Effects of Lorentz Symmetry Violation in the Spectra of Rare-Earth Ions in a Crystal Field

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We demonstrate that experiments measuring the transition energies of rare-earth ions doped in crystalline lattices are sensitive to violations of Local Lorentz Invariance and Einstein’s Equivalence Principle. Using the crystal field of LaCl₃ as an example, we calculate the frame-dependent energy shifts of the transition frequencies between low-lying states of Ce⁺³, Nd⁺³, and Er⁺³ dopants in the context of the Standard Model Extension, and show that they have high sensitivity to electron anomalies that break rotational invariance.

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Most of our day-to-day experiences are mediated by light and charged particles, and in particular its interaction with electrons. To the best of our knowledge, the physics of a system of photons and electrons is independent of the velocity and orientation of that system in absolute space, nor is it locally dependent upon where that system lies in a gravitational potential. These symmetries, respectively described as local Lorentz invariance (LLI) and Einstein’s equivalence principle (EEP), are fundamental to our modern understanding of the standard model and general relativity. It is possible, however, that these symmetries are not exact at experimentally accessible energy scales, thanks to spontaneous symmetry breaking or other physics at high energy scales [1, 2]. This possibility has driven many experimental tests of LLI and EEP [3], and motivated the development of phenomenological frameworks that can quantitatively describe the effect of LLI- and EEP-violation on known particles and fields. One such framework is provided by the standard model extension (SME) [4, 5], which has been used to analyze a wide range of experiments [6]. The SME augments the standard model Lagrangian with all combinations of known particles and fields that are not invariant under Lorentz transformations, but which preserve gauge invariance, energy and translational invariance, and the invariance of the total action [4, 5]. These terms are parameterized by Lorentz tensors that are collectively known as LLI- and EEP-violating coefficients, and are further subdivided into ‘sectors’ that deal with terms involving a particular particle. In this Letter, we focus on tests of the electron-sector $c_{\mu\nu}$ tensor, which modifies the inertial energy of electrons according to their direction of motion.

Spectroscopy of an atomic gas of neutral dysprosium has already been used to perform one of the most precise electronic tests of Lorentz invariance and the equivalence principle [7], owing to the delicate balance between the kinetic and Coulomb potential energies of bound electrons in rare earth elements. An even more sensitive measurement of the electron $c_{\mu\nu}$ coefficients has recently been performed by engineering the quantum state of a pair of trapped Ca⁺⁺ ions [8], extending precision tests of electronic LLI past the electroweak (relative to the Planck mass) scale. Both of these experiments operate at or near the interrogation-time-of-flight or atom (ion) shot-noise limit. In this Letter, we consider the possibility of using rare earth ions doped in a crystalline lattice to perform similar measurements of the electronic $c_{\mu\nu}$. Rare-earth ion-doped crystals offer substantially larger ion-number densities than are available in atomic gases, and interrogation times comparable and potentially longer than are possible in ion traps. At the same time, the resonant modes of bulk crystals have recently been shown to be excellent probes of LLI- and EEP-violating inertial energies of atomic nuclei [9], raising the possibility that rare-earth ion-doped crystals may be used as compact and comprehensive tests of LLI and EEP for normal matter. In what follows, we will focus on the orientation-dependent (LLI-violating) effects of the $c_{\mu\nu}$ tensor.

In the SME, the linearized perturbation of the electron $c_{\mu\nu}$ tensor to the Dirac Hamiltonian may be written as [4, 5, 10, 11]

$$\delta H = -(c_{00}\delta_{jk} + c_{jk})c\alpha^j p^k - (c_{0j} + c_{j0})c p^j - c_{00}mc^2\beta, \tag{1}$$

where $c_{\mu\nu}$ is a symmetric, traceless, constant background field, $c$ is the speed of light, $\alpha^j = \gamma^0\gamma^j$ and $\beta = \gamma^0$ are the usual Dirac matrices and $\delta_{jk}$ is the Kronecker symbol. Note that in general, one can define a coordinate transformation which maps the elements of $c_{\mu\nu}$ to zero, at the cost of generating new LLI-violating terms in the photon (and other matter) Hamiltonians, which in turn can be constrained by modern Michelson-Morley experiments [12]. Since our choice of coordinates is arbitrary, it follows that measurements of $c_{\mu\nu}$ can also be understood as Michelson-Morley tests, as both are only sensitive to the differences in LLI-violation in the photon and matter sectors. At first order, the last two terms of Eq. (1) do not contribute to shifts in the transition energies between different electronic bound states, and may be omitted.
We can therefore write Eq. (1) in terms of the spherical components of irreducible tensor operators as:

$$\delta H = -C_0^{(0)} T_0^{(0)} - \sum_{q=-2}^{2} (-1)^q C_q^{(2)} T_{-2}^{(2)}.$$  (2)

