Implementing the PBEc Hessian into ADF

The PBE correlation functional (DOI 10.1103/PhysRevLett.77.3865) is given by the following formula:

$$E_c = \int r \cdot \left[\epsilon_c^{unif}(w,z) + H(w,z,t)\right]$$

Here ***r*** is the density, ***w*** is the von Weisz/Seitz radius, ***z*** is the relative spin polarization, ***t*** is a dimensionless density gradient, and ***q*** the spin-scaling function (in red the variable names from the PBE paper if they differ from the variables used here):

$$w = \left(\frac{3}{4\pi}\right)^{1/3} \cdot r^{-1/3} = r_s$$

$$z = \frac{r_a - r_b}{r_a + r_b} = \zeta$$

$$t = \frac{g}{2 \cdot q \cdot r \cdot k_s} = \frac{g}{2 \cdot q \cdot r^{7/6} \cdot c_{ks}}$$

$$q(z) = \frac{(1+z)^{2/3} + (1-z)^{2/3}}{2} = \phi(\zeta)$$

$$k_F = (3\pi^2)^{1/3} \cdot r^{1/3}$$

$$k_s = \left(\frac{4}{\pi} k_F\right)^{1/2} = 2 \cdot \left(\frac{3}{\pi}\right)^{1/6} \cdot r^{1/6}$$

The formula for ***H*** satisfies a number of constraints, as can be read in the PBE paper, and is given by:

$$H = \gamma \cdot q^3 \cdot ln(1 + \delta \cdot K)$$

$$\delta = \frac{\beta}{\gamma}$$

$$K = \frac{t^2 \cdot (1 + A \cdot t^2)}{1 + A \cdot t^2 + A^2 \cdot t^4}$$

$$A = \frac{\delta}{e^y - 1}$$

$$y = -\frac{\epsilon_c^{unif}}{\gamma \cdot q^3} = -\frac{\epsilon}{\gamma \cdot q^3}$$

For the ADF implementation we need the energy, and its first and second derivatives with respect to the (spin) density, w.r.t. $\boldsymbol{g}^2$ (for convenience renamed as ***u***) and the mixed derivatives. It is easiest to separate the spin-restricted case from spin-unrestricted case. With spin-restricted case, the equations become simpler because the dependence on ***z*** and ***q*** fall away.

Let's start with the derivatives for the spin-unrestricted case, which contain everything and then for the restricted case the derivatives wr.t. z and q can be ignored.

$$z = \frac{r_a - r_b}{r_a + r_b} = \zeta \qquad (spin - restricted) \Longrightarrow z = 0$$

$$\frac{\partial z}{\partial r_a} = \frac{1}{r_a + r_b} - \frac{r_a - r_b}{(r_a + r_b)^2} = \frac{r_a + r_b}{(r_a + r_b)^2} - \frac{r_a - r_b}{(r_a + r_b)^2} = \frac{1 - z}{r}$$

$$\frac{\partial z}{\partial r_b} = \frac{-1}{r_a + r_b} - \frac{r_a - r_b}{(r_a + r_b)^2} = \frac{-r_a - r_b}{(r_a + r_b)^2} - \frac{r_a - r_b}{(r_a + r_b)^2} = \frac{-1 - z}{r}$$

$$\frac{\partial^2 z}{\partial {r_a}^2} = \frac{-\frac{\partial z}{\partial r_a}}{r} - \frac{1 - z}{r^2} = \frac{-1 + z}{r^2} - \frac{1 - z}{r^2} = \frac{2z - 2}{r^2}$$

$$\frac{\partial^2 z}{\partial {r_b}^2} = \frac{-\frac{\partial z}{\partial r_b}}{r} - \frac{-1 - z}{r^2} = \frac{1 + z}{r^2} + \frac{1 + z}{r^2} = \frac{2z + 2}{r^2}$$

$$\frac{\partial^2 z}{\partial r_a \partial r_b} = \frac{-\frac{\partial z}{\partial r_b}}{r} - \frac{1 - z}{r^2} = \frac{1 + z}{r^2} - \frac{1 - z}{r^2} = \frac{2z}{r^2}$$

$$r = r_a + r_b \rightarrow \frac{\partial r}{\partial r_a} = \frac{\partial r}{\partial r_b} = 1$$

