $h_{sr}(u)$ is $N/2$ times the system-averaged exchange-correlation hole [20].]

In Sec. II we study a particular two-electron system, the Hooke's atom, where we prove the extended cusp condition given by Eq. (5) and unimodality for the ground state for all values of the spring constant. Section III is a study of $h(u)$ for the uniform electron gas, where it is proportional to the pair distribution function, $g(u)$, which is well-known for this system. Here, we find $h_{lr}(u)$ is a constant, independent of $u$, so that all the $u$ dependence in $h$ comes from $h_{sr}(u)$. We find that the extended cusp condition is violated at high densities, and give an argument which does not depend on the details of any particular parametrization for $g(u)$. In Sec. IV we explain how the high density limit for the uniform electron gas, in which the extended cusp condition is violated, is related to the high-density limit of the Hooke's atom, in which the extended cusp condition is obeyed. We also consider how well the LSD approximation does for $h_{sr}(u)$. Section V gives our conclusions and their implications.

## II. HOOKE'S ATOM

It is not easy to find a quantum many-body system for which the Schrödinger equation may be solved analytically. However, a useful example is provided by the problem of two electrons in an external harmonic-oscillator potential, called the Hooke's atom [21–24]. The Hamiltonian for this system is

$$H = -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{1}{2} k(r_1^2 + r_2^2) + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{12}$$

where $\nabla_i = \partial/\partial \mathbf{r}_i$. In center-of-mass and relative coordinates, this becomes

$$H = -\left( \frac{1}{4} \nabla_\mathbf{R}^2 + \nabla_\mathbf{u}^2 \right) + kR^2 + \frac{k}{4} u^2 + \frac{1}{u}, \tag{13}$$

where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$. For spin singlet states, the total wave function may therefore be separated:

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \varphi(\mathbf{u}) \, \xi(\mathbf{R}) \, \chi(\sigma_1, \sigma_2), \tag{14}$$

where $\chi(\sigma_1, \sigma_2)$ is the singlet spin wave function. The motion in $\mathbf{R}$ is simply that of a three-dimensional harmonic oscillator with mass 2 and force constant $2k$. From Eq. (1) we obtain the electron-pair density

$$I(\mathbf{u}) = |\varphi(\mathbf{u})|^2, \tag{15}$$

by choosing our normalization so that $\int d^3u |\varphi(\mathbf{u})|^2 = 1$. It is possible to separate the angular and radial contributions as

$$\varphi(\mathbf{u}) = \frac{f(u)}{u} Y_{lm}(\Omega_u). \tag{16}$$

From Eq. (13), this yields a second-order differential equation for the interelectronic function $f(u)$, namely

$$\left[ -\frac{1}{2}\frac{d^2}{du^2} + \frac{1}{8}\omega^2 u^2 + \frac{1}{2u} + \frac{l(l+1)}{2u^2} \right] f(u) = \frac{\epsilon}{2} f(u), \tag{17}$$

where $\omega = \sqrt{k}$ is the oscillator frequency and $\epsilon$ is the contribution to the total energy due to the relative motion of the electrons.

For any value of the force constant $k$, at most a single differential equation needs to be solved to find the ground state of this system. This has been done numerically [21] for many values of $k$. More recently, Kais [22] and co-workers have studied the special case of $k = 1/4$, for which an analytic solution exists, while Taut [23] has shown that analytic solutions exist for an infinite, discrete set of oscillator frequencies, including both ground and excited states. Those corresponding to extremely low densities have been studied in some detail [24].

