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C. Van Alsenoy<sup>a</sup>; N. H. March<sup>bc</sup>

<sup>a</sup> Chemistry Department, University of Antwerp, Antwerp, Belgium <sup>b</sup> Oxford University, Oxford, England <sup>c</sup> Physics Department, University of Antwerp, Antwerp, Belgium

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## Non-locality in the exchange energy density of the inhomogeneous electron liquids in H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub> treated by Hartree–Fock theory

C. VAN ALSENOY\*† and N. H. MARCH‡§

†Chemistry Department, University of Antwerp, Antwerp, Belgium

‡Oxford University, Oxford, England

§Physics Department, University of Antwerp, Antwerp, Belgium

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The exchange energy density has been studied by Hartree–Fock (HF) theory in the 10-electron molecules H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub>. The local density approximation (LDA) then provides a natural starting point for interpreting the HF data. Though LDA leads to ‘shape similarity’ for the exchange density of these three molecules, there is, (a) no universality and (b) multivalued character at low densities. The low-density regime can, however, be interpreted in terms of a functional  $|\nabla\rho|/\ln\rho$ , with  $\rho$  the ground-state electron density. This functional is here provided with a firm theoretical foundation. Thus, there is a ‘cross-over’ from LDA at high densities to a low-density functional in HF theory.

*Keywords:* Inhomogeneous electron liquids; 10-Electron molecules; Exchange energy density

### 1. Background and outline

In a recent study, Wanko *et al.* [1] have criticised existing exchange-correlation functionals [2] used in practical applications of density functional theory (DFT). Especially, they have stressed the importance of accounting for non-locality. This has motivated the present study, which focuses on the non-locality of the exchange ( $x$ ) energy density, denoted below by  $\epsilon_x(\vec{r})$ . A precise definition is given in equation (4) below. Following Löwdin [3], we take Hartree–Fock (HF) theory to afford the correct treatment of exchange, without correlation. To be definite, we have chosen for the quantitative study of  $\epsilon_x(\vec{r})$  reported below the three 10-electron molecules H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub> at their equilibrium geometries.

Let us then give some theoretical background to the present study. It has been known since the pioneering work of Dirac [4] that in spin-compensated molecules and clusters whose ground-state wave function is built from a single Slater determinant

\*Corresponding author. Email: kris.vanalsenoy@ua.ac.be

via orbitals  $\psi_i(\vec{r})$ , the total exchange energy  $E_x$  is given compactly in terms of the Dirac density matrix  $\gamma(\vec{r}, \vec{r}')$  defined by

$$\gamma(\vec{r}, \vec{r}') = 2 \sum_i \psi_i(\vec{r})\psi_i(\vec{r}') \quad (1)$$

where  $i$  runs over all occupied orbitals. Then  $E_x$  has the explicit form [4,5]

$$E_x = -\frac{e^2}{4} \int \frac{\gamma^2(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad (2)$$

where  $\gamma$  satisfies the idempotency condition, which for spin-compensated systems reads

$$\frac{\gamma(\vec{r}, \vec{r}')}{2} = \int \frac{\gamma(\vec{r}, \vec{r}'')}{2} \frac{\gamma(\vec{r}'', \vec{r}')}{2} d\vec{r}'' \quad (3)$$

What we focus on in the present article is the exchange energy density  $\epsilon_x(\vec{r})$ . Though there is no unique definition of this quantity, we adopt throughout this study the form

$$\epsilon_x(\vec{r}) = -\frac{e^2}{4} \int \frac{\gamma^2(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (4)$$

which follows naturally from the result equation (2) which immediately gives back the desired result:

$$E_x = \int \epsilon_x(\vec{r}) d\vec{r} \quad (5)$$

One of us, in early work [5], argued that at sufficiently large  $\vec{r}$  (taken here to mean that we are far from all nuclei in the molecule or cluster under consideration) equation (4) simplifies to

$$\epsilon_x(\vec{r}) \rightarrow -\frac{e^2}{4r} \int \gamma^2(\vec{r}, \vec{r}') d\vec{r}' : |\vec{r}| \rightarrow \text{infinity} \quad (6)$$

