

# How to Tell an Atom From an Electron Gas: A Semi-Local Index of Density Inhomogeneity

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From a global perspective, the density of an atom is strongly inhomogeneous and not at all like the density of a uniform or nearly-uniform electron gas. But, from the semi-local or myopic perspective of standard density functional approximations to the exchange-correlation energy, it is not so easy to tell an atom from an electron gas. We address the following problem: Given the ground-state electron density  $n$  and orbital kinetic energy density  $\tau$  in the neighborhood of a point  $\mathbf{r}$ , can we construct an “inhomogeneity index”  $w(\mathbf{r})$  which approaches zero for weakly-inhomogeneous densities and unity for strongly-inhomogeneous ones? The solution requires not only the usual local ingredients of a meta-generalized gradient approximation ( $n, \nabla n, \nabla^2 n, \tau$ ), but also  $\nabla\tau$  and  $\nabla^2\tau$ . The inhomogeneity index is displayed for atoms, and for model densities of metal surfaces and bulk metals. Scaling behavior and a possible application to functional interpolation are discussed.

## I. INTRODUCTION

How can we tell an atom from a uniform electron gas, or from an electron gas of slowly-varying or nearly-uniform density? From a global perspective, the answer is trivial: The atom has a few electrons strongly confined to a small region of space, while the electron gas has an infinite number of electrons distributed smoothly over all space. But from the local or semi-local perspective of density functional theory, which looks at the electron density  $n$  and perhaps the Kohn-Sham orbital kinetic energy density  $\tau$  only in each small volume element, the answer is not so simple.

Some of the most successful density functionals for the exchange-correlation energy of a many-electron system transfer information from the slowly-varying electron gas to the densities of real atoms, molecules and solids. This is a major achievement, since most of the density of an atom is very different from that of a slowly-varying electron gas. To show this, we shall construct an “inhomogeneity index”  $w(\mathbf{r})$  which vanishes for a uniform density but approaches unity where the density is strongly inhomogeneous. No single semi-local inhomogeneity parameter suffices. A composite index (rather like a stock market index) is needed; it should approach unity when any one of its many inhomogeneity parameters is large. As we will see, the construction of an adequate inhomogeneity index from the behavior of the electron density  $n$  and orbital kinetic energy density  $\tau$  in the neighborhood

of the point  $\mathbf{r}$  is a subtle problem. It requires using all of the local ingredients of modern density functionals, and more.

The local density approximation (LDA) for exchange [1–3] has evolved over the years into the modern Kohn-Sham [3] density functional theory, the cornerstone of most electronic structure calculations in both condensed matter physics and quantum chemistry. In LDA, the exchange energy  $E_x$  and potential  $v_x(\mathbf{r})$  for a ground-state electron-density  $n(\mathbf{r})$  are approximated as

$$E_x^{\text{LDA}} = \int d^3r n(\mathbf{r}) \epsilon_x^{\text{unif}}(n(\mathbf{r})), \quad (1)$$

$$v_x^{\text{LDA}}(\mathbf{r}) = v_x^{\text{unif}}(n(\mathbf{r})), \quad (2)$$

where

$$\epsilon_x^{\text{unif}}(n) = -\frac{3}{4\pi}(3\pi^2 n)^{1/3} = -\frac{3}{4\pi}k_F \quad (3)$$

is the exchange energy per electron of an electron gas of uniform density  $n$  (in atomic units, where  $\hbar = m = e^2 = 1$ ).  $k_F$  in Eq. (3) is the Fermi wave-vector:  $n = k_F^3/3\pi^2$ . The exchange potential is

$$v_x^{\text{unif}}(n) = \partial(n\epsilon_x^{\text{unif}}(n)) = -\frac{1}{\pi}(3\pi^2 n)^{1/3} = -\frac{1}{\pi}k_F. \quad (4)$$

LDA is exact for a uniform or slowly-varying density; it assumes that each volume element  $d^3r$  is like a volume element of a uniform gas at the local density  $n(\mathbf{r})$ .

Equations (1)–(4) are also known as Gáspár-Kohn-Sham exchange. Slater [4] also pioneered the use of Eq. (4), but with a coefficient that was not quite right for a slowly-varying density [1, 3] or for an atom of large atomic number [2].

