Total kinetic energy density for closed shells in a bare Coulomb field solely in terms of *s*-state information

2002 J. Phys. A: Math. Gen. 35 L635

(http://iopscience.iop.org/0305-4470/35/45/102)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **35** (2002) L635–L639 PII: S0305-4470(02)53389-8

LETTER TO THE EDITOR

Total kinetic energy density for closed shells in a bare Coulomb field solely in terms of *s*-state information

I A Howard[1] **and N H March**[1,2]

[1] Department of Physics, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[2] Oxford University, Oxford, England, UK

Received 9 September 2002
Published 29 October 2002
Online at stacks.iop.org/JPhysA/35/L635

Abstract
The kinetic energy density $t_G(r)$, where G denotes the gradient form $(\nabla\psi)^2$, is known to be a functional of the ground-state density $\rho(r)$, but the functional remains unknown. For an arbitrary number of closed shells in a bare Coulomb field, an exact first-order differential equation is derived giving $t_G(r)$ solely in terms of *s*-state information. Numerical illustrations are given of the main analytical results.

PACS numbers: 21.10.Sf, 31.15.Ew

Some time ago, one of us [1] obtained a spatial generalization of Kato's theorem

$$\left.\frac{\partial\rho(r)}{\partial r}\right|_{r=0} = -\frac{2Z}{a_0}\rho(r)|_{r=0} \tag{1}$$

for closed shells in a bare Coulomb field as

$$\frac{\partial\rho(r)}{\partial r} = -\frac{2Z}{a_0}\rho_s(r) \tag{2}$$

where the Coulomb potential is $V(r) = -Ze^2/r$ and $\rho_s(r)$ is solely the $l = 0$ angular momentum component of the total electron density $\rho(r)$.

Of course, density functional theory then leads us to the conclusion that the positive definite kinetic energy density, $t_G(r)$ (where G—gradient—denotes that t is defined from the $(\nabla\psi)^2$ wavefunction form), is thereby determined by $\rho_s(r)$, since t_G is known to be a functional of $\rho(r)$. These, however, are formal statements, and our purpose in this letter is to make them quite explicit.

As a first step, we take the relation derived by Howard and March [2] in their work on the nuclear cusp condition in the bare Coulomb model analogous to equation (2). In their equation (12) they write the *s*-state density $\rho_s(r)$ in terms of the quantity $t'_G(r)+(2Z/a_0)t_{Gs}(r)$, the construction of which was motivated by equation (2) alone [Note: it has been brought

to our attention that in equation (13) of [2], the second term should be preceded by a minus sign.]. Their equation (12) reads

$$\rho_s(r) = \frac{a_0 r^2}{Z}\left(t'_G(r) + \frac{2Z}{a_0}t_{Gs}(r)\right) + \exp\left(-\frac{2Zr}{a_0}\right) \times \left[\rho(0) - 2\int_0^r r^2\left(t'_G(r) + \frac{2Z}{a_0}t_{Gs}(r)\right)\exp\left(\frac{2Zr}{a_0}\right)\mathrm{d}r\right]. \tag{3}$$

We shall demonstrate below that in this same model

$$t'_G(r) + \frac{2Z}{a_0}t_{Gs}(r) = -\frac{1}{r^2}\left(\frac{Z\rho}{a_0} + \frac{\rho'}{2}\right). \tag{4}$$

Assuming this result, and inserting it into equation (3), we find almost immediately that

$$\rho(r)\exp\left(\frac{2Zr}{a_0}\right) = \rho(0) - 2\int_0^r r^2\left(\frac{-V'\rho}{a_0} - \frac{\rho'}{2r^2}\right)\exp\left(\frac{2Zr}{a_0}\right)\mathrm{d}r \tag{5}$$

where $V' = Z/r^2$. Differentiating equation (5) with respect to r, it is then a simple matter to confirm that it constitutes an identity, which is the initial demonstration of the correctness of equation (4).

