Using Frequency Maps as an Excited State Potential Energy Surface

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The excited state potential is a quadratic function of the electric field

$$U = aE_H + bE_H^2, \tag{1}$$

where E_H is the electric field at the excited H position $\mathbf{r}_H$, in the direction of the excited OH bond, $\hat{\mathbf{r}}_{OH}$

$$E_H = \mathbf{E}(\mathbf{r}_H)\cdot\hat{\mathbf{r}}_{OH}. \tag{2}$$

Here, boldface denotes vectors and hats denote unit vectors. The electric field is given by

$$\mathbf{E}(\mathbf{r}_H) = \sum_j \frac{q_j \mathbf{r}_{jH}}{r_{jH}^3} \tag{3}$$

where $\mathbf{r}_{jH} = \mathbf{r}_H - \mathbf{r}_j$, so E_H is

$$E_H = \sum_j \frac{q_j \mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3}, \tag{4}$$

where the sum over j goes over all atoms within sum cutoff distance of the tagged H, except for the atoms on the same water molecule. The force on particle α due to the potential in eq. 1 is

$$\begin{align} \mathbf{F}_\alpha &= -\frac{\partial}{\partial \mathbf{r}_\alpha} U \tag{5} \\ &= -a\frac{\partial E_H}{\partial \mathbf{r}_\alpha} - 2bE_H\frac{\partial E_H}{\partial \mathbf{r}_\alpha}. \tag{6} \end{align}$$

So, we need to evaluate the derivative $\partial_{\mathbf{r}_\alpha} E_H$.

$$\frac{\partial E_H}{\partial \mathbf{r}_\alpha} = \sum_j q_j \frac{\partial}{\partial \mathbf{r}_\alpha} \frac{\mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3}. \tag{7}$$

There are three cases to consider:

1. $\alpha = j$

2. $\alpha = O$

3. $\alpha = H$

Whenever the atom α is outside the cutoff or is the other H atom on the excited molecule, $\mathbf{F}_\alpha = 0$, because the potential is independent of those atom's positions.

1 Case 1

We begin with case 1, $\alpha = j$, and focus on the derivative

$$\frac{\partial}{\partial \mathbf{r}_j} \frac{\mathbf{r}_{jH} \cdot \hat{\mathbf{r}}_{OH}}{r_{jH}^3}. \tag{8}$$

This is a vector derivative of a scalar. We begin with the x-component of this derivative

$$\frac{\partial}{\partial x_j} \frac{(x_H - x_j)x_{OH} + y_{jH}y_{OH} + z_{jH}z_{OH}}{|\mathbf{r}_H - \mathbf{r}_j|^3 r_{OH}}. \tag{9}$$

The first term is

$$\begin{aligned}
\frac{\partial}{\partial x_j} \frac{(x_H - x_j)x_{OH}}{|\mathbf{r}_H - \mathbf{r}_j|^3 r_{OH}} =& \frac{x_{OH}}{r_{OH}} \frac{\partial}{\partial x_j} (x_H - x_j)|\mathbf{r}_H - \mathbf{r}_j|^{-3} \\
=& \frac{x_{OH}}{r_{OH}} \left(\frac{-1}{|\mathbf{r}_H - \mathbf{r}_j|^3} - 3\frac{(x_H - x_j)}{|\mathbf{r}_H - \mathbf{r}_j|^4} \frac{\partial}{\partial x_j} |\mathbf{r}_H - \mathbf{r}_j| \right) \\
=& \frac{x_{OH}}{r_{OH}} \left(\frac{-1}{|\mathbf{r}_H - \mathbf{r}_j|^3} + 3\frac{(x_H - x_j)^2}{|\mathbf{r}_H - \mathbf{r}_j|^5} \right) \\
=& \frac{x_{OH}}{r_{OH}} \left(\frac{-1}{r_{jH}^3} + 3\frac{x_{jH}^2}{r_{jH}^5} \right)
\end{aligned}$$

where we used

$$\begin{aligned}
\frac{\partial}{\partial x_j} |\mathbf{r}_H - \mathbf{r}_j| =& \frac{\partial}{\partial x_j} \left((x_H - x_j) + (y_H - y_j)^2 + (z_H - z_j)^2 \right)^{1/2} && (10) \\
=& \frac{1}{2|\mathbf{r}_H - \mathbf{r}_j|} 2(x_H - x_j)(-1) && (11) \\
=& -\frac{(x_H - x_j)}{|\mathbf{r}_H - \mathbf{r}_j|} && (12)
\end{aligned}$$

