

Kinetic energy and ground-state electron densities as fingerprints of wavefunction entanglement in two-electron spin-compensated atomic models

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys. A: Math. Gen. 39 3741

(<http://iopscience.iop.org/0305-4470/39/14/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.101

The article was downloaded on 03/06/2010 at 04:17

Please note that [terms and conditions apply](#).

Kinetic energy and ground-state electron densities as fingerprints of wavefunction entanglement in two-electron spin-compensated atomic models

N H March^{1,2}, J Negro³ and L M Nieto³

¹ Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

² Oxford University, Oxford, UK

³ Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, 47071 Valladolid, Spain

E-mail: jnagro@fta.uva.es and luismi@metodos.fam.cie.uva.es

Received 12 December 2005

Published 22 March 2006

Online at stacks.iop.org/JPhysA/39/3741

Abstract

We take as a starting point the ground-state electron density in two-electron model atoms in which Coulomb confinement in the He atom is first replaced by harmonic restoring forces. Switching off electron–electron interactions, one readily constructs a third-order differential equation for the ground-state electron density, as in the recent work of March and Ludeña (2004 *Phys. Lett. A* **330** 16). We then switch on two different model interactions, first in the so-called Hookean atom going back to Kestner and Sinanoğlu (1962 *Phys. Rev.* **128** 2687), in which e^2/r_{12} is retained as in He, and secondly in the Moshinsky (1968 *Am. J. Phys.* **36** 52) atom in which $Kr_{12}^2/2$ is switched on. Some analyticity properties of the low-order linear homogeneous differential equations which result are next studied. He-like atomic ions are then treated in the limit of large atomic number Z . In this latter case, one identifies both the electron–nuclear cusp, or equivalently Kato’s theorem, and the corresponding electron–electron cusp in the ground-state spatial wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$. A final comment concerns quantum information and entanglement in relation to the recent work of Amovilli and March (2004 *Phys. Rev. A* **69** 054302).

PACS numbers: 05.30.Fk, 71.10.Ca, 31.15.Ew, 03.75.Fi

1. Background and outline

The problem of the electronic structure of the He atom remains unsolved to date, in spite of enormous efforts made since the advent of quantum mechanics. However, using the ground-state electron density $\rho(r)$ instead of the symmetrical spatial wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$

involving the coordinates of both electrons 1 and 2, important progress has been made fairly recently on model spin-compensated two-electron atoms. In particular, for the Hookean atom, going back at least to Kestner and Sinanoğlu [1], in which Coulomb confinement of electrons to the nucleus in He is now replaced by springs, but the electron–electron repulsion energy $e^2/|r_1 - r_2|$ is retained in the Hamiltonian, a third-order linear homogeneous differential equation has been derived by March *et al* [2] for the ground state density $\rho(r)$ (see equation (9) for the explicit form). Subsequently, Gál *et al* [3] have achieved the parallel result for the He-like atomic ion sequence in the limit of large atomic number Z (see equation (11) later).

In the present study, our aim is different: namely to examine the analyticity properties of these two differential equations which embrace exactly entanglement properties in the correlated wavefunctions deduced from the non-relativistic Schrödinger equation. Therefore, in section 2 almost immediately below we use this equation, together with the basic definition of $\rho(r)$ from the Schrödinger wavefunction, to deduce the shape of a final differential equation for $\rho(r)$ for spin-compensated spherical model atoms. Of course, because electron correlation affects both kinetic and potential contributions entering the Schrödinger equation, the resulting third-order differential equation for $\rho(r)$, therefore, still involves the wavefunction Ψ as well as $\rho(r)$ and its low-order derivatives. Nevertheless, section 2 provides a quite fundamental framework for assessing the effects of wavefunction entanglement on the differential equation for $\rho(r)$ (for example, one can switch off the electron–electron interaction and can vary the external potential from Coulombic attraction of electrons to the nucleus to harmonic confinement as in the Hookean atom model to be discussed in detail in section 3). Section 4 then contains a mathematical investigation of the analytic properties of the third-order differential equations currently available. A summary plus proposals for further study constitute section 5.

