$$E_{tot} = E_{TB} + E_{disp} + E_{charge} + E_{rep}$$
$$E_{TB} =$$
$$E_{disp} =$$
$$E_{charge} =$$

1 Total Energy for GFN2-xTB

$$\begin{aligned} E_{GFN2-xTB} &= E^{(0)}_{rep} + E^{(0,1,2)}_{disp} + E^{(1)}_{EHT} + E^{(2)}_{IES+IXC} + E^{(2)}_{AES+AXC} + E^{(3)}_{IES+IXC} \\ &= E_{rep} + E^{D4'}_{disp} + E_{EHT} + E_{\gamma} + E_{AES} + E_{AXC} + E^{GFN2}_{\Gamma} \end{aligned} \tag{1}$$

1.1 Repulsion Energy

$$\begin{aligned} E_{rep} &= \frac{1}{2}\sum_{A,B} \frac{Z^{eff}_A Z^{eff}_B}{R_{AB}} e^{-\sqrt{a_A a_B}(R_{AB})^{(k_f)}} \\ k_f &= \begin{cases} 1 & if A, B \in \{\mathrm{H}, \mathrm{He}\} \\ \frac{3}{2} & otherwise \end{cases} \end{aligned} \tag{2}$$

Z^{eff} and a are variables fitted for each element. A,B are the labels of atoms. Since we only have C and H in our systems we can simplify this quite a bit in code. R_{AB} is the distance between the A and B atoms.

1.2 Extended Hückel Theory Energy

$$E_{EHT} = \sum_{\mu\nu} P_{\mu\nu} + H^{EHT}_{\mu\nu} \tag{3}$$

where μ and ν are AO indecies, l and l' index shells. Both AO's are associated with an atom labled A and B.

$$\begin{aligned} P_{\mu\nu} &= P^{(0)}_{\mu\nu} + \delta P_{\mu\nu} \\ P^{(0)}_{\mu\nu} &= ?? \\ \delta P_{\mu\nu} &= ?? \\ H^{EHT}_{\mu\nu} &= \frac{1}{2} K^{ll'}_{AB} S_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}) \\ &\cdot X(EN_A, EN_B) \\ &\cdot \Pi(R_{AB}, l, l') \\ &\cdot Y(\zeta^A_l, \zeta^B_{l'}), \forall \mu \in l(A), \nu \in l'(B) \end{aligned} \tag{4}$$

$K^{ll'}_{AB}$ is a element and shell specific fitted constant however, in GFN2 it only depends on the shells. $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$ is just the overlap of the orbitals. In GFN2

$H_{\kappa\kappa} = h_A^l - \delta h_{CN'_A}^l CN'_A$ where CN'_A is the modified GFN2-type Coordinate Number for the element of atom A. h_A^l and $\delta h_{CN'_A}^l$ are both fitted constants. EN_A is the electronegativity of the element of atom A.

$$\begin{aligned} X(EN_A, EN_B) &= 1 + k_{EN} \Delta EN_{AB}^2 \\ k_{EN} &= 0.02 \text{ in GFN2} \\ \Delta EN_{AB}^2 &= (EN_A - EN_B)^2 \end{aligned} \tag{5}$$

The electronegativity for C and H are 2.55 and 2.20 according to wikipedia. Thus here is a table for the combinations we will be working with:

A	B	$X(EN_A, EN_B)$
C	C	1
C	H	$1 + 0.02 \cdot (0.35^2)$
H	C	$1 + 0.02 \cdot (0.35^2)$
H	H	1

$$\Pi(R_{AB}, l, l') = \left(1 + k_{A,l}^{\text{poly}} \left(\frac{R_{AB}}{R_{\text{cov},AB}}\right)^{\frac{1}{2}}\right) \left(1 + k_{B,l'}^{\text{poly}} \left(\frac{R_{AB}}{R_{\text{cov},AB}}\right)^{\frac{1}{2}}\right) \tag{6}$$

$R_{\text{cov},AB}$ are the summed covalent radii and taken from Reference 61[1], the covalent radii is the second number in the table for each element, $H_{\text{cov}} = 0.32$, C_{cov} =???????????????? (can be found on wiki as 0.75). $k_{A,l}^{\text{poly}}$ and $k_{B,l'}^{\text{poly}}$ are element and shell specific constants.

$$Y(\zeta_l^A, \zeta_{l'}^B) = \left(\frac{2\sqrt{\zeta_l^A \zeta_{l'}^B}}{\zeta_l^A + \zeta_{l'}^B}\right)^{\frac{1}{2}} \tag{7}$$

Here, ζ_l^A are the STO exponents of the GFN2-xTB AO basis.
Slater Type Orbitals are defined as such:

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{n-1} e^{-\zeta r}$$

N is a normalisation constant, Y are spherical harmonic funtions, n, l, m are the quantum numbers for the AO. r, θ, φ are polar 3D coordinates. ζ determines the radial extent of the STO, a large value gives rise to a function that is "tight" around the nucleus and a small value gives a more "diffuse" function. This ζ is the one mentioned in the Y term of E_{EHT} and is a value fitted when constructing the basis set.

[1] p.2109, https://www.taylorfrancis.com/books/mono/10.1201/b12286/crc-handbook-chemistry-physics-william-haynes

1.3 Isotropic electrostatic and XC energy

1.3.1 Second order

$$
\begin{aligned}
E_{\gamma} &= \frac{1}{2} \sum_{A,B}^{N_{atoms}} \sum_{l \in A} \sum_{l' \in B} q_l q_{l'} \gamma_{AB,ll'} \\
\gamma_{AB,ll'} &= \frac{1}{\sqrt{R_{AB}^2 + \eta_{AB,ll'}^{-2}}} \\
\eta_{AB,ll'} &= \frac{1}{2} \left[\eta_A (1 + k_A^l) + \eta_B (1 + k_B^{l'}) \right]
\end{aligned}
\tag{8}
$$

q_l is a partial muliken charge. η_A and η_B are element-specific fit parameters, while k_A^l and $k_B^{l'}$ are element-specific scaling factors for the individual shells ($k_A^l = 0$ when $l = 0$).

1.3.2 Third order

$$
E_{\Gamma}^{GFN2} = \frac{1}{3} \sum_{A}^{N_{atoms}} \sum_{l \in A} (q_l)^3 K_l^{\Gamma} \Gamma_A \tag{9}
$$

K_l^{Γ} is a shell specific constant common for all elements and Γ_A is an element specific constant.