$$q(z) = \frac{(1 + z)^{2/3} + (1 - z)^{2/3}}{2} \qquad (spin - restricted) \Longrightarrow q = 1$$

$$\frac{\partial q}{\partial z} = \frac{1}{3} \cdot \frac{1}{(1 + z)^{1/3}} - \frac{1}{3} \cdot \frac{1}{(1 - z)^{1/3}}$$

$$\frac{\partial^2 q}{\partial z^2} = -\frac{1}{9} \cdot \frac{1}{(1 + z)^{4/3}} - \frac{1}{9} \cdot \frac{1}{(1 - z)^{4/3}}$$

$$\frac{\partial q}{\partial r_a} = \frac{\partial q}{\partial z} \cdot \frac{\partial z}{\partial r_a}$$

$$\frac{\partial q}{\partial r_b} = \frac{\partial q}{\partial z} \cdot \frac{\partial z}{\partial r_b}$$

$$\frac{\partial^2 q}{\partial {r_a}^2} = \frac{\partial^2 q}{\partial z^2} \cdot \frac{\partial z}{\partial r_a} \cdot \frac{\partial z}{\partial r_a} + \frac{\partial q}{\partial z} \cdot \frac{\partial^2 z}{\partial {r_a}^2}$$

$$\frac{\partial^2 q}{\partial {r_b}^2} = \frac{\partial^2 q}{\partial z^2} \cdot \frac{\partial z}{\partial r_b} \cdot \frac{\partial z}{\partial r_b} + \frac{\partial q}{\partial z} \cdot \frac{\partial^2 z}{\partial {r_b}^2}$$

$$\frac{\partial^2 q}{\partial r_a \partial r_b} = \frac{\partial^2 q}{\partial z^2} \cdot \frac{\partial z}{\partial r_a} \cdot \frac{\partial z}{\partial r_b} + \frac{\partial q}{\partial z} \cdot \frac{\partial^2 z}{\partial r_a \partial r_b}$$

$$t = \frac{g}{2 \cdot q \cdot r^{7/6} \cdot c_{ks}} = \frac{u^{1/2}}{2 \cdot q \cdot r^{7/6} \cdot c_{ks}}$$

$$\frac{\partial t}{\partial r_a} = -\frac{7}{6} \cdot \frac{u^{1/2}}{2 \cdot q \cdot r^{13/6} \cdot c_{ks}} - \frac{u^{1/2}}{2 \cdot q^2 \cdot r^{7/6} \cdot c_{ks}} \cdot \frac{\partial q}{\partial r_a} = -\frac{7t}{6r} - \frac{t}{q} \cdot \frac{\partial q}{\partial r_a} = t \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_a}\right)$$

$$\frac{\partial t}{\partial r_b} = -\frac{7}{6} \cdot \frac{u^{1/2}}{2 \cdot q \cdot r^{13/6} \cdot c_{ks}} - \frac{u^{1/2}}{2 \cdot q^2 \cdot r^{7/6} \cdot c_{ks}} \cdot \frac{\partial q}{\partial r_b} = -\frac{7t}{6r} - \frac{t}{q} \cdot \frac{\partial q}{\partial r_b} = t \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_b}\right)$$

$$\frac{\partial t}{\partial u} = \frac{1}{2} \cdot \frac{u^{-1/2}}{2 \cdot q \cdot r^{7/6} \cdot c_{ks}} = \frac{t}{2 \cdot g^2}$$

$$\frac{\partial^2 t}{\partial {r_a}^2} = \frac{\partial t}{\partial r_a} \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_a}\right) + t \cdot \left(\frac{7}{6r^2} + \frac{1}{q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_a} - \frac{1}{q} \cdot \frac{\partial^2 q}{\partial {r_a}^2}\right)$$

$$\frac{\partial^2 t}{\partial {r_b}^2} = \frac{\partial t}{\partial r_b} \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_b}\right) + t \cdot \left(\frac{7}{6r^2} + \frac{1}{q^2} \cdot \frac{\partial q}{\partial r_b} \cdot \frac{\partial q}{\partial r_b} - \frac{1}{q} \cdot \frac{\partial^2 q}{\partial {r_b}^2}\right)$$

$$\frac{\partial^2 t}{\partial r_a \partial r_b} = \frac{\partial t}{\partial r_b} \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_a}\right) + t \cdot \left(\frac{7}{6r^2} + \frac{1}{q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} - \frac{1}{q} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b}\right)$$

