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ORIGINAL PAPER

Exchange energy for two closed shells generated by a bare Coulomb potential energy $-Ze^2/r$ in the limit of large Z, in two dimensions

M. L. Glasser · N. H. March · L. M. Nieto

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Abstract Two-dimensional (2D) inhomogeneous electron assemblies are becoming increasingly important in Condensed Matter and associated technologies. Here, therefore, we contribute to the Density Functional Theory of such 2D electronic systems by calculating, analytically, (i) the idempotent Dirac density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ generated by two closed shells for the bare Coulomb potential $-Ze^2/r$ and (ii) the exchange energy density $\varepsilon_x(\mathbf{r})$. Some progress is also possible concerning the exchange potential $V_x(r)$, one non-local approximation being the Slater potential $2\varepsilon_x(r)/n(r)$, with $n(r)$ the ground state electron density. However, to complete the theory of $V_x(r)$, the functional derivative of the single-particle kinetic energy per unit area $\delta t(s)/\delta n(r)$ is still required.

Keywords Exchange · Nuclear cusp condition · Slater potential

M. L. Glasser
Department of Physics, Clarkson University, Potsdam, NY 13699-5820, USA
e-mail: laryg@clarkson.edu

N. H. March
Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

N. H. March
University of Oxford, Oxford, England

N. H. March
Abdus Salam ICTP, Trieste, Italy

L. M. Nieto (✉)
Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, 47071 Valladolid, Spain
e-mail: luismi@metodos.fam.cie.uva.es

1 Background and outline

The two-dimensional (2D) electron gas is by now quite well established experimentally in a $GaAs/AlGaAs$ heterojunction. It has therefore become of considerable importance to study, from first principles, the Density Functional Theory (DFT) of the inhomogeneous electron assembly [1]. The present study is a contribution in this area, and is also relevant to quantum dots.

Thus we shall, in Sect. 2 below, set up the idempotent Dirac density matrix [2] $\gamma(\mathbf{r}, \mathbf{r}')$ defined in terms of the normalized Slater-Kohn-Sham orbitals [3,4] $\psi_i(\mathbf{r})$ as

$$\gamma(\mathbf{r}, \mathbf{r}') = 2 \sum_{\text{occ}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}'), \tag{1}$$

generated by a (as yet unknown) self-consistent one-body potential $V(r)$. The factor 2 in (1) indicates double occupation of each orbital. However, from the work of Howard et al. [5], we shall have in mind 'atomic ions' in 2D with two closed shells, but now generated in the limit of large nuclear charge Ze by the bare Coulomb potential

$$V(\mathbf{r}) = -\frac{Ze^2}{r}. \tag{2}$$

Then the Dirac matrix can be obtained analytically (see Eq. (13) below). This form is then utilized in Sect. 3 to derive the exchange energy $\varepsilon_x(r)$, also in analytic form, which is physically valid in the non-relativistic limit of large Z.

In Sect. 4 it is explored whether the entire density matrix for closed shell is determined by its s-state ($\ell = 0$) component alone (a result proved in 3D by Theophilou and March). Section 5 includes a summary of the main results of the present article and some indications for future research.

2 Idempotent Dirac density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ for two closed shells generated by the bare Coulomb potential (2) in two dimensions

The wave functions for the 2D equivalent of the H-atom with nuclear charge Ze are presently readily available. In the following, we have used the convenient treatmment given by Zaslow and Zandler [6] summarized below. If one writes the wave function in 2D generated by the potential (2) as

$$\psi(r, \phi) = R(r)\Phi(\phi), \tag{3}$$

then the angular functions are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i\ell\phi}, \tag{4}$$

where $\ell = 0, \pm 1, \pm 2, \ldots$ The radial equation for $R(r)$ in 2D then reads

$$\frac{d^2R(r)}{dr^2} + \frac{1}{r}\frac{dR(r)}{dr} + \left[\frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right) - \frac{\ell^2}{r^2}\right] R(r) = 0. \tag{5}$$