The second term is

$$\begin{aligned}
\frac{\partial}{\partial x_j}\frac{y_{jH}y_{OH}}{|\mathbf{r}_H-\mathbf{r}_j|^3 r_{OH}} =& \frac{y_{jH}y_{OH}}{r_{OH}}\frac{\partial}{\partial x_j}|\mathbf{r}_H-\mathbf{r}_j|^{-3} \\
=& \frac{3y_{jH}y_{OH}}{|\mathbf{r}_H-\mathbf{r}_j|^4 r_{OH}}\frac{\partial}{\partial x_j}|\mathbf{r}_H-\mathbf{r}_j| \\
=& \frac{3y_{jH}y_{OH}(x_H-x_j)}{|\mathbf{r}_H-\mathbf{r}_j|^5 r_{OH}} \\
=& \frac{3y_{jH}y_{OH}x_{jH}}{r_{jH}^5 r_{OH}}
\end{aligned}$$

The third term is identical, with ys replaced by zs. The full result of eq. 9 is

$$\begin{aligned}
&\frac{\partial}{\partial x_j}\frac{x_{jH}x_{OH}+y_{jH}y_{OH}+z_{jH}z_{OH}}{r_{jH}^3 r_{OH}} \\
&\quad= \frac{x_{OH}}{r_{OH}}\left(\frac{-1}{r_{jH}^3}+3\frac{x_{jH}^2}{r_{jH}^5}\right)+\frac{3y_{jH}y_{OH}x_{jH}}{r_{jH}^5 r_{OH}}+\frac{3z_{jH}z_{OH}x_{jH}}{r_{jH}^5 r_{OH}} \\
&\quad= \frac{1}{r_{jH}^3}\left[-\frac{x_{OH}}{r_{OH}}+3\frac{x_{jH}}{r_{jH}^2 r_{OH}}\left(x_{jH}x_{OH}+y_{jH}y_{OH}+z_{jH}z_{OH}\right)\right] \\
&\quad= \frac{1}{r_{jH}^3}\left(-\frac{x_{OH}}{r_{OH}}+3\frac{x_{jH}}{r_{jH}^2 r_{OH}}\mathbf{r}_{jH}\cdot\mathbf{r}_{OH}\right) \\
&\quad= \frac{1}{r_{jH}^3}\left(-\frac{x_{OH}}{r_{OH}}+3\frac{x_{jH}}{r_{jH}}\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}\right)
\end{aligned}$$

The derivatives with respect to the other two dimensions are analogous, giving

$$\frac{\partial}{\partial \mathbf{r}_j}\frac{\mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3} = \frac{3\hat{\mathbf{r}}_{jH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH})-\hat{\mathbf{r}}_{OH}}{r_{jH}^3} \tag{13}$$

Case 1 ($\alpha = j$) corresponds to α within the cutoff but not on the excited molecule. For this case, plugging the result into eq. 7 gives

$$\frac{\partial E_H}{\partial \mathbf{r}_\alpha} = \sum_j q_j \frac{\partial}{\partial \mathbf{r}_\alpha}\frac{\mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3} \tag{14}$$

$$= q_\alpha \frac{3\hat{\mathbf{r}}_{\alpha H}(\hat{\mathbf{r}}_{\alpha H}\cdot\hat{\mathbf{r}}_{OH})-\hat{\mathbf{r}}_{OH}}{r_{\alpha H}^3} \tag{15}$$

2 Case 2

We now turn to case 2, $\alpha = O$. The x-component is

$$\frac{\partial}{\partial x_O}\frac{x_{jH}(x_H-x_O)+y_{jH}y_{OH}+z_{jH}z_{OH}}{r_{jH}^3|\mathbf{r}_H-\mathbf{r}_O|}. \tag{16}$$