$$\Rightarrow \left(-\frac{7t}{6r} - \frac{t}{q} \cdot \frac{\partial q}{\partial r_b}\right) \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_a}\right) + \left(\frac{7t}{6r^2} + \frac{t}{q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} - \frac{t}{q} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b}\right)$$

$$\Rightarrow \left(\frac{49t}{36r^2} + \frac{7t}{6qr} \cdot \frac{\partial q}{\partial r_a} + \frac{7t}{6qr} \cdot \frac{\partial q}{\partial r_b} + \frac{t}{q^2} \cdot \frac{\partial q}{\partial r_b} \cdot \frac{\partial q}{\partial r_a}\right) + \left(\frac{7t}{6r^2} + \frac{t}{q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} - \frac{t}{q} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b}\right)$$

$$\Rightarrow \frac{\partial^2 t}{\partial r_a \partial r_b} = t \cdot \left(\frac{\frac{7^2}{6} + \frac{7}{6}}{r^2} + \frac{7}{6qr} \cdot \left(\frac{\partial q}{\partial r_a} + \frac{\partial q}{\partial r_b}\right) + \frac{2}{q^2} \cdot \frac{\partial q}{\partial r_b} \cdot \frac{\partial q}{\partial r_a} - \frac{1}{q} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b}\right)$$

$$\frac{\partial^2 t}{\partial u^2} = -\frac{1}{4} \cdot \frac{u^{-3/2}}{2 \cdot q \cdot r^{7/6} \cdot c_{ks}} = \frac{-\frac{\partial t}{\partial u}}{2 \cdot g^2}$$

$$\frac{\partial^2 t}{\partial r_a \partial u} = \frac{\partial t}{\partial u} \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_a}\right)$$

$$\frac{\partial^2 t}{\partial r_b \partial u} = \frac{\partial t}{\partial u} \cdot \left(-\frac{7}{6r} - \frac{1}{q} \cdot \frac{\partial q}{\partial r_b}\right)$$

For the uniform electron gas correlation energy, other routines provide derivatives with respect to ***w***, ***z***.

$$z = \frac{r_a - r_b}{r_a + r_b} = \zeta$$

$$w = \left(\frac{3}{4\pi}\right)^{1/3} \cdot r^{-1/3} = r_s$$

$$\frac{\partial w}{\partial r} = -\frac{1}{3} \cdot \left(\frac{3}{4\pi}\right)^{1/3} \cdot r^{-4/3} = -\frac{1}{3} \cdot \frac{w}{r}$$

$$\frac{\partial^2 w}{\partial r^2} = \frac{4}{9} \cdot \left(\frac{3}{4\pi}\right)^{1/3} \cdot r^{-7/3} = -\frac{4}{3} \cdot \frac{1}{r} \cdot \frac{\partial w}{\partial r}$$

$$\frac{\partial \epsilon}{\partial r_a} = \frac{\partial \epsilon}{\partial w} \cdot \frac{\partial w}{\partial r} + \frac{\partial \epsilon}{\partial z} \cdot \frac{\partial z}{\partial r_a}$$

$$\frac{\partial \epsilon}{\partial r_b} = \frac{\partial \epsilon}{\partial w} \cdot \frac{\partial w}{\partial r} + \frac{\partial \epsilon}{\partial z} \cdot \frac{\partial z}{\partial r_b}$$

$$\frac{\partial^2 \epsilon}{\partial {r_a}^2} = \frac{\partial^2 \epsilon}{\partial w^2} \cdot \frac{\partial w}{\partial r} \cdot \frac{\partial w}{\partial r} + \frac{\partial \epsilon}{\partial w} \cdot \frac{\partial^2 w}{\partial r^2} + \frac{\partial^2 \epsilon}{\partial z^2} \cdot \frac{\partial z}{\partial r_a} \cdot \frac{\partial z}{\partial r_a} + \frac{\partial \epsilon}{\partial z} \cdot \frac{\partial^2 z}{\partial {r_a}^2} + 2\left(\frac{\partial^2 \epsilon}{\partial w \partial z} \cdot \frac{\partial w}{\partial r} \cdot \frac{\partial z}{\partial r_a}\right)$$