Introducing, for $\beta_0 = 2mZe^2/\hbar^2$ and the independent variable x, defined to be

$$x = \beta_n r \quad \beta_n = \frac{\beta_0}{n - 1/2}, \tag{6}$$

into the radial Eq. (5), solutions can be obtained in the form $R(r) = \chi(x)x^{|\ell|}e^{-x/2}$, provided $\chi(x)$ satisfies

$$x\frac{d^2\chi(x)}{dx^2} + (2|\ell| + 1 - x)\frac{d\chi(x)}{dx} + (n - |\ell| - 1)\,\chi(x) = 0. \tag{7}$$

Equation (7) is satisfied by the associated Laguerre polynomials $L_k^p(x)$ where $p = 2|\ell|$ and $k = n - |\ell| - 1$. Since p and k must both be integers, with $p \leq k$, n has values $1, 2, 3, \ldots$ The energy levels E entering Eq. (5) are then given by

$$E_n = -\frac{m(Ze^2)^2}{2(n - \frac{1}{2})^2\hbar^2}, \tag{8}$$

while the corresponding normalized wave functions $\psi_{n,\ell}(r, \phi)$ can be written

$$\psi_{n,\ell}(r,\phi) = \beta_n \left[\frac{(n - 1 - |\ell|)!}{[(|\ell| + n - 1)!](2n - 1)}\right]^{1/2} e^{-\beta_n r/2}\,(\beta_n r)^{|\ell|}\,L_{n-|\ell|-1}^{2|\ell|}(\beta_n r)\,\frac{e^{i\ell\phi}}{\sqrt{2\pi}}. \tag{9}$$

2.1 Explicit form of Dirac matrix for two closed shells

The lowest closed shell in 2D corresponds to $n = 1$ and $\ell = 0$, with normalized wave function

$$\psi_{1,0}(r) = 2\beta_0\frac{e^{-\beta_0 r}}{\sqrt{2\pi}}. \tag{10}$$

The next spherically symmetric (and now degenerate) state corresponds to $n = 2$ and $\ell = 0$, with wave function

$$\psi_{2,0}(r) = \frac{2\beta_0}{3\sqrt{6\pi}}\left(1 - \frac{2}{3}\beta_0 r\right)e^{-\frac{1}{3}\beta_0 r}. \tag{11}$$

Its degenerate partners are $n = 2$, $\ell = \pm 1$ with wave functions $\psi_{2,\pm 1}(r, \phi)$ given by

$$\psi_{2,\pm 1}(r, \phi) = \frac{2\beta_0^2 r}{9\sqrt{3\pi}} e^{-\frac{1}{3}\beta_0 r} e^{\pm i\phi}. \tag{12}$$

The Dirac matrix given in (1) for the Coulomb two closed shell case is

$$\begin{aligned}\gamma(\mathbf{r}, \mathbf{r}') \equiv \gamma(r, \phi; r', \phi') &= 2[\psi_{1,0}(r)\psi_{1,0}(r') + \psi_{2,0}(r)\psi_{2,0}(r') \\ &\quad + \psi^*_{2,1}(r, \phi)\psi_{2,1}(r', \phi') + \psi^*_{2,-1}(r, \phi)\psi_{2,-1}(r', \phi')] \\ &= \frac{4\beta_0^2}{\pi}\left[e^{-\beta_0(r+r')} + \frac{1}{27}\left(1 - \frac{2}{3}\beta_0 r\right)\left(1 - \frac{2}{3}\beta_0 r'\right) e^{-\frac{1}{3}\beta_0(r+r')}\right. \\ &\quad \left. + \frac{4\beta_0^2 r r'}{243} e^{-\frac{1}{3}\beta_0(r+r')} \cos(\phi - \phi')\right].\end{aligned} \tag{13}$$

It is easily verified that the density

$$n(r) = \gamma(r, \phi; r, \phi) = \frac{4\beta_0^2}{\pi}\left[e^{-2\beta_0 r} + \frac{1}{27}\left(1 - \frac{2}{3}\beta_0 r\right)^2 e^{-\frac{2}{3}\beta_0 r} + \frac{4\beta_0^2}{243} r^2 e^{-\frac{2}{3}\beta_0 r}\right] \tag{14}$$

corresponds to the presence of 8 electrons.