2. Towards a differential equation for the ground-state density $\rho(r)$ of a spin-compensated two-electron atom

Starting from the normalized symmetrical spatial wavefunction $\Psi(r_1, r_2)$ of such a two-electron atom, the electron density $\rho(r)$ is defined by

$$\rho(r) = 2 \int \Psi^2(r, r_2) dr_2. \quad (1)$$

Taking the gradient of equation (1), we have

$$\nabla_r \rho(r) = 4 \int \Psi(r, r_2) (\nabla_r \Psi(r, r_2)) dr_2. \quad (2)$$

Forming the Laplacian $\nabla_r^2 \rho(r)$, we find

$$\nabla_r^2 \rho(r) = 4 \int (\nabla_r \Psi)^2 dr_2 + 4 \int \Psi (\nabla_r^2 \Psi) dr_2 \quad (3)$$

which has a ready interpretation as a difference between two alternative definitions of kinetic energy density (see also equation (A.8)). Taking a further gradient, the result is, with \hat{r} denoting a radial unit vector,

$$\begin{aligned} \nabla_r \{ \nabla_r^2 \rho(r) \} &= \hat{r} \left\{ \rho'''(r) + \frac{2}{r} \rho''(r) - \frac{2}{r^2} \rho'(r) \right\} \\ &= 12 \int (\nabla_r \Psi) (\nabla_r^2 \Psi) dr_2 + 4 \int \Psi (\nabla_r \{ \nabla_r^2 \Psi \}) dr_2. \end{aligned} \quad (4)$$

This is the point at which the Schrödinger equation satisfied by Ψ can be introduced: namely,

$$-\frac{1}{2}\nabla_r^2\Psi - \frac{1}{2}\nabla_{r_2}^2\Psi + [V(r) + V(r_2)]\Psi + \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}\Psi = E\Psi, \quad (5)$$

where $V(r)$ denotes the external potential, and E is the ground-state energy. Inserting this result into the right-hand side of (4), we find

$$\begin{aligned} \hat{r} \left\{ \rho'''(r) + \frac{2}{r}\rho''(r) - \frac{2}{r^2}\rho'(r) \right\} = & -24 \int (\nabla_r\Psi)(\nabla_r^2\Psi) d\mathbf{r}_2 + 24V(r) \int (\nabla_r\Psi)\Psi d\mathbf{r}_2 \\ & + 24 \int (\nabla_r\Psi)V(r_2)\Psi d\mathbf{r}_2 + 24 \int (\nabla_r\Psi)\frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}\Psi d\mathbf{r}_2 \\ & - 24E \int \Psi(\nabla_r\Psi) d\mathbf{r}_2 - 8 \int \Psi\{\nabla_r(\nabla_r^2\Psi)\} d\mathbf{r}_2 \\ & + (\nabla_r V(r)) \int \Psi(\nabla_r\Psi) d\mathbf{r}_2 + 4 \int \Psi V(r_2)(\nabla_r\Psi) d\mathbf{r}_2 \\ & + 8 \int \Psi \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}(\nabla_r\Psi) d\mathbf{r}_2 - 8E \int \Psi(\nabla_r\Psi) d\mathbf{r}_2. \end{aligned} \quad (6)$$

Grouping the kinetic energy terms together into a contribution $\hat{r}\mathcal{T}(r)$, we can write equation (6) as

$$\begin{aligned} \hat{r} \left\{ \rho'''(r) + \frac{2}{r}\rho''(r) - \frac{2}{r^2}\rho'(r) \right\} = & \hat{r}[\mathcal{T}(r) + 24V(r)\rho'] + 16 \int V(r_2)(\nabla_r\Psi^2) d\mathbf{r}_2 \\ & + 20 \int \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}(\nabla_r\Psi^2) d\mathbf{r}_2 - 24E(\nabla_r\rho(r)) - (\nabla_r V(r))\rho(r), \end{aligned} \quad (7)$$

where the spherical symmetry of the two-electron atom has now been introduced.

Quite plainly, electron correlation effects enter the kinetic contribution $\mathcal{T}(r)$ and the term

$$\int \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}(\nabla_r\Psi^2) d\mathbf{r}_2$$

involving explicitly the electron–electron interaction. In the following two sections, we therefore specialize to cases where the differential equations for $\rho(r)$, also of third order (see also [4]) as in equation (7), are already known from explicit solutions.

3. Model atoms: two differential equations for $\rho(r)$ reflecting the Coulomb repulsion $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ between electrons 1 and 2

3.1. The Hookean atom

Let us begin with the Hookean atom for a specified force constant $k = 1/4$ in the ‘external’ potential representing harmonic confinement, i.e. for

$$V(r) = \frac{1}{8}r^2. \quad (8)$$

The explicit form of the differential equation for the Hookean atom is [2]

$$\begin{aligned} (r^4 - r^2)\rho'''(r) + (4r^5 - 4r^3 - 2r)\rho''(r) \\ + (5r^6 - 4r^4 - 13r^2 + 2)\rho'(r) + (2r^7 - 10r^3)\rho(r) = 0. \end{aligned} \quad (9)$$

Because one focus of this work is entanglement, it will be instructive to compare equation (9) with the result neglecting the Coulomb interaction, when $\Psi(\mathbf{r}, \mathbf{r}_2) \rightarrow \phi(r)\phi(r_2)$: a separable

Table 1. Polynomial coefficients $P_i(r, \alpha)$ of the differential equation (11) for He-like atomic ions in the limit of large atomic number Z , with $y = Zr$, taken from equations (20)–(23) of [3].

