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# Kinetic energy density of the two-electron Hookean atom in terms of the ground-state electron density

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An explicit expression is derived for the kinetic energy density, including the correlation contribution, in terms of the ground-state electron density for the two-electron Hookean atom. This model atom has the merit that while the electrons are tied to an origin by springs, the Coulomb interaction energy between the two electrons is fully incorporated.

**KEY WORDS:** kinetic energy density, model Hookean atom, density-functional theory

## 1. Introduction

In quite recent work, Holas and March [1] achieved a synthesis of density-functional theory [2–4] with low-order density-matrix theory. In particular, they derived a formally exact expression for the force $-\partial v_{\rm xc}(\mathbf{r})/\partial\mathbf{r}$ associated with the exchange-correlation potential $v_{\rm xc}(\mathbf{r})$. Unfortunately, to date, there are only a very limited number of systems for which the essential ingredients needed to obtain the force $-\partial v_{\rm xc}(\mathbf{r})/\partial\mathbf{r}$ are available in analytical form.

This article focuses attention on one of these systems, the two-electron Hookean atom, going back to an early proposal made by Kestner and Sinanoğlu [5]. Their model was to tie the two electrons to the origin at $\mathbf{r} = \mathbf{0}$ by identical springs (a harmonic potential), but to retain the full Coulombic repulsion energy $e^2/(4\pi\varepsilon_0 r_{12})$ between the electrons at separation $r_{12}$.

For the spin-compensated ground state of this Hookean atom, with a specific choice of the force constant $k$ in the external potential energy $v_{\rm ext}(\mathbf{r})$, namely,

$$v_{\rm ext}(\mathbf{r}) = v_{\rm ext}(r) = \frac{1}{2}kr^2, \qquad k = \frac{1}{4} \tag{1}$$

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(atomic units are used here and throughout the paper), the Schrödinger equation has been solved to yield [6,7]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \widetilde{C}\left(1 + \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{2}\right) \exp\left(-\frac{\mathbf{r}_1^2 + \mathbf{r}_2^2}{4}\right), \tag{2}$$

where $\widetilde{C}$ is the normalization constant.

Returning to the form for the force $-\partial v_{\mathrm{xc}}(\mathbf{r})/\partial \mathbf{r}$ derived in [1], a basic tool was the kinetic energy density tensor $t_{\alpha\beta}(\mathbf{r})$ defined in terms of the correlated first-order density matrix $\rho(\mathbf{r}'; \mathbf{r}'')$ by

$$t_{\alpha\beta}(\mathbf{r}) = \frac{1}{4}\left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right)\rho(\mathbf{r}'; \mathbf{r}'')\big|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{3}$$

This local quantity is a real, symmetric tensor, the trace of which is the *non-negative* kinetic energy density $t(\mathbf{r}) = \sum_\alpha t_{\alpha\alpha}(\mathbf{r})$ central to this article. Therefore, in section 2 immediately below, we shall set out the form of $t_{\alpha\beta}(\mathbf{r})$ specific to the two-electron Hookean atom. The resultant kinetic energy density $t(\mathbf{r}) = t(r)$ will then be written quite explicitly in terms of the ground-state electron density $n(\mathbf{r}) = n(r)$ and its low-order derivatives as

$$t(r) = \frac{T_0(r)n(r) + T_1(r)n'(r) + T_2(r)n''(r)}{T_3(r)}, \tag{4}$$

where the functions $\{T_i(r)\}$ are low-degree polynomials in $r$ with integers as coefficients. In section 3, the kinetic energy per particle $\tau(r) = t(r)/n(r)$ will be discussed and its behavior will be analyzed in large-$r$ and small-$r$ regions. Section 4 constitutes a summary, together with proposals for future study.