In modern density functional theory, this idea is extended to include correlation, and the list of local ingredients is expanded. For example, a generalized gradient approximation (GGA) [5] uses the spin densities ( $n_\uparrow, n_\downarrow$ ) and their gradients ( $\nabla n_\uparrow, \nabla n_\downarrow$ ). The meta-GGA for exchange and correlation [6–12] is

$$E_{xc}^{\text{MGGA}} = \int d^3r n(\mathbf{r}) \times \epsilon_{xc}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \nabla^2 n_\uparrow, \nabla^2 n_\downarrow, \tau_\uparrow, \tau_\downarrow), \quad (5)$$

where

$$\tau_\sigma(\mathbf{r}) = \sum_{\alpha}^{\text{occup}} \frac{1}{2} |\nabla \psi_{\alpha\sigma}(\mathbf{r})|^2 \quad (6)$$

is the orbital kinetic energy density for electrons of spin  $\sigma$ . The  $\psi_{\alpha\sigma}(\mathbf{r})$  are the Kohn-Sham orbitals that produce the density

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{\sigma} \sum_{\alpha}^{\text{occup}} |\psi_{\alpha\sigma}(\mathbf{r})|^2, \quad (7)$$

and are themselves nonlocal functionals [3] of the density  $n(\mathbf{r})$ . In the rest of this work, we shall restrict our attention to spin-unpolarized densities ( $n_\uparrow = n_\downarrow = n/2$  and  $\tau_\uparrow = \tau_\downarrow = \tau/2$ ).

As we will see in section 2, an adequate inhomogeneity index requires not only the ingredients  $n$ ,  $\nabla n$ ,  $\nabla^2 n$ , and  $\tau$ , but also  $\nabla\tau$  and  $\nabla^2\tau$ . The last two ingredients are not currently included in the meta-GGA form of Eq. (5), but suggest a symmetry between  $n$  and  $\tau$  and arise in the density matrix expansion [13].

## II. THE MENAGERIE OF DENSITY INHOMOGENEITY PARAMETERS, WITH RESULTS FOR ATOMS

We seek an inhomogeneity index  $w(\mathbf{r})$  defined at each point  $\mathbf{r}$  of a many-electron system, and bounded in the range

$$0 \leq w \leq 1. \quad (8)$$

We want  $w(\mathbf{r})$  to be close to unity for strongly inhomogeneous densities like those of atoms, and close to zero for weakly inhomogeneous densities like those of slowly-varying or nearly-constant electron gases. (Note that nearly-constant densities need not be slowly-varying; consider a uniform density perturbed by a density wave of small amplitude but large wave-vector.) We will construct  $w$  to be of order  $\nabla^4$  in the slowly-varying limit.

We begin by defining the iso-orbital indicator [14]

$$X = \tau_W/\tau \quad (0 \leq X \leq 1), \quad (9)$$

where

$$\tau_W = |\nabla n|^2/8n \quad (10)$$

is the von Weizsäcker kinetic energy density. For any one- or two-electron ground-state density, or for any region of space in which one orbital shape dominates both  $n$  and  $\tau$ ,  $X \rightarrow 1$  [15]. For any slowly-varying density, we can replace  $\tau$  by its local-density or Thomas-Fermi approximation

$$\tau^{\text{unif}} = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3} = n \left( \frac{3}{10} k_F^2 \right), \quad (11)$$

so that

$$X \rightarrow \frac{5}{3} p, \quad \text{where } p = (|\nabla n|/2k_F n)^2 \quad (12)$$

is close to zero.

Our first guess for an inhomogeneity index is then

$$w_X \equiv X^2, \quad (13)$$

which is close to zero in a slowly-varying electron gas and equal to one in any one- or two-electron ground state. Figures 1–3 show  $w_X$  as a function of  $r$  (distance from the nucleus) for the Hartree-Fock densities [16] of the atoms Be, Ar, and Zn. Although  $w_X$  is close to one near the nucleus ( $r \rightarrow 0$ ) and in the density tail ( $r \rightarrow \infty$ ), it can be close to zero over large regions, especially intershell regions, of an atom, although the density is in fact strongly inhomogeneous in those regions. Thus  $w_X$  is inadequate as an inhomogeneity index.

