We discuss the construction of the two-flavour axion-pion effective Lagrangian at the next-to-leading order (NLO) in chiral perturbation theory and present two phenomenological applications: the scattering $a\pi \to \pi\pi$, relevant for axion thermalization in the early Universe, and the decay rate of a GeV-scale axion-like particle via the channel $a \to \pi\pi\pi$. In both cases we assess, through the NLO computation, the range of validity of the effective field theory and show that the chiral expansion breaks down earlier than what previously assumed. These results call for alternative non-perturbative approaches in order to extend the chiral description of axion-pion interactions.

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1 Introduction

The main ingredient of the axion solution to the strong CP problem [1–4] is the axion coupling to a pseudo-scalar gluon density, which sets model-independent experimental targets for the axion mass and couplings to photons, nucleons, pions and electrons. Since the axion is much lighter than the scale of chiral symmetry breaking $\Lambda_{\chi} \simeq 1$ GeV and it has the same quantum numbers of the neutral pion, chiral perturbation theory ($\chi$PT) provides a natural framework to systematically derive axion properties. In fact, those were obtained long time ago by using leading order (LO) $\chi$PT (or equivalently current algebra) in a series of renowned papers [3, 5–9]. The axion chiral potential and coupling to photons at the next-to-LO (NLO) in $\chi$PT were computed in Ref. [10] (see also [11]), but it is only more recently that the program of “precision” axion physics has restarted with Ref. [12], also motivated by the booming of the axion experimental program (see e.g. [13, 14]). State of the art axion mass calculations are now obtained by employing next-to-NLO (NNLO) $\chi$PT [15] or, alternatively, via lattice QCD techniques [16]. The axion-nucleon interaction Lagrangian instead has been derived in heavy baryon $\chi$PT up to NNLO [17, 18]. Also CP- and flavour-violating axion couplings have witnessed a resurgence of interest in the recent years, with new calculations based either on $\chi$PT or other non-perturbative approaches (see respectively Refs. [19–22] and [23–25]).

In this paper we focus on the axion-pion chiral Lagrangian at NLO. The latter was previously considered in Refs. [10, 12] in the context of the axion potential, hence limited to non-derivative axion interactions, and more generally in Ref. [26], which included also derivative axion couplings. We here expand on the derivation of the NLO axion-pion chiral Lagrangian, by providing several details which were not presented in Ref. [26].

The most interesting application of this formalism consists in the calculation of the $a\pi \rightarrow \pi\pi$ scattering, which provides the dominant channel for axion thermalization in the early Universe [27, 28], when the axion decouples from the thermal bath at temperatures below that of QCD deconfinement $T_c \simeq 155$ MeV [29–31]. The highest attainable axion mass from cosmological constraints on thermally-produced axions is known as the axion hot dark matter bound. However, as shown in Ref. [26], this bound was mainly extracted from a temperature regime, $T \gtrsim 60$ MeV, where the chiral approach to axion-pion scattering breaks down. Lacking for the moment a way to extrapolate the validity of $\chi$PT, a practical solution was given in Refs. [32, 33] which proposed an interpolation of the thermalization rate starting from the high-temperature region above $T_c$. See Refs. [34, 35] for recent cosmological analyses adopting this latter approach.

Another application of the axion-pion chiral Lagrangian arises in the context of GeV-scale axion-like particles (ALPs) which dominantly decay hadronically as soon as the phase space for the channel $a \rightarrow \pi\pi\pi$ is kinematically open. For phenomenological studies related to this channel, see e.g. Refs. [36, 37]. This process was computed at LO in $\chi$PT in Refs. [38, 39] and the chiral expansion was claimed to be valid up to ALP masses of order $4\pi f_a \simeq 1.6$ GeV. However, by explicitly computing the NLO correction, we find that the effective field theory (EFT) breaks down much earlier, namely for ALP masses just above the kinematical threshold $m_a \gtrsim 3m_\pi$. Hence, in practice, $\chi$PT never yields an accurate description for the process at hand.
The paper is structured as follows: in Sect. 2 we detail the construction of the axion-pion chiral Lagrangian, while the calculation of the two processes \( a\pi \rightarrow \pi\pi \) and \( a \rightarrow \pi\pi\pi \) up to NLO in \( \chi PT \) is provided in Sect. 3. We conclude in Sect. 4, where we highlight some general expectations for the range of validity of the EFT and advocate possible strategies to extend the validity of the chiral description. Further details on the NLO calculations are provided in Apps. A–C.

### 2 Axion-pion effective field theory

The construction of the LO axion-pion Lagrangian was originally discussed in Refs. [6, 9]. We first recall its basic ingredients (see also [27, 38–40]) in view of the extension at NLO, which was recently discussed in Ref. [26]. We here complement the latter derivation by providing several details which were omitted in Ref. [26]. In particular, we will focus on the 2-flavour formulation, which is best suited for the applications to be discussed in Sect. 3. This is because the presence of strange mesons as external states is kinematically suppressed. On the other hand, the generalization to the 3-flavour case is in principle straightforward. In the following we will generically indicate both the QCD axion and the ALP as “axion”, specifying when needed which case we are considering.

#### 2.1 Axion-QCD effective Lagrangian

The 2-flavour axion effective Lagrangian in terms of quarks and gluons reads

\[
\mathcal{L}_{QCD}^{a} = \frac{1}{2} (\partial_{\mu} a)^2 - \frac{1}{2} m_{a,0}^2 a^2 + \frac{\alpha_s}{8\pi} f_a \vec{G} \cdot \vec{G} - \bar{q}_L M_q q_R + \text{h.c.} \\
+ \frac{\partial_{\mu} a}{2f_a} q_c^0 \gamma^\mu \gamma_5 q + \frac{1}{4} g_{a\gamma}^0 a F \tilde{F},
\]

(2.1)

where \( q = (u, d)^T, M_q = \text{diag}(m_u, m_d) \), \( \vec{G} = \frac{1}{2} \epsilon^{\mu\nu\rho\sigma} G_{A\mu
u} G_{A\rho\sigma} \) and \( F \tilde{F} = \frac{1}{2} \epsilon^{\mu\nu\rho\sigma} F_{\mu\nu} F_{\rho\sigma} \), with \( \epsilon^{0123} = -1 \). For the QCD axion \( m_{a,0}^2 = 0 \), while \( m_{a,0}^2 \neq 0 \) for the ALP case. The couplings \( c^0_q = \text{diag}(c^0_u, c^0_d) \) and \( g_{a\gamma}^0 \) are model-dependent. For instance, \( c^0_u = 0 \) and \( g_{a\gamma}^0 = 0 \) in the KSVZ model [41, 42], while \( c^0_u = \frac{1}{3} \cos^2 \beta, c^0_d = \frac{1}{3} \sin^2 \beta \) and \( g_{a\gamma}^0 = \alpha/(2\pi f_a) 8/3 \) in the DFSZ model [43, 44] (with \( \tan \beta = v_u/v_d \) the ratio between the vacuum expectation values of the two Higgs doublets present in the DFSZ model).

Upon an anomalous axial rotation of the quark doublet

\[
q \rightarrow e^{i\gamma_5 \frac{2f_a}{\alpha}} Q_a q,
\]

(2.2)

with \( \text{Tr} Q_a = 1 \), the \( a\vec{G} \vec{G} \) term in Eq. (2.1) is shifted away, and the Lagrangian in Eq. (2.1) becomes

\[
\mathcal{L}_a^{QCD} = \frac{1}{2} (\partial_{\mu} a)^2 + \frac{1}{2} m_{a,0}^2 a^2 - (\bar{q}_L M_q q_R + \text{h.c.}) + \frac{\partial_{\mu} a}{2f_a} \bar{q} c^0_q \gamma^\mu \gamma_5 q + \frac{1}{4} g_{a\gamma} a F \tilde{F},
\]

(2.3)
where we have redefined the parameters as
\[ M_a = e^{i\pi_0 Q_a} M_q e^{i\pi_0 Q_a}, \quad c_q = c_q^0 - Q_a, \quad g_{a\gamma} = g_{a\gamma}^0 - \frac{3\alpha}{2\pi f_a} \text{Tr} (Q_a Q_{EM})^2, \] (2.4)
with \( Q_{EM} = \text{diag}(2/3, -1/3) \).

### 2.2 Axion-pion Lagrangian at LO

At energies \( \lesssim 1 \text{ GeV} \), the axion-QCD effective Lagrangian is replaced by the axion chiral Lagrangian, which at the LO reads
\[
\mathcal{L}_a^{(LO)} = \frac{1}{2} (\partial \mu a)^2 - \frac{1}{2} m_{a,0}^2 a^2 + \frac{f^2}{4} \text{Tr} \left[ (D^\mu U)^\dagger D_\mu U + U \chi_a^\dagger + \chi_a U^\dagger \right]
+ \frac{\partial^\mu a}{2f_a} \text{Tr} [c_q \sigma^a] J_{A,\mu}^{a|\text{LO}},
\] (2.5)
where \( f_\pi = 92.21 \text{ MeV} \), \( \chi_a = 2B_0 M_a \) (with \( B_0 \) denoting the quark condensate) and \( \sigma^a \) \((a = 1, 2, 3)\) the Pauli matrices. \( U = e^{i\pi^a \sigma^a / f_\pi} \) is the pion Goldstone matrix, with
\[
\pi^a \sigma^a = \left( \begin{array}{c} \pi_0 \\ \sqrt{2} \pi_- \end{array} \right).
\] (2.6)
The pion axial current, \( J_{A,\mu}^{a|\text{LO}} \), reads at the LO (see App. A)
\[
J_{A,\mu}^{a|\text{LO}} = \frac{i f_\pi^2}{4} \text{Tr} \left[ \sigma^a \{ U, (D_\mu U)^\dagger \} \right],
\] (2.7)
defined in terms of the covariant derivative \( D_\mu U = \partial_\mu U - ir_\mu U + iU l_\mu \), with \( r_\mu = \frac{\sigma^a}{2} a^a \) and \( l_\mu = l_\mu^a \sigma^a / 2 \) external fields which can be used to include electromagnetic or weak effects. The matching of the derivative axion term in Eq. (2.5) with the corresponding one in Eq. (2.3) has been obtained by rewriting
\[
\bar{q}_i [c_q] \gamma^\mu \gamma_5 q_j = \frac{1}{2} \left( \text{Tr} [c_q] \bar{q}_i \gamma^\mu \gamma_5 q_j + \text{Tr} [c_q \sigma^a] \bar{q}_i \gamma^\mu \gamma_5 \frac{\sigma^a}{2} q_j \right),
\] (2.8)
where we used the Fierz identity \( \sigma_{ij} \sigma_{kl} = 2(\delta_{il} \delta_{jk} - \frac{1}{2} \delta_{ij} \delta_{kl}) \). The iso-singlet current is associated to the heavy \( \eta' \) and it can be neglected for our purposes, while the iso-triplet quark axial current is replaced with the pion axial current in Eq. (2.7).

