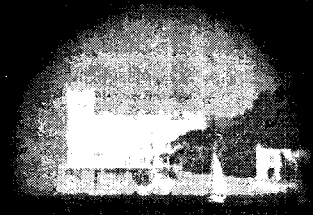




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TWO-ELECTRON ATOMS AND RELATION  
BETWEEN KINETIC ENERGY AND  
ELECTRON DENSITIES**

**N.H. March**

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United Nations Educational Scientific and Cultural Organization  
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THE ABDUS SALAM INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

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AND RELATION BETWEEN KINETIC ENERGY  
AND ELECTRON DENSITIES**

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**Abstract**

In early work, Dawson and March [J. Chem. Phys. **81**, 5850 (1984)] proposed a local energy method for treating both Hartree-Fock and correlated electron theory. Here, an exactly solvable model two-electron atom with pure harmonic interactions is treated in its ground state in the above context. A functional relation between the kinetic energy density  $t(r)$  at the origin  $r = 0$  and the electron density  $\rho(r)$  at the same point then emerges. The same approach is applied to the Hookean atom, in which the two electrons repel with Coulombic energy  $e^2/r_{12}$ , with  $r_{12}$  the interelectronic separation, but are still harmonically confined. Again the kinetic energy density  $t(r)$  is the focal point, but now generalization away from  $r = 0$  is also effected. Finally, brief comments are added about *He*-like atomic ions in the limit of large atomic number.

MIRAMARE - TRIESTE

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# 1 Background and outline

In an early study, Dawson and March<sup>1</sup> set out the so-called local energy method for treating atomic and molecular systems both at Hartree-Fock (HF) and correlated levels. The present investigation is related in that a local energy equation is first set up for treating two-electron atoms in which both ‘electron-nuclear’ and ‘electron-electron’ interactions are left to be defined.

Suppose then the ‘electron-nuclear’ potential energy is denoted by  $U(r)$  and the ‘electron-electron’ interaction energy by  $W(r_{12})$ , with  $r_{12}$  the interelectronic separation of the (assumed) spin-compensated ground state of the model atom thereby defined.

Then, if  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  and  $E$  are, respectively, the spatial (symmetric) ground-state wave function and corresponding eigenvalue, the most general local energy equation reads

$$E = \frac{H\Psi}{\Psi} \quad (1.1)$$

where  $H$  denotes the Hamiltonian operator given explicitly by

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + U(r_1) + U(r_2) + W(r_{12}) \quad (1.2)$$

While the above local energy method applies at each pair of vectors  $(\mathbf{r}_1, \mathbf{r}_2)$ , we shall now choose to integrate out information involving  $\mathbf{r}_2$ . Thus, for these two-electron atoms the ground-state electron density  $\rho(r_1)$  is given by

$$\rho(r_1) = 2 \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (1.3)$$

since the normalized ground-state wave function  $\Psi$  is real. Multiplying eqn.(1.1) by  $\Psi^2$  and integrating over all  $\mathbf{r}_2$  yields

$$\begin{aligned} \frac{E\rho(r_1)}{2} &= t(r_1) + \frac{U(r_1)\rho(r_1)}{2} + \int U(r_2)\Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ &+ \int W(r_{12})\Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 . \end{aligned} \quad (1.4)$$

It is clear that the first term on the right-hand side of eqn.(1.4) is the kinetic energy density, denoted by  $t(r_1)$ , which is precisely defined from the wave function form  $\Psi\nabla^2\Psi$ , and not from the positive-definite  $(\nabla\Psi)^2$  alternative. However, as will be invoked below, these definitions differ only by a multiple of the Laplacian of the electron density, namely  $\nabla^2\rho$ .