We prove here some general properties of the ground state, for which $l = 0$, which apply for all values of the spring constant. Taking into account Eqs. (2), (15), and (16), and the fact that $f(u)$ has no nodes for the ground state [23] (i.e., $h(u) > 0$), we rewrite Eq. (17) in terms of the electron-pair density $h(u)$:

$$\frac{u}{2}\frac{h''(u)}{h(u)} + \frac{h'(u)}{h(u)} - \frac{u}{4}\left[\frac{h'(u)}{h(u)}\right]^2 = \frac{1}{4}\omega^2 u^3 - \epsilon u + 1. \tag{18}$$

This equation may be simplified by introducing the logarithmic derivative

$$H(u) \equiv d\ln h(u)/du = h'(u)/h(u). \tag{19}$$

Inserting this definition in Eq. (18), we find

$$uH^2(u) + 4[H(u) - 1] + 2uH'(u) = u(\omega^2 u^2 - 4\epsilon). \tag{20}$$

Note that $H(u)$ has no singularities for the ground state, because $h(u)$ is strictly positive everywhere.

From Eq. (20), we are going to prove (a) the usual cusp condition $h'(0) = h(0)$, (b) the extended cusp condition $h'(u) \le h(u)$, and (c) the unimodality of $h(u)$, i.e., that $h(u)$ has precisely one maximum. In terms of the function $H(u)$, these properties are written as (a) $H(0) = 1$, (b) $H(u) \le 1$, and (c) $H(u) = 0$ once and only once.

### A. Cusp condition

The cusp condition at the origin, Eq. (4), follows directly from Eq. (20), by taking $u \to 0$. Furthermore, by dividing Eq. (20) first by $u$ and taking the same limit, one obtains

$$H'(0) = -\frac{1 + 4\epsilon}{6}. \tag{21}$$

Since $\epsilon > 0$, this implies that $H(u)$ is less than 1 for small values of $u$.

### B. Extended cusp condition

For large values of $u$, the electron-pair density $h(u)$ of a finite system monotonically decreases, or, equivalently, $H(u) \le 0$ for large $u$. Let us consider the situation of Fig. 2, in which the extended cusp condition is violated, i.e., $H(u) > 1$ in some region. But, differentiating Eq. (20), we obtain

$$H^2(u) + 2uH(u)H'(u) + 6H'(u)$$
$$+ 2uH''(u) = 3\omega^2 u^2 - 4\epsilon. \tag{22}$$

Multiplication of Eq. (22) by $u$ and subtraction of Eq. (20) leads to

$$u^2 H(u)H'(u) + 2uH'(u) + u^2 H''(u)$$
$$+ 2[1 - H(u)] = \omega^2 u^3. \tag{23}$$

At the maximum $u_0$, we have $H(u_0) > 1$ and $H'(u_0) = 0$. Taking into account that $H'(u_0) = 0$, it follows that

$$u_0^2 H''(u_0) = \omega^2 u_0^3 + 2[H(u_0) - 1]. \tag{24}$$

Since $H(u_0) > 1$, Eq. (24) implies that $H''(u_0) > 0$, which contradicts our original assumption that $u_0$ is a maximum. Thus no maximum can occur, and the extended cusp condition holds for the ground-state Hooke's atom.

### C. Unimodality of $h(u)$

In this section we prove that $H(u) = 0$ exactly once. First we note that, since $H(0) > 0$ and $\lim_{u \to \infty} H(u) \le 0$, $H(u)$ must vanish at least once.
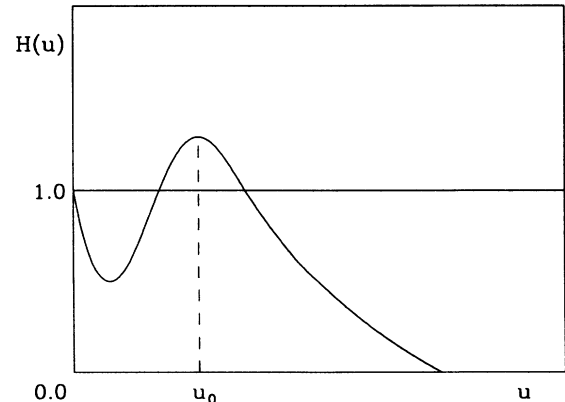


FIG. 2. Schematic of how the function $H(u)$ would behave if the extended cusp condition were violated.

