Parity Violating Energy Shifts and Berry Phases in Atoms, I

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We present a study of parity (P) violating contributions to the eigenenergies of stationary systems containing atoms in spatially inhomogeneous external electric fields. In this context the subtle interplay of P-violation and time reversal (T) invariance plays an important role. If the entire field configuration is chosen to exhibit chirality the energies are in general shifted by pseudoscalar contributions which change sign under a planar reflection of the field. In part I we consider sudden variations of the fields and calculate P-violating energy shifts using perturbation theory. In part II the adiabatic case will be treated and the connection to geometrical (Berry-) phases will be elucidated. To calculate the effects we use the standard model of elementary particle physics where the P-odd interaction arises through the exchange of Z-bosons between the quarks in the nucleus and the atomic electrons. We consider in detail hydrogen-like systems in unstable levels of principal quantum number \( n = 2 \). We study atoms with vanishing nuclear spin like \( \text{\textfrac{2}{3}} \)He\(^+\) and with nuclear spin \( I = 1/2 \) like \( \text{\textfrac{1}{2}} \)H. The nominal order of P-violating effects is \( 10^{-5} \ldots 10^{-9} \) Hz which is determined by the mixing of the \( 2S_{1/2} \) and \( 2P_{1/2} \) states. However we point out that with certain configurations of the external fields, it is possible to enhance the P-violating energy shifts dramatically! Instead of energy shifts linear in the P-violation parameters we get then shifts proportional to the square root of these parameters. Numerically we find such energy shifts which only appear for unstable states to be of order \( 10^{-5} \ldots 1 \) Hz. Under a reversal of the handedness of the external field configuration these P-violating shifts get multiplied by a phase factor \( i \), i.e. the shifts in the real and imaginary part of the complex eigenenergies are exchanged. Application of our technique to hydrogen-like atoms with a nucleus of spin \( I = 1/2 \) yields P-violating energy shifts which are very sensitive to the nuclear spin dependent P-odd force, which receives a rather large contribution from the polarized strange quark density in polarized nuclei. Thus, a measurement of these energy shifts could provide an important tool to elucidate nuclear properties connected to the so called “spin crisis”. We also present a method for treating degenerate perturbation theory which combines advantages of both, Kato’s and Bloch’s methods.

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1 Introduction

In this paper we will discuss various possibilities to obtain parity (P) violating energy shifts for atomic systems due to effects of the weak neutral current (NC) interactions. Energy shifts, i.e. frequencies can be measured in atomic physics with very high accuracy. Thus P-violating energy shifts could open up a new window for measurements of the tiny NC effects in atoms. There are some “no go” theorems for such energy shifts which are related to time reversal (T) invariance. However, each theorem needs some assumptions, and in the following we will show how the “no go” theorems can be avoided by considering situations where these assumptions are not fulfilled.

In our paper we will stay in the framework of the Standard Model (SM) of elementary particle physics [1] which led to detailed predictions of P-violating NC effects in atoms [2, 3]. By now such effects are well studied theoretically and have been verified experimentally for heavy atoms containing many electrons (for reviews cf. [1, 4, 5]). But P-violating effects have not been measured yet for hydrogen-like atoms, where theoretical calculations can be pushed to very high accuracy [4]. Proposals for P-violation experiments with hydrogenic systems have been made e.g. in [8]-[15]. In [15], a variety of P-violating polarization rotations was studied theoretically. It was also shown that, in principle, P-violating contributions to the energy levels of (unstable) hydrogen-like atoms in suitable external electric fields should exist. In the present work we will address that question in detail.

In the days of high precision tests of the SM at high energies, e.g. at LEP and SLC (cf. [16] for a review), we should list some motivations for our study:

(1) In order to check the “running” of the SM couplings as it is predicted by the renormalization theory, atomic systems should be useful, providing low energy information complementary to high energy physics measurements. In this way a very sensitive test of higher order effects in the SM and a probing for new physics beyond the SM is possible.