Using the idempotency condition equation (3) in the diagonal limit  $\vec{r}' \rightarrow \vec{r}$ , when it follows from the definition (1) that

$$\gamma(\vec{r}, \vec{r}')|_{\vec{r}'=\vec{r}} = \rho(\vec{r}), \quad (7)$$

the ground-state electron density, one finds the large  $\vec{r}$  behaviour of  $\epsilon_x(\vec{r})$  from equation (6) to be [5]

$$\epsilon_x(\vec{r}) \rightarrow -\frac{e^2}{2r} \rho(\vec{r}) : |\vec{r}| \rightarrow \text{infinity} \quad (8)$$

The outline of the present article is then as follows. In section 2, this result equation (8) is compared and contrasted with the local density approximation (LDA) for the exchange energy, which is still widely used in practical applications on especially large molecules. Section 3 then presents calculations using HF theory on the exchange energy density  $\epsilon_x(\vec{r})$  for the three 10-electron molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$ . Section 4 emphasises departures of these results for  $\epsilon_x(\vec{r})$  from the LDA result given in equation (9) below. The article concludes with section 5 that constitutes a summary plus some proposals for further work that should prove fruitful.

## 2. Relation of asymptotic form (8) of the exchange energy density to the LDA result

The LDA result for  $\epsilon_x(\vec{r})$  (equation (9)) is very simply explained using the exact result (4). One builds  $\gamma(\vec{r}, \vec{r}')$  in equation (1) from plane waves for the one-electron wave functions  $\psi(\vec{r})$ . One then finds, as discussed, for example, in the book by one of us [6], that

$$\epsilon_x^{LDA}(\vec{r}) = -\left(\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{1/3} e^2 \rho(\vec{r})^{4/3} \quad (9)$$

this result is only exact in the homogeneous electron gas limit, because of the use of free-particle eigenfunctions.

From dimensional analysis,  $\epsilon_x^{LDA}(\vec{r})$  being an exchange, energy per unit volume has dimensions  $e^2/L^4$ , where L denotes a length. In equation (9), the characteristic ‘length’ is  $\rho^{-1/3}$ , since  $\rho$  is an electron density and has dimensions  $L^{-3}$ . But the exact asymptotic result equation (8) for  $\epsilon_x^{LDA}(\vec{r})$  contains two distinct ‘lengths’,  $|\vec{r}|$  itself as well as  $\rho^{-1/3}$ . Thus equation (9) must fail in the low-density region far from nuclei.

### 2.1. Limiting form for $\epsilon_x(\vec{r})$ far from all nuclei

The aim of this sub-section, therefore, is to rewrite the exact limiting form of  $\epsilon_x(\vec{r})$  in equation (8) solely in terms of the basic variable of DFT [2], namely the electron density  $\rho(\vec{r})$ . Far from all nuclei,  $\rho(\vec{r})$  takes the form

$$\rho(\vec{r}) = A \exp\left(-2\sqrt{\frac{2Ia_0}{e^2}} \frac{r}{a_0}\right) \quad (10)$$

where  $a_0$  is the Bohr radius  $\hbar^2/me^2$ . In equation (10) we have focussed only on the exponential fall-off of the density, following the work of M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof [7],  $I$  being the ionisation potential as measured in a ‘fast’ experiment without nuclear relaxation on removing the outermost electron. From equation (10) valid far from all nuclei we readily find two further asymptotic results:

$$|\nabla\rho(\vec{r})| \rightarrow -\left[2\sqrt{\frac{2Ia_0/e^2}{a_0}}\right]\rho(\vec{r}) : |\vec{r}| \rightarrow \text{infinity} \quad (11)$$

and also

$$\ln \rho(\vec{r}) = \ln A - 2\sqrt{\frac{2Ia_0}{e^2}} \left(\frac{r}{a_0}\right). \quad (12)$$