The first term is

$$\frac{x_{jH}}{r_{jH}^3}\frac{\partial}{\partial x_O}(x_H - x_O)|\mathbf{r}_H - \mathbf{r}_O|^{-1} = \frac{x_{jH}}{r_{jH}^3}\left(\frac{-1}{|\mathbf{r}_H - \mathbf{r}_O|} - \frac{(x_H - x_O)}{|\mathbf{r}_H - \mathbf{r}_O|^2}\frac{\partial}{\partial x_O}|\mathbf{r}_H - \mathbf{r}_O|\right)$$
$$= \frac{x_{jH}}{r_{jH}^3}\left(\frac{-1}{|\mathbf{r}_H - \mathbf{r}_O|} + \frac{(x_H - x_O)^2}{|\mathbf{r}_H - \mathbf{r}_O|^3}\right)$$
$$= \frac{x_{jH}}{r_{jH}^3}\left(\frac{-1}{r_{OH}} + \frac{x_{OH}^2}{r_{OH}^3}\right)$$

The second term is

$$\frac{y_{jH}y_{OH}}{r_{jH}^3}\frac{\partial}{\partial x_O}|\mathbf{r}_H - \mathbf{r}_O|^{-1} = \frac{y_{jH}y_{OH}x_{OH}}{r_{jH}^3 r_{OH}^3}. \tag{17}$$

Again, the third term is analogous. The full x-component is

$$\frac{\partial}{\partial x_O}\frac{x_{jH}x_{OH} + y_{jH}y_{OH} + z_{jH}z_{OH}}{r_{jH}^3 r_{OH}}$$
$$= \frac{x_{jH}}{r_{jH}^3}\left(\frac{-1}{r_{OH}} + \frac{x_{OH}^2}{r_{OH}^3}\right) + \frac{y_{jH}y_{OH}x_{OH}}{r_{jH}^3 r_{OH}^3} + \frac{z_{jH}z_{OH}x_{OH}}{r_{jH}^3 r_{OH}^3}$$
$$= \frac{1}{r_{jH}^3 r_{OH}}\left(-x_{jH} + \frac{x_{jH}x_{OH}^2}{r_{OH}^2} + \frac{y_{jH}y_{OH}x_{OH}}{r_{OH}^2} + \frac{z_{jH}z_{OH}x_{OH}}{r_{OH}^2}\right)$$
$$= \frac{1}{r_{jH}^3 r_{OH}}\left[-x_{jH} + \frac{x_{OH}}{r_{OH}^2}\left(x_{jH}x_{OH} + y_{jH}y_{OH} + z_{jH}z_{OH}\right)\right]$$
$$= \frac{1}{r_{jH}^3 r_{OH}}\left(-x_{jH} + \frac{x_{OH}}{r_{OH}^2}\mathbf{r}_{jH}\cdot\mathbf{r}_{OH}\right)$$
$$= \frac{1}{r_{jH}^2 r_{OH}}\left(-\frac{x_{jH}}{r_{jH}} + \frac{x_{OH}}{r_{OH}}\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}\right)$$

So, the result for case 2 in vector form is

$$\frac{\partial}{\partial \mathbf{r}_O}\frac{\mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3} = \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{jH}}{r_{jH}^2 r_{OH}} \tag{18}$$

Case 2 ($\alpha = O$) is when α is the oxygen atom on the excited molecule. For this case, plugging the result into eq. 7 gives

$$\frac{\partial E_H}{\partial \mathbf{r}_O} = \sum_j q_j \frac{\partial}{\partial \mathbf{r}_O}\frac{\mathbf{r}_{jH}\cdot\hat{\mathbf{r}}_{OH}}{r_{jH}^3} \tag{19}$$

$$= \sum_j q_j \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{jH}}{r_{jH}^2 r_{OH}} \tag{20}$$

Here, the sum over j goes over all atoms within the cutoff, excluding the excited molecule.