(2) P-violating effects in atoms can give interesting information on properties of atoms and nuclei. The experimental study of anapole moments of nuclei has recently become possible in this way [17, 18]. P-violation in atoms may also shed light on the so-called “spin crisis” for the nucleons [18, 19].

(3) In part II we will show how P-violating energy shifts in atoms can emerge as a topological effect in quantum mechanics, i.e. as P-violating geometrical (Berry-) phases. To study such effects should be interesting in itself.

(4) There are many recent advances in experimental techniques of atomic physics, like the production and storage of “cold” heavy ion beams in storage rings (cf. [20] and references therein) and the observation of interference effects with atomic beams (cf. [21] for a review). Recent progress has been made on techniques of atomic mirrors [22], microtraps for ultracold atoms [23] and of semiconductor nano-structures, which could be used to realize experimental configurations as they will be described below. One could also imagine applications of the recently observed carbon nanotubes [24] or of the football-shaped fullerenes [25]. In a natural way they represent cavities with a diameter of a few Å, which are required for the purpose of measuring our P-violation
effects for atoms being stored inside them.

This paper continues the work done in [13, 15] and much of the formalism will be taken over from there. We are studying excited hydrogen-like atomic systems within external electric and magnetic field configurations. In the following we will briefly recall the methods including the Wigner-Weisskopf-approximation [26] for unstable states. We then examine P-violating energy shifts of atoms in external electric fields for two basically different experimental setups with either sudden or adiabatically smooth local variations of the electric field vector. Part I will be restricted to the sudden approximation case, while the adiabatic situation will be studied in part II which is in preparation. In Section 2 we consider the case of an atom inside a box with two segments only and show that there are no P-violating energy shifts due to T-invariance. In Section 3 we present results from perturbation theory for boxes with three segments. Our conclusions are drawn in Section 4, where we also discuss the relation of the P-violating energy shifts presented in our paper to those in chiral molecules.

A short account of some of the results presented in detail here has been published in [27].

From the methodological point of view we deal in Section 3 with degenerate perturbation theory, which has been treated in the classical papers by Kato and Bloch [28, 29] and which is masterly explained in [30]. We introduce a variant of degenerate perturbation theory which we find very convenient for our problems and which should be interesting for many other applications. Our ansatz is analogous to the introduction of normal coordinates in the problem of small oscillations in mechanics (cf. e.g. [31]).

In part II, which is in preparation, we will describe P-violating effects in smoothly varying fields using a WKB-approximation. We relate the energy shifts of stationary systems via boundary conditions back to geometrical phases which the atomic wave functions acquire in the external field, whose topological properties in a suitable space are crucial.

All our formulae are written in natural units, \( \hbar = c = 1 \), if other units are not explicitly indicated.

1.1 P-violation in hydrogen-like atomic systems in external fields

We consider a hydrogen-like system, i.e. a nucleus with a single electron or muon around it. It is crucial for our purpose to consider the coupling of the internal motion of the atom, in general in an unstable state, with the c.m. motion of the atom as a whole. Thus we will first discuss the formalism which we will use for describing this situation. For simplicity we will assume throughout the paper, except in Sect. 1.3, that for both, the c.m. motion and for the internal atomic motion, we can make the non-relativistic approximation.

Our system consists of two charged particles, the lepton \( \ell \) and the nucleus \( A \) with \( Z \) protons and \( N \) neutrons, where \( \ell \) and \( A \) are bound together and experience an external electromagnetic field described by a 4-vector potential \((A^0(x), \textbf{A}(x))\). As basic dynamic
variables we have the c.m. coordinate $\mathbf{R}$ and the relative coordinate $\mathbf{x}$:

$$
\mathbf{R} = \frac{m_\ell \mathbf{x}_\ell + m_A \mathbf{x}_A}{m_\ell + m_A},
$$

$$
\mathbf{x} = \mathbf{x}_\ell - \mathbf{x}_A,
$$

(1.1)

where $\mathbf{x}_\ell, \mathbf{x}_A$ are the position vectors of $\ell, A$, respectively. A simple exercise shows that in the non-relativistic case the Hamiltonian of the system can be written as follows:

$$
H = \frac{1}{2m} (\mathbf{P} - q\mathbf{A}(\mathbf{R}, t))^2 + qA^0(\mathbf{R}, t)
+ H^{INT} - \mathbf{D} \cdot \mathbf{E}(\mathbf{R}, t) - \mathbf{\mu} \cdot \mathbf{B}(\mathbf{R}, t)
+ H_0^{(\gamma)} + H_{rad}
$$