$$\frac{\partial^2 \epsilon}{\partial {r_b}^2} = \frac{\partial^2 \epsilon}{\partial w^2} \cdot \frac{\partial w}{\partial r} \cdot \frac{\partial w}{\partial r} + \frac{\partial \epsilon}{\partial w} \cdot \frac{\partial^2 w}{\partial r^2} + \frac{\partial^2 \epsilon}{\partial z^2} \cdot \frac{\partial z}{\partial r_b} \cdot \frac{\partial z}{\partial r_b} + \frac{\partial \epsilon}{\partial z} \cdot \frac{\partial^2 z}{\partial {r_b}^2} + 2\left(\frac{\partial^2 \epsilon}{\partial w \partial z} \cdot \frac{\partial w}{\partial r} \cdot \frac{\partial z}{\partial r_b}\right)$$

$$\frac{\partial^2 \epsilon}{\partial r_a \partial r_b} = \frac{\partial^2 \epsilon}{\partial w^2} \cdot \frac{\partial w}{\partial r} \cdot \frac{\partial w}{\partial r} + \frac{\partial \epsilon}{\partial w} \cdot \frac{\partial^2 w}{\partial r^2} + \frac{\partial^2 \epsilon}{\partial z^2} \cdot \frac{\partial z}{\partial r_a} \cdot \frac{\partial z}{\partial r_b} + \frac{\partial \epsilon}{\partial z} \cdot \frac{\partial^2 z}{\partial r_a \partial r_b} + \frac{\partial^2 \epsilon}{\partial w \partial z} \cdot \frac{\partial w}{\partial r} \cdot \left(\frac{\partial z}{\partial r_a} + \frac{\partial z}{\partial r_b}\right)$$

$$y = -\frac{\epsilon_c^{unif}(w,z)}{\gamma \cdot q^3} = -\frac{\epsilon}{\gamma \cdot q^3}$$

$$\frac{\partial y}{\partial r_a} = -\frac{\frac{\partial \epsilon}{\partial r_a}}{\gamma \cdot q^3} + \frac{3\epsilon}{\gamma \cdot q^4} \cdot \frac{\partial q}{\partial r_a}$$

$$\frac{\partial y}{\partial r_b} = -\frac{\frac{\partial \epsilon}{\partial r_b}}{\gamma \cdot q^3} + \frac{3\epsilon}{\gamma \cdot q^4} \cdot \frac{\partial q}{\partial r_b}$$

$$\frac{\partial^2 y}{\partial {r_a}^2} = -\frac{\frac{\partial^2 \epsilon}{\partial {r_a}^2}}{\gamma \cdot q^3} + 2\frac{3}{\gamma \cdot q^4} \cdot \frac{\partial \epsilon}{\partial r_a} \cdot \frac{\partial q}{\partial r_a} - \frac{12 \cdot \epsilon}{\gamma \cdot q^5} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_a} + \frac{3\epsilon}{\gamma \cdot q^4} \cdot \frac{\partial^2 q}{\partial {r_a}^2}$$

$$\frac{\partial^2 y}{\partial {r_b}^2} = -\frac{\frac{\partial^2 \epsilon}{\partial {r_b}^2}}{\gamma \cdot q^3} + 2\frac{3}{\gamma \cdot q^4} \cdot \frac{\partial \epsilon}{\partial r_b} \cdot \frac{\partial q}{\partial r_b} - \frac{12 \cdot \epsilon}{\gamma \cdot q^5} \cdot \frac{\partial q}{\partial r_b} \cdot \frac{\partial q}{\partial r_b} + \frac{3\epsilon}{\gamma \cdot q^4} \cdot \frac{\partial^2 q}{\partial {r_b}^2}$$

$$\frac{\partial^2 y}{\partial r_a \partial r_b} = -\frac{\frac{\partial^2 \epsilon}{\partial r_a \partial r_b}}{\gamma \cdot q^3} + \frac{3}{\gamma \cdot q^4} \cdot \left(\frac{\partial \epsilon}{\partial r_b} \cdot \frac{\partial q}{\partial r_a} + \frac{\partial \epsilon}{\partial r_a} \cdot \frac{\partial q}{\partial r_b}\right) - \frac{12 \cdot \epsilon}{\gamma \cdot q^5} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} + \frac{3\epsilon}{\gamma \cdot q^4} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b}$$