The most important single inhomogeneity parameter for the exchange energy is probably the Becke parameter [17, 18]

$$Q = \frac{5}{3} p + \frac{10}{3} q + \left(1 - \frac{\tau}{\tau^{\text{unif}}}\right), \quad (14)$$

where

$$q = \frac{\nabla^2 n}{(2k_F)^2 n} \quad (15)$$

is the reduced Laplacian and  $p$  of Eq. (12) is the square of the reduced gradient of the density. ( $p$  and  $q$  tell us how fast  $n$  varies on the scale of the  $n$ -dependent local Fermi wavelength  $2\pi/k_F$ . For further discussion, see Ref. [19].) The spherically-averaged exchange hole density for any spin-unpolarized density has the short-range behavior

$$\begin{aligned} \langle n_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) \rangle_{\text{sph. avg.}} &= -\frac{n}{2} + \frac{u^2}{3} \tau^{\text{unif}} [1 - Q] \\ &+ O(u^4), \end{aligned} \quad (16)$$

where  $u$  is distance from the electron at  $\mathbf{r}$ . Note that

$$1 - \frac{\tau}{\tau^{\text{unif}}} = 1 - \frac{5}{3} \frac{p}{X}. \quad (17)$$

In a weakly inhomogeneous region of space,  $Q^2$  and the squares of the three individual terms in  $Q$  of Eq. (14) should be much less than 1. So we define

$$Y^2 = \left(\frac{5}{3}p\right)^2 + \left(\frac{10}{3}q\right)^2 + \left(1 - \frac{\tau}{\tau^{\text{unif}}}\right)^2, \quad (18)$$

and propose our second guess for an inhomogeneity index

$$w_{XY} \equiv \frac{X^2 + Y^2}{1 + Y^2}. \quad (19)$$

Eq. (19) still makes  $w_{XY} = 1$  in any iso-orbital region ( $X = 1$ ), and it makes  $w_{XY}$  closer to one than is  $w_X$  over much more of the density of an atom (Figs. 1–3).

But there are still “outer intershell” regions of an atom where  $w_{XY} \approx 0$ . These are regions of space in which  $4\pi r^2 n(r)$  increases with  $r$ . In these regions, the usual meta-GGA parameters of Eq. (5) cannot recognize the strong inhomogeneity, and thus cannot tell an atom from an electron gas; indeed,  $p$  and  $q$  are small there and  $\tau \approx \tau^{\text{unif}}$ , yet these regions are *not* electron-gas-like.

For example, consider the outer intershell region of the Be atom, where  $n = n_{1s} + n_{2s}$  is dominated by  $n_{2s}$ , but  $n_{2s}$  maximizes so that  $\tau = |\nabla n_{1s}|^2/8n_{1s} + |\nabla n_{2s}|^2/8n_{2s}$  is dominated by  $n_{1s}$ . In this region,  $X$  of Eq. (9) is necessarily small. What tells us that this is a region of strong inhomogeneity? In this region,  $\tau$  is decaying rapidly, with a length scale characteristic of  $n_{1s}$ , so it is the derivatives of  $\tau$  that are needed to tell this atomic region from an electron gas.

The previous paragraph suggests that we need for  $\tau$  the analogs of the dimensionless derivatives of Eqs. (12) and (15):

$$p_\tau = \left(\frac{|\nabla\tau|}{2k_\tau\tau}\right)^2, \quad q_\tau = \frac{\nabla^2\tau}{(2k_\tau)^2\tau}, \quad (20)$$

where  $k_\tau$  is defined by

$$\tau = \frac{3}{10}k_\tau^2 \left(\frac{k_\tau^3}{3\pi^2}\right). \quad (21)$$

( $p_\tau$  and  $q_\tau$  tell us how fast  $\tau$  varies on the scale of the  $\tau$ -dependent Fermi wavelength  $2\pi/k_\tau$ .) By analogy to  $Y^2$  of Eq. (18), we define

$$Z^2 = \left(\frac{5}{3}p_\tau\right)^2 + \left(\frac{10}{3}q_\tau\right)^2, \quad (22)$$

and propose our final inhomogeneity index

$$w_{XYZ} \equiv \frac{X^2 + Y^2 + Z^2}{1 + Y^2 + Z^2}. \quad (23)$$

$w_{XYZ}$  is “balanced” between or symmetric in the  $n$  and  $\tau$  variables. It is small where the reduced gradient and Laplacian of  $n$  and  $\tau$  are small in the same sense, and  $\tau \approx \tau^{\text{unif}}$ , and  $X^2 \ll 1$ . These conditions are easy to satisfy in an electron gas, but not in an atom. Figures 1–3 show that  $w_{XYZ}$  is close to unity over most of an

atom, including the “difficult” intershell regions.  $w_{XYZ}$  dips below one in the valence-shell region of the atom, suggesting that this region is slightly more homogeneous than the rest of the atom, as one might expect. The dip in the valence-shell region seems shallowest for s electrons, deeper for p electrons, and still deeper for d electrons, reflecting the increasing orbital overlap from s to p and p to d shells.