(1.2)

Here $m$ and $q$ are the total mass and charge of the atom:

$$
m = m_A + m_\ell
$$

$$
q = (Z - 1)e.
$$

(1.3)

We denote by $e$ ($e > 0$) the proton charge. The components of the momentum operator for the c.m. motion are

$$
P_j = \frac{1}{i} \frac{\partial}{\partial R_j}, \quad (j = 1, 2, 3).
$$

(1.4)

The Hamiltonian for the internal motion in the c.m. system in the absence of external fields is denoted by $H^{INT}$. The electric and magnetic dipole moment operators are $\mathbf{D}$ and $\mathbf{\mu}$, respectively, and $\mathbf{E}(\mathbf{R}, t), \mathbf{B}(\mathbf{R}, t)$ are the electric and magnetic fields at the c.m. position:

$$
\mathbf{E}(\mathbf{R}, t) = -\nabla A^0(\mathbf{R}, t) - \frac{\partial}{\partial t} \mathbf{A}(\mathbf{R}, t),
$$

$$
\mathbf{B}(\mathbf{R}, t) = \nabla \times \mathbf{A}(\mathbf{R}, t).
$$

(1.5)

Finally $H_0^{(\gamma)}$ is the Hamiltonian of the free photons and $H_{rad}$ describes the coupling of the atom to the photons.

In (1.2) we have neglected the variation of the electric and magnetic fields over the atomic dimensions. We have also neglected terms proportional to $\dot{\mathbf{R}} \times \mathbf{E}$ and $\dot{\mathbf{R}} \times \mathbf{B}$ coming from the fact that the electric and magnetic fields felt by the atom are those in its actual rest system. Such terms give rise to the motional Stark and Zeeman effects. Thus for our purpose the motion of the atom should be very slow. Since we are interested here in the principle of P-violating energy shifts, we want to study the simplest possible cases. We only have to make sure that our approximations do not introduce any spurious sources of P-violation.

Let us now have a closer look at the Hamiltonian of the internal atomic motion which we write as

$$
H^{INT} = H_0^{INT} + H_{PV},
$$

(1.6)

\footnote{A detailed discussion of the c.m. and relative coordinates for relativistic systems including spin can be found in [32].}
where $H_{\nu}^{NT}$ is the P-conserving piece and $H_{\nu}$ the P-violating one.

In the framework of the SM the relevant effective P-violating Hamiltonian $H_{\nu}$ is — to leading order — due to $Z$ exchange between the atomic lepton and the quarks in the nucleus. In the non-relativistic limit one finds (cf. e.g. [15]: we use the notation as in Section 2 of [15]):

$$H_{\nu} = H_{\nu}^{(1)} + H_{\nu}^{(2)},$$

$$H_{\nu}^{(1)} = \frac{G}{4\sqrt{2} m_\ell} Q_{w}^{(1)}(Z, N) \cdot \left\{ \delta^3(x)(\sigma \cdot p) + (\sigma \cdot p)\delta^3(x) \right\},$$

$$H_{\nu}^{(2)} = \frac{G}{4\sqrt{2} m_\ell} Q_{w}^{(2)}(Z, N) \cdot \left\{ \delta^3(x)(I \cdot \sigma)(\sigma \cdot p) + (\sigma \cdot p)(I \cdot \sigma)\delta^3(x) \right\},$$