$$A = \frac{\delta}{e^y - 1} \quad \Leftrightarrow \quad \frac{\partial A}{\partial u} = 0$$

$$\frac{\partial A}{\partial r_a} = \frac{-\delta}{(e^y - 1)^2} \cdot \frac{\partial y}{\partial r_a}$$

$$\frac{\partial A}{\partial r_b} = \frac{-\delta}{(e^y - 1)^2} \cdot \frac{\partial y}{\partial r_b}$$

$$\frac{\partial^2 A}{\partial {r_a}^2} = \frac{2 \cdot \delta}{(e^y - 1)^3} \cdot \frac{\partial y}{\partial r_a} \cdot \frac{\partial y}{\partial r_a} + \frac{-\delta}{(e^y - 1)^2} \cdot \frac{\partial^2 y}{\partial {r_a}^2}$$

$$\frac{\partial^2 A}{\partial {r_b}^2} = \frac{2 \cdot \delta}{(e^y - 1)^3} \cdot \frac{\partial y}{\partial r_b} \cdot \frac{\partial y}{\partial r_b} + \frac{-\delta}{(e^y - 1)^2} \cdot \frac{\partial^2 y}{\partial {r_b}^2}$$

$$\frac{\partial^2 A}{\partial r_a \partial r_b} = \frac{2 \cdot \delta}{(e^y - 1)^3} \cdot \frac{\partial y}{\partial r_a} \cdot \frac{\partial y}{\partial r_b} + \frac{-\delta}{(e^y - 1)^2} \cdot \frac{\partial^2 y}{\partial r_a \partial r_b}$$

$$K = \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} = \frac{N}{D}$$

$$\frac{\partial N}{\partial A} = t^4$$

$$\frac{\partial N}{\partial t} = 2t + 4At^3$$

$$\frac{\partial D}{\partial A} = t^2 + 2At^4$$

$$\frac{\partial D}{\partial t} = 2At + 4A^2 t^3$$

$$\frac{\partial^2 N}{\partial A^2} = 0$$

$$\frac{\partial^2 N}{\partial t^2} = 2 + 12At^2$$

$$\frac{\partial^2 N}{\partial A \partial t} = 4t^3$$

$$\frac{\partial^2 D}{\partial A^2} = 2t^4$$

$$\frac{\partial^2 D}{\partial t^2} = 2A + 12A^2 t^2$$

$$\frac{\partial^2 D}{\partial A \partial t} = 2t + 8At^3$$

$$\frac{\partial K}{\partial A} = \frac{\frac{\partial N}{\partial A} D - N\frac{\partial D}{\partial A}}{D^2}$$

$$\frac{\partial K}{\partial t} = \frac{\frac{\partial N}{\partial t} D - N\frac{\partial D}{\partial t}}{D^2}$$

$$\frac{\partial^2 K}{\partial A^2} = \frac{2N\frac{\partial D}{\partial A}\frac{\partial D}{\partial A} - 2D\frac{\partial N}{\partial A}\frac{\partial D}{\partial A} + D^2\frac{\partial^2 N}{\partial A^2} - ND\frac{\partial^2 D}{\partial A^2}}{D^3} \qquad \frac{\partial^2 N}{\partial A^2} = 0$$

$$\frac{\partial^2 K}{\partial t^2} = \frac{2N\frac{\partial D}{\partial t}\frac{\partial D}{\partial t} - 2D\frac{\partial N}{\partial t}\frac{\partial D}{\partial t} + D^2\frac{\partial^2 N}{\partial t^2} - ND\frac{\partial^2 D}{\partial t^2}}{D^3}$$

$$\frac{\partial^2 K}{\partial A \partial t} = \frac{2N\frac{\partial D}{\partial A}\frac{\partial D}{\partial t} - D\frac{\partial N}{\partial A}\frac{\partial D}{\partial t} - D\frac{\partial N}{\partial t}\frac{\partial D}{\partial A} + D^2\frac{\partial^2 N}{\partial A \partial t} - ND\frac{\partial^2 D}{\partial A \partial t}}{D^3}$$

$$\frac{\partial K}{\partial r_a} = \frac{\partial K}{\partial A}\cdot\frac{\partial A}{\partial r_a} + \frac{\partial K}{\partial t}\cdot\frac{\partial t}{\partial r_a}$$