$P_0(r, \alpha) = 4[9 + 72\alpha + (18 + 240\alpha)y - (48 - 384\alpha)y^2 - (144 - 384\alpha)y^3 - (160 - 256\alpha)y^4]$
$P_1(r, \alpha) = 2[9 + 144\alpha + 528\alpha y - (138 - 912\alpha)y^2 - (360 - 960\alpha)y^3 - (400 - 640\alpha)y^4]/(Z - \alpha)$
$P_2(r, \alpha) = 2[36\alpha - (9 - 168\alpha)y - (54 - 336\alpha)y^2 - (144 - 384\alpha)y^3 - (160 - 256\alpha)y^4]/(Z - \alpha)^2$
$P_3(r, \alpha) = [24\alpha y - (9 - 72\alpha)y^2 - (36 - 96\alpha)y^3 - (40 - 64\alpha)y^4]/(Z - \alpha)^3$

function. The corresponding differential equation for this independent-particle model with the same force constant $k = 1/4$ can be extracted from the study of Howard *et al* [5] and reads

$$r^2 \rho''' + 16r \rho'' + [-16 + 8r^2 - r^4] \rho' + 3r^3 \rho = 0. \quad (10)$$

In section 4, the analyticity of equation (9) derived from a wavefunction involving entanglement due to the Coulombic repulsion between electrons will be compared and contrasted with the independent particle equation (10). But first let us turn to the important sequence of He-like atomic ions.

3.2. He atomic ions in the limit of large atomic number Z

An equation paralleling equation (9) for the Hookean atom model has been derived subsequently by Gál *et al* [3] for the He-like atomic ion sequence in the limit of large atomic number Z . Of course, it is just in this large Z limit that relativistic effects become significant, so we shall term it a ‘non-relativistic’ model. We quote first the third-order differential equation of the form

$$\sum_{i=0}^3 P_i(r) \rho^{(i)}(r) = 0, \quad (11)$$

where the polynomials $P_i(r)$ are collected in table 1, using the work of Gál *et al* [3]. The quantity α in table 1 indicates that the ‘unperturbed’ solution, before switching on the Coulomb repulsion, involves the ‘screening’ of $-Ze^2/r$ to $-(Z - \alpha)e^2/r$ (see also Hall *et al* [6]).

Again, this equation (11) stems from a wavefunction involving entanglement, but now due to a ‘weak’ electron–electron interaction because of the large Z limit (see the initial derivation of an explicit form of the ground-state electron density $\rho(r)$ by Schwartz [7]).

We aim in section 4 to compare and contrast the analyticity properties of equation (11) with the corresponding independent particle model. This can be obtained, after a short calculation, from the work of Howard *et al* [8] and reads, in a form corresponding to the exact equation (11) in this large Z limit including electron–electron interaction, but now for $\alpha = 0$ only:

$$r^2 \rho''' + (3Zr^2 - 4r) \rho'' + (2Z^2r^2 - 10Zr + 6) \rho' - (4Z^2r - 12Z) \rho = 0, \quad (12)$$

the differences between equation (11) for $\alpha = 0$ and equation (12) reflecting again, of course, electron–electron repulsion.

4. Non-analyticity properties of the Hookean atom and He-like large Z limit models

Our purpose in this section is now to study the analyticity properties of equations (9) and (11) for the Hookean atom and for He-like atomic ions in the limit of large Z , respectively. Both of these density differential equations result from wavefunctions with entanglement.

4.1. The Hookean atom

The most relevant difference between equation (9) for the ground-state density of the Hookean atom and for the limiting equation (10) when the interaction e^2/r_{12} between the two electrons

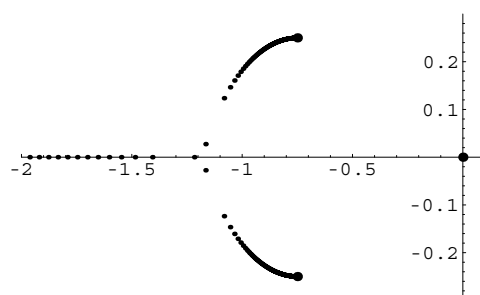


Figure 1. Solutions of $P_3(r, \alpha) = 0$ for different non-zero values of α are shown. For $\alpha = 5/8$, there are two complex roots in addition to a double root at $\alpha = 0$. Increasing α , we find two complex roots of decreasing imaginary part and a real negative root (all the three approaching a negative real value as $\alpha \rightarrow (3 + 2\sqrt{3})/8$), plus a root which remains at the origin.