As an immediate example of the utility of this latter equation, let us insert the spatial generalization of Kato's theorem embodied in equation (2) into the right-hand side of equation (4) to find, for an arbitrary number of closed shells,

$$t'_G(r) + \frac{2Z}{a_0}t_{Gs}(r) = -\frac{Z}{a_0 r^2}\rho_{l\neq 0} \tag{6}$$

where evidently $\rho_{l\neq 0} = \rho - \rho_s$. For the K shell alone, evidently $\rho_{l\neq 0} = 0$, and we have the analogue of equation (2) for the kinetic energy densities. For the K + L shell case [3, 4], $\rho_{l\neq 0} \equiv \rho_p(r)$, where p denotes $l = 1$ as usual, and since this is proportional to r^2 near the nucleus, $t'_G + (2Z/a_0)t_{Gs}$ now tends to a constant at the origin $r = 0$.

We next appeal to the result [5] that

$$t_{Gs}(r) = \frac{1}{4}\frac{\rho_{l\neq 0}(r)}{r^2} + \frac{\rho''_s(r)}{8} \tag{7}$$

and using equation (7) to remove $\rho_{l\neq 0}/r^2$ from equation (6) yields

$$t'_G(r) = -\frac{6Z}{a_0}t_{Gs} + \frac{Z}{2a_0}\rho''_s \tag{8}$$

which determines the total kinetic energy density $t_G(r)$ solely in terms of s-state information, and is one of the key results of the present letter.

As a non-trivial example of the use of equation (8), let us consider the Heilmann–Lieb (HL) density [6], which we shall denote by $\rho_\infty(r)$, since these workers summed over the entire bound-state spectrum $\epsilon_n = -Z^2/2n^2$ from $n = 1$ to infinity. While HL gave two alternative integral expressions for $\rho_\infty(r)$, we have found for computational purposes that it is very useful to write the s-state density, from the HL equation (12) giving $\mathrm{d}\rho/\mathrm{d}r$ (and therefore ρ_s from equation (2)), in terms of the Whittaker functions $\mathcal{M}(a, b, z)$ [7] as

$$\rho_{s\,\infty}(r) = \frac{1}{4\pi r^2}\sum_{n=1}^{\infty}\frac{1}{n}\left[\mathcal{M}\left(n, \frac{1}{2}, \frac{2r}{n}\right)\right]^2. \tag{9}$$

We have then obtained analytically a power series expansion in r of $\rho_{s\,\infty}(r)$ in terms of the Riemann zeta function $\zeta(m)$, and the low-order terms only are reproduced below:

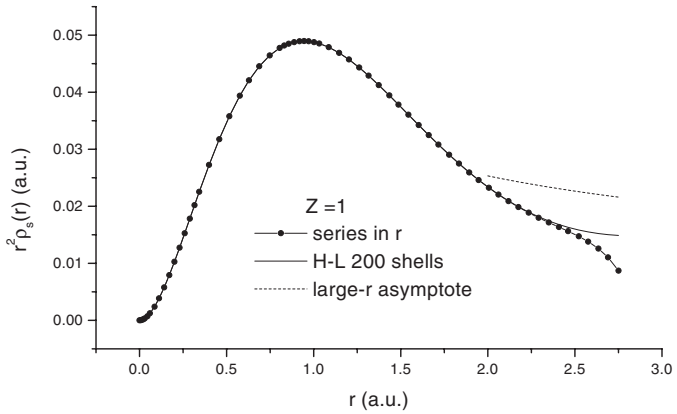

Figure 1. s-state density $\rho_s(r)$ times r^2 for an infinite number of bound states in a bare Coulomb field. The Heilmann–Lieb exact result is shown (summed to 200 shells), and for comparison the series expansion has been employed, the low-order terms of which are given in equation (10).

