We'll look at the left weak order. This choice is of no substance; $x \leq y$ in the left weak order iff $x^{-1} \leq y^{-1}$ in the right weak order.

In the left weak order on the symmetric group $S_{n}$, given any $w \in S_{n}$ and any $s_{i}$, there exists a covering relation in one direction or the other between $w$ and $s_{i} w$, according to whether $l\left(s_{i} w\right)$ is greater or less than $l(w)$. In either case, the graph arising from the covering relations has an edge $\left(w, s_{i} w\right)$. These are all the covering relations, so these are all the edges.

Left-multiplication by a Coxeter generator $s_{i}=(i i+1)$ has the effect of switching which elements are mapped to $i$ and $i+1$, i.e. exchanging two consecutive integers $i$ and $i+1$ wherever they appear in the permutation
when written out as a list of images. This then is the condition for two permutations $\pi, \pi^{\prime} \in S_{n}$ to be joined by an edge in the weak order.

We claim the same condition identifies the edges of the permutahedron $\Pi_{n}$. We'll identify a permutation $\pi$ with the point $(\pi(1), \ldots, \pi(n))$ whose coordinates it gives.

The edges of $\Pi_{n}$ are by definition exactly the one-dimensional faces, i.e. the one-dimensional subpolytopes which can be realised as the intersection of $\Pi_{n}$ with a hyperplane. So let be given two permutations $\pi, \pi^{\prime} \in S_{n}$, and let $H$ be a hyperplane that intersects $\Pi_{n}$ only in the edge $\left(\pi, \pi^{\prime}\right)$, i.e. such that one of the two open halfspaces delimited by $H$ contains all permutations other than $\pi$ and $\pi^{\prime}$.

Choosing a normal vector $a$ to $H$ of suitable sign, we may assume $\langle\pi, a\rangle=$ $\left\langle\pi^{\prime}, a\right\rangle=: b$ and $\langle\sigma, a\rangle<b$ for any other permutation $\sigma \in S_{n}$. Thus for any $i<j$ in $[n]$ we must have $a_{\pi^{-1}(i)} \leq a_{\pi^{-1}(j)}$, otherwise the permutation $(i j) \pi$, which switches the preimages of $i$ and $j$, would achieve $\langle(i j) \pi, a\rangle>\langle\pi, a\rangle$. For the same reason we have strict inequality $a_{\pi^{-1}(i)}<a_{\pi^{-1}(j)}$ unless $\pi^{\prime}=$ ( $i j$ ) $\pi$. The same is true using $\pi^{\prime}$ in place of $\pi$. Therefore at least two entries of $a$ must be equal, since there's at least one pair $i<j$ such that $\pi^{-1}(i)$ and $\pi^{-1}(j)$ compare in the opposite sense to $\pi^{\prime-1}(i)$ and $\pi^{\prime-1}(j)$. Thus we do have an equality of form $\pi^{\prime}=(i j) \pi$. Furthermore, $i$ and $j$ must be consecutive integers, otherwise we'd have $a_{\pi^{-1}(i)}<a_{\pi^{-1}(i+1)}<a_{\pi^{-1}(j)}=$ $a_{\pi^{-1}(i)}$.

This shows that any edge $\left(\pi, \pi^{\prime}\right)$ of $\Pi_{n}$ has $\pi^{\prime}=(i i+1) \pi$ for some $i$. This is in fact also a sufficient condition. We claim that if we choose $a$ to be any vector with its entries suitably ordered, i.e. such that $a_{\pi^{-1}(i)}=a_{\pi^{-1}(i+1)}$ and $a_{\pi^{-1}(j)}<a_{\pi^{-1}(j+1)}$ for $j \neq i$, and take $b$ to be $\langle\pi, a\rangle=\left\langle\pi^{\prime}, a\right\rangle$, we will realise the edge $\left(\pi, \pi^{\prime}\right)$ as the face defined by the hyperplane $\langle\sigma, a\rangle=b$.

For any $\sigma_{0} \in S_{n}$ distinct from $\pi, \pi^{\prime}$, there will be some pair $i^{\prime}<j^{\prime}$ in $[n]$ not equal to $(i, i+1)$ such that $\sigma_{0}\left(\pi^{-1}(i)\right)>\sigma_{0}\left(\pi^{-1}(i+1)\right)$; and then $\sigma_{1}:=\left(i^{\prime} j^{\prime}\right) \sigma_{0}$ satisfies $\left\langle\sigma_{1}, a\right\rangle>\left\langle\sigma_{0}, a\right\rangle$. Iterating in this way, define a sequence of permutations $\left(\sigma_{k}\right)$ : if ever some $\sigma_{k}$ is $\pi$ or $\pi^{\prime}$, let the sequence terminate; otherwise construct $\sigma_{k+1}$ so that $\left\langle\sigma_{k+1}, a\right\rangle>\left\langle\sigma_{k}, a\right\rangle$. If ever the sequence does terminate, by transitivity among all these inequalities we get $\left\langle\sigma_{0}, a\right\rangle<b$. Otherwise, since $S_{n}$ is finite we must have distinct indices $k, k^{\prime}$ with $\sigma_{k}=\sigma_{k^{\prime}}$; but then transitivity of inequalities gives the contradiction $\left\langle\sigma_{k^{\prime}}, a\right\rangle>\left\langle\sigma_{k}, a\right\rangle$. We conclude that every permutation $\sigma$ other than $\pi$ and $\pi^{\prime}$ lies in the open halfspace $\langle\sigma, a\rangle<b$, as claimed.