From eqn.(1.4), the local energy equation at the heart of the present study of two-electron atoms reads

$$\begin{aligned} E &= \frac{2t(r_1)}{\rho(r_1)} + U(r_1) + \frac{2}{\rho(r_1)} \int U(r_2)\Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ &+ \frac{2}{\rho(r_1)} \int W(r_{12})\Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 . \end{aligned} \quad (1.5)$$

The outline of the rest of this paper is then as follows. In section 2 immediately below eqn.(1.5) is applied to a model atom in which both  $U(r)$  and  $W(r_{12})$  are harmonic in form, such

a proposal going back at least to Moshinsky <sup>2,3</sup>. The main result we focus on relates to the limit  $r_1 \rightarrow 0$  of the ratio of  $t(r_1)$  to  $\rho(r_1)$ . Section 3 utilizes eqn.(1.5) for the so-called Hookean atom, going back to Kestner and Sinanoshu <sup>4-6</sup>. Here, harmonic springs still tie electrons 1 and 2 to the ‘nucleus’ at the origin  $r = 0$ , but the interaction potential energy  $W(r_{12})$  is now the Coulombic repulsion  $e^2/r_{12}$ . Again, the kinetic energy density  $t(r)$  is the main focus of attention. Section 4 treats then, but now quite briefly, *He*-like atomic ions with large atomic number  $Z$  although, as throughout the paper, non-relativistic quantum mechanics is retained. Section 5 constitutes a summary, plus some suggestions for future studies.

## 2 Two-electron atom with purely harmonic interactions

For the atom proposed by Moshinsky <sup>2,3</sup>, the choices of ‘external’ potential  $U(r)$  and interaction term  $W(r_{12})$  are as follows:

$$U(r) = \frac{1}{2}r^2; \quad W(r_{12}) = \frac{1}{2}Kr_{12}^2, \quad (2.1)$$

where  $K$  evidently measures the relative strength of  $U$  and  $W$ . The spatial form of the ground-state wave function is known to be

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \pi^{-3/2}(1+2K)^{3/8} \exp\left(-\frac{r_1^2+r_2^2}{2}\right) \\ &\times \exp\left(-\frac{1}{2}\{\alpha-1\}|\mathbf{r}_1-\mathbf{r}_2|^2\right), \end{aligned} \quad (2.2)$$

the quantity  $\alpha$ , which measures the ground-state energy  $E$  through

$$E = 3\alpha, \quad (2.3)$$

being defined as a function of  $K$  by

$$\alpha = \frac{1}{2} \left[ (1+2K)^{1/2} + 1 \right]. \quad (2.4)$$

In principle, one can insert directly eqns.(2.1) - (2.4) into the local energy eqn.(1.4). However, we shall restrict ourselves in the present section to taking the limit of the r.h.s. of eqn.(1.4) as  $r_1 \rightarrow 0$ , and shall thereby focus all attention on the calculation of the limit

$$\lim_{r_1 \rightarrow 0} \frac{t(r_1)}{\rho(r_1)} \equiv \frac{t(0)}{\rho(0)}. \quad (2.5)$$

Since  $U(r_1)$  from eqn.(2.1) tends to zero as  $r_1 \rightarrow 0$ , we readily obtain

$$\begin{aligned} \frac{t(0)}{\rho(0)} &= \frac{E}{2} - \frac{1}{\rho(0)} \int \frac{1}{2}r_2^2\Psi^2(0, \mathbf{r}_2)d\mathbf{r}_2 \\ &\quad - \frac{1}{\rho(0)} \int \frac{1}{2}Kr_2^2\Psi^2(0, \mathbf{r}_2)d\mathbf{r}_2. \end{aligned} \quad (2.6)$$

Evidently, the calculation of the ratio of kinetic energy density  $t$  to electron density  $\rho$  at the origin  $r = 0$  reduces to the evaluation of the integral  $I$  defined by

$$I = \int r_2^2 \Psi^2(0, r_2) dr_2 . \quad (2.7)$$

From eqn.(2.2),

$$\Psi^2(0, r_2) = n^2 \exp(-\alpha r_2^2) : \quad (2.8)$$

where  $n^2 = \pi^{-3}(1 + 2K)^{3/4}$ .