3 Analytic form of exchange energy density

The exchange energy/unit area can be evaluated directly from (13) using

$$\varepsilon_x(r) = -\frac{e^2}{4}\int \frac{\gamma^2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{15}$$

from which we obtain by insertion of Eq. (13) the result, in terms of the scaled variable $x = \beta_0 r$,

$$\varepsilon_x(r) = -\frac{16e^2}{\pi^2}\beta_0^3 e^{-2x/3}[H_1(x) + H_2(x) + H_3(x)], \tag{16}$$

where

$$H_1(x) = \int_0^\infty dt\, \frac{te^{-2t/3}}{x + t}\left[e^{-2(x+t)/3} + \frac{1}{27}\left(1 - \frac{2}{3}x\right)\left(1 - \frac{2}{3}t\right)\right]^2 \mathbf{K}\left(2\frac{\sqrt{xt}}{x + t}\right), \tag{17}$$

$$H_2(x) = \frac{4}{243}\int_0^\infty dt\, \frac{te^{-2t/3}}{x + t}\left[e^{-2(x+t)/3} + \frac{1}{27}\left(1 - \frac{2}{3}x\right)\left(1 - \frac{2}{3}t\right)\right]$$

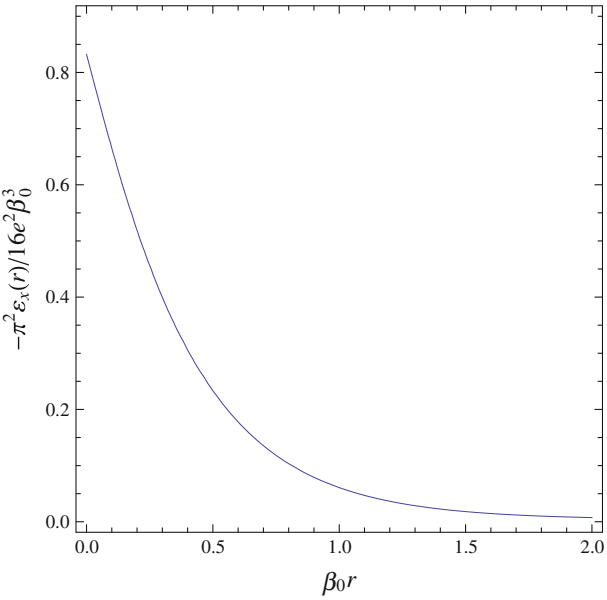

Fig. 1 The normalized exchange energy per unit area $-\varepsilon_x(r)/(16e^2\beta_0^3/\pi^2)$ versus $\beta_0 r$

$$\times\left[(x^2+t^2)\mathbf{K}\left(2\frac{\sqrt{xt}}{x+t}\right)-(x+t)^2\mathbf{E}\left(2\frac{\sqrt{xt}}{x+t}\right)\right], \tag{18}$$

$$H_3(x)=\frac{1}{6}\left(\frac{4}{243}\right)^2\int_0^\infty dt\,\frac{te^{-2t/3}}{x+t}\left[(x^4+4x^2t^2+t^4)\mathbf{K}\left(2\frac{\sqrt{xt}}{x+t}\right)\right.$$
$$\left.-(x^2+t^2)(x+t)^2\mathbf{E}\left(2\frac{\sqrt{xt}}{x+t}\right)\right], \tag{19}$$

where **K** and **E** are complete elliptic integrals of the first and second kind, respectively.

For $r=0$, one readily finds that $H_1(0)=515\pi/1,944$ and $H_2(0)=H_3(0)=0$. Indeed, $\varepsilon_x(r)$ can be expressed explicitly in terms of modified Bessel functions, as indicated in the "Appendix"; however, the result is quite complicated and so we present the numerical value in Figs. 1, 2. For small r the density is dominated by the term containing $H_1(x)$ and the approach in the Appendix gives

$$\varepsilon_x(r)=\varepsilon_x(0)[1-2\beta_0 r+\frac{392}{515}\beta_0^2 r^2\log(\beta_0 r)+O(r^2)] \tag{20}$$