At  $r$  sufficiently large to neglect the  $\ln A$  term, we can rewrite equation (12) in the unorthodox form

$$2\sqrt{\frac{2Ia_0}{e^2}} \frac{r}{a_0} = -\ln \rho(\vec{r}) : |\vec{r}| \rightarrow \text{infinity} \quad (13)$$

Returning now to equation (8) we have at sufficiently large  $r$  the form

$$\epsilon_x(\vec{r}) \rightarrow -\frac{e^2}{2} \frac{\rho(\vec{r})2\sqrt{2Ia_0/e^2}}{a_0 \ln \rho(\vec{r})}. \quad (14)$$

But we want a ‘universal’ form of  $\epsilon_x(\vec{r})$  at large  $r$ , and so we next remove the ionisation potential term in equation (14) by appealing to equation (11). This yields the desired result that

$$\epsilon_x(\vec{r}) \rightarrow \frac{e^2}{2} \frac{|\nabla \rho(\vec{r})|}{\ln \rho(\vec{r})} : |\vec{r}| \rightarrow \text{infinity} \quad (15)$$

which must only be used at sufficiently large  $\vec{r}$  such that  $\ln \rho(\vec{r})$  is negative. This formally exact ‘universal’ limit in equation (15) shows, of course, why the LDA form (9) must fail in the low-density regime far from all nuclei. It is therefore, as a further step in ‘refining’ the LDA result in equation (9), suggestive to propose a new ansatz, albeit approximate, that

$$\epsilon_x(\vec{r}) = -\frac{e^2}{a_0^4} \epsilon \left( a_0^4 \rho^{4/3}; \frac{|a_0^4 \nabla \rho|}{\ln(a_0^3 \rho)} \right) \quad (16)$$

where  $\epsilon$  is now dimensionless and is a function (not functional!) of two variables as shown, both of these also written here in dimensionless form.

We must expect in high-density regions that generally the dominant variable is the LDA form  $a_0^4 \rho^{4/3}$ . But in the low-density regime far from the nuclei, the ‘gradient’ variable  $|\nabla \rho|/\ln(\rho)$  must become the dominant one. Perhaps also, to at least reflect Kato’s cusp condition [8] approximately, near nuclei this gradient variable will again play a significant role.

### 3. Hartree–Fock results for exchange energy density $\epsilon_x(\vec{r})$ related to $\rho(\vec{r})$ in $\text{H}_2\text{O}$ , $\text{NH}_3$ and $\text{CH}_4$

Turning next to specific HF results, the relationship between the exchange density  $\epsilon_x(\vec{r})$  and  $\rho(\vec{r})$  has been examined for the three 10-electron systems  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$ . Using a aug-cc-pVTZ basis set as implemented in the Gaussian03 program [9] the

geometry of these molecules was optimised at the Hartree–Fock level and the resulting orbitals used to evaluate the electron density  $\rho(\vec{r})$  as well as the exchange density  $\epsilon_x(\vec{r})$  as defined in equation (17) below:

$$\epsilon_x(\vec{r}) = -\frac{e^2}{4} \sum_{i < j} \int \frac{\varphi_i(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_i(\vec{r}) \varphi_j(\vec{r}) \quad (17)$$

which is a realisation of the Dirac density matrix in terms of HF-orbitals.

In order to limit required computation time, plots were generated for points in a planar rectangular grid ( $(x, y)$ -plane for the molecules oriented in their centre of mass system), with a spacing of 0.05 au. For a given grid point  $\vec{r}$  the integrals

$$\int \frac{\chi_\mu(\vec{r}') \chi_\nu(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (18)$$

were calculated over the atomic orbitals  $\chi_\mu$  and  $\chi_\nu$  then transformed to the molecular orbital basis, and multiplied with the values of the MO's  $\varphi_i(\vec{r})$  and  $\varphi_j(\vec{r})$  in position  $\vec{r}$ . The resulting plots are depicted in figures 1–3, respectively, for  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$ . From these figures the ‘non-universality’ as well as the multivalued character