Next suppose that $H(u) = 0$ more than once, as shown in the hypothetical schematic of Fig. 3. We will show, by contradiction, that this situation is impossible.

We begin with the last zero of $H(u)$, which is labeled $u_C$. At $u_C$, $H(u_C) = 0$, so that Eq. (20) yields

$$2u_C H'(u_C) = \omega^2 u_C^3 - 4\epsilon u_C + 4. \qquad (25)$$

But $H'(u_C) \leq 0$, so that $\omega^2 u_C^2 - 4\epsilon \leq -4/u_C$. Since $u_C > 0$, this means that

$$u_C < \frac{2\sqrt{\epsilon}}{\omega}. \qquad (26)$$

So, we have proven that $H(u)$ has no zeros [i.e., that $h(u)$ is monotonically decreasing] beyond the point $u = 2\sqrt{\epsilon}/\omega$.

Next we consider other possible roots of $H(u) = 0$. For the moment, we assume that $H'(u_C) < 0$, and we address the case $H'(u_C) = 0$ later. In that case, $H(u)$ is positive and rising as a function of $u_C - u$ for $u$ close to, but smaller than, $u_C$. To produce another zero between 0 and $u_C$, $H(u)$ must turn back down toward the axis, so that there must be a point $u_B$ at which there is a maximum in $H(u)$, i.e., $H'(u_B) = 0$. At such a point, Eq. (24) holds, and may be rearranged to yield

$$\omega^2 u^3 - 2 = u^2 H''(u) - 2H(u). \qquad (27)$$

This result is valid for any extremum of $H(u)$. In the present case, $H(u_B) > 0$, while $H''(u_B) \leq 0$, so that

$$u_B \leq (2/\omega^2)^{1/3}. \qquad (28)$$

Now, for $H(u)$ to have another zero, the function must either touch or cross the axis, and then turn back up again as a function of $u_B - u$, in order to satisfy the cusp condition at the origin, $H(0) = 1$. We denote this minimum by $u_A$, and apply Eq. (27). Since $H(u_A) \leq 0$, and $H''(u_A) \geq 0$, we find

$$u_A \geq (2/\omega^2)^{1/3}. \qquad (29)$$

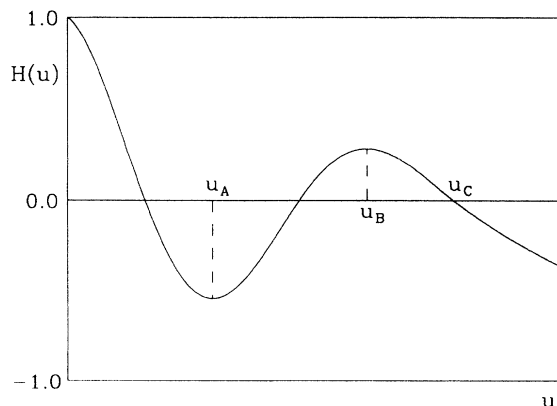But $u_B \geq u_A$ by construction, and $u_A = u_B$ is impossi-

ble, as $H(u_B) > 0$, while $H(u_A) \leq 0$. Thus there can be no more zeros of $H(u)$ for $u < u_C$, assuming $H'(u_C) \neq 0$.

Lastly, we show that $H'(u_C) = 0$ also leads to a contradiction. This would be the case if $u_B$ were merged into $u_C$ in Fig. 3. If that were true, then Eq. (27) would also apply to $u_C$. But $H(u_C) = 0$ and $H''(u_C) < 0$, since $H(u)$ approaches 0 from below as $u \to u_C$. Thus

$$u_C < (2/\omega^2)^{1/3}. \qquad (30)$$

For some value of $u < u_C$, there must be a point like $u_A$ in the figure, which obeys Eq. (29), and therefore produces a contradiction. Thus we have shown both that $h(u)$ is unimodal, and that its only extremum is for $u < 2\sqrt{\epsilon}/\omega$.