with

$$\varepsilon_x(0)=-\frac{16e^2\beta_0^3}{\pi^2}\frac{515\pi}{1,944}. \tag{21}$$

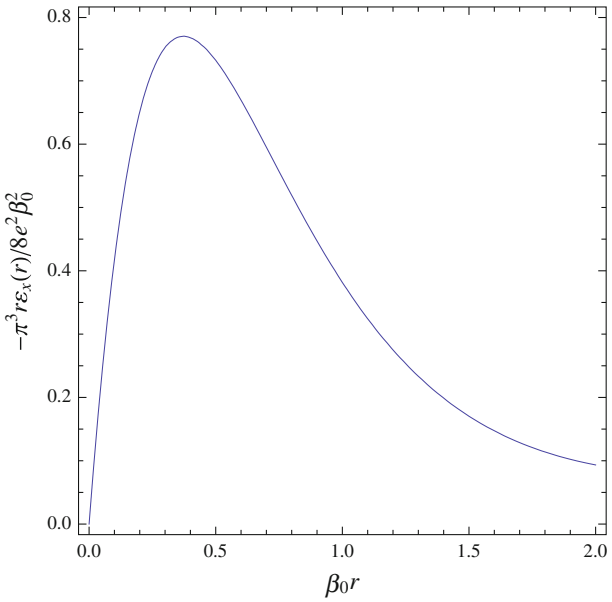

Fig. 2 The quantity $-2\pi r\varepsilon_x(r)/(16e^2\beta_0^2/\pi^2)$ versus $\beta_0 r$

For large values of r we must have

$$\varepsilon_x(r) \to -\frac{e^2}{4r}\int \gamma^2(\mathbf{r},\mathbf{r}')d\mathbf{r}' = -\frac{e^2}{2r}n(r). \tag{22}$$

This is easily verified by explicit integration using (13), where $n(r)$ is given in (14). This relation is demonstrated in Fig. 3.

For a uniform two-dimensional electron gas of density $n(r)$, the exact exchange energy per unit area is [7]

$$\varepsilon_x^{LDA}(r) = -(e^2/\pi^2)(2\pi n(r))^{3/2}. \tag{23}$$

The local density approximation in this case, obtained by replacing n by $n(r)$ in (14), is illustrated in Fig. 4.

To conclude this section, we note that Eq. (16) has already embodied in it the nuclear cusp condition on the exchange energy derived by March et al. [8] (see their Eq. (3.18)). This appears to be the source of the nonanalytic behavior displayed in (17).

4 Relating to the Theophilou–March generalization for a two-dimensional system: the Green function as a tool

It seems of interest, at this point, to discuss whether, as Theophilou and March [9] found in three dimensions, the 'spherical' part of (13) is sufficient to determine the total Dirac matrix (13). All important is whether key variables are again in 2D

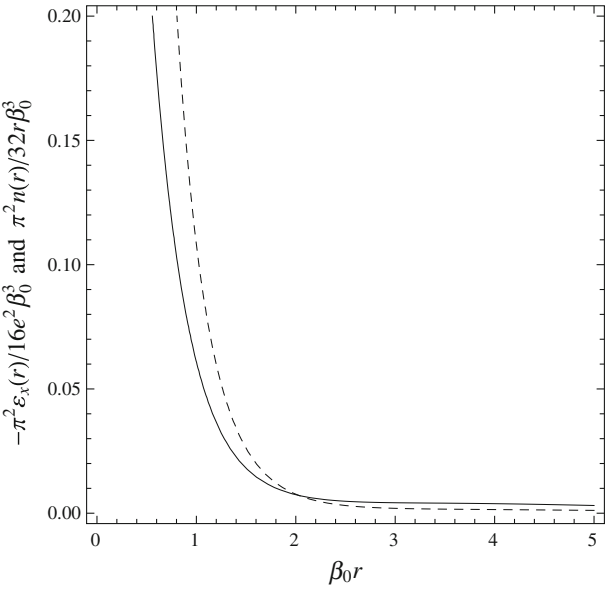

Fig. 3 Comparison of $-\varepsilon_x(r)/(16e^2\beta_0^3/\pi^2)$ with $(-e^2/2r)\int\gamma^2(\mathbf{r},\mathbf{r}')d\mathbf{r}'$ (*dashed curve*), both versus $\beta_0 r$