In the following, we set \( Q_a = M_q^{-1}/\text{Tr} M_q^{-1} \), so that terms linear in \( a \) (including \( a-\pi^0 \) mass mixing) drop out from Eq. (2.5) and the only linear axion term arise from the derivative interaction with the pion axial current. Explicitly, the derivative axion coupling reads
\[
\text{Tr} [c_q \sigma^a] = \left( \frac{m_u - m_d}{m_u + m_d} + c_u^0 - c_d^0 \right) \delta^{a3}.
\] (2.9)
Expanding the pion axial current \( J_{A,\mu}^{a}|_{\text{LO}} = f_{\pi} \partial_{\mu} \bar{\pi}^{a} - \frac{1}{f_{\pi}} \pi^{2} \partial_{\mu} \pi^{a} - \frac{3}{2f_{\pi}} \pi^{a} \partial_{\mu} \pi^{2} + \ldots \), with \( \pi = \sqrt{\pi_{0}^{2} + 2\pi_{+}\pi_{-}} \), the axion-pion derivative terms are given by
\[
\frac{\partial^{\mu} a}{2f_{a}} \text{Tr} \left[ c_{q} \sigma^{a} \right] J_{A,\mu}^{a}|_{\text{LO}} \simeq -\frac{1}{2} \left( \frac{m_{d} - m_{u}}{m_{u} + m_{d}} + c_{d}^{0} - c_{u}^{0} \right) \frac{f_{\pi}}{f_{a}} \partial_{\mu} a \partial^{\mu} \pi_{0}^{a} \frac{1}{3} \left( \frac{m_{d} - m_{u}}{m_{u} + m_{d}} + c_{d}^{0} - c_{u}^{0} \right) \frac{1}{f_{a} f_{\pi}} \partial_{\mu} \left( 2\partial^{\mu} \pi_{0} \partial_{\mu} \pi_{-}^{0} - \pi_{0} \partial_{\mu} \pi_{+}^{0} - \pi_{0} \pi_{+}^{0} \partial_{\mu} \pi_{-}^{0} \right).
\]

The first operator introduces a kinetic mixing between the axion and the neutral pion, parametrized by the coefficient
\[
\epsilon \equiv -\frac{f_{\pi}}{2f_{a}} \left( \frac{m_{d} - m_{u}}{m_{d} + m_{u}} + c_{d}^{0} - c_{u}^{0} \right).
\]

At the quadratic level the \( a-\pi_{0}^{0} \) Lagrangian reads
\[
\mathcal{L}_{a-\pi_{0}^{0}}^{\text{quad}} = \frac{1}{2} \left( \partial_{\mu} a \partial_{\mu} \pi_{0}^{0} \right) K_{\text{LO}}^{a} \left( \partial^{\mu} a \partial_{\mu} \pi_{0}^{0} \right) - \frac{1}{2} \left( a \pi_{0}^{0} \right) M_{\text{LO}}^{2} \left( a \pi_{0}^{0} \right),
\]
with
\[
K_{\text{LO}}^{a} = \begin{pmatrix} 1 & \epsilon \\ \epsilon & 1 \end{pmatrix}, \quad M_{\text{LO}}^{2} = \begin{pmatrix} m_{a}^{2} & 0 \\ 0 & m_{\pi}^{2} \end{pmatrix}
\]
and \( m_{a}^{2} = m_{a,0}^{2} + m_{a,\text{QCD}}^{2} \), where
\[
m_{a,\text{QCD}}^{2} = \frac{m_{u} m_{d}}{(m_{u} + m_{d})^{2}} \frac{m_{\pi}^{2} f_{\pi}^{2}}{f_{a}^{2}} \simeq 5.7 \left( \frac{10^{12} \text{ GeV}}{f_{a}} \right) \mu \text{eV},
\]
is the QCD axion mass squared at the LO. The procedure in order to diagonalize the quadratic Lagrangian in Eq. (2.12) consists of three steps: \( i \) diagonalization of the kinetic term by an orthogonal transformation, \( ii \) re-scaling of the fields to have a canonical kinetic term and \( iii \) diagonalization of the mass matrix (rotated and re-scaled after steps \( i \) and \( ii \)). The first orthogonal rotation
\[
R_{1} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}
\]
gives
\[
R_{1}^{T} K_{\text{LO}} R_{1} = \begin{pmatrix} 1 - \epsilon & 0 \\ 0 & 1 + \epsilon \end{pmatrix}.
\]

Therefore the re-scaling is given by (fields need to be multiplied by the inverse of \( W \))
\[
W = \begin{pmatrix} \frac{1}{\sqrt{1 - \epsilon}} & 0 \\ 0 & \frac{1}{\sqrt{1 + \epsilon}} \end{pmatrix}.
\]
The action of $R_1$ and $W$ on the mass matrix puts it in the form

$$\hat{M}_{\text{LO}}^2 = W R_1^T M_{\text{LO}}^2 R_1 W = \frac{1}{2} \begin{pmatrix} m_a^2 + m_\pi^2 & m_a^2 - m_\pi^2 \\ m_\pi^2 - m_a^2 & m_a^2 + m_\pi^2 \end{pmatrix} \begin{pmatrix} \frac{1 - \epsilon}{\sqrt{1 - \epsilon^2}} & \frac{\sqrt{1 - \epsilon^2}}{m_a^2 + m_\pi^2} \\ \frac{\sqrt{1 - \epsilon^2}}{m_a^2 - m_\pi^2} & \frac{1 + \epsilon}{\sqrt{1 - \epsilon^2}} \end{pmatrix}, \quad (2.18)$$

whose eigenvalues are $m_\pi^2$ and $m_a^2$ plus corrections of $O(\epsilon^2)$ for the pion and ALP masses, and $O(\epsilon^4)$ for the QCD axion mass (considering $m_a/m_\pi \sim O(\epsilon)$ in the QCD axion case).

Denoting by $R_2$ the matrix that diagonalizes Eq. (2.18) as $R_2^T \hat{M}_{\text{LO}}^2 R_2$, one obtains that the complete rotation that needs to be applied to the fields $(a, \pi_0)$ in order to fully diagonalize the quadratic Lagrangian in Eq. (2.12) is given by

$$R = (R_1 W R_2)^{-1} = \begin{pmatrix} 1 - \frac{\epsilon m_a^4}{2(m_a^2 - m_\pi^2)^2} & -\frac{\epsilon m_\pi^2}{m_a^2 - m_\pi^2} \\ \frac{\epsilon m_a^4}{m_a^2 - m_\pi^2} & 1 + \frac{\epsilon^2 m_\pi^4}{2(m_a^2 - m_\pi^2)^2} \end{pmatrix}. \quad (2.19)$$

Neglecting $O(\epsilon^2)$ terms in $R^{-1}$, we finally obtain

$$a = a_{\text{phys}} + \frac{\epsilon m_\pi^2}{m_a^2 - m_\pi^2} \pi_{0\text{phys}}, \quad (2.20)$$

$$\pi_0 = \pi_{0\text{phys}} - \frac{\epsilon m_a^4}{m_a^2 - m_\pi^2} a_{\text{phys}}, \quad (2.21)$$

where $(a_{\text{phys}}, \pi_{0\text{phys}})$ denote fields with diagonal propagators. In the following, we drop the subscript “phys” when working in the diagonal basis.