## 2. Relation between the kinetic energy density and the electron density

In the Hookean atom model, the wave function $\Psi$, equation (2), is readily utilized to construct the first-order density matrix $\rho(\mathbf{r}'; \mathbf{r}'') = 2\int \mathrm{d}^3 r_2\, \Psi(\mathbf{r}', \mathbf{r}_2)\Psi(\mathbf{r}'', \mathbf{r}_2)$ entering the definition (3) of the kinetic energy density tensor $t_{\alpha\beta}(\mathbf{r})$. With the resulting $\rho$ inserted in equation (3), the shape of $t_{\alpha\beta}$ is then immediately clear as

$$t_{\alpha\beta}(\mathbf{r}) = \frac{r_\alpha r_\beta}{r^2} f(r) + \delta_{\alpha\beta} k(r). \tag{5}$$

The spherical symmetry of the ground-state electron density $n(r)$ has its analogue in equation (5) in that the two functions $f$ and $k$ appearing there are functions only of $r = |\mathbf{r}|$. Separate forms of $f(r)$ and $k(r)$ are available in terms of the error function and Dawson's integral, from the recent investigation of Qian and Sahni [8]. The latter integral can fortunately be by-passed by taking immediately the trace of the tensor in equation (5) as

$$t(r) = f(r) + 3k(r). \tag{6}$$

The cancellation of Dawson's integral already referred to leaves the result for the interacting-system kinetic energy density $t(r)$ in the form

$$t(r) = \frac{1}{8}r^2 n(r) + \frac{C}{4}\left[2\left(1-r^2\right)g_1(r) - g_2(r) + \left(\frac{1}{r} - r\right)g_3(r)\right], \tag{7}$$

where

$$C = \pi(2\pi)^{1/2}\widetilde{C}^2 = \frac{1}{[2^{3/2}\pi(8+3\pi^{1/2})]}, \tag{8}$$

$$g_1(r) = \exp\left(-\frac{r^2}{2}\right), \tag{9}$$

$$g_2(r) = 4\left(\frac{2}{\pi}\right)^{1/2}\left[g_1(r)\right]^2, \tag{10}$$

$$g_3(r) = 4g_1(r)\,\mathrm{erf}\left(\frac{r}{2^{1/2}}\right), \tag{11}$$

in terms of the error function

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x \mathrm{d}y\,\exp\left(-y^2\right). \tag{12}$$

Similarly to $t(r)$, equation (7), the electron number density $n(r)$ is also a linear combination of the functions $\{g_i(r)\}$ [8]:

$$n(r) = C\left[\left(7+r^2\right)g_1(r) + g_2(r) + \left(\frac{1}{r} + r\right)g_3(r)\right]. \tag{13}$$

Since the derivatives of the functions $\{g_i(r)\}$ are linear combinations of the same functions with simple $r$-dependent coefficients: $g_1'(r) = -rg_1(r)$, $g_2'(r) = -2rg_2(r)$, $g_3'(r) = g_2(r) - rg_3(r)$, therefore, each one of three functions $n(r)$, $n'(r)$ and $n''(r)$ can be represented as a linear combination of the functions $\{g_i(r)\}$ with simple $r$-dependent coefficients. These three linear relations can be inverted to obtain $g_1(r)$, $g_2(r)$ and $g_3(r)$ as linear combinations of $n(r)$, $n'(r)$ and $n''(r)$. Therefore, $t(r)$, equation (7), can be expressed as such a combination, equation (4).

As the first step towards this goal, $g_3(r)$ is eliminated from equation (7) by combining it with equation (13), what results in

$$\frac{4(1+r^2)[t(r) - (r^2/8)n(r)]}{C} = \frac{(1-r^2)n(r)}{C} - \left(5 - 6r^2 + r^4\right)g_1(r) - 2g_2(r). \tag{14}$$