In the spherical operator form used in this Letter, the elements of $c_{\mu\nu}$ are written as $[13, 14]$

$$C_0^{(0)} = c_{00} + \frac{2}{3} c_{zz} - \frac{2}{3} c_{00}$$
$$C_0^{(2)} = \frac{1}{3} (3c_{zz} - c_{zz})$$
$$C_{\pm 1}^{(2)} = \pm (c_{xz} \pm ic_{zy})$$
where double roman indexes indicate a sum over the spatial components of $c_{\mu\nu}$, and $U$ is the local Newtonian gravitational potential.

The problem of a rare-earth ion in a crystal field has been well studied $[15, 17]$. The total Hamiltonian of a rare-earth ion in a crystal field may be written as $H = H_f + V$, where $H_f$ is the free ion Hamiltonian and $V$ is the electrostatic potential due to the crystal environment. The states of free ions are spherically symmetric, and designated by their total angular momentum $J$ and its projection $M$. When the ions are inserted into a crystal, the ambient crystal field $V$ breaks spherical symmetry, partially lifting the $(2J + 1)$-fold degeneracy of the free ions’ energy levels $[13, 16]$. The crystal potential $V$ can be written as

$$V = \sum_{k} \sum_{q=-k}^{k} B_q^{k} C_q^{(k)},$$

where $C_q^{(k)} = 4\pi/(2k+1) Y_{kq}$ are normalized spherical harmonics, and $Y_{kq}$ are spherical tensor operators of rank $k$. The summation over $k$ is restricted to even numbers because the contribution of $V$ to leading order energy shifts must come from its even-parity components, and $k \leq 6$ due to the triangle condition for spherical harmonic integrals (since $l = 3$ for rare-earth ions with configuration $4f^N$). The number of terms in Eq. (3) may be further reduced using the discrete point symmetry of the crystal. The $B_q^{k}$ coefficients, also known as the crystal field parameters, depend on the structure of the crystal and the electronic wave functions’ radial components. They are determined by a least-squares fit to the experimental energy levels of the ion in the crystal. The crystal field potential is assumed to act only on the electrons in an open shell, i.e. $4f^N$ for rare-earth ions.

The crystal field-induced energy splitting may be obtained using the secular determinant $|\langle JM| V |J'M'\rangle - \lambda \delta_{JJ'} \delta_{MM'}| = 0$ acting on the free ion states $|JM\rangle$. The split eigenstates $|\psi\rangle$ can be obtained by diagonalizing the interaction $V$ separately within each $J$-manifold, and thus $|\psi\rangle = \sum_{JM} a_{JM} |JM\rangle$. Thus the non-zero matrix elements of $V$ are restricted to $\langle JM | T_{q}^{2} | J'M'\rangle$, with $q = M - M'$, and $|q| \leq 2$.