After the LO diagonalization procedure, the LO chiral Lagrangian containing the axion-pions interaction terms is given by (including the contribution due to Eq. (2.21) from the standard 4-pion Lagrangian)

$$L_{a\pi}^{\chi(\text{LO})} = \frac{C_{a\pi}}{2 f_a f_\pi (m_a^2 - m_\pi^2)} \left\{ (m_a^2 - 2m_\pi^2) \partial_\mu a \left( 2 \partial_\mu \pi_0 \pi_+ \pi_- - \pi_0 \partial_\mu \pi_+ \pi_- - \pi_0 \pi_+ \partial_\mu \pi_- \right) + m_a^2 a \left( m_\pi^2 (\pi_0 \pi_+ \pi_- + \frac{1}{2} \pi_0^3) - 2 \pi_0 \partial_\mu \pi_+ \partial^\mu \pi_- + \partial_\mu \pi_0 (\partial^\mu \pi_+ \pi_- + \partial^\mu \pi_- \pi_+) \right) \right\}, \quad (2.22)$$

with

$$C_{a\pi} = \frac{1}{3} \left( \frac{m_d}{m_u + m_d} + c_d^0 - c_u^0 \right). \quad (2.23)$$

The QCD axion case is recovered in the $m_a^2 \to 0$ limit.
2.3 Axion-pion Lagrangian at NLO

The axion-pion Lagrangian beyond LO requires two ingredients: the $\mathcal{O}(p^4)$ chiral Lagrangian with the axion-dressed coefficient $\chi_a = 2B_0 M_a$ (cf. Eq. (2.4)) and the derivative axion interaction with the NLO pion axial current. The 2-flavour chiral Lagrangian at NLO can be expressed in various equivalent bases. Here we stick to the expression given by Gasser and Leutwyler [45], which in the standard trace notation reads [46]

$$\mathcal{L}_a^{(\text{NLO})} = \frac{\ell_1}{4} \left\{ \text{Tr} \left[ D_\mu U (D^\mu U) \right] \right\}^2 + \frac{\ell_2}{4} \text{Tr} \left[ D_\mu U (D^\nu U) \right] \text{Tr} \left[ D^\mu U (D^\nu U) \right]$$

$$+ \frac{\ell_3}{16} \left[ \text{Tr} \left( \chi_a U^\dagger + U \chi_a \right)^2 \right] + \frac{\ell_4}{4} \text{Tr} \left[ D_\mu U (D^\mu \chi_a) + D_\mu \chi_a (D^\mu U) \right]$$

$$+ \ell_5 \left[ \text{Tr} \left( f_{\mu \nu}^R f_{\nu L}^\mu \right) - \frac{1}{2} \text{Tr} \left( f_{\mu \nu}^L f_{\nu L}^\mu + f_{\mu \nu}^R f_{\nu R}^\mu \right) \right]$$

$$+ \frac{i \ell_6}{2} \text{Tr} \left[ f_{\mu \nu}^R D^\mu U (D^\nu U) + f_{\mu \nu}^L (D^\mu U)^\dagger D^\nu U \right]$$

$$- \frac{\ell_7}{16} \left[ \text{Tr} \left( \chi_a U^\dagger - U \chi_a \right)^2 \right] + \frac{h_1 + h_3}{4} \text{Tr} \left( \chi_a U^\dagger \chi_a \right) + \frac{h_1 - h_3}{16} \left[ \text{Tr} \left( \chi_a U^\dagger + U \chi_a \right)^2 \right]$$

$$+ \left[ \text{Tr} \left( \chi_a U^\dagger - U \chi_a \right)^2 \right] - 2 \text{Tr} \left( \chi_a U^\dagger \chi_a U^\dagger + U \chi_a U \chi_a \right) \right\} - 2h_2 \text{Tr} \left( f_{\mu \nu}^L f_{\nu L}^\mu + f_{\mu \nu}^R f_{\nu R}^\mu \right)$$

$$+ \frac{\partial^\mu a}{2f_a} \text{Tr} \left[ c_\sigma a \sigma^a \right] J_{A,\mu}^{a} (\text{NLO}).$$

The low-energy constants $\ell_1, \ell_2, \ldots, \ell_7$ are not fixed by chiral symmetry, but they need to be determined from experimental data or lattice QCD. The constants $h_1, h_2, h_3$ are coupled to pion-independent terms (see Eq. (2.26) below). Hence, in a theory without axions they would be of no physical relevance. The $f_{\mu \nu}^{R,L}$ are the field strength tensors associated to the fields $r_\mu$ and $l_\mu$ appearing in the covariant derivative (see [45] for details).

The NLO chiral left (right) current is obtained by differentiating the NLO Lagrangian with respect to the external field $l_\mu$ ($r_\mu$). Taking the axial combination of the chiral currents (see App. A) one obtains

$$J_{A,\mu}^{a} (\text{NLO}) = i \frac{\ell_2}{2} \text{Tr} \left[ \sigma^a \{ D_\mu U^\dagger, U \} \right] \text{Tr} \left[ D_\nu U D^\nu U^\dagger \right]$$

$$+ i \frac{\ell_2}{4} \text{Tr} \left[ \sigma^a \{ D^\nu U^\dagger, U \} \right] \text{Tr} \left[ D_\mu U D^\nu U^\dagger + D_\nu U D^\mu U \right]$$

$$- i \frac{\ell_4}{8} \text{Tr} \left[ \sigma^a \{ D_\mu U, \chi_a \} - \sigma^a \{ U, D_\mu \chi_a \} + \sigma^a \{ D_\mu \chi_a, U^\dagger \} \right]$$

$$+ \frac{\ell_6}{4} \text{Tr} \left[ f_{\mu \nu}^{R} \{ \sigma^a, D^\nu U \} U^\dagger + f_{\mu \nu}^{R} U \{ D^\nu U^\dagger, \sigma^a \} + f_{\mu \nu}^{L} U^\dagger \{ \sigma^a, D^\nu U \} + f_{\mu \nu}^{L} [D^\nu U^\dagger, \sigma^a] U \right].$$

Being interested only in axion-pion interactions, from now on we will set to zero the field strength tensors as well as the external currents. Then the axion-pion Lagrangian up to NLO is given by the sum $\mathcal{L}_a^{(\text{LO})} + \mathcal{L}_a^{(\text{NLO})}$. 

7
Note that the NLO terms reintroduce a quadratic mixing of the axion field with the neutral pion. In App. B we explicitly repeat the diagonalization procedure at NLO, including as well one-loop terms from the LO chiral Lagrangian. In fact, the choice $Q_a = M_a^{-1}/\text{Tr} M_a^{-1}$ allows us to eliminate only some of the mass mixing terms at NLO. On the other hand, no axion-pion mixing arises from the term proportional to $h_1 - h_3$ in Eq. (2.24), since the latter does not depend on the pion field. This is readily seen by using the identity

\[
\left[ \text{Tr} \left( \chi_a U^\dagger + U \chi_a^\dagger \right) \right]^2 + \left[ \text{Tr} \left( \chi_a U^\dagger - U \chi_a^\dagger \right) \right]^2 - 2\text{Tr} \left( \chi_a U^\dagger \chi_a U^\dagger + U \chi_a^\dagger U \chi_a^\dagger \right)
= \left[ \text{Tr}(\chi_a) \right]^2 + \left[ \text{Tr}(\chi_a^\dagger) \right]^2 - \left[ \text{Tr}(\sigma_a^\dagger \chi_a^\dagger) \right]^2.
\]

(2.26)

The remaining axion-pion mass mixing is found to be

\[
\mathcal{L}_a^{(\text{NLO})} \supset a \pi_0 \frac{m_\pi^4}{\ell_4 f_\pi (m_a^2 - m_\pi^2)} \left\{ - 3C_{a\pi} \ell_3 m_a^2 + \ell_7 (m_d - m_u) \left[ 3C_{a\pi} \frac{m_a^2}{m_u + m_d} - \frac{4m_d m_u m_\pi^2}{(m_d + m_u)^2} \right] \right\}.
\]

(2.27)

Considering instead derivative terms, at NLO the pion axial current gives rise to the following kinetic mixing term

\[
\frac{\partial \mu a}{2f_a} \left[ c_q \sigma^a \right] J_{A,\mu}^{a\pi} |_{\text{NLO}} \supset - \frac{3}{2} \frac{m_\pi^2}{\ell_4 f_\pi} C_{a\pi} q^\mu \partial_\mu \pi_0.
\]

(2.28)

Besides those tree-level mixings, the axion and the neutral pion also mix through one-loop diagrams, generated by the LO terms in Eq. (2.22).

### 3 Two applications at NLO

We next present two applications of the axion-pion chiral Lagrangian at NLO. The first one is the calculation of the $a\pi \rightarrow \pi \pi$ scattering, previously computed at LO in Refs. [27, 28], which is a crucial ingredient for the axion thermalization rate in the early Universe. The latter can be cast as an expansion in $T/f_\pi$, and through the explicit calculation of the NLO correction we will show that the chiral expansion breaks down for $T \gtrsim 60 \text{ MeV}$ [26]. The second application consists in the calculation of the decay rate $a \rightarrow \pi \pi \pi$, that is one of the leading hadronic channels for GeV-scale ALPs. This process has been previously computed at the LO in Refs. [38, 39]. In this case we will show, through the NLO calculation, that the $\chi$PT expansion breaks just above the kinematical threshold $m_a \gtrsim 3m_\pi$.

The two calculations, which share similar technical issues, will be carried out by retaining the axion-pion mixing at NLO explicitly, i.e. through the Lehmann-Symanzik-Zimmermann (LSZ) formalism [49]. In App. B we provide instead an alternative calculation (only for the case of $a\pi \rightarrow \pi \pi$ scattering) in which the axion-pion mixing is first removed via a direct NLO diagonalization of the axion-pion propagator.
3.1 $a\pi \to \pi\pi$ scattering

Considering different charge eigenstates, we want to compute the processes $a\pi_0 \to \pi_+\pi_-$, $a\pi_+ \to \pi_+\pi_0$ and $a\pi_- \to \pi_-\pi_0$, and the corresponding sum of squared matrix elements

$$\sum |M|^2 = |M_{a\pi_0 \to \pi_+\pi_-}|^2 + |M_{a\pi_+ \to \pi_+\pi_0}|^2 + |M_{a\pi_- \to \pi_-\pi_0}|^2,$$

(3.1)

which enters into the axion-pion thermalization rate (cf. Eq. (3.19)). After briefly recalling the LO result, we will present the calculation of the NLO amplitudes and their contribution to the axion-pion thermalization rate.

