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\skewchar $\langle font \rangle$ [$\langle number \rangle$ parameter]

The \skewchar of a font is the character in the font whose kerns, as defined in the font's metrics file, determine the positions of math accents. That is, suppose that TEX is applying a math accent to the character 'x'. TEX checks if the character pair 'x\skewchar' has a kern; if so, it moves the accent by the amount of that kern. The complete algorithm that TEX uses to position math accents (which involves many more things) is in Appendix G of The TEXbook.

If the value of \s takes the kern value to be zero.

Note that $\langle font \rangle$ is a control sequence that names a font, not a $\langle font-name \rangle$ that names font files. Beware: an assignment to \skewchar is not undone at the end of a group. If you want to change \skewchar locally, you'll need to save and restore its original value explicitly.