where $H_{\nu}^{(2)}$ depends on the nucleus’ spin $I$ and $H_{\nu}^{(1)}$ does not. $G$ is Fermi’s constant, furthermore, $p$ and $\sigma$ are the momentum and spin operators of the lepton $\ell$ and $Q_{w}^{(1,2)}$ are the weak charges of the nucleus

$$Q_{w}^{(1)}(Z, N) = \frac{1}{4}(1 - 4 \sin^2 \theta_w) - N,$$

$$Q_{w}^{(2)}(Z, N) = \frac{1}{7}(1 - 4 \sin^2 \theta_w) \left[ \Delta u(Z, N) - \Delta d(Z, N) - \Delta s(Z, N) \right],$$

where $\theta_w$ is the weak angle and the $\Delta q$ are defined as the “total polarizations” carried by the quark species $q = u, d, s$. It is assumed in [11] that possible contributions of the $c, b$ and $t$ quarks in the nucleus can be neglected. We refer the reader to [15] and to the references therein for more details.

The energy levels of the hydrogen-like atom in the Coulomb approximation are $1S, 2S, 2P$ etc., where $2S$ and $2P$ are degenerate. These levels are split by the fine structure, the Lamb shift and further QED effects as well as by the hyperfine structure if the nuclear spin $I \neq 0$. The resulting near degeneracy of the opposite parity states $2S$ and $2P$ makes the $n = 2$ levels in principle ideal candidates for looking for P-violating effects. Also, the $2S$ state is long lived. Thus we will concentrate on the atoms in $n = 2$ states in the following.

The relevant dimensionless parameters measuring the “wrong” parity admixture in the $n = 2$ states are $\delta_i(Z, N)$, $i = 1, 2$, defined in (3.17) of [13], which are proportional to $Q_{w}^{(i)}(Z, N)$. For electronic atoms we have approximately (cf. (3.21) of [15]):

$$\delta_i(Z, N) \simeq -Q_{w}^{(i)}(Z, N) \cdot 6.14 \times 10^{-12}.\tag{1.12}$$

Let us discuss next the Hilbert space of state vectors for our system. We will consider atoms in $n = 2$ states, denoted $|2, a\rangle$, $a = 1, 2, \ldots$ (cf. Sect. 3.1 of [15]), and at arbitrary c.m. position $R$, and their decay products, i.e. atoms in $n = 1$ states plus photons. A basis in our Hilbert space is then provided by the vectors

$$|R; 2, a\rangle,$$

$$|R; 1, b; \gamma, k\rangle,\tag{1.13}$$

where we label by $k = 1, 2, \ldots$ a convenient basis set of photon states and by $b = 1, 2, \ldots$, the internal $n = 1$ atomic states. We assume these states to be normalized to

$$\langle R'; 2, a'| R; 2, a\rangle = \delta^{(3)}(R' - R) \delta_{a'a},$$

$$\langle R'; 1, b'; \gamma, k'| R; 1, b; \gamma, k\rangle = \delta^{(3)}(R' - R) \delta_{\gamma\gamma} \delta_{k'k},\tag{1.14}$$
with all other scalar products vanishing.

Consider now a general state vector \( | t \rangle \) at some time \( t \). The part of the state vector describing the undecayed \( n = 2 \) atoms is (cf. (3.6), (3.7) of \[15\]):

\[
\Psi(R, t) = \sum_a \psi_a(R, t) | 2, a \rangle,
\]

(1.15)

where

\[
\psi_a(R, t) = \langle R; 2, a | t \rangle.
\]

(1.16)

The wave function \( \Psi \) can be thought of as a Schrödinger wave function for the c.m. motion, but with a number of components equal to the number \( N \) of linearly independent \( n = 2 \) states labeled by \( a \). Thus we can also write \( \Psi \) as an \( N \)-component wave function:

\[
\Psi(R, t) \leftrightarrow \begin{pmatrix}
\psi_1(R, t) \\
\psi_2(R, t) \\
\vdots \\
\psi_N(R, t)
\end{pmatrix}.
\]