$$\frac{\partial K}{\partial r_b} = \frac{\partial K}{\partial A}\cdot\frac{\partial A}{\partial r_b} + \frac{\partial K}{\partial t}\cdot\frac{\partial t}{\partial r_b}$$

$$\frac{\partial K}{\partial u} = \frac{\partial K}{\partial A}\cdot\frac{\partial A}{\partial u} + \frac{\partial K}{\partial t}\cdot\frac{\partial t}{\partial u} \qquad \frac{\partial A}{\partial u} = 0$$

$$\frac{\partial^2 K}{\partial {r_a}^2} = \frac{\partial^2 K}{\partial A^2}\cdot\frac{\partial A}{\partial r_a}\cdot\frac{\partial A}{\partial r_a} + \frac{\partial K}{\partial A}\cdot\frac{\partial^2 A}{\partial {r_a}^2} + \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial r_a}\cdot\frac{\partial t}{\partial r_a} + \frac{\partial K}{\partial t}\cdot\frac{\partial^2 t}{\partial {r_a}^2} + \frac{\partial^2 K}{\partial A \partial t}\cdot\left(\frac{\partial A}{\partial r_a}\cdot\frac{\partial t}{\partial r_a} + \frac{\partial A}{\partial r_a}\cdot\frac{\partial t}{\partial r_a}\right)$$

$$\frac{\partial^2 K}{\partial {r_b}^2} = \frac{\partial^2 K}{\partial A^2}\cdot\frac{\partial A}{\partial r_b}\cdot\frac{\partial A}{\partial r_b} + \frac{\partial K}{\partial A}\cdot\frac{\partial^2 A}{\partial {r_b}^2} + \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial r_b}\cdot\frac{\partial t}{\partial r_b} + \frac{\partial K}{\partial t}\cdot\frac{\partial^2 t}{\partial {r_b}^2} + \frac{\partial^2 K}{\partial A \partial t}\cdot\left(\frac{\partial A}{\partial r_b}\cdot\frac{\partial t}{\partial r_b} + \frac{\partial A}{\partial r_b}\cdot\frac{\partial t}{\partial r_b}\right)$$

$$\frac{\partial^2 K}{\partial r_a \partial r_b} = \frac{\partial^2 K}{\partial A^2}\cdot\frac{\partial A}{\partial r_a}\cdot\frac{\partial A}{\partial r_b} + \frac{\partial K}{\partial A}\cdot\frac{\partial^2 A}{\partial r_a \partial r_b} + \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial r_a}\cdot\frac{\partial t}{\partial r_b} + \frac{\partial K}{\partial t}\cdot\frac{\partial^2 t}{\partial r_a \partial r_b} + \frac{\partial^2 K}{\partial A \partial t}\cdot\left(\frac{\partial A}{\partial r_b}\cdot\frac{\partial t}{\partial r_a} + \frac{\partial A}{\partial r_a}\cdot\frac{\partial t}{\partial r_b}\right)$$

$$\frac{\partial^2 K}{\partial u^2} = \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial u}\cdot\frac{\partial t}{\partial u} + \frac{\partial K}{\partial u}\cdot\frac{\partial^2 t}{\partial u^2}$$

$$\frac{\partial^2 K}{\partial u \partial r_a} = \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial u}\cdot\frac{\partial t}{\partial r_a} + \frac{\partial K}{\partial t}\cdot\frac{\partial^2 t}{\partial u \partial r_a} + \frac{\partial^2 K}{\partial t \partial A}\cdot\frac{\partial t}{\partial u}\cdot\frac{\partial A}{\partial r_a}$$

$$\frac{\partial^2 K}{\partial u \partial r_b} = \frac{\partial^2 K}{\partial t^2}\cdot\frac{\partial t}{\partial u}\cdot\frac{\partial t}{\partial r_b} + \frac{\partial K}{\partial t}\cdot\frac{\partial^2 t}{\partial u \partial r_b} + \frac{\partial^2 K}{\partial t \partial A}\cdot\frac{\partial t}{\partial u}\cdot\frac{\partial A}{\partial r_b}$$