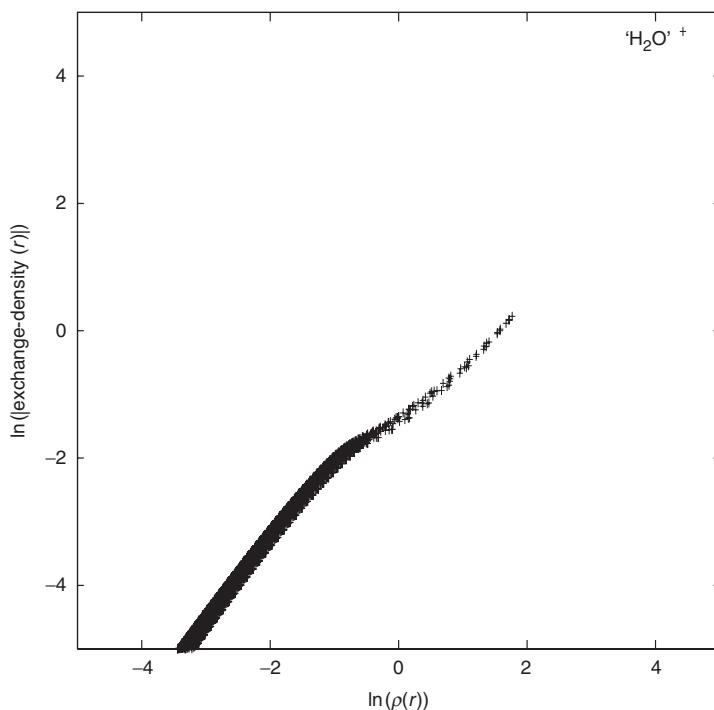


Figure 1. Plot of  $\ln |\epsilon_x(\vec{r})|$  vs.  $\ln \rho(\vec{r})$  for  $\text{H}_2\text{O}$ , where  $\epsilon_x(\vec{r})$  and  $\rho(\vec{r})$  are from HF calculations.

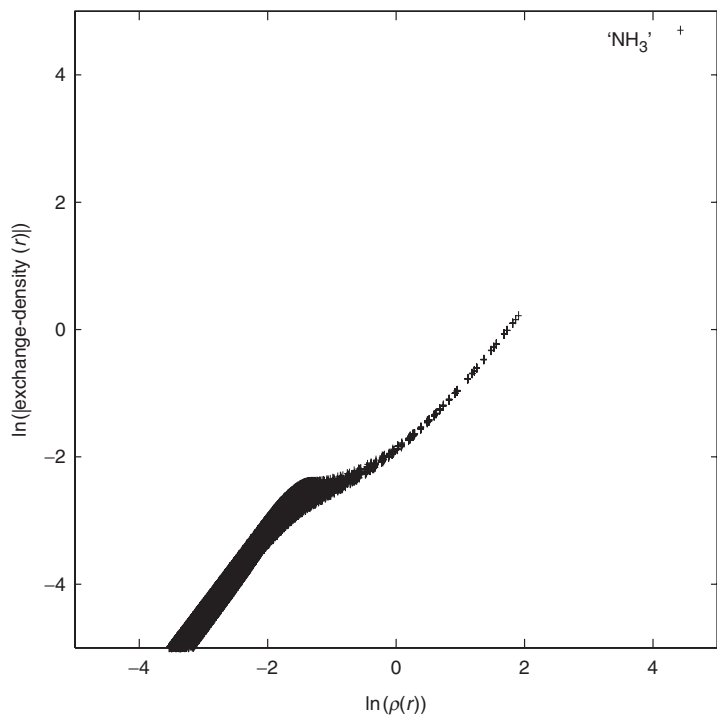


Figure 2. Plot of  $\ln|\epsilon_x(\vec{r})|$  vs.  $\ln\rho(\vec{r})$  for  $\text{NH}_3$ , where  $\epsilon_x(\vec{r})$  and  $\rho(\vec{r})$  are from HF calculations.