at separation r_{12} is ‘switched-off’ is that the highest order derivative ρ''' is multiplied by the polynomial $(r^4 - r^2)$ for equation (9) with interaction and simply by r^2 for the non-interacting limit (10). Therefore, dividing through to remove these factors, it becomes clear that whereas $r = 0$ is a singular point of both equations (9) and (11), a new singularity is introduced by the polynomial $(r^4 - r^2)$, that on the positive real axis being evidently at $r = 1$. This is clearly then the ‘fingerprint’ for the Hookean atom of the electron–electron interaction, which was quite evident in the ground-state wavefunction $\Psi(r_1, r_2)$ entering equation (1), before integrating over r_2 to obtain the electron density $\rho(r)$. The new ‘singularity’ we suggest is coming from the electron–electron cusp which occurs in the wavefunction $\Psi(r_1, r_2)$, as $r_1 - r_2$ tends to zero. This leaves, as already stressed, its fingerprints in equation (9) which are, of course, lost in the independent-particle limiting equation (10).

4.2. He-like ions at large atomic number Z

We next turn to the He-like differential equation (11), with the polynomials given in table 1. The aim again is to compare and contrast this (now from a weakly entangled wavefunction, because of the large Z limit) equation (11) with the corresponding non-interacting limit (12).

For orientation, let us put $\alpha = 0$ in $P_3(r, \alpha)$ recorded in table 1 to find, with $y = Zr$,

$$P_3(r, 0) = (-9y^2 - 36y^3 - 40y^4)/Z^3. \quad (13)$$

This is to be contrasted with the non-interacting equation (12) where the highest derivative ρ''' is again multiplied by r^2 as in the non-interacting counterpart (10) for the Hookean atom already treated.

The solutions of equation (13) equated to zero are such that one obvious solution is $y = r = 0$. The marked difference from the Hookean atom equation (9) is that there are now no other solutions of equation (13) for real positive r , though, of course, non-analyticities exist in the complex plane.

Because of this, we have examined further the effect of re-defining the ‘unperturbed’ solution, before switching on the Coulombic inter-electronic repulsion characterized by the constant α introduced following equation (11), and altering the polynomials $P_i(r, \alpha)$ as recorded in table 1. We have examined the solutions of $P_3(r, \alpha) = 0$ for various values of α , especially for $\alpha \geq 5/8$. Figure 1 is designed to show the general effect of α when $P_3(r, \alpha)$ in table 1 is used to transcend equation (13) for $\alpha \neq 0$.

5. Summary and future directions

The non-analyticity of the third-order differential equations (9) and (11) embodying the Coulomb repulsion energy e^2/r_{12} between electrons 1 and 2 at separation r_{12} is best seen by comparing the coefficients of the highest derivative ρ''' with the corresponding non-interacting limits. Thus, for the Hookean atom, with differential equation (9), ρ''' is multiplied by the polynomial $(r^4 - r^2)$ in the presence of the Coulomb interaction, whereas in equation (10), the non-interacting limit of equation (9), there is only the factor r^2 . For equation (9), there is now non-analytic behaviour when $(r^4 - r^2) = 0$, i.e. in particular at the physically significant solutions $r = 0$ and $r = 1$. The latter solution is entirely due to the Coulombic correlation between the two electrons, and thus is a quite clear fingerprint of entanglement in the ground-state wavefunction of the Hookean atom.

Turning to the non-relativistic ‘model’ of the He-like atomic ion sequence in the limit of large atomic number Z , the differential equation (11), with polynomials $P_i(r)$ recorded in table 1, embodies wavefunction entanglement, whereas equation (12) records the corresponding independent-particle limit. Again, for equation (12), the only non-analyticity is at $r = 0$, whereas the polynomial $P_3(r)$ recorded in table 1 has non-analyticity away from $r = 0$, but not on the real axis as is the case for the Hookean atom.

As to future directions, it would, of course, be of outstanding interest if the large Z limit of the He-like sequence of atomic ions could be relaxed, even to the next lowest order in $1/Z$. The coefficient of ρ''' appears all important with regard to the non-analytic behaviour induced by electron–electron interaction, and even the inclusion of the next order in $1/Z$ should be illuminating for the long-standing problem of the He atom itself. Finally, we think also that it would be interesting for the future if work along the lines reported in the present study could be brought into close contact with the recent ideas of Amovilli and March [9] on entanglement and quantum information. The considerations of the present study suggest that the first-order density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ (see also appendices A and C) may be the appropriate tool to use in forging such a link.

Acknowledgments

JN and LMN acknowledge the support of the Spanish MEC (project MTM2005-09183) and Junta de Castilla y León (VA013C05). NHM wishes to thank the Department of Theoretical Physics of the University of Valladolid, and especially Professors J A Alonso and M Santander, both for very generous hospitality and for the stimulating atmosphere in which the contribution of NHM to this study was carried out. Finally, NHM wishes to acknowledge his indebtedness to Drs C Amovilli and T Gál, and to Professors A Holas, I A Howard and Á Nagy for invaluable discussions over some years on the general area embraced by the present work.