Thus, by simple quadrature one has the explicit result

$$\frac{I}{4\pi n^2} = \int_0^\infty r^4 \exp(-\alpha r^2) dr = \frac{3}{8} \frac{\pi^{1/2}}{\alpha^{5/2}} . \quad (2.9)$$

Using next a result of the study of March *et al.* <sup>7</sup>, one may write the normalization factor  $n$  in terms of the electron density  $\rho(0)$  at the origin  $r = 0$  as

$$n^2 = \left[ \frac{\rho(0)}{2} \right] \left[ \frac{\alpha}{\pi} \right]^{3/2} \quad (2.10)$$

Hence by substituting eqn.(2.10) into eqn.(2.9) we readily find

$$I = \frac{3}{4} \frac{\rho(0)}{\alpha} . \quad (2.11)$$

Returning to the local energy equation in the form (2.6), and utilizing eqns.(2.7) and eqn.(2.11), one finds the ratio  $t(0)/\rho(0)$  to be given by

$$\frac{t(0)}{\rho(0)} = \frac{3\alpha}{2} - \frac{3}{8\alpha}(1 + K) . \quad (2.12)$$

The final step in obtaining a physically significant relation between  $t(0)$  and  $\rho(0)$  in this model two-electron atom is to express the r.h.s. of eqn.(2.12) solely in terms of  $\rho(0)$  itself.

First of all, from eqn.(2.4) it follows readily that

$$K = 2\alpha^2 - 2\alpha \quad (2.13)$$

and using eqn.(2.13) in eqn.(2.12) then yields the result

$$\frac{t(0)}{\rho(0)} = \frac{3}{8} \left[ 2\alpha + 2 - \frac{1}{\alpha} \right] . \quad (2.14)$$

But from eqn.(10) of March *et al.* <sup>7</sup>, one can write

$$\frac{1}{\alpha} = 2 - \pi \left\{ \frac{\rho(0)}{2} \right\}^{2/3} . \quad (2.15)$$

Using eqn.(2.15) in eqn.(2.14), it is evident that  $t(0)/\rho(0)$  is a simple function of  $\rho(0)^{2/3}$ , namely

$$\frac{t(0)}{\rho(0)} = \frac{3}{8} \frac{\left[ 2 + 2\pi \left\{ \frac{\rho(0)}{2} \right\}^{2/3} - \pi^2 \left\{ \frac{\rho(0)}{2} \right\}^{4/3} \right]}{\left[ 2 - \pi \left\{ \frac{\rho(0)}{2} \right\}^{2/3} \right]} . \quad (2.16)$$

Since one of the current aims of density functional theory is to obtain the kinetic energy density  $t$  as a functional of the ground-state density  $\rho$ , eqn.(2.16) for the interacting two-electron 'harmonic' atom is a significant result in that context.

### 3 Local energy equation plus kinetic energy density for two-electron Hookean atom

Let us turn to the second of the model atoms already referred to in section 1, namely the two-electron Hookean atom. While characterized in general by the choices of external potential  $U(r)$  and electron-electron interaction  $W(r_{12})$ :

$$U(r) = \frac{1}{2}kr^2; \quad W(r_{12}) = e^2/r_{12}, \quad (3.1)$$

we shall content ourselves with the solvable case<sup>5,6</sup> when  $k = 1/4$ . The important point to be stressed here is the retention of the Coulombic repulsion energy  $e^2/r_{12}$  in this model atom, which then subsumes the key electron-electron cusp condition.

For the above choice of force constant  $k = 1/4$ , the spatial ground-state wave function is known to be<sup>5,6</sup>

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = n \exp\left(-\frac{|\mathbf{r}_1 + \mathbf{r}_2|^2}{8}\right) \exp(-|\mathbf{r}_2 - \mathbf{r}_1|^2/8) \left(1 + \frac{|\mathbf{r}_2 - \mathbf{r}_1|}{2}\right), \quad (3.2)$$

the normalization factor  $n$  having the value

$$n = 1 / \left[ 2\pi^{5/4} (5\pi^{1/2} + 8)^{1/2} \right]. \quad (3.3)$$

The ground-state electron density in this model with  $k = 1/4$  is given by<sup>6</sup>

$$\rho(r) = \frac{\pi(2\pi)^{1/2}n^2}{r} \exp\left(-\frac{r^2}{2}\right) \left\{ 7r + r^3 + \left(8/(2\pi)^{1/2}\right) r \exp\left(-\frac{r^2}{2}\right) + 4(1 + r^2) \operatorname{erf}(r/2^{1/2}) \right\} \quad (3.4)$$

where the error function is defined as

$$\operatorname{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-y^2) dy. \quad (3.5)$$