$$\rho_{s\,\infty}(r) = \frac{\zeta(3)}{\pi} - 2\zeta(3)\frac{r}{\pi} + \left[\frac{5}{3}\zeta(3) + \frac{1}{3}\zeta(5)\right]\frac{r^2}{\pi} - \left[\frac{7}{9}\zeta(3) + \frac{5}{9}\zeta(5)\right]\frac{r^3}{\pi} + \left[\frac{7}{30}\zeta(3) + \frac{7}{18}\zeta(5) + \frac{2}{45}\zeta(7)\right]\frac{r^4}{\pi} - \left[\frac{11}{225}\zeta(3) + \frac{7}{45}\zeta(5) + \frac{14}{225}\zeta(7)\right]\frac{r^5}{\pi} + \mathcal{O}(r^6). \tag{10}$$

We have plotted in figure 1 (for $Z = 1$) essentially the HL s-state density $\rho_{s\,\infty}(r)$ by summing over $n = 1$ to 200 (actually in terms of Laguerre polynomials). This is compared with the series expansion (10), taken however in our computations up to 20th order in r. As can be seen in figure 1, this series starts to deviate from the exact HL density $\rho_{s\,\infty}(r)$ around $r = 2.2$ a.u. Also shown in figure 1 at the largest r-value plotted is the large-r asymptote of HL, namely [6, 8] for $Z = 1$,

$$\rho_{s\,\infty}(r) = \frac{3}{4}\frac{\sqrt{2}}{3\pi^2}r^{-5/2} \qquad r \to \infty \tag{11}$$

but one will approach this limit very slowly since the quantity $r^2\rho_{s\,\infty}(r)$ plotted behaves as

$$r^2\rho_{s\,\infty}(r) = \frac{3}{4}\frac{\sqrt{2}}{3\pi^2}r^{-1/2} \qquad r \to \infty. \tag{12}$$

Relation (4) has proved central to this letter and therefore we shall now give a full proof below in which we appeal to the study of March and Santamaria [9] on this bare Coulomb model. These authors used the kinetic energy density $t(r)$ defined from the wavefunction form $(\psi\nabla^2\psi)$ and considered first the nth closed shell (later we shall again sum over shells). Denoting kinetic and particle densities by t_n and ρ_n for this shell, it was proved in [9] that (see also [10])

$$\frac{t_n}{\rho_n} = \frac{t_{ns}}{\rho_{ns}}. \tag{13}$$

But evidently

$$t_{ns} = -\tfrac{1}{2}\psi_{n00}\nabla^2\psi_{n00} \tag{14}$$

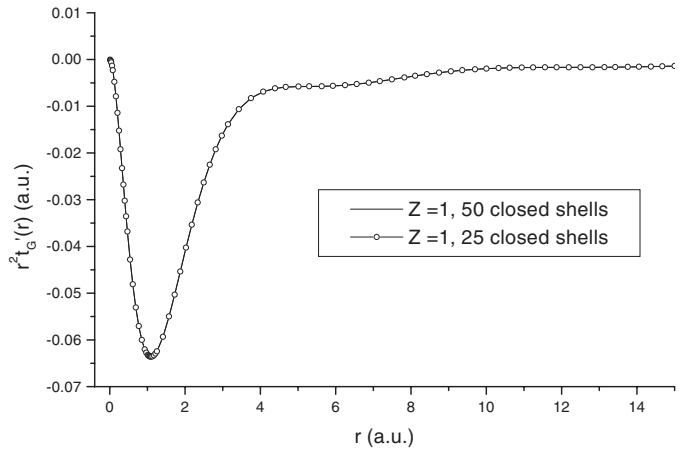

Figure 2. Derivative $t'_G(r)$ of kinetic energy density, times r^2, plotted for the case $Z = 1$ for a bare Coulomb field. Results, calculated from equation (8) and the Heilmann–Lieb expression for $\rho_s(r)$, are compared for 25 and 50 closed shells.