Next, use is made of results obtained by March et al. [9], who investigated the same Hookean system. Their equations (6) and (5), rewritten in our notation as

$$\frac{(2r+2r^3)n(r) + (2+3r^2)n'(r) + rn''(r)}{C} = -r\left(1-r^2\right)g_1(r), \tag{15}$$

$$\frac{4r^3 n(r) + (2+3r^2+r^4)n'(r) + (r+r^3)n''(r)}{C} = \left(-15r + 8r^3 - r^5\right)g_1(r) - 4rg_2(r), \tag{16}$$

allow for immediate determination of $g_1(r)$ from the first,

$$g_1(r) = -\frac{1}{1-r^2}\frac{(2+2r^2)n(r) + (2/r+3r)n'(r) + n''(r)}{C}, \tag{17}$$

and then of $g_2(r)$ by substituting the previous result to the second,

$$4g_2(r) = \frac{1}{C}\frac{1}{1-r^2}\Bigg[\left(30+10r^2-10r^4+2r^6\right)n(r) + \left(\frac{28}{r}+28r-20r^3+4r^5\right)n'(r) + \left(14-8r^2+2r^4\right)n''(r)\Bigg]. \tag{18}$$

After inserting these results into equation (14), the expression (4) for $t(r)$ is obtained with coefficient functions given by

$$T_0(r) = -8r^1 - 17r^3 - 8r^5 + r^7, \tag{19}$$

$$T_1(r) = -8r^0 - 22r^2 - 12r^4 + 2r^6, \tag{20}$$

$$T_2(r) = -4r^1 - 4r^3, \tag{21}$$

$$T_3(r) = +8r^1 + 0r^3 - 8r^5. \tag{22}$$

This then constitutes the desired explicit relation allowing the kinetic energy density to be calculated solely from the ground-state density.

Of course, in this relation the correlation kinetic energy density $t_c(r)$ is completely incorporated thereby, from the knowledge of the ground-state density. In the case of the two-electron system in the spin-compensated ground state, this energy can be easily separated, because the noninteracting kinetic energy density $t_s$ equals simply the von Weizsäcker energy, which for spherically symmetric density is given by

$$t_s(r) = t_W(r) = \frac{1}{8}\frac{[n'(r)]^2}{n(r)}. \tag{23}$$

So, the correlation kinetic energy density

$$t_c(r) = t(r) - t_s(r) \tag{24}$$

is also expressible in terms of $n(r)$, $n'(r)$ and $n''(r)$.

To complete the electron density theory of the kinetic energy density presented here, we note that in earlier work [9] the Euler equation satisfied by the ground-state electron density has been shown to be of third-order linear homogeneous form

$$N_3(r)n'''(r) + N_2(r)n''(r) + N_1(r)n'(r) + N_0(r)n(r) = 0, \tag{25}$$

with the following polynomials, which were determined in [9]:

$$N_0(r) = +0r^1 - 10r^3 + 0r^5 + 2r^7, \tag{26}$$

$$N_1(r) = +2r^0 - 13r^2 - 4r^4 + 5r^6, \tag{27}$$

$$N_2(r) = -2r^1 - 4r^3 + 4r^5, \tag{28}$$

$$N_3(r) = +0r^0 - 1r^2 + 1r^4. \tag{29}$$

## 3. The kinetic energy per particle

Besides the kinetic energy density $t(r)$, there is known also another local characteristic of the kinetic energy of the system, namely, the local kinetic energy per particle $\tau(r) = t(r)/n(r)$. As will be shown, the influence of the Coulombic electron–electron interaction on the kinetic energy can be well demonstrated in terms of $\tau(r)$ and its components $\tau_s(r) = t_s(r)/n(r)$ and $\tau_c(r) = t_c(r)/n(r)$.