Appendix A. Harmonic confinement with general interparticle interaction

The purpose of this appendix is two-fold. First, we relate the Hookean model, given some prominence in the main text, to the model of Moshinsky [10]. Both are built around harmonic confinement, but the difference between the two models resides in different interparticle interactions: Coulombic repulsion for the Hookean model and harmonic for the Moshinsky case. Secondly, having forged the relation for these two models, we treat harmonic confinement for general interparticle $u(r_{12})$ within the present context, drawing on the first-principles theory set out by Holas *et al* [11].

The point we wish to stress, from section 2, is that $\nabla^2\rho$ is related to the difference between two definitions of kinetic energy density. These are written in section 2 in terms of the Schrödinger wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$, but it will be helpful below, for compactness, to write them in terms of the exact first-order density matrix $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ discussed by Holas *et al* [11].

Then, we have that

$$\frac{1}{4}\nabla^2\rho(\mathbf{r}_1) = -\frac{\hbar^2}{2m}[\nabla_{\mathbf{r}_1}^2\gamma(\mathbf{r}_1, \mathbf{r}_2) - \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_2}\gamma(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_2=\mathbf{r}_1}. \quad (\text{A.1})$$

To avoid repetition, we emphasize at once that in Holas *et al* [11] the common element connecting $\rho(\mathbf{r}_1)$ and $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the relative motion (RM) wavefunction. Thus, in terms of relative coordinates $\mathbf{r}_1 - \mathbf{r}_2$ and centre-of-mass (CM) coordinate $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ separates as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi^{\text{RM}}(r)\Psi^{\text{CM}}(R), \quad (\text{A.2})$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and $R = |\mathbf{R}|$. Writing $\Psi^{\text{RM}}(r)$ in terms of $\psi^{\text{RM}}(r)$ defined by

$$\psi^{\text{RM}}(r) = \sqrt{4\pi r}\Psi^{\text{RM}}(r), \quad (\text{A.3})$$

normalized to $\int_0^\infty dr[\psi^{\text{RM}}(r)]^2 = 1$, this relative motion wavefunction is shown by Holas *et al* [11] to satisfy the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d}{dr}\right)^2 + V_{\text{eff}}(r)\right]\psi^{\text{RM}}(r) = E^{\text{RM}}\psi^{\text{RM}}(r). \quad (\text{A.4})$$

In equation (A.4), $V_{\text{eff}}(r)$ is given explicitly by

$$V_{\text{eff}}(r) = \frac{m_{\text{RM}}\omega_0^2 r^2}{2} + u(r), \quad m_{\text{RM}} = \frac{m}{2}, \quad (\text{A.5})$$

with $u(r_{12})$, as noted above, the general interparticle interaction. What is now to be emphasized in the present context is that Holas *et al* [11] determine both $\rho(\mathbf{r}_1)$ and $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ entering equation (A.1) in terms of $\psi^{\text{RM}}(r)$ and explicitly known functions. We write the simplest diagonal form only here, namely

$$\rho(r_1) = \frac{8}{\sqrt{\pi}} \exp\left(\frac{-r_1^2}{a_{\text{CM}}^2}\right) \int_0^\infty y^2 e^{-\frac{y^2}{4}} [\Psi^{\text{RM}}(a_{\text{CM}}y)]^2 \frac{\sinh(r_1 y/a_{\text{CM}})}{(r_1 y/a_{\text{CM}})} dy. \quad (\text{A.6})$$

Here a_{CM} has dimensions of length and is defined by

$$a_{\text{CM}} = \sqrt{\frac{\hbar}{m_{\text{CM}}\omega_0}}, \quad m_{\text{CM}} = 2m, \quad \omega_0^2 = km^{-1}. \quad (\text{A.7})$$

Evidently, since $\gamma(\mathbf{r}_1, \mathbf{r}_2)$, as shown in [11], is also characterized by $\Psi^{\text{RM}}(r)$ plus known functions, one can regard, in this context of harmonic confinement, $\gamma(\mathbf{r}_1, \mathbf{r}_2) = \gamma(\mathbf{r}_1, \mathbf{r}_2, [\rho])$, the essential link between γ and ρ being Ψ^{RM} characterized by equations (A.4) and (A.5). Using the form of $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ obtained by Holas *et al* [11] for this harmonic confinement model and given explicitly in their equation (20), we can write equation (A.1), for the specific case of the Hookean atom where $u(r_{12}) = e^2/r_{12}$, as

$$\frac{1}{4}\nabla^2\rho(\mathbf{r}_1) = t_g(r) - t(r), \quad (\text{A.8})$$

where $t(r)$ is the first term on the right-hand side of equation (A.1) which we calculate directly as

$$t(r) = -C^2 \frac{\pi e^{-r^2}}{16r} \left\{ 8r(-8 + r^2) + \sqrt{2\pi} e^{r^2/2} (-34r - 3r^3 + r^5) + 4\sqrt{2\pi} e^{r^2/2} (-7r^2 + r^4) \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) \right\}. \quad (\text{A.9})$$