(1.17)

Similarly, the \( n = 1 \) states plus photons are described by multi-component wave functions (cf. (3.8) of \[15\])

\[
\Phi_k(R, t) = \left( \langle R; 1, b; \gamma, k | t \rangle \right).
\]

(1.18)

The general methods \[26\] for obtaining the non-hermitian mass matrix can now be applied (cf. Sect. 3.2 of \[15\]). Starting from the Hamiltonian (1.2) this gives us an effective Schrödinger equation for the state vector \( \Psi(R, t) \) as follows:

\[
i \frac{\partial}{\partial t} \Psi(R, t) = (H_{\text{eff}} \Psi)(R, t),
\]

(1.19)

where \( H_{\text{eff}} \) is a non-hermitian operator:

\[
H_{\text{eff}} = \frac{1}{2m} (P - qA(R, t))^2 + qA^0(R, t) + \mathcal{M}(R, t),
\]

(1.20)

\[
\mathcal{M}(R, t) = \mathcal{M}_0 - D \cdot \mathcal{E}(R, t) - \mu \cdot \mathcal{B}(R, t),
\]

(1.21)

\[
\mathcal{M}_0 = \left( (2, a | H_0^{\text{INT}} + H_{\text{PV}} | 2, b) \right) - \frac{i}{2} \Gamma,
\]

\[
D = \left( (2, a | D | 2, b) \right),
\]

\[
\mu = \left( (2, a | \mu | 2, b) \right).
\]

(1.22)

As in \[15\], quantities with a bar underneath denote matrices in the space of \( n = 2 \) states. Thus \( D \) and \( \mu \) are the corresponding matrices of the electric and magnetic dipole operators, respectively. In (1.22) the matrix \( \Gamma \) is the decay rate matrix for the \( n = 2 \) states as defined in (3.13) of \[15\]. Here we have assumed that the decay rates from specific states \( | 2, a \rangle \) do not depend on their c.m. motional state. This is an approximation which neglects e.g. relativistic time dilatation effects. But again, no spurious P-violation is introduced in this way.
In the following we will be concerned with finding solutions to (1.19) for various field configurations. In particular, we will be interested in electric and magnetic field configurations which are constant in time and consider the eigenstates $\Psi(R)$ of $H_{\text{eff}}$ for this situation:

$$H_{\text{eff}}\Psi(R) = E \Psi(R).$$

(1.23)

In general the eigenvalue $E$ is, of course, complex. The wave functions $\Psi(R)$ satisfying (1.23) correspond to states with single exponential decay. We note that a non-hermitian operator $O$ does not need to be diagonalizable, i.e. in general there will be no linear operator $V$ satisfying $V^{-1}OV = \text{diagonal operator}$. A finite $N$-dimensional non-hermitian matrix is always diagonalizable if it has $N$ different eigenvalues. In the case of degeneracies of eigenvalues diagonalization is in general not possible even for finite $N$, and the right (left) eigenstates form no longer a basis (cf. e.g. [33]). In the following we will in the general analysis always assume that all non-hermitian matrices/operators occurring are diagonalizable. In the specific examples discussed we check explicitly that this assumption is valid.

The basic question which we study in this paper is as follows: under what circumstances can the complex energy eigenvalue $E$ have linear terms in the $P$-violation parameters $\delta_1, \delta_2(Z,N)$. Since these parameters are very small, we will neglect terms quadratic in $\delta_1, \delta_2$ in our calculations below. How could experimentalists look for terms linear in $\delta_1, \delta_2$? The typical strategy which we have in mind is as follows. Consider an electric field arrangement $\mathcal{E}(x)$ and the parity-transformed one:

$$\mathcal{E}_p(x) = -\mathcal{E}(-x).$$

(1.24)