### III. RESULTS FOR MODEL DENSITIES OF METAL SURFACES AND BULK METALS

In section 2, we applied our inhomogeneity indices to atoms, which have a discrete spectrum of Kohn-Sham orbital energies and are strongly-inhomogeneous throughout space. Here we will turn to systems that have a continuous spectrum, and can be either strongly or weakly inhomogeneous.

In the infinite barrier model (IBM) [20] of a jellium surface, the non-interacting or Kohn-Sham electrons are confined to the half-space  $z > 0$  by the effective potential  $v_{\text{eff}}(z) = 0$  (for  $z > 0$ ) and  $+\infty$  (for  $z < 0$ ). The density  $n(z)$  then vanishes for  $z \leq 0$ , and tends to a constant  $\bar{n} = \bar{k}_F^3/3\pi^2$  as  $z \rightarrow \infty$ , with a first Friedel peak at  $2\bar{k}_F z = 6$  and smaller Friedel oscillations for larger  $z$ . Figure 4 shows that the surface region is one of strong inhomogeneity, while the bulk region is one of weak inhomogeneity, as expected. Note however that the IBM surface is more inhomogeneous than the self-consistent [21, 22] jellium surface (Fig. 5) or the surface of a real free-electron-like metal.

We now turn to the Mathieu Gas (MG) model system, which is defined by the effective potential

$$v_{\text{eff}}(\mathbf{r}) = \frac{1}{2}\bar{k}_F^2\bar{\lambda}[1 - \cos(2\bar{k}_F\bar{p}z)] \quad (24)$$

applied to non-interacting electrons of initially uniform density  $\bar{n} = \bar{k}_F^3/3\pi^2$  (i.e.,  $n(\mathbf{r}) \rightarrow \bar{n}$  as  $\bar{\lambda} \rightarrow 0$ ).

Its main properties are determined by the dimensionless parameters  $\bar{\lambda}$  and  $\bar{p}$ . The inhomogeneity indices are independent of the overall scale, which is set by  $\bar{k}_F$ . Reference 23 gives more details on the MG model system, the role of its parameters, and the calculation of the Kohn-Sham orbitals. Here, we simulate bulk Na and Ca by making the MG effective potential reproduce the corresponding pseudopotential’s first non-zero Fourier term for a direction perpendicular to a lattice plane. From tabulated coefficients [24] we get the following parameter values (using bcc monovalent Na with  $r_s = 3.93$ , and fcc divalent Ca with  $r_s = 3.27$ )

$$\text{Bulk Na model: } \bar{\lambda} = 0.17, \bar{p} = 1.140, \quad (25)$$

$$\text{Bulk Ca model: } \bar{\lambda} = 0.087, \bar{p} = 0.880. \quad (26)$$

For these parameters, the separable MG energy band structure along the  $k_z$  direction shows some resemblance to bulk Na and Ca, with the Fermi level of Na just below,

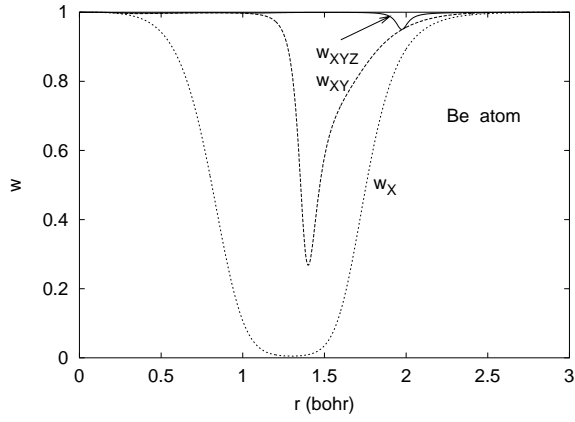


FIG. 1: The inhomogeneity indices  $w_X$  (Eq. (13)),  $w_{XY}$  (Eq. (19)), and  $w_{XYZ}$  (Eq. (23)) for the Hartree-Fock density of the Be atom. The 2s valence orbital has  $\langle r^{-1} \rangle^{-1} = 1.91$  bohr, close to the outer maximum of  $4\pi r^2 n(r)$ .