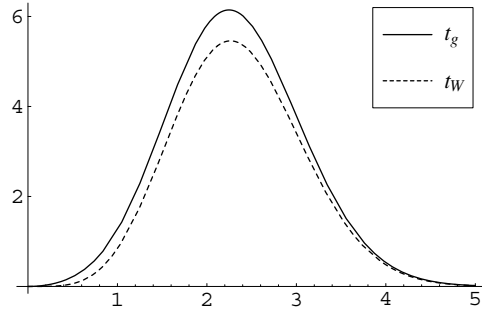


Figure 2. Correlated radial kinetic energy contribution $4\pi r^2 t_g(r)$ compared with single-particle counterpart $4\pi r^2 t_W(r)$, for the Hookean atom with force constant $k = 1/4$. Difference between these two kinetic energy densities is a quantitative measure of entanglement.

The corresponding result for $t_g(r)$, deriving from the gradient of the wavefunction form of kinetic energy, is

$$t_g(r) = C^2 \frac{\pi e^{-r^2}}{16r} \left\{ 8r(-2 + r^2) + \sqrt{2\pi} e^{r^2/2} (4r + 3r^3 + r^5) + 4\sqrt{2\pi} e^{r^2/2} (2 - r^2 + r^4) \operatorname{erf}\left(\frac{r}{\sqrt{2}}\right) \right\}, \quad (\text{A.10})$$

where $C^2 = 1/[2\pi^{5/4}(5\pi^{1/2} + 8)^{1/2}]$.

We have then shown that $\partial_r(t - t_g)$ can be written solely in terms of the density ρ and its low-order derivatives. Equation (9) follows using equation (A.8).

Using the positive-definite kinetic energy $t_g(r)$ in equation (A.10), we have plotted in figure 2 the radial distribution $4\pi r^2 t_g(r)$ versus r . For comparison, we have used the known analytic form of the ground state density $\rho(r)$ to compare with the single-particle kinetic energy which has the Weizsäcker form $t_W(r) = (1/8)(\nabla\rho)^2/\rho$. The difference between these two curves is a clear measure of entanglement.

To conclude this appendix, we turn to discuss results corresponding to equations (A.9) and (A.10) for the so-called Moshinsky atom. Here, the external potential is $V(r) = \frac{1}{2}r^2$ and

$$u(r_{12}) = \frac{1}{2}Kr_{12}^2. \quad (\text{A.11})$$

Then

$$\rho(r) = 2 \left(\frac{\beta}{\pi} \right)^{3/2} \exp(-\beta r^2), \quad (\text{A.12})$$

with $\beta = (2\alpha - 1)/\alpha$ while

$$\alpha = \frac{1}{2}[(1 + 2K)^{1/2} + 1]. \quad (\text{A.13})$$

The differential equation for $\rho(r)$ is readily verified to be

$$\nabla^2 \rho = (-6\beta + 4\beta^2 r^2)\rho \quad (\text{A.14})$$

and hence from equation (A.8) it follows that

$$4[t_g(r) - t(r)] = (-6\beta + 4\beta^2 r^2)\rho. \quad (\text{A.15})$$

Holas, Howard and March [11] give the explicit form of $t_g(r)$ as

$$t_g(r) = \frac{1}{2}\rho(r) \left[\frac{3(\alpha - 1)^2}{2\alpha} - \frac{(2\alpha - 1)}{\alpha} \ln \left(\frac{\rho(r)}{\rho(0)} \right) \right], \quad (\text{A.16})$$

where, from equation (A.12), $\rho(0) = 2(\beta/\pi)^{3/2}$.

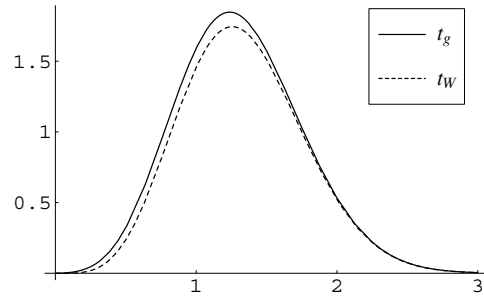


Figure 3. As in figure 2, but now for the Moshinsky model atom. The parameter α defined in equation (A.13) for plot of $4\pi r^2 t_g(r)$ is taken for the case $K = 1$. The single-particle kinetic energy contribution $4\pi r^2 t_W(r)$ corresponds to $t_W(r) = (1/8)(\nabla\rho)^2/\rho$ for the same density.