Following section 2, we shall again focus on the consequences of the local energy eqn.(1.4) at the origin  $r = 0$ . Then we may write, using  $k = 1/4$  in eqn.(3.1),

$$E = \frac{2t(0)}{\rho(0)} + \frac{2}{\rho(0)} \int \frac{1}{8} r_2^2 \Psi^2(0, r_2) dr_2 + \frac{2}{\rho(0)} \int \frac{e^2}{r_2} \cdot \Psi^2(0, r_2) dr_2. \quad (3.6)$$

But from eqn.(3.2)

$$\Psi^2(0, r_2) = n^2 \exp\left(-\frac{1}{2}r_2^2\right) \left(1 + \frac{r_2}{2}\right)^2 \quad (3.7)$$

and for the density  $\rho(0)$  at the origin one finds from eqn.(3.4) the explicit form

$$\rho(0) = n^2 \left[ 7 \cdot 2^{1/2} \pi^{3/2} + 16\pi \right] \quad (3.8)$$

which can be viewed as the analogue of eqn.(2.15) obtained earlier for the Moshinsky atom.

### 3.1 Kinetic energy density related to electron density for all values of $r$

Instead of focussing solely on  $t(0)$  appearing in the local energy form (3.6), it will be instructive below to study  $t(r)$  for all  $r$ . While this is directly accessible from the local energy eqn.(1.4) by inserting eqns.(3.1) and (3.2), one can also obtain it via the kinetic energy density tensor  $t_{\alpha\beta}(r)$  defined by Holas and March <sup>8</sup>, though its trace now corresponds to the positive-definite form of kinetic energy density proportional to  $(\text{grad } \psi)^2$  in wave function terms: we shall denote this form by  $t_{grad}(r) \equiv t_g(r)$ . The explicit relation between  $t(r)$  appearing in the local energy eqn.(1.4) and  $t_g(r)$  is

$$t(r) = t_g(r) - \frac{1}{4} \nabla^2 \rho(r) . \quad (3.9)$$

For a convenient form of  $t_{\alpha\beta}(r)$  for present purposes, we next appeal to the work of Qian and Sahni <sup>9</sup>, and in particular to their eqn.(A18) to write

$$t_g(r) = f(r) + 3k(r) , \quad (3.10)$$

where in ref.10 explicit expressions are recorded in eqns.(A19) and (A20) for  $f$  and  $k$  respectively. Forming the combination  $f + 3k$  appearing in eqn.(3.10) leads to the important simplification that Dawson's integral appearing in the separate expressions for  $f$  and  $k$  cancels in  $f + 3k$ , and only  $\text{erf}(r/2^{1/2})$  appearing in  $\rho(r)$  given in eqn.(3.4) above remains, apart from simple explicit functions. We then obtain  $t_g(r)$  from eqn.(3.10) as

$$\begin{aligned} t_g(r) = & \frac{r^2 \rho(r)}{8} - \frac{\pi^{3/2}}{2^{1/2}} n^2 r^2 \exp\left(-\frac{r^2}{2}\right) + 2^{1/2} \pi^{3/2} n^2 \frac{(1-r^2)}{r} \text{erf}(r/2^{1/2}) \\ & - 2\pi n^2 \exp(-r^2) + \frac{\pi^{3/2}}{2^{1/2}} n^2 \exp\left(-\frac{r^2}{2}\right) . \end{aligned} \quad (3.11)$$

It is now a fairly straightforward matter to take the limit of  $t_g(r)$  as  $r \rightarrow 0$ , the definition (3.5) being invoked in the process, as well as the value of  $n^2$  given in eqn.(3.3). The desired result is then found to be

$$t_g(0) = \frac{\pi^{3/2} n^2}{2^{1/2}} = \frac{1}{2^{5/2} \pi [5\pi^{1/2} + 8]} . \quad (3.12)$$

Finally, we invoke eqn.(3.9) to obtain  $t(0)$  from  $t_g(0)$ , via the Laplacian of the density  $\rho(r)$ , the 'correction' to  $t_g(0)$  being

$$-\frac{1}{4} \nabla^2 \rho|_{r=0} = \frac{\left[\frac{15}{16} \left(\frac{\pi}{2}\right)^{1/2} + 1\right] 2\pi^{3/2}}{[5\pi^{1/2} + 8]} . \quad (3.13)$$