3.1.1 LO amplitude

Let us start by considering the amplitude $a(p_1)\pi_0(p_2) \to \pi_+(p_3)\pi_-(p_4)$. We will consistently neglect terms of $\mathcal{O}(1/f_a)^2$. From the contact interaction in Eq. (2.22) (with $m_a \to 0$) one gets the matrix element

$$iM_{a\pi_0 \to \pi_+\pi_-} = -i\frac{C_{a\pi}}{f_a f_\pi} [2p_1 \cdot p_2 + p_1 \cdot p_3 + p_1 \cdot p_4] = i\frac{C_{a\pi}}{f_a f_\pi} \frac{3}{2} [m_\pi^2 - s],$$

(3.2)

where in the last step we have employed the Mandelstam variables, defined as

$$s = (p_1 + p_2)^2 = 2p_1 \cdot p_2 + m_\pi^2,$$

$$t = (p_1 - p_3)^2 = -2p_1 \cdot p_3 + m_\pi^2,$$

$$u = (p_1 - p_4)^2 = -2p_1 \cdot p_4 + m_\pi^2.$$

(3.3)

The crossed amplitude $a\pi_+ \to \pi_+\pi_0$ ($a\pi_- \to \pi_-\pi_0$) is obtained replacing $p_2 \leftrightarrow -p_4$ ($p_2 \leftrightarrow -p_3$), which is equivalent to substituting $s$ with $u$ ($t$), namely

$$iM_{a\pi_+ \to \pi_+\pi_0} = i\frac{C_{a\pi}}{f_a f_\pi} \frac{3}{2} [m_\pi^2 - u],$$

(3.4)

$$iM_{a\pi_+ \to \pi_+\pi_0} = i\frac{C_{a\pi}}{f_a f_\pi} \frac{3}{2} [m_\pi^2 - t].$$

(3.5)

Summing the squared matrix elements leads to the LO result [27, 28]

$$\sum |M|_{LO}^2 = \left( C_{a\pi} \frac{3}{2} \frac{C_{a\pi}}{f_a f_\pi} \right)^2 \frac{9}{4} [s^2 + t^2 + u^2 - 3m_\pi^4].$$

(3.6)

3.1.2 NLO amplitude

We now consider the NLO axion-pion scattering amplitude, retaining explicitly the $a-\pi_0$ mixing at one loop. It is convenient to work in a basis where the lowest-order, $\mathcal{O}(p^2)$, mixing has been diagonalized via Eqs. (2.20)–(2.21) and the remaining mixing is of $\mathcal{O}(p^4)$. Employing the LSZ reduction formula [49] the amplitude is given by (focussing e.g. on the $a\pi_0 \to \pi_+\pi_-$ channel, see Fig. 1)

$$M_{a\pi_0 \to \pi_+\pi_-} = \frac{1}{\sqrt{Z_a Z_\pi}} \Pi_{a=1}^4 \lim_{p_0^2 \to m_a^2} (p_0^2 - m_0^2) \times G_{a\pi_0 \to \pi_+\pi_-}(p_1, p_2, p_3, p_4),$$

(3.7)
The index $\alpha$ runs over the external particles, $Z_a$ ($Z_\pi$) is the wave-function renormalization of the axion (pion) field defined via the residue of the 2-point Green’s functions

$$G_{\alpha\alpha}(p^2_{\alpha} \simeq m_{\alpha}^2) = \frac{iZ_{\alpha}}{p^2_{\alpha} - m_{\alpha}^2}, \quad (3.8)$$

while the full 4-point Green’s function is given by

$$G_{a\pi_0 \rightarrow \pi_+ \pi_-} = \sum_{i,j=a,\pi_0} G_{ij \rightarrow \pi_+ \pi_-} \times G_{\pi_+ \pi_+}(m_{\pi}^2)G_{\pi_- \pi_-}(m_{\pi}^2)G_{a\pi}(m_{a}^2 = 0)G_{\pi_0 j}(m_{\pi}^2). \quad (3.9)$$

The first term is the amputated 4-point function, multiplied by the 2-point functions of the external legs with the axion mass set to zero. Working with LO diagonal propagators, the 2-point amplitude for the $a-\pi_0$ system reads

$$\mathcal{P}_{ij} = \text{diag}(p^2, p^2 - m_{\pi}^2) - \Sigma_{ij}, \quad (3.10)$$

where $\Sigma_{ij}$ encodes NLO corrections including mixings. The 2-point Green’s function is hence

$$G_{ij} = (-i\mathcal{P})^{-1}_{ij} = i \begin{pmatrix} \frac{1}{p^2} & \frac{\Sigma_{\pi\pi}}{p^2(p^2 - m_{\pi}^2 - \Sigma_{\pi\pi})} \\ \frac{\Sigma_{a\pi}}{p^2(p^2 - m_{\pi}^2 - \Sigma_{\pi\pi})} & \frac{1}{p^2 - m_{\pi}^2 - \Sigma_{a\pi}} \end{pmatrix}. \quad (3.11)$$

Expanding the diagonal terms around the physical masses we get (see Eq. (B.7))

$$Z_a = 1 \quad Z_\pi = 1 + \Sigma'_{\pi\pi}(m_{\pi}^2), \quad (3.12)$$

with primes indicating derivatives with respect to $p^2$. Then, by plugging Eq. (3.9) and (3.11) into the LSZ formula for the scattering amplitude and neglecting $O(1/f_a)^2$ terms,
one finds

\[ \mathcal{M}_{a\pi_0\rightarrow\pi_+\pi_-} = \left(1 + \frac{3}{2} \Sigma'_{\pi\pi}(m_\pi^2)\right) G_{a\pi_0\rightarrow\pi_+\pi_-}^{\text{LO}} - \frac{\Sigma_{a\pi}(m_\pi^2 = 0)}{m_\pi^2} G_{0\pi_0\rightarrow\pi_+\pi_-}^{\text{LO}} + G_{a\pi_0\rightarrow\pi_+\pi_-}^{\text{NLO}}, \]  

(3.13)

where the \( G \)'s are evaluated at the physical masses of the external particles.

We report here the expressions of the LO Green’s functions and the NLO two points functions, which are given by

\[ G_{a\pi_0\rightarrow\pi_+\pi_-}^{\text{LO}} = \frac{C_{a\pi}}{f_\pi f_a} \frac{3}{2} \left[m_\pi^2 - s\right], \]  

(3.14)

\[ G_{0\pi_0\rightarrow\pi_+\pi_-}^{\text{LO}} = \frac{2m_\pi^2 - 3s}{3f_\pi^2}, \]  

(3.15)

\[ \Sigma'_{\pi\pi} = \frac{2I}{3f_\pi^2}, \]  

(3.16)

\[ \Sigma_{a\pi}(p^2) = 3C_{a\pi} p^2 \left[\frac{\ell_i m_\pi^2}{2f_a f_\pi} - \frac{2I}{3f_a f_\pi}\right] - \frac{4\ell_i (m_d - m_u) m_a m_d m_\pi^4}{f_a f_\pi (m_u + m_d)^3}, \]  

(3.17)

with \( I \) defined in Eq. (B.4). The one-loop diagrams entering the Green’s function \( G_{a\pi_0\pi_+\pi_-}^{\text{NLO}} \) are shown in Fig. 2, and the full renormalized NLO amplitude for the \( a\pi_0 \rightarrow \pi_+\pi_- \) process (and its crossed channels) is given in Eq. (B.23).

The one-loop amplitudes have been computed in dimensional regularization. To carry out the renormalization procedure in the (modified) \( \text{MS} \) scheme, we define the scale-independent parameters \( \ell_i \) as \( [45] \)

\[ \ell_i = \frac{\gamma_i}{32\pi^2} \left[\ell_i + R + \ln \left(\frac{m_\pi^2}{\mu^2}\right)\right], \]  

(3.18)

with \( R = \frac{2}{d-4} - \log(4\pi) + \gamma_E - 1 \), in order to cancel the divergent terms (in the limit \( d = 4 \)) with a suitable choice of the \( \gamma_i \) coefficients. Eventually, only the terms proportional to \( \ell_{1,2,7} \) contribute to the NLO amplitude, which is renormalized for \( \gamma_1 = 1/3, \gamma_2 = 2/3 \) and \( \gamma_7 = 0 \) (see App. B). The latter coefficients coincide with the values obtained for the standard chiral theory \( [45] \).
3.1.3 Axion-pion thermalization rate

The crucial quantity needed to extract the axion hot dark matter bound is the axion decoupling temperature, $T_D$, obtained via the freeze-out condition $\Gamma_a(T_D) \simeq H(T_D)$, where $H(T)$ is the Hubble expansion rate and $\Gamma_a$ is the axion-pion thermalization rate, defined as

$$\Gamma_a = \frac{1}{n_{eq}^a} \int \frac{d^3p_1}{(2\pi)^3} \frac{d^3p_2}{(2\pi)^3} \frac{d^3p_3}{(2\pi)^3} \frac{d^3p_4}{(2\pi)^3} \sum |M|^2 (2\pi)^4 \delta^4(p_1 + p_2 - p_3 - p_4) f_1 f_2 (1 + f_3) (1 + f_4),$$  

(3.19)

with $n_{eq}^a = (\zeta_3/\pi^2)T^3$ and $f_i = 1/(e^{E_i/T} - 1)$.

In the following, we will only consider the interference between the LO and NLO terms in the squared matrix elements, $\sum |M|^2 \simeq \sum |M|_{LO}^2 + \sum 2 \text{Re}[M_{LO} M_{NLO}^*]$, since the NLO squared correction is of the same order of the NNLO-LO interference, which we neglect. Moreover, we will set the model-dependent axion couplings $c_{u,d}^0 = 0$ (see Eq. (2.23)), in order to comply with the standard setup considered in the literature [27, 28]. We will also neglect thermal corrections to the scattering matrix element, since those are small for $T \lesssim m_\pi$ [50–52].