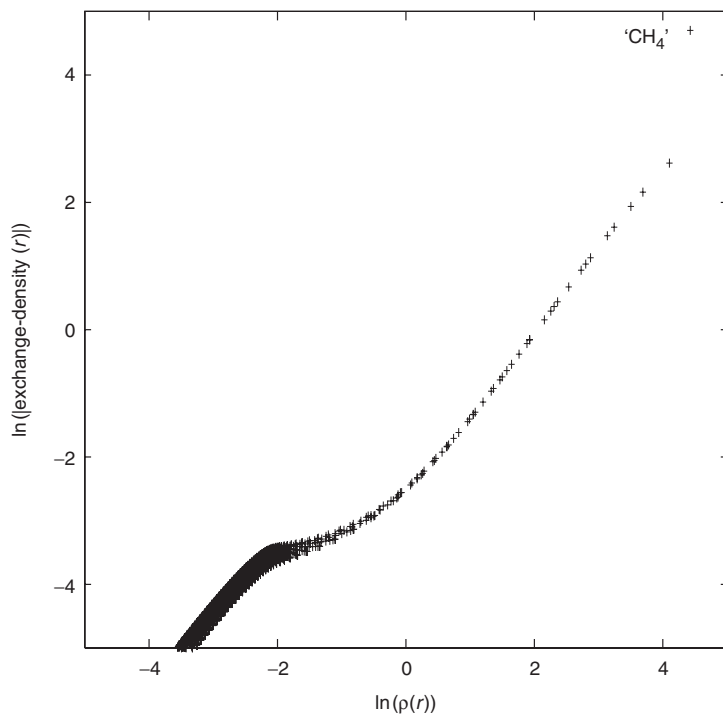


Figure 3. Plot of  $\ln|\epsilon_x(\vec{r})|$  vs.  $\ln\rho(\vec{r})$  for  $\text{CH}_4$ , where  $\epsilon_x(\vec{r})$  and  $\rho(\vec{r})$  are from HF calculations.

aforementioned are easily recognised. Nevertheless, there is a remarkable ‘shape similarity’ between the figures for the HF exchange energy density.

#### 4. Summary and proposals for further work

The main achievements of the present study are as follows:

- (i) The demonstration of non-locality in the HF exchange energy density  $\epsilon_x(\vec{r})$  for the isoelectronic molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$  in figures 1–3.
- (ii) The recognition that at low densities, the HF functional  $\epsilon_x[\rho]$  must tend, when sufficiently far from the nuclei, to the universal form (15).
- (iii) The proposal, albeit now approximate, that in HF theory the exchange energy density function (16) may provide a quantitative route in the absence of the exact functional  $\epsilon_x[\rho]$ .

Relating loosely to (iii) above, we have included in the Appendix some discussion of a solvable non-relativistic analytic example, but this time for 10-electron Ne-like atomic ions with large atomic number  $Z$ . This example could play a role, we believe, in the future, in relation to (iii) above, though we must stress that the Dirac density matrix used is now the leading term in the  $1/Z$  expansion of atomic theory, and hence has no Fock operator contribution.

Finally, it is, of course, important for the future to study the non-locality of the Löwdin correlation energy,  $E_c$  say, to be added to  $E_x$  defined in equations (4) and (5) above. By analogy with equation (5), we can write

$$E_c = \int \epsilon_c(\vec{r}) d\vec{r} \quad (19)$$

The important question for the future is to assess the importance of non-locality in the correlation energy density  $\epsilon_c(\vec{r})$ .

Our proposal for a modest start to provide an answer to this question in the future, is to utilise Möller–Plesset (MP) perturbation theory, which is the natural starting point for correcting HF theory for Löwdin electron correlation energy. Of course, we recognise that low-order MP theory will only give a fraction of the total Löwdin correlation energy, but nevertheless, if this fraction of  $\epsilon_c(\vec{r})$  could be eventually extracted from MP2 (plus perhaps MP4 if it proves interesting) the question of the importance of non-locality of  $\epsilon_c(\vec{r})$  could be answered with some certainty.