For the reason of this demonstration, let us consider first the same system of two electrons tied to the center by the harmonic potential $v_{ext}(r)$, equation (1), but with the electron–electron interaction absent (all characteristics of this system will be distinguished by the subscript 0). Its density is

$$n_0(r) = \frac{2}{(2\pi)^{3/2}} g_1(r), \tag{30}$$

[compare with equation (13)], see equation (9) for $g_1(r)$. Because this is the noninteracting-electron system, its kinetic energy density is just the von Weizsäcker energy, equation (23), so $\tau_{0c}(r) = 0$ and

$$\tau_0(r) = \tau_{0s}(r) = \frac{1}{8}\left(\frac{n_0'(r)}{n_0(r)}\right)^2 = \frac{1}{8}\left(\frac{g_1'(r)}{g_1(r)}\right)^2 = \frac{1}{8}r^2. \tag{31}$$

By comparing this result with equation (1), we conclude that

$$\tau_0(r) = v_{ext}(r), \tag{32}$$

i.e., the local kinetic energy per particle at the position $r$ equals the potential energy at the same position. This relation represents locally what is known globally as the virial equation for the harmonic oscillator: the total kinetic energy equals the total potential energy.

Of course, for the original, interacting system, there is no simple analytical result for $\tau(r)$ at arbitrary $r$, like equation (32) for noninteracting system. However, the results in the form of series can be obtained in the large-$r$ and small-$r$ regions. This will make possible comparison of $\tau(r)$ with $\tau_0(r)$.

The large-$r$ expansion of the function $g_3(r)$, equations (11), (12), which enters expressions for $t(r)$ and $n(r)$, equations (7) and (13), can be obtained from the asymptotic series for the error function [10]

$$\operatorname{erf}(x) \asymp 1 - \pi^{-1/2}x^{-1}\exp\bigl(-x^2\bigr)\bigl[1 - 2^{-1}x^{-2} + 2^{-2}3x^{-4} - \cdots\bigr], \tag{33}$$

which leads to

$$g_3(r) = 4g_1(r)\left\{1 - \left(\frac{2}{\pi}\right)^{1/2} r^{-1}g_1(r)\bigl[1 + \mathrm{O}\bigl(r^{-2}\bigr)\bigr]\right\}. \tag{34}$$

After inserting this result into equations (7) and (13) we obtain

$$t(r) = \frac{r^2}{8} n(r) + \frac{C}{4} g_1(r)\left[-2r^2 - 4r + 2 + 4r^{-1} + \mathrm{O}\left(r^{-2} g_1(r)\right)\right], \tag{35}$$

$$n(r) = C g_1(r)\left[r^2 + 4r + 7 + 4r^{-1} + \mathrm{O}\left(r^{-2} g_1(r)\right)\right], \tag{36}$$

so the interacting kinetic energy per particle in the large-$r$ region can readily be obtained as

$$\begin{aligned} \tau(r) &= \frac{t(r)}{n(r)} \\ &= 8^{-1} r^2 + 0r - 2^{-1} + r^{-1} + 0r^{-2} - 4r^{-3} + \mathrm{O}\left(r^{-4}\right) \\ &= \left[1 - 4r^{-2} + \mathrm{O}\left(r^{-3}\right)\right] \tau_0(r), \end{aligned} \tag{37}$$

and its noninteracting partner as

$$\begin{aligned} \tau_{\mathrm{s}}(r) &= \frac{1}{8}\left(\frac{n'(r)}{n(r)}\right)^2 \\ &= 8^{-1} r^2 + 0r - 2^{-1} + r^{-1} + 0r^{-2} - 4r^{-3} + \mathrm{O}\left(r^{-4}\right). \end{aligned} \tag{38}$$

We see that these two functions are very close in this region, so that the correlation kinetic energy per particle happens to be very small there:

$$\begin{aligned} \tau_{\mathrm{c}}(r) &= \tau(r) - \tau_{\mathrm{s}}(r) \\ &= \mathrm{O}\left(r^{-4}\right) = \tau_0(r)\left[\mathrm{O}\left(r^{-6}\right)\right]. \end{aligned} \tag{39}$$

By comparing $\tau(r)$, equation (37), with $\tau_0(r)$, equation (31), we conclude that the presence of the electron–electron Coulombic interaction in the system modifies the kinetic energy per particle with the term $[-4r^{-2} + \mathrm{O}(r^{-3})]\tau_0(r)$ which is, in the large-$r$ region, much smaller than the leading term $\tau_0(r)$.