## III. UNIFORM ELECTRON GAS

In this section, we discuss the extended cusp condition [Eq. (5)] for the case of a uniform electron gas. Because the system is translationally invariant, Eq. (7) becomes

$$h(u) = \frac{1}{2} n N g(r_s, \zeta, u), \qquad (31)$$

where $n$ is the (uniform) density of the system, and $g(r_s, \zeta, u)$ is the pair distribution function in a uniform gas of density $n = 3/(4\pi r_s^3)$ and relative spin polarization $\zeta$, at separation $u$. This function has been the subject of intense study for many years, as it leads to the correlation energy per particle of the uniform gas, a key ingredient in constructing the local density approximation of density-functional theory. A recent accurate parametrization for $g(r_s, \zeta, u)$ has been given by Perdew and Wang [25], and encoded by He [26], based on known limits and scaling relations; it agrees well with existing Monte Carlo data [27–30].

We first note that unimodality is not obeyed by the uniform gas. This is because $g(u)$ contains Friedel oscillations at large values of $u$, due to the presence of a Fermi surface. These oscillations have wave vector equal to $2k_F$, where $k_F = (3\pi^2 n)^{1/3}$ is the Fermi wave vector. Note that the parametrization of Perdew and Wang used here does not include these oscillations, which are usually insignificant in determining the exchange-correlation energy, and are irrelevant to the discussion given below.

Next we consider the extended cusp condition. In Fig. 4, we plot the function $g(u) - g'(u)$ for various values of $r_s$, with $\zeta = 0$. We see that, for sufficiently low densities, i.e., large $r_s$, the extended cusp condition Eq. (5) is satisfied, but for high densities, it is violated. In Fig. 5, we keep $r_s = 0.5$, and plot $g(u) - g'(u)$ for various values of $\zeta$. We find violations of Eq. (5) for all spin polarizations.

To understand why the extended cusp condition is violated at high densities, we separate $g(u)$ into its exchange and correlation contributions,

$$g(u) = g_x(u) + g_c(u). \qquad (32)$$

In the high density limit, $g_x(u)$ dominates. Now $g_x(u)$ varies between $1/2$ and $1$ on a length scale of order $1/(2k_F)$, and so $g'_x(u) \approx O(2k_F)$. We also know $g'_x(u)$ must be positive for some value of $u$. Thus, as $k_F \to \infty$,



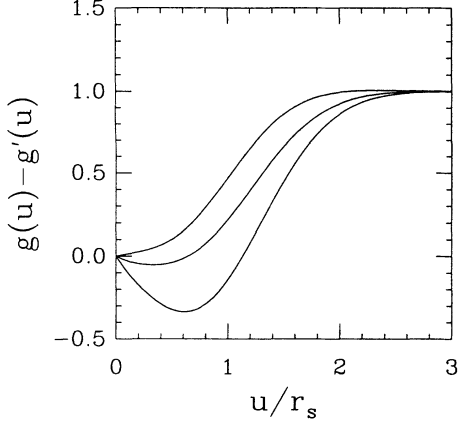FIG. 3. Schematic of how $H(u)$ might behave if unimodality were violated.

FIG. 4. Plots of $g(u) - g'(u)$ with $\zeta = 0$ and $r_s = 0.5$ (lowest line), $r_s = 1.0$ (middle line), or $r_s = 5.0$ (upper line) for the uniform gas.

$g'_x(u)$ becomes very large and positive, while $g_x(u) \approx 1$, so that the extended cusp condition is violated. It is straightforward to check explicitly the well-known formula for $g_x(u)$ for the uniform gas [25] to see that it has these properties.