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### Appendix: Exchange energy for non-relativistic 10-electron neon-like atomic ions in the limit of large atomic number $Z$

March and Santamaria [10] derived the Dirac density matrix  $\gamma(\vec{r}, \vec{r}')$  analytically for K plus L closed shells in a bare Coulomb potential in the limit of large atomic number  $Z$ . Then from the  $1/Z$  expansion of atomic theory, one can construct  $\gamma$  in leading order from bare Coulomb wave functions.

Then one can use equation (4) above to calculate, also analytically, the exchange energy density  $\epsilon_x(\vec{r})$  for this spherically symmetric 10-electron atomic ion. This was done by Howard *et al.* and is given explicitly in their equation (2.2) [11]. The corresponding ground-state electron density  $\rho(\vec{r})$  takes the form

$$\rho(r) = \left(\frac{2}{\pi}\right) \left(\frac{Z}{a_0}\right)^3 \exp\left(\frac{-2Zr}{a_0}\right) + \left(\frac{1}{4\pi}\right) \left(\frac{Z}{a_0}\right)^3 \exp\left(\frac{-Zr}{a_0}\right) \left[1 - \frac{Zr}{a_0} + \frac{1}{2} \left(\frac{Zr}{a_0}\right)^2\right]. \quad (\text{A1})$$

To illustrate the low density function  $|\nabla\rho|/\ln(\rho)$ , we first take the large  $r$  limit of equation (A1) to find

$$\rho(r) = \left(\frac{1}{4\pi}\right) \left(\frac{Z}{a_0}\right)^3 \exp\left(\frac{-Zr}{a_0}\right) \frac{1}{2} \left(\frac{Zr}{a_0}\right)^2 : r \rightarrow \text{infinity}. \quad (\text{A2})$$

Then the leading term in  $|\nabla\rho|$  at large  $r$  from equation (A2) is readily found as

$$|\nabla\rho| = \frac{Z}{a_0} \rho(r). \quad (\text{A3})$$

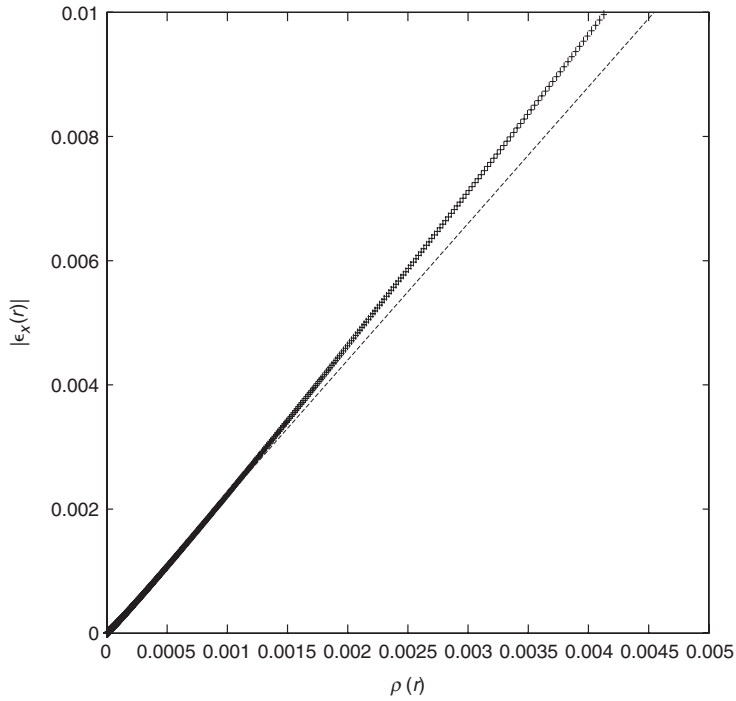


Figure A1. Plot of  $|\epsilon_x(r)|$  vs.  $\rho(r)$  for the exact model with  $Z=92$ , a trendline ( $y=2.2x$ ) is included to guide the eye.