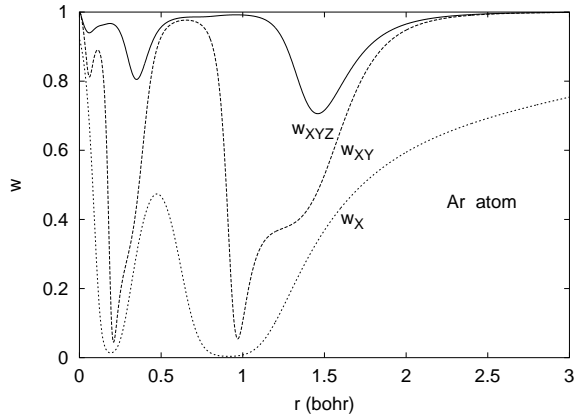


FIG. 2: Same as Fig. 1, but for the Ar atom. The 2p valence orbital has  $\langle r^{-1} \rangle^{-1} = 1.23$  bohr, close to the outer maximum of  $4\pi r^2 n(r)$ .

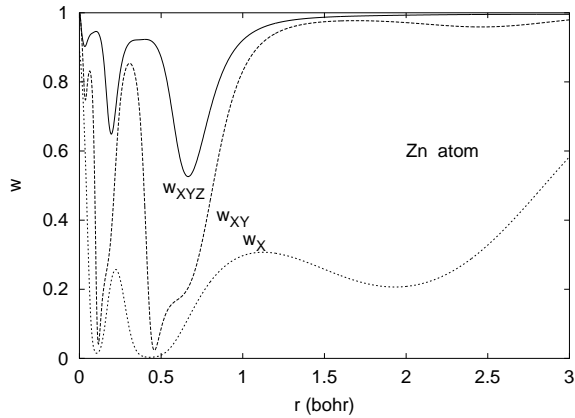


FIG. 3: Same as Fig. 1, but for the Zn atom. The 3d valence orbital has  $\langle r^{-1} \rangle^{-1} = 0.65$  bohr, close to the outer maximum of  $4\pi r^2 n(r)$ .

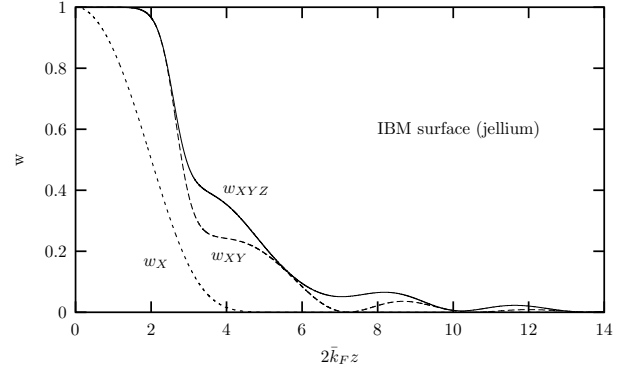


FIG. 4: The inhomogeneity indices  $w_X$  (Eq. (13)),  $w_{XY}$  (Eq. (19)), and  $w_{XYZ}$  (Eq. (23)) in the infinite barrier model. The electron density vanishes for  $z < 0$ , and approaches a constant  $\bar{n} = \bar{k}_F^3/3\pi^2$  as  $z \rightarrow \infty$ , with a first Friedel peak at  $2\bar{k}_F z = 6$ . The neutralizing uniform positive background fills the half space  $2\bar{k}_F z > 3\pi/4 \approx 2.36$ .

and that of Ca just above, the first band gap. Figures 6 and 7 show the inhomogeneity indices in the MG bulk Na and Ca models over half a period of  $v_{\text{eff}}$ , i.e., from  $z = 0$  to  $z = \pi/(2\bar{k}_F \bar{p})$ . As expected for these electron-gas-like systems, all the indices are close to zero over the whole range. The indices are significantly lower for the Ca model than for Na. This is explained by the observation that, for MG systems, placing the Fermi level successively higher in the energy band structure describes a path towards the limit of slowly-varying densities ( $\bar{p} \rightarrow 0$ ,  $\lambda \rightarrow 0$ ) [23]. Hence, the Ca bulk model is expected to be closer to the slowly-varying limit than the Na model.