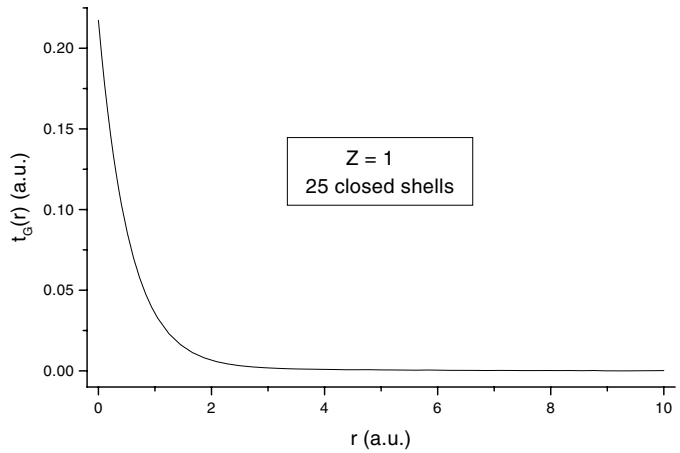

Figure 3. Total kinetic energy density $t_G(r)$ for 25 closed shells, constructed solely from s-state information.

and using the Schrödinger equation for the (normalized) s-state wavefunction ψ_{n00} of the nth closed shell one finds, with $\rho_{ns} = \psi^2_{n00}$,

$$\frac{t_{ns}}{\rho_{ns}} = (\epsilon_n - V(r)) \qquad \epsilon_n = -\frac{Z^2}{2n^2} \quad V(r) = -\frac{Z}{r}. \tag{15}$$

Hence, one has the result that for the nth closed shell

$$t_n(r) = [\epsilon_n - V(r)]\rho_n(r). \tag{16}$$

But the spatial generalization (2) of Kato's theorem is known to apply shell by shell, and hence by differentiation of equation (16) and use of this theorem one finds

$$t'_n(r) = -2Z\epsilon_n\rho_{ns}(r) - [V\rho_n(r)]'. \tag{17}$$

Using equation (15) for $\epsilon_n \rho_{ns}$ one readily reaches the result, after summing over an arbitrary number of closed shells, that

$$t'(r) + 2Zt_s + V'\rho = 0. \tag{18}$$

But t and t_G are well known to be related by

$$t_G(r) = t(r) + \frac{\nabla^2 \rho}{4} \tag{19}$$

and using the result in equation (18) one is led back to equation (4) after some quite straightforward manipulation. This therefore completes the proof of equation (4), which has been illustrated already by the calculation of t'_G (or t_G), actually from the derived equation (8) using equations (2) and (4), shown in figures 2 and 3.

In summary, some general analytical results have been presented for an arbitrary number of closed shells in a bare Coulomb field, the most notable of which are embodied in equations (4) and (8). In particular, equation (8) shows that the total kinetic energy density $t_G(r)$ can be obtained from t_{Gs} and ρ_s (plus Z), i.e. from s-state information. Figures 1 to 3 illustrate the analysis presented here in the Heilmann–Lieb limit [6].

Acknowledgments

IAH acknowledges support from the IWT—Flemish region. NHM wishes to acknowledge partial financial support from the Office of Naval Research for work on density functional theory. Especial thanks are due to Dr P Schmidt of that office for his continuing motivation and encouragement.

References

[1] March N H 1986 *Phys. Rev.* A **33** 88
[2] Howard I A and March N H 2002 *Phys. Lett.* A **296** 214
[3] March N H and Santamaria R 1988 *Phys. Rev.* A **38** 5002
[4] Howard I A, March N H, Senet P and Van Doren V E 2000 *Phys. Rev.* A **62** 062512
[5] Howard I A, March N H and Van Doren V E 2001 *Phys. Rev.* A **63** 062501
[6] Heilmann O J and Lieb E H 1995 *Phys. Rev.* A **52** 3628
[7] Abramowitz M J and Stegun I A 1970 *Handbook of Mathematical Functions* (New York: Dover) ch 13
[8] March N H 1996 *Phys. Rev.* A **54** 5415
[9] March N H and Santamaria R 1989 *Phys. Rev.* A **39** 2835
[10] Cooper I L 1994 *Phys. Rev.* A **50** 1040