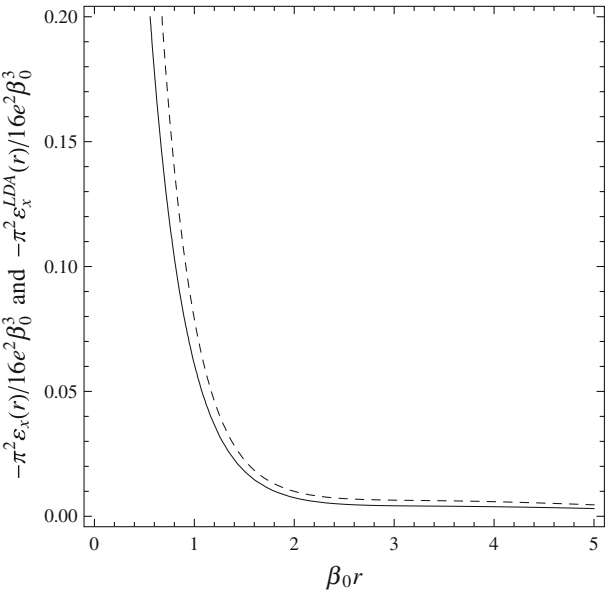

Fig. 4 Comparison of the LDA (*dashed curve*) with the exact exchange energy, both versus $\beta_0 r$

$$x = r + r' + |\mathbf{r} - \mathbf{r}'|, \qquad y = r + r' - |\mathbf{r} - \mathbf{r}'|. \tag{24}$$

In this connection we note that (13) can be written

$$\gamma(\mathbf{r}, \mathbf{r}') = n\left(\frac{r + r'}{2}\right) - \frac{8e^2\beta_0^4}{243\pi} e^{-\frac{2}{3}\frac{(r+r')}{2}} |\mathbf{r} - \mathbf{r}'|^2. \tag{25}$$

The Dirac matrix is the two-sided inverse Laplace transform of the Green function

$$\gamma(\mathbf{r}, \mathbf{r}') = \lim_{\eta \to 0^+} \int_{c-i\infty}^{c+i\infty} \frac{ds}{2\pi i} e^{\eta s} G(\mathbf{r}, \mathbf{r}'; s), \tag{26}$$

where [10]

$$G(\mathbf{r}, \mathbf{r}'; E) = \frac{\sqrt{2}m}{i\hbar^2} \frac{e^{-\pi\eta}}{\cosh(\pi\eta)} \times \int_{\infty}^{1^+} \frac{dz}{2\pi i} \left(\frac{z+1}{z-1}\right)^{i\eta} e^{ik(r+r')z} \frac{\cos[2k\sqrt{rr'}\cos[(\phi - \phi')/2]\sqrt{z^2-1}]}{\sqrt{z^2-1}}, \tag{27}$$

or

$$G(x, y; E) = \frac{2m}{i\hbar^2} \tanh(\pi\eta) \int_0^{\infty} du \coth^{2i\eta}(u/2) e^{ik(\frac{x+y}{2})\cosh u} \cos[k\sqrt{xy}\sinh u]. \tag{28}$$

Here $k = \sqrt{2mE/\hbar^2}$, $\eta = mZe^2/k\hbar^2$. The poles of G are $\eta = (n - 1/2)i$, giving energy levels

$$E_n = -\frac{m(Ze^2)^2}{2(n-1/2)^2\hbar^2} \tag{29}$$

in agreement with (8). It thus appears that

$$G(\mathbf{r}, \mathbf{r}'; E) = G\left(\frac{x+y}{2}, \sqrt{xy}; E\right). \tag{30}$$

We note for future reference that the $\ell = 0$ contribution to the Green function is (in atomic units)

$$G_0(r, r'; E) = \frac{\Gamma(1/2 + a)}{\sqrt{-2Err'}} W_{-a,0}(2r_>/a) M_{-a,0}(2r_</a), \tag{31}$$

where W and M denote Whittaker functions and $a = (-2E)^{-1/2}$. As usual, $r_{\{>,<\}}$ denotes $\{max,\ min\}$ of r, r', respectively.