Note that such considerations do not apply to the cusp condition at the origin, which the uniform gas *does* obey. This is because $g_x(u)$ has no cusp at the origin, i.e., $g'_x(0) = 0$. Here the correlation contribution becomes significant, and in fact must suffice to fulfill the cusp condition. Since it is known that, as $r_s \to 0$,

$$g(0) = \frac{1}{2}(1 - \alpha r_s), \tag{33}$$

where $\alpha = 2(4/9\pi)^{1/3} (\pi^2 + 6\ln 2 - 3)/(5\pi)$ for the uniform electron gas [31,32], and is generally system dependent [33], we deduce that, for $u \ll r_s \ll 1$,

$$g_c(u) = \frac{-\alpha r_s + u(1 - \alpha r_s)}{2} + O(u^2) \tag{34}$$
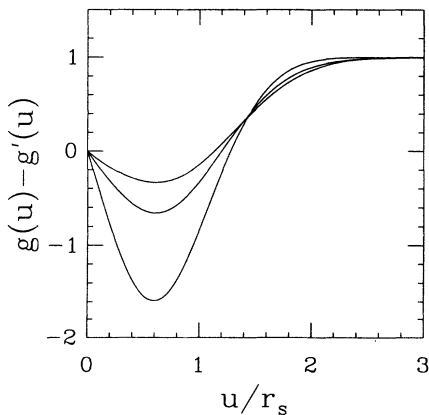
in the high density limit.



FIG. 5. Plots of $g(u) - g'(u)$ with $r_s = 0.5$ and $\zeta = 0$ (smallest dip), $\zeta = 0.5$ (middle dip), or $\zeta = 1.0$ (largest dip) for the uniform gas.

## IV. LONG- AND SHORT-RANGE CONTRIBUTIONS TO $h(u)$

The preceding two sections suggest a possible contradiction. In Sec. III we showed that, at high densities, the uniform gas violates the extended cusp condition, and gave a compelling argument for this result. However, in Sec. II, we showed that the Hooke's atom obeys the extended cusp condition for all values of the spring force constant, including large values which produce a very high density. We discuss in the present section a qualitative difference between these two systems which explains why one violates the extended cusp condition, while the other does not.

Recall the separation in Sec. I of $h(u)$ into short- and long-ranged contributions. Consider how these separate contributions behave in the high-density limit of a two-electron system. Again, exchange dominates, but now $g_x(u) = 1/2$ everywhere. Thus we find, from Eqs. (7)-(10),

$$h(u) = \frac{1}{2}h_{lr}(u) = -h_{sr}(u). \tag{35}$$

Clearly, if $h(u)$ then obeys the extended cusp condition, so also does $h_{lr}(u)$; but $h_{sr}(u) - h'_{sr}(u) \leq 0$ for all $u$. In the particular case of the Hooke's atom, the high density (or noninteracting) limit is just a pair of three-dimensional harmonic oscillators. The ground-state wave functions are simple Gaussians, yielding a density

$$n(r) = \frac{2}{u_0^3}\left(\frac{2}{\pi}\right)^{3/2} \exp(-2\, r^2/u_0^2), \tag{36}$$

where $u_0 = (4/k)^{1/4}$ is a measure of the radius of the system. Equation (10) then yields

$$h_{lr}(u) = \frac{2}{u_0^3}\left(\frac{1}{\pi}\right)^{3/2} \exp(-u^2/u_0^2). \tag{37}$$

Now, for $u$ finite (and nonzero) on the scale of $u_0$, we find $h'_{lr}(u)/h_{lr}(0) \approx O(1/u_0)$, which becomes very large and negative for small $u_0$. But from Eq. (35), $h_{sr}(u) = -h_{lr}(u)/2$. Thus the extended cusp condition is obeyed by the total $h(u)$, but $h_{sr}(u)$ alone contains an extreme violation of the extended cusp condition.