And then finally, to put everything together:

$$H = \gamma \cdot q^3 \cdot ln(1 + \delta \cdot K)$$

$$\frac{\partial H}{\partial K} = \frac{\delta \cdot \gamma \cdot q^3}{1 + \delta \cdot K}$$

$$\frac{\partial H}{\partial q} = \gamma \cdot 3q^2 \cdot ln(1 + \delta \cdot K)$$

$$\frac{\partial^2 H}{\partial K^2} = \frac{-\delta^2 \cdot \gamma \cdot q^3}{(1 + \delta \cdot K)^2}$$

$$\frac{\partial^2 H}{\partial q^2} = \gamma \cdot 6q \cdot ln(1 + \delta \cdot K)$$

$$\frac{\partial^2 H}{\partial K \partial q} = \frac{\delta \cdot \gamma \cdot 3q^2}{1 + \delta \cdot K}$$

$$\frac{\partial H}{\partial r_a} = \frac{\partial H}{\partial K} \cdot \frac{\partial K}{\partial r_a} + \frac{\partial H}{\partial q} \cdot \frac{\partial q}{\partial r_a}$$

$$\frac{\partial H}{\partial r_b} = \frac{\partial H}{\partial K} \cdot \frac{\partial K}{\partial r_b} + \frac{\partial H}{\partial q} \cdot \frac{\partial q}{\partial r_b}$$

$$\frac{\partial H}{\partial u} = \frac{\partial H}{\partial K} \cdot \frac{\partial K}{\partial u}$$

$$\frac{\partial^2 H}{\partial {r_a}^2} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial r_a} \cdot \frac{\partial K}{\partial r_a} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial {r_a}^2} + \frac{\partial^2 H}{\partial q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_a} + \frac{\partial H}{\partial q} \cdot \frac{\partial^2 q}{\partial {r_a}^2} + \frac{\partial^2 H}{\partial K \partial q} \cdot \left(\frac{\partial K}{\partial r_a} \cdot \frac{\partial q}{\partial r_a} + \frac{\partial K}{\partial r_a} \cdot \frac{\partial q}{\partial r_a}\right)$$

$$\frac{\partial^2 H}{\partial {r_b}^2} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial r_b} \cdot \frac{\partial K}{\partial r_b} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial {r_b}^2} + \frac{\partial^2 H}{\partial q^2} \cdot \frac{\partial q}{\partial r_b} \cdot \frac{\partial q}{\partial r_b} + \frac{\partial H}{\partial q} \cdot \frac{\partial^2 q}{\partial {r_b}^2} + \frac{\partial^2 H}{\partial K \partial q} \cdot \left(\frac{\partial K}{\partial r_b} \cdot \frac{\partial q}{\partial r_b} + \frac{\partial K}{\partial r_b} \cdot \frac{\partial q}{\partial r_b}\right)$$

$$\frac{\partial^2 H}{\partial r_a \partial r_b} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial r_a} \cdot \frac{\partial K}{\partial r_b} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial r_a \partial r_b} + \frac{\partial^2 H}{\partial q^2} \cdot \frac{\partial q}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} + \frac{\partial H}{\partial q} \cdot \frac{\partial^2 q}{\partial r_a \partial r_b} + \frac{\partial^2 H}{\partial K \partial q} \cdot \left(\frac{\partial K}{\partial r_a} \cdot \frac{\partial q}{\partial r_b} + \frac{\partial K}{\partial r_b} \cdot \frac{\partial q}{\partial r_a}\right)$$

$$\frac{\partial^2 H}{\partial u^2} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial u} \cdot \frac{\partial K}{\partial u} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial u^2}$$

$$\frac{\partial^2 H}{\partial u \partial r_a} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial u} \cdot \frac{\partial K}{\partial r_a} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial u \partial r_a} + \frac{\partial^2 H}{\partial K \partial q} \cdot \frac{\partial K}{\partial u} \cdot \frac{\partial q}{\partial r_a}$$

$$\frac{\partial^2 H}{\partial u \partial r_b} = \frac{\partial^2 H}{\partial K^2} \cdot \frac{\partial K}{\partial u} \cdot \frac{\partial K}{\partial r_b} + \frac{\partial H}{\partial K} \cdot \frac{\partial^2 K}{\partial u \partial r_b} + \frac{\partial^2 H}{\partial K \partial q} \cdot \frac{\partial K}{\partial u} \cdot \frac{\partial q}{\partial r_b}$$