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In[1]:= ClearAll["Global`*"]
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$$V = -\frac{1}{2} \mu^2 (\pi^2 + (v + \sigma)^2) + \frac{\lambda}{4} (\pi^2 + (v + \sigma)^2)^2;$$

$$V /. \left\{ v \rightarrow \frac{\mu}{\sqrt{\lambda}} \right\} // \text{FullSimplify} // \text{Expand}$$

$$\text{Out[3]} = \frac{\pi^4 \lambda}{4} - \frac{\mu^4}{4 \lambda} + \pi^2 \sqrt{\lambda} \mu \sigma + \frac{1}{2} \pi^2 \lambda \sigma^2 + \mu^2 \sigma^2 + \sqrt{\lambda} \mu \sigma^3 + \frac{\lambda \sigma^4}{4}$$