We note in passing that, just as in the uniform gas, the exchange contribution alone violates the exact cusp condition at the origin, where its derivative vanishes. In the Appendix we give the details of a perturbation calculation, in which the Coulomb repulsion is treated to first order, and show that the leading correlation contribution restores the cusp condition at the origin, again just as in the case of the uniform gas.

To compare this high density behavior with that of the uniform gas, note that the short-range $h_{sr}(u)$ behaves quite similarly in both systems, while $h_{lr}(u)$ is very different. In fact, we can make an LSD approximation to $h_{sr}(u)$ for nonuniform systems, by defining

$$h_{sr}^{LSD}(u) = \frac{1}{2}\int d^3r\; n^2(\mathbf{r})[g(r_s(\mathbf{r}), \zeta(\mathbf{r}), u) - 1], \tag{38}$$

where $g[r_s(\mathbf{r}), \zeta(\mathbf{r}), u]$ is the uniform gas pair distribution function, $r_s(\mathbf{r}) = [4\pi n(\mathbf{r})/3]^{-1/3}$, and $\zeta(\mathbf{r})$ is the relative spin polarization at $\mathbf{r}$. In Fig. 6, we plot both $h_{sr}(u)$ and $h_{sr}^{LSD}(u)$ for the high density limit of the Hooke's atom, where the density is given by Eq. (36), $\zeta = 0$, $h_{sr}(u)$ is given by Eqs. (35) and (37), and $g$ appearing in Eq. (38) contains only the exchange contribution. We see that the LSD approximation is generally good, especially in regions where $h_{sr}(u)$ is large. One of the reasons for its success is that $h_{sr}^{LSD}(u)$ integrates to $-1$, just as the exact $h_{sr}(u)$ does. Furthermore, for high densities, $g(r_s, \zeta = 0, u = 0) = 1/2$, so that $h_{sr}^{LSD}(u = 0) = h_{sr}(u = 0)$. (At lower densities, the LSD value at the origin is expected to be approximately correct [8].) Note that, while the decay in $h_{sr}(u)$ is due entirely to the falloff in density of the Hooke's atom, as its pair distribution function $g = 1/2$ everywhere, the decay in $h_{sr}^{LSD}(u)$ is due to the decay in the uniform gas value of $g - 1$.

The above analysis explains why the uniform gas behaves so differently from the Hooke's atom in the high density limit. In both systems, $h_{sr}(u)$ behaves very similarly, developing a large, positive derivative for finite $u$ as $n \to \infty$. However, the Hooke's atom $h'(u)$ also contains contributions from $h'_{lr}(u)$ due to the density gradient, which have no analog in the uniform electron gas. These are sufficient to cancel the contributions from $h'_{sr}(u)$, so that the extended cusp condition remains valid for this system.

Another useful separation which highlights the deviations from behavior similar to the uniform gas, and which may be applied to any system, is

$$h(u) = h_0(u) + h_2(u), \qquad (39)$$

where

$$h_0(u) = \frac{1}{2} \int d^3r \, n(\mathbf{r}) \int \frac{d\Omega_u}{4\pi} \, n(\mathbf{r} + \mathbf{u})[g(\mathbf{r}, \mathbf{r} + \mathbf{u}) - 1]$$
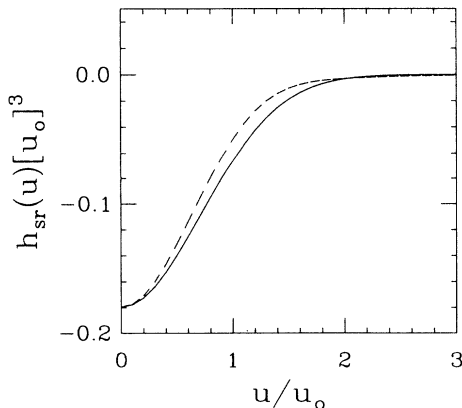$$+ \frac{1}{2} \int d^3r \, n^2(\mathbf{r}), \qquad (40)$$

and

$$h_2(u) = \frac{1}{2} \int d^3r \, n(\mathbf{r}) \int \frac{d\Omega_u}{4\pi} \, [n(\mathbf{r} + \mathbf{u}) - n(\mathbf{r})]. \quad (41)$$