The LLI-violating correction $\delta\omega_{nm} = \langle \delta E_n - \delta E_m \rangle / \hbar$ to the transition frequency $\omega_{nm}$ between each pair of levels $n$ and $m$ in the ion in the crystal field is a linear combination of the spatial components of the $c_{\mu\nu}$ tensor, which is itself a frame-dependent quantity. This energy shift also varies as a function of the ion’s position in an external gravitational field, although as we will see, this effect is smaller than the frame-dependent phenomena for the transitions of interest. To uniquely specify the value of $c_{\mu\nu}$, we must also specify the inertial frame in which it is defined. This frame is typically taken to be approximated by the rest frame of the Sun: specifically the sun-centered celestial equatorial frame (SCCEF), denoted by coordinates $(T, X, Y, Z)$, while the local laboratory frame coordinates are denoted as $(t, x, y, z)$. For a terrestrial laboratory, the lab-frame values of the tensor’s dominant spatial components $c_{\mu\nu}^{lab}$ depend upon the orientation of the lab with respect to the SCCEF, and thus modulate with characteristic frequency $\Omega \approx 2 \times 2\pi/(23 \text{ h } 56 \text{ min})$, or twice every sidereal day. The value of the anomalous tensor in the lab-frame can be related to that in the SCCEF via $c_{\mu\nu}^{lab} = \Lambda_{\mu}^{\mu} \Lambda_{\nu}^{\nu} c_{\mu\nu}^{SCCEF}$, where $\Lambda_{\mu}^{\nu}$ is the standard Lorentz boost plus rotation from the SCCEF to the lab frame $[3, 10, 18]$. Thanks to the Earth’s orbital velocity, the boost $\Lambda_{\mu}^{\nu}$ mixes the time and spatial components of $c_{\mu\nu}^{SCCEF}$ into the spatial components of $c_{\mu\nu}^{lab}$. This gives a measurement that searches for yearly modulations of $\delta H$ access to the parity-odd $c_{\mu\nu}^{SCCEF}$ and the isotropic $c_{\mu\nu}^{SCCEF}$ components of the anomalous tensor, albeit with a sensitivity that is suppressed by one and two factors of the Earth’s orbital boost velocity $\beta \approx 1 \times 10^{-4}$. Here, we will focus on the laboratory-frame values of $c_{\mu\nu}$ and the corresponding spherical operator elements $C_0^{(0)}$ and $C_q^{(2)}$, and drop the frame-identifying superscript.

To calculate the perturbation $\delta\omega_{nm}$ due to Eq. (2), we must first calculate the eigenstates of the rare-earth ions in their host crystal field. For trivalent rare earth ions $(R^{3+})$ in the LaCl$_3$ lattice (see, e.g., $[16]$, pg. 149), the crystal field has the point symmetry $C_{6h}$, and is determined by four crystal field parameters $B_q^k$:

$$V = B_0^2 c_{00}^{(2)} + B_4^4 c_{04}^{(4)} + B_6^6 c_{06}^{(6)} + B_6^6 c_{66}^{(6)} + c_{66}^{(6)}.$$  (4)

The simplest rare earth ion to which Eq. (4) applies is Ce$^{3+}$, with configuration $4f^1$. Following the labeling and methods of $[12]$, the eigenstates and corresponding energies of Ce$^{3+}$ are presented in Table I. In the first column of the table, labels of the states are taken from the Ref. $[17]$. The eigenstates are also distinguished by their crystal quantum number $\mu$.

For brevity, we restrict the crystal quantum number to $-\mu$ because both degenerate states get the same shift from the LLI-violating perturbation. The eigenstates $|I\rangle$, $|a\rangle$, and $|c\rangle$ are presented in Ref. $[17]$: $|\psi_{-\mu}\rangle = \xi|7/2, -7/2\rangle + \eta|7/2, 5/2\rangle + \zeta|5/2, 5/2\rangle$,  (5)

with expansion coefficients $\xi$, $\eta$ and $\zeta$ listed in Tab. I tabulated from $[17]$. Similarly, the remaining eigenstates $|II\rangle$, $|III\rangle$, $|b\rangle$, and $|d\rangle$ are (see Table I):

$$|\psi_{-\mu}\rangle = \xi|7/2, m\rangle + \zeta|5/2, m\rangle,$$  (6)
TABLE I. Experimental crystal-field splitting and calculated wave functions for Ce$^{3+}$ ($4f^3$) ions in LaCl$_3$ from reference [7]. $B_{0}^{0} = 129$, $B_{0}^{1} = -329$, $B_{0}^{2} = -997$, and $B_{0}^{3} = 403$ in cm$^{-1}$ are used in the crystal field [31]. The LLI-violating shifts of the energy levels from Eqs. (11), (12), and (13) are presented in the last column. Note that the eigenstates are doubly degenerate in non-magnetic crystals.