Then the kinetic energy density  $t(r)$  at the origin  $r = 0$  has the value

$$t(0) = \frac{1}{2^{5/2} \pi [5\pi^{1/2} + 8]} \left[ 1 + 2^{7/2} \pi^{5/2} \left\{ 1 + \frac{15}{16} \left(\frac{\pi}{2}\right)^{1/2} \right\} \right] . \quad (3.14)$$

Thus, from eqns.(3.3), (3.8), (3.12), and (3.14) we obtain the analogue of eqn.(2.12) derived earlier for the Moshinsky atom, when eqn.(3.8) is used directly for  $\rho(0)$ .

Returning to the basic  $r$ -dependent eqn.(3.11), let us multiply throughout by  $r$  to find

$$\begin{aligned} r t_g(r) &= \frac{r^3 \rho(r)}{8} - \frac{\pi^{3/2}}{2^{1/2}} n^2 r^3 \exp(-r^2/2) \\ &+ 2^{1/2} \pi^{3/2} n^2 (1 - r^2) \operatorname{erf}(r/2^{1/2}) - 2\pi n^2 r \exp(-r^2) \\ &+ \frac{\pi^{3/2}}{2^{1/2}} n^2 r \exp\left(-\frac{r^2}{2}\right). \end{aligned} \quad (3.15)$$

It turns out that, to eliminate the error function, one needs to differentiate eqn.(3.15) three times, the result being set out in eqn.(A6) of the Appendix. The desired result relating  $t_g(r)$  and  $\rho(r)$  is then of the form

$$(r^4 - r^2)t_g''' + 3(r^3 - r)t_g'' = R_0(r)\rho + R_1(r)\rho' + R_2(r)\rho'' + R_3(r)\rho''' . \quad (3.16)$$

Here the  $R_i(r)$  denote polynomials in  $r$ , which are recorded explicitly in the Appendix. Eqn.(3.16) represents the functional relation between the positive definite kinetic energy density  $t_g(r)$  and the electron density  $\rho(r)$  plus its low-order derivatives. It completes the sought-after density functional result for the two-electron Hookean atom. One boundary condition which  $t_g(r)$  must satisfy on integration of eqn.(3.16) is the form (3.12) for  $t_g(0)$ .

#### 4 *He*-like atomic ions for large atomic number $Z$

Let us first neglect the electron-electron interaction term  $e^2/r_{12}$  relative to the electron-nuclear coupling  $-Ze^2/r$ , an approximation which becomes increasingly valid for large  $Z$ . Then with  $U(r) = -Ze^2/r$ , one can derive a differential equation for the kinetic energy density  $t(r)$  in terms of  $U$  and the electron density  $\rho(r)$  as <sup>11</sup>

$$t'(r) = -\frac{3}{2} U'(r)\rho - \frac{\rho'}{4r^2} - \frac{\rho''}{2r} - \frac{\rho'''}{8} . \quad (4.1)$$

Let us form  $t_g(r)$  using eqn.(3.9) as

$$t_g' = -\frac{3}{2} U'(r)\rho - \frac{3\rho'}{4r^2} + \frac{\rho'''}{8} . \quad (4.2)$$

But  $U'(r) = Ze^2/r^2$  in this case, and therefore multiplying (4.2) by  $\frac{r^2}{\rho}$  yields

$$\frac{r^2 t_g'}{\rho} = -\frac{3}{2} Ze^2 - \frac{3\rho'}{4\rho} + \frac{r^2 \rho'''}{8\rho} . \quad (4.3)$$

Differentiating with respect to  $r$  given the differential equation relating  $t_g$  and  $\rho$  in the large  $Z$  limit of non-relativistic quantum mechanics as

$$r^2 \rho t_g'' + [2r\rho - r^2 \rho'] t_g' = \frac{3}{4} \rho'^2 - \frac{3}{4} \rho \rho'' + \frac{1}{4} r \rho \rho''' + \frac{r^2 \rho \rho^{IV}}{8} - \frac{r^2}{8} \rho' \rho''' . \quad (4.4)$$

Again, but now in the limit  $Z \rightarrow \infty$  for *He*-like atomic ions, one has a functional relationship between the kinetic energy density  $t_g(r)$  and the electron density  $\rho(r)$ ; the counterpart of the



exact eqn.(3.16) for the Hookean atom. It would seem interesting for the future to make use of the Schwartz <sup>12</sup> density  $\rho(r)$  which subsumes  $e^2/r_{12}$  in lowest order. But presently, there is no route of equivalent reliability for the calculation of  $t_g(r)$  with inclusion of  $e^2/r_{12}$ , and so we shall not pursue the matter further here.