The picture in the small-$r$ region is quite different. Expansions for $t(r)$ and $n(r)$ can be found easily from equations (7)–(13), and they are

$$t(r) = C\left\{\left[\frac{1}{2} + \frac{1}{8} r^2 + \mathrm{O}\left(r^4\right)\right] + \left[0 + \frac{1}{3} r^2 + \mathrm{O}\left(r^4\right)\right]\eta\right\}, \tag{40}$$

$$n(r) = C\left\{\left[7 - \frac{5}{2} r^2 + \mathrm{O}\left(r^4\right)\right] + \left[8 - \frac{8}{3} r^2 + \mathrm{O}\left(r^4\right)\right]\eta\right\}, \tag{41}$$

where

$$\eta = \left(\frac{2}{\pi}\right)^{1/2} \approx 0.7979. \tag{42}$$

The expressions for the kinetic energy per particle and its components follow immediately from these expansions and equations (23) and (24):

$$\tau(r) = a_0 + a_2 r^2 + \mathrm{O}\big(r^4\big), \tag{43}$$

$$\tau_{\mathrm{s}}(r) = \frac{b_2}{8} r^2 + \mathrm{O}\big(r^4\big) = \big[b_2 + \mathrm{O}\big(r^2\big)\big]\tau_0(r), \tag{44}$$

$$\tau_{\mathrm{c}}(r) = a_0 + c_2 r^2 + \mathrm{O}\big(r^4\big), \tag{45}$$

where

$$a_0 = \frac{1}{14 + 16\eta} \approx 0.03736, \tag{46}$$

$$a_2 = a_0 \left\{ \left[ \frac{1}{4} + \frac{2}{3}\eta \right] + \frac{5/2 + (8/3)\eta}{7 + 8\eta} \right\} \approx 0.04213, \tag{47}$$

$$b_2 = \left\{ \frac{5 + (16/3)\eta}{7 + 8\eta} \right\}^2 \approx 0.4783, \tag{48}$$

$$c_2 = a_2 - \frac{b_2}{8} \approx -0.01766. \tag{49}$$

By comparing $\tau(r) = \tau_{\mathrm{s}}(r) + \tau_{\mathrm{c}}(r)$, equations (43)–(45), with $\tau_0(r) = \tau_{0\mathrm{s}}(r)$, equation (31), we conclude that the electron–electron interaction plays a crucial role in the small-$r$ region: (i) the correlation term $\tau_{\mathrm{c}}(r)$, which arises solely due to the this interaction, represents the dominant component of $\tau(r)$, (ii) this interaction induces also a damping factor $[b_2 + \mathrm{O}(r^2)]$, which scales the noninteracting-system kinetic energy $\tau_0(r)$ to $\tau_{\mathrm{s}}(r)$ – the noninteracting component of $\tau$, equation (44).

## 4. Summary and future directions

In summary, the major result of the present study is equation (4), where the polynomials $\{T_i(r)\}$ are given explicitly in equations (19)–(22). This result determines the interacting-system kinetic energy density $t(r)$ in terms of the electron number density $n(r)$. In conjunction with the differential equation (25) for $n(r)$, one has therefore a complete theory of the kinetic energy density in this model. Naturally, however, the polynomials in $r$ appearing in both equations (4) and (25) are characteristics of the Hookean atom with the specific choice of the spring constant given in equation (1).

It would be of obvious interest for the future, if one could demonstrate, for the two-electron Hookean model on which all attention has focused here, that the "shape" rather than the fine details, of the basic equation (4) was robust against changes in the force constant $k$. Naturally (but one must expect in longer expressions), it would be of great interest if the present result could be extended to an $N$-electron model atom, for $N > 2$.

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