Substituting equation (A.16) into (A.15), we thus obtain the alternative form of kinetic energy density $t(r)$ as

$$t(r) = t_g(r) + \left(\frac{3}{2}\beta + \beta^2 r^2\right) \rho(r) = \frac{1}{2}\rho(r) \left[\frac{3}{2} \frac{(\alpha - 1)^2}{\alpha} + 3\beta + 2\beta^2 r^2 \right] - \frac{(2\alpha - 1)}{2\alpha} \rho(r) \ln\left(\frac{\rho(r)}{\rho(0)}\right). \quad (\text{A.17})$$

That equations (A.16) and (A.17) have connections with information theory is apparent from the appearance of a term proportional to $\rho(r) \ln \rho(r)$ in both these forms of kinetic energy density for the Moshinsky model of the two-electron spin-compensated atom.

In figure 3, kinetic energy densities are again plotted, to display entanglement.

Appendix B. Case when repulsive interparticle interaction $u(r_{12}) = \lambda r_{12}^{-2}$

Again, with harmonic confinement, Capuzzi, March and Tosi [12] have obtained the ground-state density $\rho(r)$ when the external potential $V(r) = m\omega^2 r^2/2$ and the repulsive interaction $u(r_{12})$ is determined by

$$u(r_{12}) = \lambda r_{12}^{-2}. \quad (\text{B.1})$$

Capuzzi *et al* [12] obtain the density as

$$\rho(r) = \frac{1}{2^{\alpha-1}\pi^{3/2}} \left(\frac{m\omega}{\hbar}\right)^{3/2} \exp(-2m\omega r^2/\hbar) {}_1F_1\left(\frac{3}{2} + \alpha; \frac{3}{2}; \frac{m\omega r^2}{\hbar}\right). \quad (\text{B.2})$$

These workers then derive the second-order linear homogeneous differential equation

$$\frac{\hbar}{4m\omega} r \rho''(r) + \left[\frac{\hbar}{2m\omega} + \frac{3}{2}r^2\right] \rho'(r) + r \left[\frac{3}{2} - \alpha + \frac{2m\omega}{\hbar} r^2\right] \rho(r) = 0 \quad (\text{B.3})$$

satisfied by $\rho(r)$ in equation (B.2).

Our purpose below is to use equation (3), and the wavefunction $\Psi(\mathbf{r}, \mathbf{r}_2)$ of this model to derive the two alternative definitions of the kinetic energy density. The first of these is the positive definite form

$$t_g(r) = \int (\nabla_{\mathbf{r}} \Psi(\mathbf{r}, \mathbf{r}_2))^2 d\mathbf{r}_2, \quad (\text{B.4})$$

while the other takes the form

$$t(r) = - \int \Psi(\mathbf{r}, \mathbf{r}_2) \nabla_{\mathbf{r}}^2 \Psi(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2. \quad (\text{B.5})$$

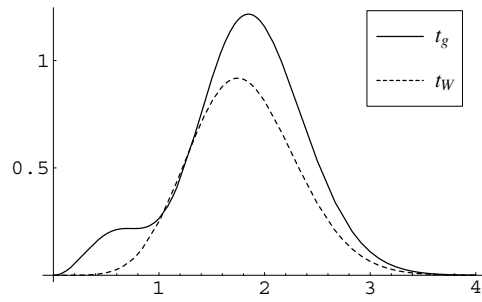


Figure 4. Kinetic energy densities $4\pi r^2 t_g(r)$ and single-particle counterpart $4\pi r^2 t_W(r)$ for inverse square-law repulsion. Correlated $t_g(r)$ curve now shows structure whereas $t_W(r)$ is smooth. Again difference between $t_g(r)$ and $t_W(r)$ reflects entanglement in the wavefunction (B.6). The parameter value $\lambda m/\hbar^2$ in equation (B.7) is chosen equal to 2, while $m\omega/\hbar$ is taken as unity.