| Config. | State | $\mu$ | $m_{\pi}/2$ | $m_{\eta}/2$ | $m_{\zeta}/2$ | $E$ (cm$^{-1}$) | $\delta E$ ($C_{q}^{(2)} \times 10^6$ cm$^{-1}$) |
|---------|-------|-------|-------------|-------------|-------------|----------------|-----------------------------------|
| $^4$F$_{7/2}$ | | | | | | | |
| $|$d$|$ | $\pm3/2$ | $\mp3/2$ | $\mp5/2$ | $\mp5/2$ | $\mp3/2$ | 2399.5 | 1.54 |
| | | $\pm3/2$ | $\mp5/2$ | $\mp5/2$ | $\mp5/2$ | 2282.6 | -2.52 |
| $|$b$|$ | $\pm5/2$ | $\mp5/2$ | $\mp5/2$ | $\mp5/2$ | $\mp5/2$ | 2166.0 | -1.56 |
| $|$a$|$ | | $\pm7/2$ | $\mp7/2$ | $\mp5/2$ | $\mp5/2$ | $\mp5/2$ | $\mp5/2$ | 0 | -3.16 |

where $m = 1/2$ or $3/2$, as shown in Tab. I. These basis states are approximated by the relativistic, four-component spinor Hartree-Fock (HF) orbitals of the free Ce$^{3+}$ ion.

$\psi_{nm}(r) = \frac{1}{r} \left( \frac{f_{n\kappa}(r)\Omega_{\kappa m}(\theta, \phi)}{i\alpha g_{nm}(r)\Omega_{-\kappa m}(\theta, \phi)} \right),  \quad (7)$

where the non-relativistic two-component spinor is defined by

$\Omega_{\kappa m}(\theta, \phi) = \left( \begin{array}{c} \pm \sqrt{\frac{\kappa+1/2-m}{2\kappa+1}} Y_{l,m-1/2}(\theta, \phi) \\ \sqrt{\frac{\kappa+1/2+m}{2\kappa+1}} Y_{l,m+1/2}(\theta, \phi) \end{array} \right),  \quad (8)$

and $\kappa = \mp(j+1/2)$ (for $j = l \pm 1/2$) is the unified quantum number denoting angular momentum and parity.

For transitions between states with the same quantum number $n$ and total angular momentum $J$, the main contribution of the LLI-violating perturbation of Eq. (2) comes from the tensor $T_q^{(2)}$ operator. Its matrix elements may be written as

$\langle n'k'm' | T_q^{(2)} | n\kappa m \rangle = (-1)^{J'-m'} \left( \begin{array}{c} j' \ 2 \\ -m' \ 0 \end{array} \right) \times \langle k' \ | c_q^{(2)} \ | \ k \rangle I(k', \kappa),  \quad (9)$

where $I(k', \kappa)$ represents a radial integral [19], given explicitly in the Supplement. The reduced matrix element of the tensor $c_q^{(2)}$ is

$\langle k' \ | c_q^{(2)} \ | \ k \rangle = (-1)^{J'+\mp} \sqrt{|j'\cdot j|} \left( \begin{array}{c} j' \ j \ k \\ -1 \ 1 \ 0 \end{array} \right),  \quad (10)$

where $[j', j] \equiv (2j'+1)(2j+1)$.

The energy shifts due to LLI violation can be calculated using equations (2), (9), and (10). In terms of the expansion coefficients and radial integrals $I(a, b)$ defined in the Supplement, the shifts of the states $|I\rangle$, $|a\rangle$, and $|c\rangle$ in Eq. (10) are

$\delta E = \frac{C_q^{(2)}}{21} \left( \begin{array}{c} (7\xi^2 + \eta^2)(I(-4, -4) + 6\zeta^2I(3, 3) + 2\sqrt{6}\zeta\eta I(-4, 3)) \end{array} \right),  \quad (11)$

Two other states $|IJ\rangle$ and $|b\rangle$ have the shifts

$\delta E = -\frac{C_q^{(2)}}{21} \left( \begin{array}{c} (5\xi^2I(-4, -4) + \frac{24}{5}\zeta^2I(3, 3) - 4\sqrt{\frac{5}{6}}\zeta I(-4, 3)) \end{array} \right),  \quad (12)$

with $m = 1/2$ in Eq. (6), while the states $|III\rangle$ and $|d\rangle$ have the energy shifts of the levels

$\delta E = -\frac{C_q^{(2)}}{21} \left( \begin{array}{c} (3\xi^2I(-4, -4) + \frac{6}{5}\zeta^2I(3, 3) - 6\sqrt{\frac{5}{3}}\zeta I(-4, 3)) \end{array} \right),  \quad (13)$