5 Summary and future directions

We have presented here an analytic derivation of the exchange energy density for two closed shells generated by a bare Coulomb potential in two dimensions. The essential ingredient in the calculation is the Dirac density matrix given in Eq. (13). In relation to this quantity, it seemed of interest in Sect. 4 to explore whether a parallel existed in 2D of the Theophilou-March 3D result: namely that the entire density matrix for closed shell is determined by its s-state ($\ell = 0$) component alone. Though this result is not directly generalizable to the 2D case of the bare Coulomb potential, it has led us to the result (30) for the Green function, in terms of the key 2D variables x and y introduced in Eq. (24). Finally, it is, of course, of considerable interest for the future to study further the exchange potential $V_x(r)$ given by the functional derivative of the total exchange energy $E_x = \int \varepsilon_x(r)\, d\mathbf{r}$ with respect to the density $n(r)$. To date, we have only obtained the so-called Slater approximation to $V_x(r)$, namely $2\varepsilon_x(r)/n(r)$. To do so requires knowledge of the functional derivative of the single-particle kinetic energy per unit area, which is an important problem for future study.

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Appendix

The integrals in $H_j(x)$, $j = 1, 2, 3$ in (17)–(19) are all of the forms

$$M_n(a,x) = \int_0^\infty dt\ e^{-at}\frac{t^n}{x+t}\mathbf{K}\left(\frac{2\sqrt{xt}}{x+t}\right) = (-1)^n\frac{\partial^n}{\partial a^n}M_0(a,x), \tag{A.1}$$

$$N_n(a,x) = \int_0^\infty dt\ e^{-at}\frac{t^n}{x+t}\mathbf{E}\left(\frac{2\sqrt{xt}}{x+t}\right) = (-1)^n\frac{\partial^n}{\partial a^n}N_0(a,x), \tag{A.2}$$

which can be expressed as modified Bessel functions. For example, to evaluate $M_0(a,x)$, we first make the substitution $t = xk$ and then decompose the range of integration $[0,\infty] = [0,1] \cup [1,\infty]$. In the first part we apply Landen's transformation in the form

$$\mathbf{K}\left(\frac{2\sqrt{k}}{1+k}\right) = (1+k)\mathbf{K}(k) \tag{A.3}$$

and in the second part, first let $k \to 1/k$ and then apply (A.3). This results in [11]

$$M_0(a,x) = \int_0^1 \left(e^{-axk} + k^{-1}e^{-ax/k}\right)\mathbf{K}(k)dk = \frac{\pi}{2} I_0(ax/2)K_0(ax/2). \quad \text{(A.4)}$$

This is significant, in that $K_0(z)$ is logarithmically singular for $z \to 0$. Consequently, the exchange density is non-analytic for small r, as indicated in the text. Proceeding in this way, the exact exchange energy density in terms of the scaled radius x

$$\varepsilon_x(r) = \varepsilon_x(0)x\left[\frac{2}{515}e^{-4x/3}h_1(x) - \frac{2}{125145}e^{-2x/3}h_2(x) + \frac{486}{515}e^{-2x}h_3(x)\right], \quad \text{(A.5)}$$

where

$$\begin{aligned}
h_1(x) &= I_0\left(\frac{2x}{3}\right)\left[(8x^2-6x+9)K_1\left(\frac{2x}{3}\right) + (8x^2-12x)K_0\left(\frac{2x}{3}\right)\right] \\
&\quad - I_1\left(\frac{2x}{3}\right)\left[8x^2K_1\left(\frac{2x}{3}\right) + (8x^2-6x+9)K_0\left(\frac{2x}{3}\right)\right], \\
h_2(x) &= I_1\left(\frac{x}{3}\right)\left[(32x^4+108x^2-108x+81)K_0\left(\frac{x}{3}\right)\right. \\
&\quad \left. + (32x^4+48x^3+216x^2+54x)K_1\left(\frac{x}{3}\right)\right] \\
&\quad - I_0\left(\frac{x}{3}\right)\left[(32x^4-48x^3+72x^2-54x)K_0\left(\frac{x}{3}\right)\right. \\
&\quad \left. + (32x^4+108x^2-108x+81)K_1\left(\frac{x}{3}\right)\right], \\
h_3(x) &= I_0(x)K_1(x) - I_1(x)K_0(x).
\end{aligned}$$

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