3 Case 3

We now turn to case 3, $\alpha = H$. The x-component is

$$\frac{\partial}{\partial x_H}\frac{(x_H - x_j)(x_H - x_O) + y_{jH}y_{OH} + z_{jH}z_{OH}}{|\mathbf{r}_H - \mathbf{r}_j|^3|\mathbf{r}_H - \mathbf{r}_O|}. \tag{21}$$

The first term is

$$\begin{aligned}
&\frac{\partial}{\partial x_H}(x_H - x_j)(x_H - x_O)|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1} \\
&\quad = (x_H - x_O)|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1} + (x_H - x_j)\frac{\partial}{\partial x_H}(x_H - x_O)|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1} \\
&\quad = \frac{x_{OH}}{r_{jH}^3 r_{OH}} + x_{jH}\left(|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1} + (x_H - x_O)\frac{\partial}{\partial x_H}|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1}\right) \\
&\quad = \frac{x_{OH}}{r_{jH}^3 r_{OH}} + x_{jH}\left[\frac{1}{r_{jH}^3 r_{OH}} + x_{OH}\left(|\mathbf{r}_H - \mathbf{r}_j|^{-3}\frac{\partial}{\partial x_H}|\mathbf{r}_H - \mathbf{r}_O|^{-1} + |\mathbf{r}_H - \mathbf{r}_O|^{-1}\frac{\partial}{\partial x_H}|\mathbf{r}_H - \mathbf{r}_j|^{-3}\right)\right] \\
&\quad = \frac{x_{OH}}{r_{jH}^3 r_{OH}} + x_{jH}\left[\frac{1}{r_{jH}^3 r_{OH}} + x_{OH}\left(-\frac{x_{OH}}{r_{jH}^3 r_{OH}^3} - 3\frac{x_{jH}}{r_{OH} r_{jH}^5}\right)\right] \\
&\quad = \frac{1}{r_{jH}^3 r_{OH}}\left[x_{OH} + x_{jH} - x_{jH}x_{OH}\left(\frac{x_{OH}}{r_{OH}^2} + 3\frac{x_{jH}}{r_{jH}^2}\right)\right]
\end{aligned}$$

The second term is

$$\begin{aligned}
y_{jH}y_{OH}\frac{\partial}{\partial x_H}|\mathbf{r}_H - \mathbf{r}_j|^{-3}|\mathbf{r}_H - \mathbf{r}_O|^{-1} &= y_{jH}y_{OH}\left(-\frac{x_{OH}}{r_{jH}^3 r_{OH}^3} - 3\frac{x_{jH}}{r_{OH} r_{jH}^5}\right) \\
&= -\frac{y_{jH}y_{OH}}{r_{jH}^3 r_{OH}}\left(\frac{x_{OH}}{r_{OH}^2} + 3\frac{x_{jH}}{r_{jH}^2}\right)
\end{aligned}$$

where we used the result from the 3rd through 5th lines above. The full result for the x-component is

$$\begin{aligned}
&\frac{\partial}{\partial x_H}\frac{x_{jH}x_{OH} + y_{jH}y_{OH} + z_{jH}z_{OH}}{r_{jH}^3 r_{OH}} \\
&\quad = \frac{1}{r_{jH}^3 r_{OH}}\left[x_{OH} + x_{jH} - \left(\frac{x_{OH}}{r_{OH}^2} + 3\frac{x_{jH}}{r_{jH}^2}\right)(x_{jH}x_{OH} + y_{jH}y_{OH} + z_{jH}z_{OH})\right] \\
&\quad = \frac{1}{r_{jH}^3 r_{OH}}\left[x_{OH} + x_{jH} - \left(\frac{x_{OH}}{r_{OH}^2} + 3\frac{x_{jH}}{r_{jH}^2}\right)\mathbf{r}_{jH}\cdot\mathbf{r}_{OH}\right]
\end{aligned}$$

Putting all the components together, we have

$$\begin{aligned}
\frac{\partial}{\partial \mathbf{r}_H} \frac{\mathbf{r}_{jH} \cdot \hat{\mathbf{r}}_{OH}}{r_{jH}^3} =& \frac{1}{r_{jH}^3 r_{OH}} \left[\mathbf{r}_{OH} + \mathbf{r}_{jH} - \left(\frac{\mathbf{r}_{OH}}{r_{OH}^2} + 3 \frac{\mathbf{r}_{jH}}{r_{jH}^2} \right) \mathbf{r}_{jH} \cdot \mathbf{r}_{OH} \right] \\
=& \frac{1}{r_{jH}^2} \left[\frac{\hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{jH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3 \frac{\hat{\mathbf{r}}_{jH}}{r_{jH}} \right) \hat{\mathbf{r}}_{jH} \cdot \hat{\mathbf{r}}_{OH} \right]
\end{aligned}$$