By integrating numerically the phase space in Eq. (3.19) we find (see Refs. [26, 53] for the analytical treatment of the phase space integral)

$$\Gamma_a(T) = \left(\frac{C_{a\pi}}{f_a f_\pi}\right)^2 0.212 T^5 \left[h_{LO}(m_\pi/T) - 2.92 \frac{T^2}{f_\pi} h_{NLO}(m_\pi/T)\right],$$  

(3.20)

where for the numerical evaluation we used the central values of the LECs $\bar{\ell}_1 = -0.36(59)$ [54], $\bar{\ell}_2 = 4.31(11)$ [54], $\bar{\ell}_3 = 3.53(26)$ [55], $\bar{\ell}_4 = 4.73(10)$ [55] and $\bar{\ell}_7 = 2.5(1.4) \times 10^{-3}$ [56], $m_u/m_d = 0.50(2)$ [55], $f_\pi = 92.1(8)$ MeV [57] and $m_\pi = 137$ MeV (corresponding to the average neutral/charged pion mass). The $h$-functions are normalized to $h_{LO}(0) = h_{NLO}(0) = 1$ and they are plotted in the left panel of Fig. 3. It should be noted that Eq. (3.20) is meaningful only for $m_\pi/T \gtrsim 1$, since at higher temperatures above $T_c \simeq 155$ MeV pions are deconfined and the axion thermalization rate should be computed from the interactions with a quark-gluon plasma. Nevertheless, we are interested in extrapolating the behaviour of Eq. (3.20) from the low-temperature regime, where the chiral approach is reliable.

In the right panel of Fig. 3 we compare the LO and NLO rates contributing to $\Gamma_a = \Gamma_a^{LO} + \Gamma_a^{NLO}$. In particular, the $|\Gamma_a^{NLO}/\Gamma_a^{LO}|$ ratio does not depend on $f_a$. Requiring as a loose criterium that the NLO correction is less than 50% of the LO one, yields $T_\chi \simeq 62$ MeV as the maximal temperature at which the chiral description of the thermalization rate can be reliably extended.
3.2 \(a \to \pi\pi\pi\) decay

The ALP decay rate in three pions is obtained by integrating the differential rate (see e.g. Sect. 48 in [57])

\[
d\Gamma_{a \to 3\pi} = \frac{1}{(2\pi)^3} \frac{1}{32m_a^2} |M_{a \to 3\pi}|^2 du ds,
\]

where there are two possible decay channels: \(a \to \pi_0\pi^+\pi^-\) and \(a \to \pi_0\pi_0\pi_0\). In the following, we present the calculation of the ALP decay amplitudes and compare the LO to the NLO decay rate.

3.2.1 LO amplitude

The LO amplitudes are obtained from the interaction terms in Eq. (2.22) and are found to be

\[
M^{LO}_{a \to \pi_0\pi^+\pi^-} = \frac{3C_{a\pi}m_\pi^2(m_\pi^2 - s)}{2f_\pi f_a (m_a^2 - m_\pi^2)},
\]

\[
M^{LO}_{a \to \pi_0\pi_0\pi_0} = \frac{-3C_{a\pi}m_\pi^2 m_a^2}{2f_\pi f_a (m_a^2 - m_\pi^2)}.
\]

Note that the neutral pion channel (Eq. (3.23)) is proportional to \(m_a^2\), since it stems entirely from \(a-\pi_0\) mixing.

3.2.2 NLO amplitude

To compute the ALP decay into three pions at NLO we use again the LSZ formula in Eq. (3.7) with ALP-pion propagators diagonalized at the LO. Considering the ALP-pion
mixings at the NLO, the ALP-decay amplitudes are given by

\[
M_{a \rightarrow \pi^0 \pi^+ \pi^-} = \left(1 + \frac{3}{2} \Sigma'_{\pi \pi}\right) G_{a \rightarrow \pi^0 \pi^+ \pi^-}^{\text{LO}} + \frac{\Sigma_{a \pi}(p^2 = m_a^2)}{m_a^2 - m^2_\pi} G_{\pi^0 \rightarrow \pi^0 \pi^+ \pi^-}^{\text{LO}} + G_{a \rightarrow \pi^0 \pi^+ \pi^-}^{\text{NLO}},
\]

(3.24)

with \((i, j) = (+, -)\) or \((0, 0)\). Defining the invariant mass of the two-pions systems \(\pi_i^\alpha \pi_j^\beta\) as \(\left(p_{\pi_i^\alpha} + p_{\pi_j^\beta}\right)^2 = m_{\pi_i^\alpha \pi_j^\beta}^2 \equiv s, t, u\) with, respectively, \((\alpha, \beta) = (+, -), (0, +), (0, -)\), we obtain

\[
G_{a \rightarrow \pi^0 \pi^+ \pi^-}^{\text{LO}} = \frac{3C_{a \pi} m^2_\pi \left(m^2_\pi - s\right)}{2f_\pi f_a \left(m_a^2 - m^2_\pi\right)},
\]

(3.25)

\[
G_{\pi^0 \rightarrow \pi^0 \pi^+ \pi^-}^{\text{LO}} = \frac{m_a^2 + 2m^2_\pi - 3s}{3f_\pi},
\]

(3.26)

\[
G_{a \rightarrow \pi^0 \pi^0 \pi^0}^{\text{LO}} = -\frac{m^2_\pi}{f_\pi},
\]

(3.27)

\[
G_{\pi^0 \rightarrow \pi^0 \pi^0 \pi^0}^{\text{LO}} = -\frac{m^2_\pi}{f_\pi},
\]

(3.28)

\[
\Sigma'_{\pi \pi} = \frac{2I}{3f^2_\pi},
\]

(3.29)

\[
\Sigma_{a \pi}(p^2) = \frac{C_{a \pi}}{f_\pi f_a} \left(\frac{3\ell_3 m^4_a m^2_\pi}{m^2_a - m^2_\pi} + \frac{3\ell_4 m^2_\pi p^2}{2} - \frac{I \left(4p^2 \left(m^2_a - 2m^2_\pi\right) + m^2_\pi m^2_a\right)}{4 \left(m^2_a - m^2_\pi\right)} \right)
- \frac{\ell_7 m^4_a \left(m_d - m_u\right) \left(m^2_a (m_d + m_u)^2 - 4m^2_\pi m_d m_u\right)}{f_\pi f_a \left(m^2_a - m^2_\pi\right) (m_d + m_u)^3}.
\]

(3.30)

The one-loop diagrams entering the Green’s function \(G_{a \rightarrow \pi^0 \pi^+ \pi^-}^{\text{NLO}}\) are shown in Fig. 4, and the full NLO decay amplitudes are reported in Eqs. (C.1)–(C.2).

To carry out the renormalization procedure in dimensional regularization we shift the LECs as in Eq. (B.8) and we fix \(\gamma_1 = 1/3, \gamma_2 = 2/3, \gamma_3 = -1/2\) and \(\gamma_4 = 2\), consistently with the values found in literature for the standard chiral theory [45].
3.2.3 ALP decay rate: LO vs. NLO

At LO we reproduce the decay rates given in Refs. [38, 39], that in our notation read

\[ \Gamma_{a \to \pi\pi\pi}^{\text{LO}} = \frac{3C_{a\pi}^2}{4096\pi^3} \frac{m_a m_{\pi}^4}{f_{\pi}^2 f_a^2} g_{ij0}^{\text{LO}}(m_a), \]  

(3.31)

with the numerical functions \( g_{ij0}^{\text{LO}}(m_a) \) shown in the left panel of Fig. 5. Note that the \( g_{000}^{\text{LO}}(m_a) \) function includes the symmetry factor \( 1/6 \).

At NLO we need to consider the interference between the LO and NLO amplitudes, since NLO\(^2\) terms are formally of higher order. Then the LO+NLO rates can be written as

\[ \Gamma_{a \to \pi\pi\pi}^{\text{LO+NLO}} = \frac{3C_{a\pi}^2}{4096\pi^3} \frac{m_a m_{\pi}^4}{f_{\pi}^2 f_a^2} \left[ g_{ij0}^{\text{LO}}(m_a) + \frac{1}{16\pi^2} \frac{m_a^2}{f_{\pi}^2} g_{ij0}^{\text{NLO}}(m_a) \right], \]  

(3.32)

where the NLO functions \( g_{ij0}^{\text{LO}} \) are obtained by numerically integrating the NLO amplitudes in Eqs. (C.1)–(C.2). Their profile is shown in the left panel of Fig. 5, for comparison with the LO counterparts. Although the expansion parameter in Eq. (3.32) is formally written as \( (m_a/4\pi f_{\pi})^2 \), the actual calculation of the NLO rate shows (cf. right panel of Fig. 5) that the NLO correction becomes of the same order of the LO result already for ALP masses just above the kinematical threshold \( m_a \gtrsim 3m_{\pi} \). This is reflected by a somewhat larger value of the NLO \( g \)-functions compared to the LO ones, as shown in Fig. 5.

Thus we conclude the \( \chi \)PT description of the \( a \to \pi\pi\pi \) decay rate breaks down for ALP masses much smaller than \( 4\pi f_{\pi} \simeq 1.6 \) GeV [39]. This earlier breakdown of \( \chi \)PT is also found in SM processes that are similar to the ALP decay into pions considered here, as e.g. \( \eta \to \pi\pi\pi \) (see e.g. [58, 59]). For instance, the NNLO rate for \( \eta \to \pi\pi\pi \) was found to be a factor \( \approx 4.5 \) larger than the LO one [58].

