[1] **Local Spin Density Approximation**\ $\underline{Exchange\ energy}$ - **Slater Exchange**

$E_x(n) = -\frac{9}{8}\alpha(\frac{3}{\pi})^{\frac{1}{3}}n^{\frac{1}{3}}$\ with $\alpha = \frac{2}{3}$ and n = $n(r)$ as density.

$\underline{exchange\ potential}$ is given by

$$V_x(r)) = E_x(n) + n\frac{\partial E_x(n)}{\partial n}$$

$$= E_x(n) + n\frac{1}{3}(-\frac{9}{8}\alpha(\frac{3}{\pi})^{\frac{1}{3}})n^{-\frac{2}{3}} = E_x(n) + \frac{1}{3}E_x(n) = \frac{4}{3}E_x(n)$$

$\underline{Correlation\ energy}$ - **VWN3 Functional**

The relevent paper is 'Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis' by S.H. Vosko, L. Wilk and M. Nusair https://escholarship.org/content/qt23j4q7zm/qt23j4q7zm.pdf?t=obc5l4

We define the Seitz radius as\ $r_s = (\frac{3}{4\pi n})^{\frac{1}{3}}$

$$E_c(n) = A\{log_e\frac{x^2}{X(x)} + \frac{2b}{Q}tan^{-1}\frac{Q}{2x+b} - \frac{bx_0}{X(x_0)}\left[log_e\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}tan^{-1}\frac{Q}{2x+b}\right]\}$$

$Q = \sqrt{4c-b^2}$ $\qquad X(x) = x^2 + bx + c \qquad x = \sqrt(r_s)$

Parameterization:\ paramagnetic $x_0 = -0.409286, b = 13.0720, c = 42.7198, A = 0.0310907$\ ferromagnetic $x_0 = -0.743294, b = 20.1231, c = 101.578, A = 0.01554535$

$\underline{Correlation\ potential}$

Note $\frac{d\ log_e x}{dx} = \frac{1}{x}$ and $\frac{d\ tan^{-1}x}{dx} = \frac{1}{1+x^2}$

Rearranging E_c to collect tan^{-1} terms we have\

$$E_c = A\{log_e\frac{x^2}{X(x)} - \frac{bx_0}{X(x_0)}log_e\frac{(x-x_0)^2}{X(x)} + \left[\frac{2b}{Q} - \frac{bx_0}{X(x_0)}\frac{2(b+2x_0)}{Q}\right]tan^{-1}\frac{Q}{2x+b}\}$$

Partial derivatives of the terms in above expression with respect to x are

$$(i) \quad \frac{\partial\ log_e\frac{x^2}{X(x)}}{\partial x} = \frac{X(x)}{x^2}\left[\frac{2x}{X(x)} - \frac{x^2}{X(x)^2}(2x+b)\right] = \left[\frac{2}{x} - \frac{(2x+b)}{X(x)}\right]$$

$$(ii) \quad \frac{\partial\ log_e\frac{(x-x_0)^2}{X(x)}}{\partial x} = \frac{X(x)}{(x-x_0)^2}\left[\frac{2(x-x_0)}{X(x)} - \frac{(x-x_0)^2(2x+b)}{X(x)^2}\right] = \left[\frac{2}{(x-x_0)} - \frac{(2x+b)}{X(x)}\right]$$

$$(iii) \quad \frac{\partial\ tan^{-1}\frac{Q}{2x+b}}{\partial x} = \frac{1}{1+(\frac{Q}{2x+b})^2}\left(\frac{-2Q}{(2x+b)^2}\right) = \frac{-2Q}{Q^2+(2x+b)^2} = \frac{-2Q}{4c-b^2+4x^2+4bx+b^2} = \frac{-2Q}{4(x^2+bx+c)} = -\frac{Q}{2X(x)}$$\

And\ $\frac{d\ x}{dn} = (\frac{3}{4\pi})^{\frac{1}{6}}(-\frac{1}{6}n^{-\frac{7}{6}}) = -\frac{1}{6n}(\frac{3}{4\pi n})^{\frac{1}{6}} = -\frac{x}{6n}$

By the chain rule we have $n\frac{d\ E_c}{dn} = n\frac{\partial E_c}{\partial x}\frac{dx}{dn} = -\frac{x}{6}\frac{\partial E_c}{\partial x}$

(i) can be written as $\frac{2x^2+2bx+2c-2x^2-bx}{xX(x)} = \frac{bx+2c}{xX(x)}$

(iii) can be written with it's prefactor as

$$-\frac{Q}{2X(x)}(\frac{2b}{Q})\left[1 - \frac{x_0(b+2x_0)}{X(x_0)}\right] = -\frac{b}{X(x)}\frac{1}{X(x_0)}\left[x_0^2 + bx_0 + c - bx_0 - 2x_0^2\right] = -\frac{b}{X(x)X(x_0)}(c - x_0^2)$$

putting the above two equations over a common denominator of $xX(x)X(x_0)$ gives a numerator of

$$(bx + 2c)(x_0^2 + bx_0 + c) - bx(c - x_0^2) = bxx_0^2 + b^2xx_0 + bcx + 2cx_0^2 + 2cbx_0 + 2c^2 - bcx + bxx_0^2 = 2c(x_0^2 + bx_0 + c) + bxx_0(2x_0 + b)$$

now make the denominator $xX(x)X(x_0)(x - x_0)$ so above expression for numerator becomes

$$(iv) \quad 2cX(x_0)(x - x_0) + bxx_0(x - x_0)(2x_0 + b) = 2cX(x_0)(x - x_0) + (2bx^2x_0^2 + b^2x^2x_0 - 2bxx_0^3 - b^2xx_0^2)$$

(ii) can be written with it's prefactor as $-\frac{bxx_0}{xX(x_0)X(x)(x-x_0)}\left[2X(x) - (x - X_0)(2x + b)\right]$

this numerator is $bxx_0(2x^2 + 2bx + 2bc - 2x^2 - bx + 2xx_0 + bx_0) = bxx_0(bx + 2bc + 2xx_0 + bx_0)$

the above equation and (iv) have the same denominator so combining we have

$2cX(x_0)(x - x_0) + (2bx^2x_0^2 + b^2x^2x_0 - 2bxx_0^3 - b^2xx_0^2) + bxx_0(bx + 2bc + 2xx_0 + bx_0)$ rearranging

$$2cX(x_0)(x - x_0) + \left[-2bxx_0^3 + (2bx^2x_0^2 - 2bx^2x_0^2) - (b^2xx_0^2 + b^2xx_0^2) + (b^2x^2x_0 - b^2x^2x_0) - 2bcxx_0\right] = 2cX(x_0)(x - x_0)$$
$$- 2bxx_0\left[x_0^2 + bx_0 + c\right] = 2cX(x_0)(x - x_0) - 2bxx_0X(x_0)$$

so $\frac{\partial E_c}{\partial x} = A\{\frac{2cX(x_0)(x-x_0)-2bxx_0X(x_0)}{xX(x)X(x_0)(x-x_0)}\} = A\{\frac{2c(x-x_0)-2bxx_0}{xX(x)(x-x_0)}\}$

and $n\frac{d\ E_c}{dn} = A\frac{2c(x-x_0)-2bxx_0}{xX(x)(x-x_0)}(-\frac{x}{6n})$ =

$$-\frac{A}{3}\{\frac{c(x-x_0)-bxx_0}{(x-x_0)X(x)}\}$$

Finally $V_c = E_c - \frac{A}{3}\{\frac{c(x-x_0)-bxx_0}{(x-x_0)X(x)}\}$