For a density wave of relative amplitude  $A$  and wavevector  $\mathbf{k}$  superposed on a uniform density  $\bar{n} = \bar{k}_F^3/3\pi^2$ , i.e.,  $n(\mathbf{r}) = \bar{n}[1 + A \cos(kz)]$ , we note that  $p \propto A^2(k/\bar{k}_F)^2$

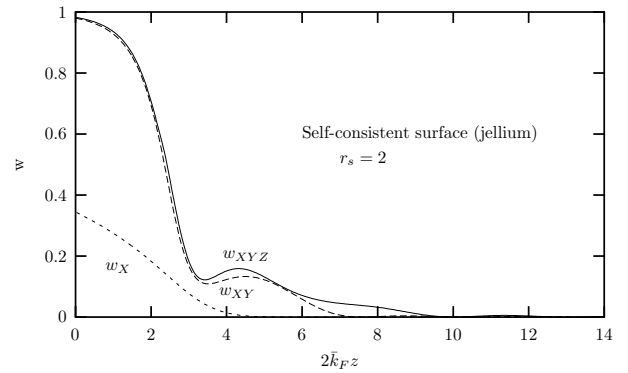


FIG. 5: Same as Fig. 4 but for the self-consistent jellium surface with bulk density parameter  $r_s = 2 = (3/4\pi n)^{1/3}$ . The neutralizing uniform positive background fills the half space  $2\bar{k}_F z > 3\pi/4 \approx 2.36$ , as in Fig. 4.

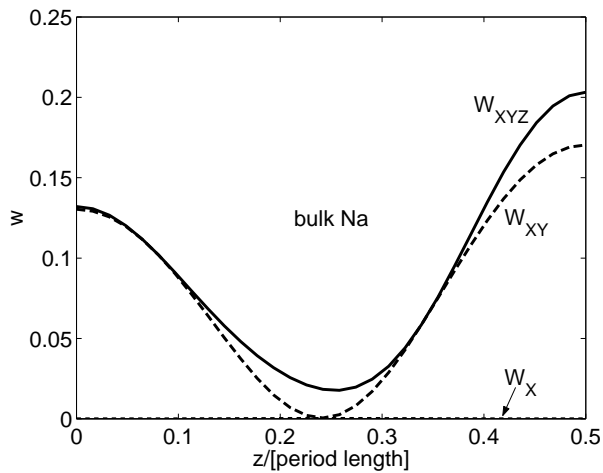


FIG. 6: The inhomogeneity indices for the Na bulk model density, obtained from the system described by the MG effective potential  $v_{\text{eff}}$  in Eqs. (24) and (25). The plot ranges over half a period of the system, from the density maximum at  $z = 0$  (at the  $v_{\text{eff}}$  minimum) to the density minimum (at the  $v_{\text{eff}}$  maximum).

and  $q \propto A(k/\bar{k}_F)^2$ . For  $|A| \ll 1$ , we shall have  $p \ll |q|$  and  $w_X \ll w_{XY}$ , as can be seen in the right half of Fig. 4 or 5 and in Figs. 6 and 7. *Either*  $|A| \ll 1$  or  $k/\bar{k}_F \ll 1$  can make  $p$  and  $|q|$  small, although only  $k/\bar{k}_F \ll 1$  is the limit of slowly-varying densities.

In the slowly-varying limit, we can use the second-order gradient expansion [25]

$$\tau \rightarrow \tau^{\text{unif}} \left[ 1 + \frac{5}{27}p + \frac{20}{9}q \right] \quad (27)$$

to express

$$X^2 \rightarrow 2.78p^2, \quad (28)$$

$$Y^2 \rightarrow 2.81p^2 + 0.82pq + 16.05q^2, \quad (29)$$

$$Z^2 \rightarrow 35.15p^2 + 41.15pq + 30.86q^2, \quad (30)$$

where  $p$  and  $q$  are both small. (For the densities of Figs. 6 and 7,  $Z^2$  is not well-represented by Eq. (30). The expansions (27)–(30) have not been used in any of our figures.)