Figure 5: Left panel: Numerical profile of \( g_{000}^{\text{NLO}} \) and \( g_{+-0}^{\text{NLO}} \), in red and blue respectively, compared to their LO counterparts in light and dark grey. Right panel: Ratio of the NLO to LO rates for the two possible decay channels. The vertical grey line indicates the kinematical threshold for the \( a \to \pi\pi\pi \) decay, with \( m_{\pi} = 137 \) MeV corresponding to the average neutral/charged pion mass (at leading order in the isospin breaking).
4 Conclusions

In this paper we have discussed the formulation of the axion-pion Lagrangian at the NLO in $\chi$PT and considered two applications of phenomenological relevance: the $a\pi \to \pi\pi$ scattering, which is the most important thermalization channel for the so-called axion hot dark matter bound, and the ALP decay $a \to \pi\pi\pi$, which is one of the main hadronic channels for GeV-scale ALPs. The calculation of these two processes presents several common aspects and in both cases we have estimated, through the inclusion of the NLO correction, the range of applicability of the chiral expansion. In the case of axion-pion scattering we have found that the axion-pion thermalization rate can be cast as an expansion in powers of $T/f_\pi$ and that $\chi$PT breaks down for temperatures $T \gtrsim 60$ MeV (cf. right panel in Fig. 3). In the case of the ALP decay instead the chiral EFT fails for ALP masses already just above the kinematical threshold of $3m_\pi$ (cf. right panel in Fig. 5). In both cases, these results show an earlier breakdown of the chiral EFT compared to naive expectations based on previous LO calculations, see respectively Refs. [27, 28] for $a\pi \to \pi\pi$ and Refs. [38, 39] for $a \to \pi\pi\pi$. We conclude that the range of applicability of the axion-pion chiral Lagrangian is rather limited for the two relevant processes discussed above and hence alternative non-perturbative approaches (based either on dispersion relations or lattice QCD techniques) which extend the validity of the chiral description of axion-pion interactions are called for.

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A Pion axial current

In this Appendix we provide the derivation of the pion axial current at the NLO. The currents associated to the Left and Right chiral rotations

\[ L = \exp \left(-i \Theta^a_L \frac{\sigma^a}{2} \right), \quad R = \exp \left(-i \Theta^a_R \frac{\sigma^a}{2} \right), \quad (A.1) \]

acting on the Goldstone matrix as $U \to RUL^\dagger$, are easily computed promoting the global symmetries to local ones, and computing the variation $\delta \mathcal{L}$ of the Lagrangian under the given transformation. From Noether’s theorem, the Left and Right currents are given by

\[ J^\mu_{L,R} = - \frac{\partial \delta \mathcal{L}}{\partial \partial^\mu \Theta^a_{L,R}(x)}. \quad (A.2) \]

Let us consider the LO chiral Lagrangian

\[ \mathcal{L}_\chi = \frac{f^2}{4} \text{Tr} \left[ \partial^\mu U^\dagger \partial_\mu U + U \chi^\dagger + \chi U^\dagger \right]. \quad (A.3) \]
To compute e.g. the Right current, we set $\Theta_R^a(x) = 0$ and perform an infinitesimal Right transformation
\[
U \rightarrow \left(1 - i\Theta_R^a(x)\frac{\sigma^a}{2}\right)U.
\] (A.4)
The variation of $L_\chi$ is
\[
\delta L_\chi = i\frac{f_\pi^2}{4}\partial_{\mu}\Theta_R^a(x)\text{Tr}\left[\vartheta^\mu U U^\dagger \sigma^a\right],
\] (A.5)
and therefore $J^\mu_R$ is given by
\[
J^\mu_R = -i\frac{f_\pi^2}{4}\text{Tr}\left[\vartheta^\mu U U^\dagger \sigma^a\right].
\] (A.6)

With an analogous procedure one obtains
\[
J^\mu_L = -i\frac{f_\pi^2}{4}\text{Tr}\left[\vartheta^\mu U U^\dagger \sigma^a\right].
\] (A.7)
The $R-L$ combination of these two currents provides the pion axial current at LO
\[
J^\mu_A = i\frac{f_\pi^2}{4}\text{Tr}\left[\sigma^a\{U, \vartheta^\mu U^\dagger\}\right].
\] (A.8)
The procedure can be repeated at the NLO by employing the shift of the $\mathcal{O}(p^4)$ chiral Lagrangian in Eq. (2.24), which yields
\[
J^\mu_R (\text{NLO}) = +i\frac{\ell_1}{2}\text{Tr}\left[\sigma^a U D^\mu U^\dagger\right]\text{Tr}\left[D_\nu U D^\nu U^\dagger\right]
\]
\[
+ i\frac{\ell_2}{4}\text{Tr}\left[\sigma^a U D^\mu U^\dagger\right]\text{Tr}\left[D^\mu U D_\nu U^\dagger + D_\nu U D^\mu U^\dagger\right]
\]
\[
+ i\frac{\ell_4}{8}\text{Tr}\left[\sigma^a D^\mu U \chi U^\dagger - \sigma^a U D^\mu \chi U^\dagger + \sigma^a D^\mu \chi U^\dagger - \sigma^a \chi D^\mu U^\dagger\right]
\]
\[
+ i\frac{\ell_6}{4}\text{Tr}\left[f^R_{\mu\nu}\left(\sigma^a D^\nu U U^\dagger + U D^\nu U^\dagger \sigma^a\right) + f^L_{\mu\nu}\left(U^\dagger \sigma^a D^\nu U + D^\nu U^\dagger \sigma^a U\right)\right],
\] (A.9)
and
\[
J^\mu_L (\text{NLO}) = -i\frac{\ell_1}{2}\text{Tr}\left[\sigma^a D^\mu U^\dagger U\right]\text{Tr}\left[D_\nu U D^\nu U^\dagger\right]
\]
\[
- i\frac{\ell_2}{4}\text{Tr}\left[\sigma^a D^\mu U^\dagger U\right]\text{Tr}\left[D_\nu U D_\mu U^\dagger + D_\mu U D_\nu U^\dagger\right]
\]
\[
- i\frac{\ell_4}{8}\text{Tr}\left[\sigma^a \chi^\dagger D^\mu U - \sigma^a D^\mu \chi U^\dagger + \sigma^a U^\dagger D^\mu \chi - \sigma^a D^\mu U^\dagger \chi\right]
\]
\[
+ i\frac{\ell_6}{4}\text{Tr}\left[f^R_{\mu\nu}\left(D^\nu U \sigma^a U^\dagger + U \sigma^a D^\nu U^\dagger\right) + f^L_{\mu\nu}\left(U^\dagger D^\nu U \sigma^a + \sigma^a D^\nu U^\dagger U\right)\right].
\] (A.10)

Combining the left and right currents we obtain the axial current in Eq. (2.25).

## B Axion-pion mixing at NLO

We explicitly perform here the NLO diagonalization of the axion and neutral pion propagators and discuss as well an alternative way to compute the $a\pi \rightarrow \pi\pi$ scattering without employing the LSZ formula. We focus for simplicity on the case of the QCD axion, for which $m_a^2 \ll m_\pi^2$. 

17
B.1 NLO diagonalization

The axion-neutral pion Lagrangian up to order $1/f_a$ (hence neglecting $m_a^2$ terms) is given by

$$\mathcal{L}_{a-\pi_0} = \frac{1}{2} (\partial_\mu a)^2 + \frac{1}{2} (\partial_\mu \pi_0b)^2 - \frac{1}{2} m_\pi^2 \pi_0b + \mathcal{L}_{\text{int}}$$

where the subscript $b$ stands for bare fields\(^1\) and the interaction Lagrangian reads explicitly

$$\mathcal{L}_{\text{int}} = a \pi_0b \ell_7 \frac{4m dm_n m_\pi (m_d - m_u)}{f_a f_\pi (m_d + m_u)^4} - 3 C a \pi \partial_\mu a \partial_\mu \pi_0b \left( f_\pi + \ell_4 m_\pi^2 \right)$$

$$+ \frac{2 C a \pi}{f_a f_\pi} \partial_\mu a \partial_\mu \pi_0b \pi_+ \pi_- + \frac{1}{24 f_\pi^2} m_\pi^2 \pi_0b^2 - \frac{1}{3 f_\pi^2} \pi_0b \partial_\mu \pi_+ \partial_\mu \pi_-$$

$$+ \frac{1}{6 f_\pi^2} m_\pi^2 \pi_+ \pi_- b^2 - \frac{1}{3 f_\pi^2} \pi_+ \pi_- \partial_\mu \pi_0b \partial_\mu \pi_0b - \ell_3 m_\pi^2 \pi_0b^2 + \ell_7 \pi_0b (m_d - m_u)^2 \frac{m_\pi^4}{f_\pi^2 (m_u + m_d)^2}.$$  \hspace{1cm} (B.2)

Note that $\mathcal{L}_{\text{int}}$ contains all the terms which contribute to the two-point functions of the neutral scalar fields, i.e. LO tree-level mixings, LO terms giving the one-loop corrections and NLO terms. The latter provide the counterterms needed to reabsorb the loop divergences.