Case 3 ($\alpha = H$) is when α is the excited hydrogen atom. For this case, plugging the result into eq. 7 gives

$$\frac{\partial E_H}{\partial \mathbf{r}_H} = \sum_j q_j \frac{\partial}{\partial \mathbf{r}_H} \frac{\mathbf{r}_{jH} \cdot \hat{\mathbf{r}}_{OH}}{r_{jH}^3} \tag{22}$$

$$= \sum_j q_j \frac{1}{r_{jH}^2} \left[\frac{\hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{jH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3 \frac{\hat{\mathbf{r}}_{jH}}{r_{jH}} \right) \hat{\mathbf{r}}_{jH} \cdot \hat{\mathbf{r}}_{OH} \right] \tag{23}$$

Here, the sum over j goes over all atoms within the cutoff, excluding the excited molecule.

4 Summary

So, the force on particle α is given by

$$\mathbf{F}_\alpha = -a \frac{\partial E_H}{\partial \mathbf{r}_\alpha} - 2b E_H \frac{\partial E_H}{\partial \mathbf{r}_\alpha}, \tag{24}$$

where the derivative $\partial_{\mathbf{r}_\alpha} E_H$ is given by

$$\frac{\partial E_H}{\partial \mathbf{r}_\alpha} = \begin{cases}
q_\alpha \dfrac{3\hat{\mathbf{r}}_{\alpha H}(\hat{\mathbf{r}}_{\alpha H} \cdot \hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{OH}}{r_{\alpha H}^3} & \alpha = \text{different molecule} \\
\displaystyle\sum_j q_j \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH} \cdot \hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{jH}}{r_{jH}^2 r_{OH}} & \alpha = \text{excited O} \\
\displaystyle\sum_j q_j \frac{1}{r_{jH}^2} \left[\frac{\hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{jH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3 \frac{\hat{\mathbf{r}}_{jH}}{r_{jH}} \right) \hat{\mathbf{r}}_{jH} \cdot \hat{\mathbf{r}}_{OH} \right] & \alpha = \text{excited H} \\
0 & \alpha = \text{outside cutoff} \\
0 & \alpha = \text{other H on excited molecule}
\end{cases}$$

Here, the sums over j go over all atoms within the cutoff, excluding the excited molecule.

5 Conservation

The total force on the system should be zero.

$$\sum_\alpha \mathbf{F}_\alpha =$$

$$= \sum_j q_j \frac{3\hat{\mathbf{r}}_{jH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{OH}}{r_{jH}^3} + \sum_j q_j \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{jH}}{r_{jH}^2 r_{OH}}$$

$$+ \sum_j q_j \frac{1}{r_{jH}^2}\left[\frac{\hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{jH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3\frac{\hat{\mathbf{r}}_{jH}}{r_{jH}}\right)\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}\right]$$

$$= \sum_j \frac{q_j}{r_{jH}^2}\left[\frac{3\hat{\mathbf{r}}_{jH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}) - \hat{\mathbf{r}}_{jH}}{r_{OH}} + \frac{\hat{\mathbf{r}}_{OH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{jH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3\frac{\hat{\mathbf{r}}_{jH}}{r_{jH}}\right)\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}\right]$$

$$= \sum_j \frac{q_j}{r_{jH}^2}\left[\frac{3\hat{\mathbf{r}}_{jH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH})}{r_{jH}} + \frac{\hat{\mathbf{r}}_{OH}(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH})}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3\frac{\hat{\mathbf{r}}_{jH}}{r_{jH}}\right)\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH}\right]$$

$$= \sum_j \frac{q_j}{r_{jH}^2}\left[\frac{3\hat{\mathbf{r}}_{jH}}{r_{jH}} + \frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} - \left(\frac{\hat{\mathbf{r}}_{OH}}{r_{OH}} + 3\frac{\hat{\mathbf{r}}_{jH}}{r_{jH}}\right)\right](\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH})$$

$$= \sum_j \frac{q_j}{r_{jH}^2}(0)(\hat{\mathbf{r}}_{jH}\cdot\hat{\mathbf{r}}_{OH})$$

$$= 0$$