We note finally as an alternative to eqn.(4.4), that for the non-interacting case when  $e^2/r_{12}$  is omitted the positive definite kinetic energy  $t_g(r)$  is explicitly given by the von Weizsäcker form <sup>13</sup>

$$t_g(r) = \frac{1}{8} \frac{\rho'^2}{\rho} \quad (4.5)$$

and hence

$$t'_g(r) = \frac{1}{4} \frac{\rho'\rho''}{\rho} - \frac{1}{8} \frac{\rho'^3}{\rho^2}. \quad (4.6)$$

Multiplying (4.6) through by  $\rho^2$  and differentiating the result with respect to  $r$  readily yields, after multiplying finally by  $r^2$ :

$$r^2 \rho^2 t''_g + 2r^2 \rho \rho' t'_g = \frac{r^2}{4} \rho \rho''^2 - \frac{r^2}{8} \rho'^2 \rho'' + r^2 \frac{\rho \rho' \rho'''}{4}. \quad (4.7)$$

Subtracting eqn.(4.7) from eqn.(4.4) times  $\rho(r)$  then gives

$$\begin{aligned} [2r\rho^2 - 3r^2\rho\rho']t'_g &= \frac{3}{4}\rho\rho'^2 - \frac{3}{4}\rho^2\rho'' + \frac{1}{4}r\rho^2\rho''' + \frac{r^2\rho^2\rho^{IV}}{8} \\ &\quad - \frac{r^2}{4}\rho\rho''^2 + \frac{r^2}{8}\rho'^2\rho'' - \frac{3}{8}r^2\rho\rho'\rho''' \end{aligned} \quad (4.8)$$

which is a functional relationship between  $t'_g$  and electron density  $\rho$  plus its derivatives up to, and including,  $\rho^{IV}$ . From Kato's theorem <sup>14</sup>, we have that

$$\left. \frac{\partial \rho}{\partial r} \right|_{r=0} = -\frac{2Z}{a_0} \rho(r=0) \quad (4.9)$$

and hence, by combining eqns.(4.5) and (4.9):

$$t_g(r=0) = \frac{1}{2} \frac{Z^2}{a_0^2} \rho(r=0). \quad (4.10)$$

Thus  $t_g(r=0)$  is fixed from knowledge of  $\rho(r=0)$ , plus however the value of the atomic number  $Z$ .

## 5 Summary and future directions

The main results of the present study of two-electron atoms are:

- (i) The local energy eqn.(1.4) for general 'external' potential  $U(r)$  and 'electron-electron' interaction  $W(r_{12})$ .
- (ii) The density functional relationship (2.16) between the kinetic energy density  $t(0)$  and  $\rho(0)$ , for the Moshinsky atom for which both  $U$  and  $W$  are of harmonic form.

- (iii) The functional relationship between the positive definite kinetic energy density  $t_g(r)$  and the electron density  $\rho(r)$  embodied in the exact differential eqn.(3.16) for the Hookean atom, for which  $U$  is still harmonic, but  $W(r_{12}) = e^2/r_{12}$ , the electron-electron cusp condition thereby being subsumed completely.
- (iv) For helium-like atomic ions in the limit of sufficiently large atomic number  $Z$  that  $e^2/r_{12}$  can be neglected, the differential eqn.(4.4), or its alternative form (4.8), relating  $t_g(r)$  to  $\rho(r)$ .

For the future, it would seem to be of some interest to attempt the generalization of eqns.(4.4) and/or (4.8) to include the electron-electron interaction to lowest order, for large atomic number  $Z$ . Further results for the Moshinsky atom which would be worthwhile in the future involve the generalization of eqn.(2.16) away from  $r = 0$ , and in particular the connected study of non-locality in relating  $t(r)$  and  $\rho(r)$  which is not apparent from this equation.