#### IV. SCALING, FUNCTIONAL INTERPOLATION, AND OTHER DISCUSSION

Consider a uniform density scaling

$$n(\mathbf{r}) \rightarrow n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \quad (31)$$

where  $\gamma$  is a positive parameter. The number of electrons  $\int d^3r n_\gamma(\mathbf{r}) = \int d^3r n(\mathbf{r})$  is unchanged, but the density is uniformly compressed ( $\gamma > 1$ ) or expanded ( $\gamma < 1$ ). It

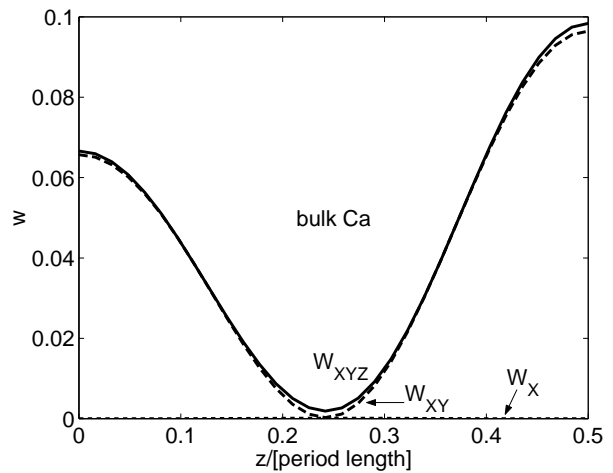


FIG. 7: The inhomogeneity indices for the Ca bulk model. The plot is similar to Fig. 6, but uses a  $v_{\text{eff}}$  with parameters from Eq. (26).

is easy to see that all three of our inhomogeneity indices scale:

$$w(\mathbf{r}) \rightarrow w(\gamma\mathbf{r}), \quad (32)$$

i.e., the system does not become any more or less inhomogeneous under uniform density scaling.

Under the transformation of Eq. (31), the exchange energy has a simple scaling [26]:

$$E_x[n] \rightarrow E_x[n_\gamma] = \gamma E_x[n]. \quad (33)$$

If we write

$$E_x = \int d^3r n(\mathbf{r}) \epsilon_x(\mathbf{r}), \quad (34)$$

then

$$\epsilon_x(\mathbf{r}) \rightarrow \gamma \epsilon_x(\gamma\mathbf{r}). \quad (35)$$

If we know  $\epsilon_x(\mathbf{r})$  in both the strongly-inhomogeneous (SI) and weakly-inhomogeneous (WI) limits, we might make an interpolation

$$\epsilon_x(\mathbf{r}) = w(\mathbf{r}) \epsilon_x^{\text{SI}}(\mathbf{r}) + [1 - w(\mathbf{r})] \epsilon_x^{\text{WI}}(\mathbf{r}), \quad (36)$$

which preserves the scaling behavior of Eq. (35).

A very accurate non-empirical meta-GGA for  $E_{xc}[n]$  [12] can be constructed using just the local ingredients  $n(\mathbf{r})$ ,  $\nabla n(\mathbf{r})$ , and  $\tau(\mathbf{r})$ , without the other ingredients  $\nabla^2 n$ ,  $\nabla \tau$ , and  $\nabla^2 \tau$  needed to complete our inhomogeneity index  $w_{XYZ}$  of Eq. (23). A possible explanation is as follows: The only parts of an atom where  $w_{XY}$  of Eq. (19) is small are the “outer intershell regions”, in which  $p$  of Eq. (12) and  $q$  of Eq. (15) are small, as are  $X$  of Eq. (9) and  $(1 - \tau/\tau^{\text{unif}})$  of Eq. (14). In these regions, the exchange energy densities predicted by LDA, by the non-empirical PBE GGA [5], and by the non-empirical TPSS meta-GGA [12] will all agree closely

with one another, and the short-range behavior of the exact exchange hole (Eq. (16)) will be LDA-like. It is very possible then that LDA, GGA and meta-GGA are all correct in these regions, even though these regions are decidedly not electron-gas-like. This suggests using  $w_{XY}$  in place of  $w_{XYZ}$  in the interpolation of Eq. (36).

Fortunately, inhomogeneity effects can be weak even when the inhomogeneity is not. For example, the Gáspár-Kohn-Sham LDA of Eq. (1) for the exchange energy, applied to atoms, never makes an error of more than about 14 %, and usually much less. The relative error seems to be very small for an atom of large atomic number [2]. Our inhomogeneity index shows what a remarkable achievement that really is.

Finally, we can define a global inhomogeneity index

$$\bar{w}_P = \int d^3r n(\mathbf{r})^P w(\mathbf{r}) / \int d^3r n(\mathbf{r})^P, \quad (37)$$

where  $P = 4/3$  would be the natural choice for a discussion of the exchange energy.

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