Here the radial integrals can be obtained from the formulae $I_5$ and $I_1$ in the Supplement, and are taken over HF wave functions. Their numerical values are $I(3, 3) = -50.0$, $I(-4, -4) = -49.33$, and $I(-4, 3) = -49.58$ in atomic units (a.u.). The total shift of each state is presented in the rightmost column of Tab. I. The largest relative energy shift is that between the ground $|I\rangle$ state and the low-lying $|II\rangle$ state, with $\delta \omega_{I,II} = (2\pi)C_q^{(2)}(2.76 \times 10^{16})$. A similarly large LLI-violating energy shift is observed for the $|I\rangle$ to $|b\rangle$ transition.

In contrast to the case of neutral dysprosium, the contribution of the scalar $T_0^{(0)}$ component of the LLI-violating perturbation in Eq. (2) to the ions' transition energies is smaller than that of the tensor operator $T_q^{(2)}$ [1]. This is due to the fact that the low-lying
ion excitations are largely between states with the same
quantum number $n$ and total angular momentum $J$. In
the non-relativistic limit, the scalar operator $\tau_0^{(0)}$ is pro-
torical to the sum of the bound electrons’ kinetic en-
nergy $\sum_i \frac{p_i^2}{2m}$. Using the virial theorem in a Coulomb po-
tential, the electrons’ binding energy is approximately
equal to their kinetic energy. The LLI-violating change
in the transition energy between bound states with the
same $n$ and different $J$ is therefore expected to scale as
$\delta \omega_{nm} \approx C_0^{(0)} (6 \times 10^{13} \text{Hz})$. This, combined with the com-
paratively small range of variation in $U/e^2$ accessible to a
terrestrial laboratory ($\sim 10^{-10}$ in the Sun’s potential over
a year), implies this ion could serve as a stable reference

$$
\delta E(J, \mu) = -C_0^{(2)} \langle \mu J \parallel T^{(2)} \parallel \mu J \rangle - \frac{3 \sum_M a_M^2 M^2 - J(J+1)}{(2J+3)(J+1)(2J+1)J(2J-1)}
$$

where $a_M$ are the coefficients for the wave functions pre-
sented in Tab. I. Inspection of Tab. I reveals that the max-
imal change in the ions’ transition frequencies due to
LLI-violation is $\delta \omega_{bc} = 2\pi C_0^{(2)} (5.6 \times 10^{16} \text{Hz})$ for Nd$^{3+}$
and $\delta \omega_{bc} = 2\pi C_0^{(2)} (11 \times 10^{16} \text{Hz})$ for Er$^{3+}$. As in the case
of Ce$^{3+}$, the scalar shift proportional to $C_0^{(0)}$ is expected
to be comparatively negligible.

A dedicated experiment measuring the THz-scale en-
ergy splitting between the $| e \rangle$ and $| e \rangle'$ states of Er$^{3+}$ at
the level of 1 mHz would be sensitive to $C_0^{(2)}$ as small
as $10^{-20}$. To estimate the reach of existing experimental
measurements of Er$^{3+}$ transitions, we have also consid-
ered optical transitions in Er$^{3+}$:Y$_2$SiO$_5$ [21]. Because
of the lower symmetry $C_{2h}$ of the crystal Y$_2$SiO$_5$ field,
We have demonstrated that the ground state spectrum of rare earth ions doped in a crystalline host can be used to perform a sensitive test of LLI. We have taken advantage of existing work on the spectrum of Er$^{3+}$, Nd$^{3+}$, and Ce$^{3+}$ to perform an explicit calculation of these ions’ energy shifts in response to LLI-violation when doped in LaCl$_3$. The energy levels and sensitivities of Ce$^{3+}$, Nd$^{3+}$, and Er$^{3+}$ ions are expected to be similar when doped in different crystalline media. Er$^{3+}$ is a particularly interesting case, as the optical coherence of the $J = 15/2 ightarrow J = 13/2$ transition is particularly long-lived at 4.4 ms for 0.001% doping concentration Er$^{3+}$:Y$_2$SiO$_5$. An experiment that is sensitive to a 1 mHz orientation-dependent modulation of the $Z_1 ightarrow Y_1$ optical transition in Er$^{3+}$:Y$_2$SiO$_5$ could measure spatial components of the electronic $c_{\mu \nu}$ tensor as small as $10^{-10}$, improving upon existing limits by an order of magnitude. An experiment measuring orientation-dependent modulations of the THz-scale energy difference between the $|c\rangle$ and $|e\rangle$ states (see Tab. I) at the mHz would be more sensitive still, probing the LLI-violating $c_{\mu \nu}$ tensor at the level of $10^{-20}$. We note that dynamic decoupling techniques, which switch between states with quantum numbers of equal magnitude and opposite sign do not suppress the LLI-violating signal proportional to the quadrupole component of $C_0^{(2)}$ of $c_{\mu \nu}$. Other rare earth ion-doped materials may also prove to be useful for testing this and other aspects of LLI, and are a promising area for future work.