Using the unnormalized spatial symmetric wavefunction for the ground state given by Crandall *et al* [13], namely

$$\Psi(\mathbf{r}, \mathbf{r}_2) = \exp(-m\omega r^2/2\hbar) \exp(-m\omega r_2^2/2\hbar) |\mathbf{r} - \mathbf{r}_2|^\alpha, \quad (\text{B.6})$$

where

$$\alpha = [(1 + 4\lambda m/\hbar^2)^{1/2} - 1]/2, \quad (\text{B.7})$$

we find

$$\nabla_r \Psi(\mathbf{r}, \mathbf{r}_2) = \hat{\mathbf{r}}(-m\omega r/\hbar)\Psi(\mathbf{r}, \mathbf{r}_2) + \frac{\alpha}{|\mathbf{r} - \mathbf{r}_2|} (\nabla_r |\mathbf{r} - \mathbf{r}_2|)\Psi(\mathbf{r}, \mathbf{r}_2). \quad (\text{B.8})$$

Hence, from equation (B.4), we find

$$t_g(r) = \frac{m^2\omega^2 r^2}{\hbar^2} \int \Psi^2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2 + \int \frac{\alpha^2}{|\mathbf{r} - \mathbf{r}_2|^2} (\nabla_r |\mathbf{r} - \mathbf{r}_2|)^2 \Psi^2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2 - 2\alpha \int \frac{1}{|\mathbf{r} - \mathbf{r}_2|} \frac{m\omega r}{\hbar} (\hat{\mathbf{r}} \cdot \nabla_r |\mathbf{r} - \mathbf{r}_2|) \Psi^2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2. \quad (\text{B.9})$$

The first integral on the right-hand side of equation (B.9) is equal to $\rho(r)/2$, where $\rho(r)$ is given by equation (B.2).

Figure 4 shows plots of correlated and single-particle kinetic energy densities.

Appendix C. Entanglement: inequality relating electron density to first-order density matrix

For a two-electron spin-compensated system without entanglement, the first-order density matrix $\gamma/2$ is idempotent. When entanglement is introduced by switching on an interparticle interaction $u(r_{12})$ between the two ‘electrons’ at separation r_{12} , then

$$\int \frac{\gamma(\mathbf{r}, \mathbf{r}_2)}{2} \frac{\gamma(\mathbf{r}_2, \mathbf{r}')}{2} d\mathbf{r}_2 < \frac{\gamma(\mathbf{r}, \mathbf{r}')}{2}. \quad (\text{C.1})$$

The simplest consequence in the present framework built round the ground-state electron density $\rho(r) \equiv \gamma(\mathbf{r}, \mathbf{r})$ is evidently

$$\rho(r) > \frac{1}{2} \int \gamma^2(\mathbf{r}, \mathbf{r}_2) d\mathbf{r}_2. \quad (\text{C.2})$$

As the most elementary example of the cases treated in the present paper, let us return to the Moshinsky model, for which the ground-state electron density $\rho(r)$ is of the Gaussian form both with or without the harmonic interparticle interaction $u(r_{12}) = Kr_{12}/2$. One of us [14] demonstrated in earlier work on this model that $\gamma(\mathbf{r}, \mathbf{r}')$ could, in fact, be written explicitly in terms of $\rho(r)$ (see also [11], especially equation (36)). For $u(r_{12}) = 0$, i.e. $K = 0$,

$$\gamma_{u=0}(\mathbf{r}, \mathbf{r}_2) = \rho(r)^{1/2}\rho(r_2)^{1/2}, \quad (\text{C.3})$$

and insertion into the right-hand side of the inequality (C.2) gives immediately $\frac{1}{2}\rho(r) \int \rho(r_2) d\mathbf{r}_2 = \rho(r)$ from the normalization of the density for the two-electron atom. From the result (36) of [11], the inequality (C.2) is recovered with entanglement, i.e. when $K \neq 0$.

To date, from the other entangled models discussed here, we have not achieved explicitly the function $\gamma = \gamma[\rho]$ exhibited in [14] for the Moshinsky model.

References

- [1] Kestner N R and Sinanoğlu O 1962 *Phys. Rev.* **128** 2687
- [2] March N H, Gál T and Nagy Á 1998 *Chem. Phys. Lett.* **292** 384
- [3] Gál T, March N H and Nagy Á 1999 *Chem. Phys. Lett.* **305** 429
- [4] March N H and Ludeña E V 2004 *Phys. Lett. A* **330** 16
- [5] Howard I A, March N H and Nieto L M 2002 *Phys. Rev. A* **66** 054501
- [6] Hall G G, Jones L L and Rees D 1965 *Proc. R. Soc. A* **283** 194
- [7] Schwartz C 1959 *Ann. Phys., NY* **2** 156
- [8] Howard I A, March N H and Van Doren V E 2001 *Phys. Rev. A* **63** 062501
- [9] Amovilli C and March N H 2004 *Phys. Rev. A* **69** 054302
- [10] Moshinsky M 1968 *Am. J. Phys.* **36** 52
- [11] Holas A, Howard I A and March N H 2003 *Phys. Lett. A* **310** 451
- [12] Capuzzi P, March N H and Tosi M P 2005 *J. Phys. A: Math. Gen.* **38** L439
- [13] Crandall R, Whitnell R and Bettega R 1984 *Am. J. Phys.* **52** 438
- [14] March N H 2002 *Phys. Lett. A* **306** 63