We next define the renormalization conditions. Firstly, it is important to note that in $\chi$PT the pion mass $m_\pi$ as well as the pion decay constant $f_\pi$ do not get renormalized. This can be easily understood by observing that, at NLO, $m_\pi$ and $f_\pi$ are corrected by terms proportional to the bare low-energy constants $\ell_3$, $\ell_4$ and $\ell_7$ (see Eqs. (B.11)–(B.12)). Therefore, since the divergences come from loops of $\mathcal{L}_a^{\chi(LO)}$, it is sufficient to extract the counterterms from $\ell_3$, $\ell_4$ and $\ell_7$. Hence, $m_\pi$ and $f_\pi$ are the physical pion mass and decay constant at LO. Let us now denote by $-i \Sigma_{ij}(p^2)$ (with $i,j = a, \pi_0$) the 1-particle-irreducible (1PI) self-energy correction. The net effect of this correction is encoded in the effective Lagrangian

$$\mathcal{L}^{\text{eff}}_{a-\pi} = \frac{1}{2} a \left( \frac{p^2}{a} \right) a + \frac{1}{2} \pi_0 \left( a^2 - m_\pi^2 + (p^2 - m_\pi^2) \delta Z_\pi - \Sigma_{\pi\pi}(p^2) \right) \pi_0$$

$$- a \Sigma_{a\pi}(p^2) \left( 1 + \frac{1}{2} \delta Z_\pi \right) \pi_0,$$  \hspace{1cm} (B.3)

where we employed the pion wave-function renormalization, $\pi_0b \rightarrow (1 + \frac{1}{2} \delta Z_\pi) \pi_0$, defined as $\delta Z_\pi = \partial \Sigma_{\pi\pi}(p^2)/\partial p^2$. The one-loop self-energies $\Sigma_{ij}(p^2)$ can be computed from the interaction Lagrangian in Eq. (B.2). Defining

$$I = \frac{m_\pi^2}{16 \pi^2} \left[ R + \log \left( \frac{m_\pi^2}{\mu^2} \right) \right],$$  \hspace{1cm} (B.4)

with $R = \frac{2}{\pi^2} - \log(4\pi) + \gamma_E - 1$, and using dimensional regularization we find

$$\Sigma_{\pi\pi}(p^2) = I \frac{1}{6 f_\pi^2} [4p^2 - m_\pi^2] + 2 \ell_4 m_\pi^4 f_\pi^2 - 2 \ell_7 (m_d - m_u)^2 m_\pi^4 f_\pi^2 (m_u + m_d)^2,$$  \hspace{1cm} (B.5)

$$\Sigma_{a\pi}(p^2) = 3 C a \pi \left[ \frac{f_\pi}{2 f_a} + \frac{4 \ell_4 m_\pi^2}{3 f_a f_\pi} - \frac{2 I}{3 f_a f_\pi} \right] - \frac{4 \ell_7 (m_d - m_u) m_u m_d m_\pi^4}{f_a f_\pi (m_u + m_d)^3}.$$  \hspace{1cm} (B.6)

\(^1\)We dropped the $b$ subscript for the axion field, since quantum corrections of $\mathcal{O}(1/f_a^2)$ are systematically neglected.
from which we get
\[ \delta Z_{\pi} = \frac{2I}{3f_{\pi}^2}. \] (B.7)

Therefore, we define the scale-independent parameters \( \ell_i \) and \( h_i \) in such a way that the \( R + \log(m_{\pi}^2/\mu^2) \) factor is subtracted [45]
\[
\ell_i = \frac{\gamma_i}{32\pi^2} \left[ \ell_i + R + \log \left( \frac{m_{\pi}^2}{\mu^2} \right) \right],
\]
\[
h_i = \frac{\delta_i}{32\pi^2} \left[ h_i + R + \log \left( \frac{m_{\pi}^2}{\mu^2} \right) \right].
\] (B.8)

Plugging these definitions in Eqs. (B.5)–(B.6) and substituting back into Eq. (B.3) we find that in order to renormalize \( \Sigma_{\pi\pi} \) and \( \Sigma_{a\pi} \) we need to set
\[
\gamma_3 = -\frac{1}{2}, \quad \gamma_4 = 2.
\] (B.9)

Thus the renormalized effective Lagrangian becomes
\[
L_{a-\pi_0}^{\text{eff}} = \frac{1}{2} a \left( p^2 \right) a + \frac{1}{2} \pi_0 \left( p^2 - m_{\pi}^2 \right) \pi_0 - a \left( p^2 3C_{a\pi} \frac{\tilde{f}_{\pi}}{f_{a\pi} f_{\pi}} - \frac{4\ell_7 (m_d - m_u) m_u m_d m_{\pi}^4}{f_{a\pi} f_{\pi} (m_u + m_d)^3} \right) \pi_0,
\] (B.10)
with
\[
\tilde{m}_{\pi}^2 = m_{\pi}^2 - \frac{m_{\pi}^2 \ell_3}{32\pi^2 f_{\pi}^2} - \frac{2\ell_7 (m_d - m_u)^2 m_{\pi}^4}{f_{\pi}^2 (m_u + m_d)^2},
\] (B.11)
and
\[
\tilde{f}_{\pi} = f_{\pi} + \frac{\ell_4 m_{\pi}^2}{16\pi^2 f_{\pi}}.
\] (B.12)

We observe that \( \ell_7 \) is not renormalized, since in the LO Lagrangian the \( m_d - m_u \) terms are all momentum dependent. So we are left with a non-zero off-diagonal two-point function. In order to eliminate the mixing, we can rotate the axion and the pion fields as
\[
a \to a - \beta_1 \pi_0,
\]
\[
\pi_0 \to \pi_0 - \beta_2 a.
\] (B.13)

yielding
\[
L_{a-\pi_0}^{\text{eff}} \to \frac{1}{2} a \left( p^2 \right) a + \frac{1}{2} \pi_0 \left( p^2 - \tilde{m}_{\pi}^2 \right) \pi_0
\]
\[
- a \left( \beta_1 p^2 + \beta_2 (p^2 - m_{\pi}^2) + p^2 3C_{a\pi} \frac{\tilde{f}_{\pi}}{f_{a\pi} f_{\pi}} - \frac{4\ell_7 (m_d - m_u) m_u m_d m_{\pi}^4}{f_{a\pi} f_{\pi} (m_u + m_d)^3} \right) \pi_0.
\] (B.14)

Hence, to cancel the mixing term it is sufficient to set
\[
\beta_1 = -3C_{a\pi} \frac{\tilde{f}_{\pi}}{f_{a\pi} f_{\pi}} + \frac{4\ell_7 (m_d - m_u) m_u m_d}{f_{a\pi} f_{\pi} (m_u + m_d)^3},
\] (B.15)
\[
\beta_2 = -\frac{4\ell_7 (m_d - m_u) m_u m_d m_{\pi}^2}{f_{a\pi} f_{\pi} (m_u + m_d)^3}.
\] (B.16)
B.2 NLO amplitude without LSZ

We now provide an alternative calculation of the $a\pi \rightarrow \pi \pi$ amplitude without employing the LSZ formula, namely via the NLO diagonalization of the axion-pion quadratic terms provided in App. B.1. At NLO we need to consider two contributions: tree-level amplitudes from the NLO Lagrangian and loop amplitudes from the LO Lagrangian. In what follows we still neglect contributions of $O(1/f_a^2)$. First, we report the relevant terms for the scattering process stemming from $\mathcal{L}_{\text{NLO}}$ and $J_{A,\mu|\text{NLO}}^a$; after the NLO diagonalization:

$$
\mathcal{L}_{a}\overset{\text{(NLO)}}{=}-\ell_1 \frac{8m_dm_u(m_d-m_u)m_A^2}{3f_A^3(m_d+m_u)^2}a\pi_0 (2\pi_+\pi_- + \pi_0\pi_0), \quad (B.17)
$$

and

$$
\frac{\partial^\mu a}{f_a} \text{Tr} \frac{1}{2} [c_\sigma, J_A^{a|\text{NLO}}] \supset \frac{1}{f_A f_\pi^3} \left( \frac{m_d-m_u}{m_d+m_u} + c_d - c_u \right) \partial^\mu a \left\{ 2 \ell_1 \left( \partial_\mu \pi_0 \partial_\nu \pi_0 \partial^\nu \pi_0 + 2 \partial_\mu \pi_0 \partial_\nu \pi_- \partial^\nu \pi_+ \right) \\
+ 4 \ell_2 \left( \partial_\mu \pi_0 \partial_\nu \pi_0 \partial^\nu \pi_0 + \partial_\mu \pi_+ \partial_\nu \pi_- \partial^\nu \pi_0 + \partial_\mu \pi_- \partial_\nu \pi_+ \partial^\nu \pi_0 \right) \\
+ \frac{\ell_4}{12} m_A^2 \left( 2 \pi_+ \pi_0 \partial_\mu \pi_- + 2 \pi_- \pi_0 \partial_\mu \pi_+ + 2 \pi_+ \pi_- \partial_\mu \pi_0 + 3 \pi_0 \pi_0 \partial_\mu \pi_0 \right) \right\}. \quad (B.18)
$$

From Eq. (B.17) it follows that at NLO there is a new channel, $a\pi_0 \rightarrow \pi_0\pi_0$, not present at LO. However, this does not interfere with the LO and hence it is formally of higher-order in the chiral expansion. The calculation of the scattering amplitudes (there are in total 25 loop diagrams contributing to the four possible axion-pion scattering processes) has been carried out using the computational tools FeynRules [60, 61], FeynArts [62], FeynCalc [63–65] and Package-X [66].