Similarly, from equation (2.2) of Howard *et al.* [11], the large  $r$  limit of the exchange energy density is

$$\epsilon_x(r) = -\frac{e^{-Zr/a_0}[972(\alpha r)^2]}{15,552} \left( \frac{e^2 \alpha^3}{\pi r} \right). \quad (\text{A4})$$

Removing the  $r$  dependence from the numerator of equation (A4) in favour of  $\rho(r)$  in equation (A2) readily yields

$$\epsilon_x(r) = -\frac{e^2}{2r} \rho(r) \quad (\text{A5})$$

which recovers equation (8) of the main text as it must.

Evidently, from equation (A2) we find

$$\ln \rho(r) = -\frac{Zr}{a_0} + O(\ln r) : r \rightarrow \text{infinity}. \quad (\text{A6})$$

Hence equation (A5) can be rewritten, using equation (A3) and (A6) in the limit when the  $O(\ln r)$  term is negligible, as

$$\epsilon_x(r) \rightarrow \frac{e^2}{2} \frac{|\nabla \rho|}{\ln \rho(r)} \quad (\text{A7})$$

which recovers equation (15) of the main text.

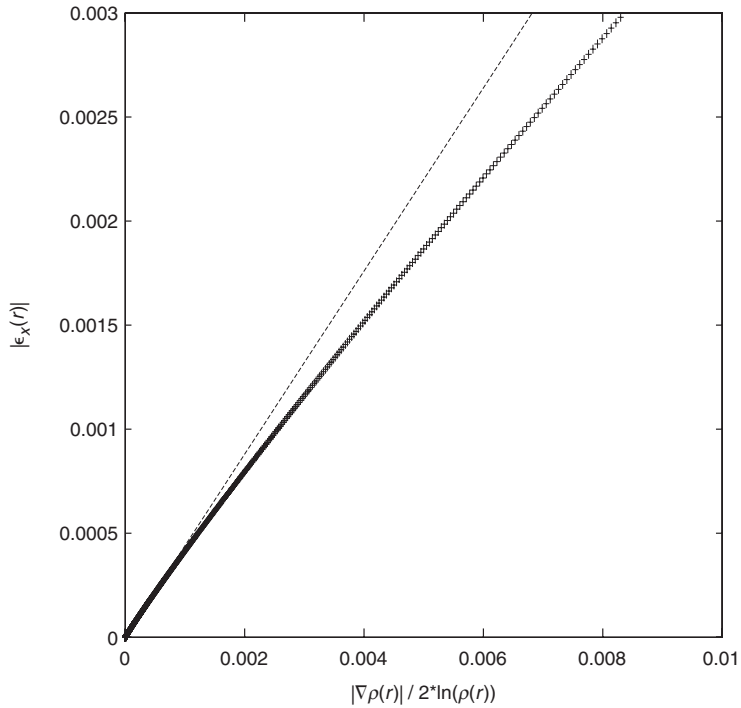


Figure A2. Plot of  $|\epsilon_x(r)|$  vs.  $|\nabla\rho|/2\ln(\rho(r))$  for the exact model with  $Z=92$ , a trendline ( $y=0.44x$ ) is included to guide the eye.

For this exact model, figures A1 and A2 display respectively, for  $Z=92$ ,  $\epsilon_x(r)$  versus  $\rho(r)$  and  $\epsilon_x(r)$  versus  $|\nabla\rho|/2\ln\rho(r)$ .

For the future, it may be worthwhile to make plots of  $\epsilon_x$  with  $x=a_0^4\rho^{4/3}$  and  $y=|a_0^4\nabla\rho|/\ln(a_0^3\rho)$ , thereby generalising figures 1–3 shown above, though the  $y$  variable is only to be included at sufficiently low density.