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## Appendix A

Some details on Hookean atom including explicit forms of polynomials  $R_i(r)$  in differential eqn.(3.16) for kinetic energy density  $t_g(r)$ .

The detailed way in which one passes from eqn.(3.15) to the final differential eqn.(3.16) giving the kinetic energy density  $t_g(r)$  has been deferred to this Appendix.

The first stage of the derivation involves differentiating eqn.(3.15) three times. Omitting the details, this process then yields the result

$$\begin{aligned}
 rt_g''' + 3t_g'' &= \frac{3}{4}\rho + \frac{9}{4}r\rho' + \frac{9r^2}{8}\rho'' + \frac{r^3}{8}\rho''' \\
 -n^2e^{-r^2/2} &\left[ \frac{9\pi^{3/2}}{2^{1/2}} + 14\pi \right] + n^2r^2e^{-r^2/2} \left[ \frac{33\pi^{3/2}}{2^{1/2}} + 16\pi \right] \\
 &+ 12\pi n^2e^{-r^2} - 48\pi n^2r^2e^{-r^2} + 16\pi n^2r^4e^{-r^2} \\
 -n^2r^4e^{-r^2/2} &\left[ \frac{13\pi^{3/2}}{2^{1/2}} + 2\pi \right] + n^2r^6e^{-r^2/2} \left[ \frac{\pi^{3/2}}{2^{1/2}} \right]
 \end{aligned} \tag{A1}$$

Next, we employ eqn.(4) of ref.10 to remove  $\exp(-r^2)$ :

$$2\exp(-r^2) = \left\{ c^{-1} [(1+r^2)\rho(r) + (r+r^3)\rho'] - \frac{1}{4} \left(\frac{\pi}{2}\right)^{1/2} (7-4r^2+r^4) \exp\left(-\frac{r^2}{2}\right) \right\} \tag{A2}$$

where

$$c = 2\pi^{3/2} / \left[ 5\pi^{1/2} + 8 \right] \tag{A3}$$

Thus, rewriting eqn.(A1) using eqn.(A2) leads to the form

$$\begin{aligned}
 rt_g''' + 3t_g'' &- \frac{3}{4}\rho + \frac{9}{4}r\rho' + \frac{9r^2}{8}\rho'' + \frac{r^3}{8}\rho''' \\
 -8\pi n^2r^4 &[c^{-1} \{(1+r^4)\rho(r) + (r+r^3)\rho'(r)\}] \\
 +24\pi n^2r^2 &\left[ c^{-1} \{(1+r^4)\rho(r) + (r+r^3)\rho'(r)\} - 6\pi n^2r^2 \left(\frac{\pi}{2}\right)^{1/2} (7-4r^2+r^4) \exp\left(-\frac{r^2}{2}\right) \right] \\
 +2\pi n^2r^4 &\left[ \left(\frac{\pi}{2}\right)^{1/2} (7-4r^2+r^4) \exp\left(-\frac{r^2}{2}\right) \right] + \frac{3\pi}{2} n^2 \left(\frac{\pi}{2}\right) (7-4r^2+r^4) \exp -\frac{r^2}{2} \\
 -n^2e^{-r^2/2} &\left[ \frac{9\pi^{3/2}}{2^{1/2}} + 14\pi \right] + n^2r^2e^{-r^2/2} \left[ \frac{33\pi^{3/2}}{2^{1/2}} + 6\pi \right]
 \end{aligned}$$

or

$$\begin{aligned}
 rt_g''' + 3t_g'' &- \frac{3}{4}\rho + \frac{9}{4}r\rho' + \frac{9r^2}{8}\rho'' + \frac{r^3}{8}\rho''' \\
 +24\pi n^2c^{-1}r^2 &[\{1+r^4\}\rho(r) + (r+r^3)\rho'(r)] - 8\pi n^2c^{-1}r^4 [\{1+r^4\}\rho(r) + (r+r^3)\rho'(r)] \\
 -6\pi n^2c^{-1} &[(1+r^4)\rho(r) + (r+r^3)\rho'(r)]
 \end{aligned}$$

$$\begin{aligned}
&= -6\pi \left(\frac{\pi}{2}\right)^{1/2} n^2 [7r^2 - 4r^4 + r^6] \exp\left(-\frac{r^2}{2}\right) \\
&\quad + 2\pi \left(\frac{\pi}{2}\right)^{1/2} n^2 [7r^4 - 4r^6 + r^8] \exp\left(-\frac{r^2}{2}\right) \\
&\quad + \frac{3\pi}{2} \left(\frac{\pi}{2}\right)^{1/2} n^2 [7 - 4r^2 + r^4] \exp\left(-\frac{r^2}{2}\right)
\end{aligned} \tag{A4}$$

