First observe that the trace of R_q is given by

$$\mathrm{tr}(R_q) = 3a^2 - b^2 - c^2 - d^2,$$

but since $a^2 + b^2 + c^2 + d^2 = 1$, we get $\mathrm{tr}(R_q) = 4a^2 - 1$, so

$$a^2 = \frac{\mathrm{tr}(R_q) + 1}{4}.$$

If $R \in \mathbf{SO}(3)$ is any rotation matrix and if we write

$$R = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33}, \end{pmatrix}$$

we are looking for a unit quaternion $q \in \mathbf{SU}(2)$ such that $R_q = R$. Therefore, we must have

$$a^2 = \frac{\mathrm{tr}(R) + 1}{4}.$$

We also know that

$$\mathrm{tr}(R) = 1 + 2\cos\theta,$$

where $\theta \in [0, \pi]$ is the angle of the rotation R, so we get

$$a^2 = \frac{\cos\theta + 1}{2} = \cos^2\left(\frac{\theta}{2}\right),$$

which implies that

$$|a| = \cos\left(\frac{\theta}{2}\right) \quad (0 \leq \theta \leq \pi).$$

Note that we may assume that $\theta \in [0, \pi]$, because if $\pi \leq \theta \leq 2\pi$, then $\theta - 2\pi \in [-\pi, 0]$, and then the rotation of angle $\theta - 2\pi$ and axis determined by the vector (b, c, d) is the same as the rotation of angle $2\pi - \theta \in [0, \pi]$ and axis determined by the vector $-(b, c, d)$. There are two cases.

Case 1. $\mathrm{tr}(R) \neq -1$, or equivalently $\theta \neq \pi$. In this case $a \neq 0$. Pick

$$a = \frac{\sqrt{\mathrm{tr}(R) + 1}}{2}.$$

Then by equating $R - R^\top$ and $R_q - R_q^\top$, we get

$$\begin{aligned} 4ab &= r_{32} - r_{23} \\ 4ac &= r_{13} - r_{31} \\ 4ad &= r_{21} - r_{12}, \end{aligned}$$