Within the LSD approximation of Eq. (38),

$$h_0^{LSD}(u) = \frac{1}{2} \int d^3r \, n^2(\mathbf{r}) \, g[r_s(\mathbf{r}), \zeta(\mathbf{r}), u] \qquad (42)$$

is a system average of the uniform gas $h(u)$, which violates the extended cusp condition Eq. (5) for sufficiently high densities, and $h_2(u)$ is an inhomogeneity correction. Taylor expansion of $n(\mathbf{r} + \mathbf{u})$ to second order in $\mathbf{u}$, and subsequent integration by parts, gives

$$h_2(u) - h'_2(u) = \frac{u}{6} \int d^3r |\nabla n|^2 \geq 0, \qquad (43)$$

to first order in $u$. Thus the $h_2(u)$ term by itself satisfies the extended cusp condition for small $u$, and so helps $h(u)$ to satisfy this condition at small $u$ for a rapidly varying $n(\mathbf{r})$.

Although both $h_{lr}(\mathbf{r})$ and $h_2(\mathbf{r})$ satisfy the extended cusp condition for small $u$, they can still violate it at large $u$. For example, consider a system composed of two fragments, each of radius $R$, with centers separated by a distance $a \gg 2R$. If the density of each fragment vanishes outside its own radius, then $h_{lr}(u)$ vanishes for $2R < u < a - 2R$, but rises again as $u$ exceeds $a - 2R$, making $h_{lr}(u) - h'_{lr}(u) < 0$ for $u \approx a - 2R$.

## V. CONCLUSIONS

Clearly, the most important conclusion from this work is that the extended cusp condition is not true for the ground state of all inhomogeneous systems. It may be true in more limited cases, e.g., for all two-electron systems, or perhaps for all atoms and ions. We can expect violations of the extended cusp condition in systems which have sufficiently large and slowly varying densities. This is not the case for the high-density limit of few-electron ions, where the density never becomes nearly uniform. For the Hooke's atom discussed here, Eq. (36) shows that the density always varies on the length scale $u_0$, the "radius" of the atom. We also showed that unimodality is trivially not obeyed by the uniform gas. These examples illustrate the danger of assuming that conditions which are obeyed by specific classes of systems can be transferred to all inhomogeneous electron systems.

## APPENDIX

In this Appendix, we show how the leading corrections to the high-density limit of the Hooke's atom ensure that



FIG. 6. Comparison of $h_{sr}(u)$ (solid line) and $h_{sr}^{LSD}(u)$ (dashed line) for the high-density Hooke's atom.

$h(u)$ obeys the cusp condition at the origin. We treat the Coulomb repulsion as a weak perturbation on the noninteracting system, and write

$$h(u) = h^{(0)}(u) + h^{(1)}(u) + \cdots, \tag{A1}$$

where the superscripts label powers of $e^2$. By expanding the definition of $h(u)$, Eqs. (1) and (2), we find

$$h^{(1)}(u) = \int \frac{d\Omega_u}{4\pi} \int d^3R \ 2\,\mathrm{Re}\big[\Psi_0^{(0)*}(\mathbf{u,R})\Psi_0^{(1)}(\mathbf{u,R})\big], \tag{A2}$$

where the subscripts label the particular eigenstate, e.g., 0 labels the ground state, and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the center-of-mass coordinate. The leading correction to the ground-state wave function may be expanded in terms of the excited states of the unperturbed system in the usual way:

$$\Psi_0^{(1)}(\mathbf{u,R}) = \sum_{\nu \neq 0} c_\nu \Psi_\nu^{(0)}(\mathbf{u,R}), \tag{A3}$$