The final step is to use eqn.(6) of ref.10 to eliminate  $\exp\left(-\frac{r^2}{2}\right)$  from eqn.(A4), namely

$$\left(\frac{\pi}{2}\right)^{1/2} \exp\left(-\frac{r^2}{2}\right) = \frac{4}{(r^3 - r)} c^{-1} [(2r + 2r^3)\rho(r) + (2 + 3r^2)\rho' + r\rho''] \tag{A5}$$

It is natural to multiply through by the factor  $(r^3 - r)$  appearing in the denominator of eqn.(A5) and then we obtain

$$\begin{aligned}
&(r^4 - r^2)t_g''' + 3(r^3 - r)t_g'' - \frac{3}{4}(r^3 - r)\rho + \frac{9}{4}(r^4 - r^2)\rho' \\
&+ \frac{9}{8}(r^5 - r^3)\rho'' + \frac{(r^6 - r^4)}{8}\rho''' + 24\pi n^2 c^{-1}(r^3 - r)(r^2 + r^6)\rho(r) \\
&+ 24\pi n^2 c^{-1}(r^3 + r^5)(r^3 - r)\rho' - 8\pi n^2 c^{-1}(r^4 + r^8)(r^3 - r)\rho(r) \\
&\quad - 8\pi n^2 c^{-1}(r^5 + r^7)(r^3 - r)\rho' - 6\pi n^2 c^{-1}(1 + r^4)(r^3 - r)\rho \\
&\quad \quad - 6\pi n^2 c^{-1}(r^3 - r)(r^3 + r)\rho' \\
&= -6\pi n^2(7r^2 - 4r^4 + r^6)4c^{-1} [(2r + 2r^3)\rho(r) + (2 + 3r^2)\rho' + r\rho''] \\
&+ 2\pi n^2(7r^4 - 4r^6 + r^8)4c^{-1} [(2r + 2r^3)\rho + (2 + 3r^2)\rho' + r\rho' + r\rho''] \\
&\quad + \frac{3\pi}{2}n^2(7 - 4r^2 + r^4)4c^{-1} [(2r + 2r^3)\rho + (2 + 3r^2)\rho' + r\rho''] .
\end{aligned} \tag{A6}$$

Hence the results for  $R_i(r)$  are found to be as in the following eqns.(A7)-(A10).

Since  $n^2 c^{-1} \pi = (8\pi^3)^{-1}$  one finds first of all that

$$R_0(r) = \left[-\frac{3}{4}r + \frac{3}{4}r^3\right] + (8\pi^3)^{-1}[78r - 20r^3 + 34r^5 + 242r^7 - 88r^9 + 24r^{11}] \tag{A7}$$

which is evidently an odd polynomial of  $O(r^{11})$ .

Finding the coefficient of  $\rho'$  from eqn.(A6) yields the result

$$R_1(r) = -\frac{9}{4}r^2 + \frac{9}{4}r^4 - (8\pi^3)^{-1}[390r^2 + 236r^4 - 368r^6 + 176r^8 - 32r^{10}] \tag{A8}$$

i.e. an even polynomial of  $O(r^{10})$ .

Similarly  $R_2(r)$  is found to be the 9<sup>th</sup> order polynomial

$$R_2(r) = -\frac{9}{8}r^3 + \frac{9}{8}r^5 - (8\pi^3)^{-1}[42r - 192r^3 + 158r^5 - 56r^7 + 8r^9] \tag{A9}$$

and finally

$$R_3(r) = -\frac{r^4}{8} + \frac{r^6}{8} . \tag{A10}$$

This completes the result (3.16), giving the kinetic energy density  $t_g(r)$  in terms of  $\rho(r)$  and its low-order derivatives.

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