Let us focus for definiteness on the $a\pi_0 \rightarrow \pi_+\pi_-$ channel and describe in more detail how the renormalization procedure is implemented. Considering the pion wave-function renormalization in Eq. (B.7), the divergent part from the LO amplitude is

$$
M_{\text{tree}}^{\text{UV}} = -IC_a \pi \frac{3(2m_\pi^2 - u - t)}{2f_A^2 f_\pi}, \quad (B.19)
$$

with $I$ defined in Eq. (B.4) and $C_a \pi$ in Eq. (2.23). The UV divergence of the one-loop amplitude is instead

$$
M_{1-\text{loop}}^{\text{UV}} = IC_a \pi \frac{-9m_\pi^2(u + t) + 12m_\pi^4 + 2(u^2 + ut + t^2)}{2m_A^2 f_\pi^3 f_A}, \quad (B.20)
$$

while the NLO amplitude provides the $\gamma_1$ and $\gamma_2$ counterterms (see Eq. (B.8))

$$
M_{\text{NLO}}^{\text{UV}} = -IC_a \pi \frac{3 \left[ 4m_\pi^4(\gamma_1 + \gamma_2) + 4\gamma_1 tu + (2\gamma_1 + \gamma_2)(-3m_\pi^2(t + u) + t^2 + u^2) \right]}{4f_A f_\pi^3 m_A^2}. \quad (B.21)
$$

To renormalize the $a\pi_0 \rightarrow \pi_+\pi_-$ amplitude $\gamma_1$ and $\gamma_2$ must be chosen so that the sum $M_{\text{tree}}^{\text{UV}} + M_{1-\text{loop}}^{\text{UV}} + M_{\text{NLO}}^{\text{UV}}$ vanish, which happens for

$$
\gamma_1 = \frac{1}{3}, \quad \gamma_2 = \frac{2}{3}. \quad (B.22)
$$
The same relation is found by considering the renormalization of the crossed channels. As a result, considering the NLO corrections to $f_\pi$ (see Eq. (B.12)) inside $\mathcal{M}_{\text{LO}}$ and neglecting the charged-neutral pion mass difference arising at second order in the isospin breaking parameter $m_d - m_u$, the full amplitude for the $a\pi_0 \to \pi_+ \pi_-$ channel reads

\[
\mathcal{M}^{\text{NLO}}_{a\pi_0 \to \pi_+ \pi_-} = \frac{C_{a\pi}}{192\pi^2 f_\pi^4 f_a} \left\{ 15m_\pi^2(u + t) - 11u^2 - 8ut - 11t^2 - 6\ell_4 m_\pi^2(m_\pi^2 - s) (2m_\pi^2 - s) - 6\ell_2 (-3m_\pi^2(u + t) + 4m_\pi^4 + u^2 + t^2) + 18\ell_4 m_\pi^2(m_\pi^2 - s) \right. \\
+ 3 \left[ 3\sqrt{1 - \frac{4m_\pi^2}{s}} s (m_\pi^2 - s) \ln \left( \frac{\sqrt{s} (s - 4m_\pi^2) + 2m_\pi^2 - s}{2m_\pi^2} \right) \right. \\
+ \sqrt{1 - \frac{4m_\pi^2}{t}} (m_\pi^2(t - 4u) + 3m_\pi^4 + t(u - t)) \ln \left( \frac{\sqrt{t} (t - 4m_\pi^2) + 2m_\pi^2 - t}{2m_\pi^2} \right) \\
+ \sqrt{1 - \frac{4m_\pi^2}{u}} (m_\pi^2(u - 4t) + 3m_\pi^4 + u(t - u)) \ln \left( \frac{\sqrt{u} (u - 4m_\pi^2) + 2m_\pi^2 - u}{2m_\pi^2} \right) \right\} \\
+ 4\ell_7 m_\pi^2 m_d (s - 2m_\pi^2) m_u (m_d - m_u) \\
\left. \frac{f_\pi^3 f_a}{(m_d + m_u)^3} \right\}.
\]

(B.23)

The crossed amplitudes $a\pi_+ \to \pi_+ \pi_0$ and $a\pi_- \to \pi_- \pi_0$ are obtained by replacing $s \leftrightarrow u$ and $s \leftrightarrow t$, respectively.

### C ALP decay amplitudes

Following Eq. (3.24), the full ALP decay amplitudes up to NLO are given by

\[
\mathcal{M}_{a \to \pi_0 \pi_+ \pi_-} = \frac{3C_{a\pi} m_\pi^2 (m_\pi^2 - s)}{2f_a f_\pi (m_d^2 - m_u^2)} + \frac{C_{a\pi}}{32\pi^2 f_a f_\pi^3 (m_d^2 - m_u^2)} \left\{ \ell_4 m_\pi^2 (2m_\pi^2 - s) (m_a^2 + m_\pi^2 - s) \right. \\
+ \ell_2 m_\pi^2 (m_a^2 (2m_\pi^2 - s) + m_a^4 - 3m_a^2 s + 5m_\pi^4 - u^2 - t^2) \\
+ \frac{3}{2} \ell_3 m_a^2 m_\pi^4 + 3\ell_4 m_\pi^2 (m_a^2 + m_\pi^2) (m_\pi^2 - s) \\
+ \frac{1}{6} m_\pi^2 (45m_\pi^2 - 29s) + 11m_a^4 - 15m_a^2 s + 45m_\pi^4 - 11t^2 - 8tu - 11u^2 \right\}.
\]

21
\[- \frac{1}{2} \log \left( \frac{2m_{\pi}^2 - u + \sqrt{u(2u - 4m_{\pi}^2)}}{2m_{\pi}^2} \right) \sqrt{1 - \frac{m_{\pi}^2}{u} \left( 3m_{\pi}^4 + (u - 4t)m_{\pi}^2 \right)} \]

\[+ (t - u)u + m_a^2 \left( u - m_{\pi}^2 \right) m_{\pi}^2 \]

\[- \frac{1}{2} \log \left( \frac{2m_{\pi}^2 - t + \sqrt{t(t - 4m_{\pi}^2)}}{2m_{\pi}^2} \right) \sqrt{1 - \frac{m_{\pi}^2}{t} \left( 3m_{\pi}^4 + (t - 4u)m_{\pi}^2 \right)} \]

\[+ (u - t)t + m_a^2 \left( t - m_{\pi}^2 \right) m_{\pi}^2 \]

\[+ \frac{3}{2} \log \left( \frac{2m_{\pi}^2 - s + \sqrt{s(s - 4m_{\pi}^2)}}{2m_{\pi}^2} \right) \sqrt{1 - \frac{m_{\pi}^2}{s} \left( m_a^2 + s \right) \left( m_a^2 + s \right) m_{\pi}^2} \]

\[+ \ell_t \frac{(m_d - m_a)m_{\pi}^4}{3f_a f_{\pi}^3 (m_a^2 - m_{\pi}^2)^2 (m_d + m_a)^3} \left[ \left( m_a^2 \left( 3s(m_d + m_a)^2 - 4m_{\pi}^2 \right) \left( m_a^2 + 7m_d m_a + m_u^2 \right) \right) \right. \]

\[+ m_a^4 \left( m_d^2 + 10m_d m_a + m_u^2 \right) + 12m_d m_a^2 m_u \left( 2m_{\pi}^2 - s \right) \right] , \quad \text{(C.1)} \]

and

\[M_{a \rightarrow \pi_0 \pi_0 \pi_0} = - \frac{3C_{\alpha \pi}^2 m_{\pi}^2 m_a^2}{2f_{\pi} f_a (m_a^2 - m_{\pi}^2)} \]

\[+ \frac{C_{\alpha \pi}}{32\pi^2 f_a f_{\pi}^3 \left( m_a^2 - m_{\pi}^2 \right)^2} \left\{ 2\bar{f}_1 m_{\pi}^2 \left( m_a^2 \left( 3m_{\pi}^2 - s \right) + m_a^4 - 3m_{\pi}^4 s + 6m_{\pi}^4 t^2 - tu - u^2 \right) \right\} \]

\[+ 4\bar{f}_2 m_{\pi}^2 \left( m_a^2 \left( 3m_{\pi}^2 - s \right) + m_a^4 - 3m_{\pi}^4 s + 6m_{\pi}^4 t^2 - tu - u^2 \right) \]

\[+ \frac{9}{2} \ell_2 m_a^2 m_{\pi}^4 - 3\bar{f}_4 m_a^2 m_{\pi}^2 \left( m_a^2 + m_{\pi}^2 \right) \]

\[+ \frac{3}{2} \log \left( \frac{\sqrt{s(s - 4m_{\pi}^2)} + 2m_{\pi}^2 - s}{2m_{\pi}^2} \right) m_{\pi}^2 \sqrt{1 - \frac{m_{\pi}^2}{s} \left( m_a^2 m_a^2 + 2 \left( m_{\pi}^2 - s \right)^2 \right)} \]

\[+ \frac{3}{2} \log \left( \frac{\sqrt{t(t - 4m_{\pi}^2)} + 2m_{\pi}^2 - t}{2m_{\pi}^2} \right) m_{\pi}^2 \sqrt{1 - \frac{m_{\pi}^2}{t} \left( m_a^2 m_a^2 + 2 \left( m_{\pi}^2 - t \right)^2 \right)} \]

\[+ \frac{3}{2} \log \left( \frac{\sqrt{u(u - 4m_{\pi}^2)} + 2m_{\pi}^2 - u}{2m_{\pi}^2} \right) m_{\pi}^2 \sqrt{1 - \frac{m_{\pi}^2}{u} \left( m_a^2 m_a^2 + 2 \left( m_{\pi}^2 - u \right)^2 \right)} \]

\[+ \frac{3}{2} m_{\pi}^2 \left( -4s \left( m_a^2 + 3m_{\pi}^2 \right) + 13m_a m_{\pi}^2 + 2m_a^4 + 24m_{\pi}^4 - 4 \left( t^2 + tu + u^2 \right) \right) \} \]

\[22\]
\[ \ell_\gamma m_\pi^4 \left( 4m_a^2 - 3m_b^2 \right) (m_d - m_u) \left( m_a^2(m_d + m_u)^2 - 4m_d m_a^2 m_u \right) \]
\[ + \frac{f_\pi^3}{f_\pi} \left( m_a^2 - m_b^2 \right)^2 (m_d + m_u)^3. \]

(C.2)

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