where $\nu$ labels all the noninteracting system eigenstates, and

$$c_\nu = \int d^3u \int d^3R \ \Psi_0^{(0)*}(\mathbf{u,R})\frac{e^2}{u}\Psi_\nu^{(0)}(\mathbf{u,R})/(E_0 - E_\nu), \tag{A4}$$

where $E_\nu$ is the eigenvalue of the $\nu$th noninteracting state. Since both the potential $e^2/u$ and the ground state are spherically symmetric in $\mathbf{u}$, and the potential is independent of $\mathbf{R}$, the only nonzero values of $c_\nu$ are those corresponding to spherically symmetric states in $\mathbf{u}$, and the ground state in $\mathbf{R}$. We label these nonzero coefficients with the $u$ radial quantum number $n$. Then $E_0 - E_n = 3\omega/2 - (2n + 3/2)\omega = -2n\omega$, and

$$c_n = -\frac{2\pi}{n\omega} \int_0^\infty du \ u \ \phi_0^*(u) \ \phi_n(u), \tag{A5}$$

where the state $\phi_n(u)$ is the $n$th spherically symmetric eigenstate of a three dimensional oscillator with reduced mass $\mu = 1/2$, and is given by [34]

$$\phi_n(u) = b_n \ L_n^{(1/2)}\Big(\frac{u^2}{u_0^2}\Big) \ e^{-u^2/2u_0^2}, \tag{A6}$$

where $L_n^{(1/2)}(x)$ is the associated Laguerre polynomial

of order 1/2 [35], and the normalization constant $b_n$ is given by $b_n = \big[n!/(2\pi\Gamma(n + 3/2)u_0^3)\big]^{1/2}$. The integral appearing in Eq. (A5) may be easily evaluated using the generating function for these polynomials [35], and we find

$$c_n = -\frac{u_0 \ \sqrt{(2n+1)!/\pi}}{n! \ n \ (2n+1) \ 2^{n+1}}. \tag{A7}$$

Inserting this result in Eq. (A2), we find that the first correction to the angle-averaged pair density has the form

$$h^{(1)}(u) = -u_0 \ h^{(0)}(u) \ f(u/u_0), \tag{A8}$$

where

$$f(x) = \frac{1}{\sqrt{\pi}} \sum_{n=1}^\infty \frac{L_n^{(1/2)}(x^2)}{n \ (2n+1)}. \tag{A9}$$

The individual Laguerre polynomials in the sum in Eq. (A9) each have a well-defined Taylor expansion about the origin. However, the sum does not, as may be seen by performing the expansion, and finding that the coefficient of $x^2$ is a diverging sum. We may still extract the cusp contribution by use of the following identity:

$$x = \frac{2}{\sqrt{\pi}} \sum_{n=0}^\infty \frac{L_n^{(1/2)}(x^2)}{1 - 4n^2}, \tag{A10}$$

which can be proven using the generating function [35]. Note that the coefficients in this sum decay as $(-1/2n^2)$ for large $n$, the same behavior as in $f(x)$. We can therefore deduce that $f(x)$ indeed contains a term linear in $x$, and can find its contribution analytically by subtracting $x$ and adding the sum on the right-hand side of Eq. (A10). This yields

$$f(x) = \frac{2}{\sqrt{\pi}} - x - \frac{1}{4\sqrt{\pi}} \sum_{n=1}^\infty \frac{L_n^{(1/2)}(x^2)}{(n + 1/2) \ n \ (n - 1/2)}. \tag{A11}$$

Because the coefficients in the sum now fall off more rapidly for large $n$, that term in Eq. (A11) contains no linear contribution.

Finally, we insert this form of $f(x)$ into Eq. (A8) and consider small values of $u$. Since $df/dx = -1$ at $x = 0$, we find that the cusp condition at the origin, Eq. (4), is indeed obeyed to leading order in $u_0$.

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