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**SUPPLEMENT**

The radial integrals included in Eq. (9) are from Ref. [19], and are summarized in this Supplement for convenience. According to the quantum numbers $\kappa'$ and $\kappa$, [1] V.A. Kostelecký and S. Samuel, Phys. Rev. Lett. 63, 224 (1989); Phys. Rev. D 40, 1886 (1989).
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the radial integrals take one of the following forms:

\[
I_1 = \frac{\alpha}{\hbar} \int_0^\infty dr \left((2\kappa - 1)g_{n'\kappa'} \frac{\partial f_{n\kappa}}{\partial r} + (2\kappa + 3)f_{n'\kappa'} \frac{\partial g_{n\kappa}}{\partial r} - \frac{(2\kappa - 1)(\kappa + 1)}{r} g_{n'\kappa'} f_{n\kappa} - \frac{(2\kappa + 3)\kappa}{r} f_{n'\kappa'} g_{n\kappa}\right)
\]

for \(\kappa' = -\kappa + 2\), and

\[
I_4 = -\frac{\alpha}{\hbar} \int_0^\infty dr \left(\frac{\partial f_{n\kappa}}{\partial r} + \frac{\kappa + 1}{r} g_{n'\kappa'} f_{n\kappa}\right)
\]

for \(\kappa' = \kappa + 2\), and

\[
I_5 = -\frac{\alpha}{\hbar} \int_0^\infty dr \left(\frac{\partial f_{n\kappa}}{\partial r} + \frac{\kappa}{r} g_{n'\kappa'} f_{n\kappa} + \frac{\kappa}{r} f_{n'\kappa'} g_{n\kappa}\right)
\]

for \(\kappa' = \kappa\). In the nonrelativistic limit the matrix element \(\langle \phi | c \alpha j p^k | \phi \rangle\) becomes \(\langle \phi | p^j p^k | m | \phi \rangle\). This changes the radial integrals in Eq. (9). Only the radial integrals differ between the relativistic and the nonrelativistic limits, while the angular parts of the matrix elements are the same. In the non-relativistic limit, \(I_1\) and \(I_5\) reduce to

\[
I_1 = \hbar^2 \int_0^\infty dr \left(\frac{\partial f_{n'\kappa'}}{\partial r} \frac{\partial f_{n\kappa}}{\partial r} + \frac{\kappa(\kappa + 1)}{r^2} f_{n'\kappa'} f_{n\kappa}\right)
\]

\(I_2\) and \(I_3\) become

\[
I_2 = \hbar^2 \int_0^\infty dr \left(\frac{\partial f_{n'\kappa'}}{\partial r} \frac{\partial f_{n\kappa}}{\partial r} - \frac{2\kappa - 1}{r} f_{n'\kappa'} \frac{\partial f_{n\kappa}}{\partial r} - \frac{\kappa(\kappa - 2)}{r^2} f_{n'\kappa'} f_{n\kappa}\right)
\]

and \(I_4\) takes the form of

\[
I_3 = \hbar^2 \int_0^\infty dr \left(\frac{\partial f_{n'\kappa'}}{\partial r} \frac{\partial f_{n\kappa}}{\partial r} + \frac{2\kappa + 3}{r} f_{n'\kappa'} \frac{\partial f_{n\kappa}}{\partial r} - \frac{(\kappa + 3)(\kappa + 1)}{r^2} f_{n'\kappa'} f_{n\kappa}\right).
\]