Let $E(\mathcal{E}, \delta_1, \delta_2)$ be the energy eigenvalue of some level in the field $\mathcal{E}(x)$ and $E(\mathcal{E}_p, \delta_1, \delta_2)$ the eigenvalue of the corresponding level in the field $\mathcal{E}_p(x)$. The basic observable to study experimentally is the energy difference:

$$\Delta E = E(\mathcal{E}, \delta_1, \delta_2) - E(\mathcal{E}_p, \delta_1, \delta_2).$$

(1.25)

Clearly, in order for $\Delta E$ to have a chance to be nonzero, the field configurations $\mathcal{E}(x)$ and $\mathcal{E}_p(x)$ must be essentially different, i.e. they should not be transformable into each other by a proper rotation. In other words: the field configuration $\mathcal{E}(x)$ must have handedness or chirality.

Now we note that from considering a P-transformation we get:

$$E(\mathcal{E}, \delta_1, \delta_2) = E(\mathcal{E}_p, -\delta_1, -\delta_2).$$

(1.26)

This leads to

$$E(\mathcal{E}, 0, 0) = E(\mathcal{E}_p, 0, 0).$$

(1.27)

If we first exclude the case where there is a degeneracy of levels for $\delta_{1,2} = 0$, the eigenvalues $E$ are differentiable in $\delta_{1,2}$ at this point (cf. appendix C of [13]) and we get:

$$\Delta E = 2 \sum_{i=1,2} \delta_i \frac{\partial E(\mathcal{E}, \delta_1, \delta_2)}{\partial \delta_i} \bigg|_{\delta_{1,2}=0} + \mathcal{O}(\delta_1^2, \delta_1 \delta_2, \delta_2^2).$$

(1.28)
Thus, the measurable asymmetry (1.25) is directly related to the terms in the energy eigenvalues $E(\mathcal{E},\delta_1,\delta_2)$ which are linear in $\delta_1,\delta_2$. In practice degeneracies of levels for $\delta_{1,2} = 0$ do occur and have to be dealt with carefully. As we will show, such degeneracies can be used to obtain $P$-violating energy differences (1.25) which are proportional to $\sqrt{\delta_i}$. Thus we get huge enhancements of $P$-violating energy shifts of order $1/\sqrt{\delta_i} \approx 10^6$ for special external field arrangements. Varying the fields around these special values one should observe sharp resonance type phenomena.

Of course, instead of the asymmetry (1.25) we could consider the asymmetry of the energies in the field $\mathcal{E}(x)$ and a field $\mathcal{E}_R(x)$ obtained from $\mathcal{E}$ by reflection on some plane. Maybe it is also possible to make a continuous change from $\mathcal{E}(x)$ to $\mathcal{E}_v(x)$ or $\mathcal{E}_R(x)$ and observe the corresponding continuous change of the energy eigenvalues.

1.2 Atoms in a constant electric field

Let us consider a simple case to start with: an atom in a constant electric field $\mathcal{E}$. We assume the atom to be confined inside a region $B$ which can be of arbitrary shape. This confinement of the atom in $B$ could, for instance, be realized by having the walls of a suitable trap containing the atom built as “mirrors” (cf. [22]). We represent the “vessel” or “trap” containing the atom by a potential $V_b(R)$ which is zero inside the vessel and infinite outside. This leads to the following boundary condition for the wave function $\Psi(R)$:

$$\Psi(R) = 0 \quad \text{for} \quad R \in \partial B$$

(1.29)

where $\partial B$ denotes the boundary of $B$. In the following (1.29) is always understood to be imposed. The effective Hamiltonian (1.20) reads now

$$H_{\text{eff}} = \frac{P^2}{2m} - q R \cdot \mathcal{E} + M_0 - D \cdot \mathcal{E}.$$  

(1.30)

The eigenvalue equation (1.23) can easily be discussed for this case. Clearly, we can diagonalize the operators governing the c.m. motion,

$$H^{\text{EXT}} = \frac{P^2}{2m} - q R \cdot \mathcal{E},$$

(1.31)

and the internal motion,

$$\mathcal{M} = M_0 - D \cdot \mathcal{E},$$

(1.32)

separately, form the tensor product of the corresponding eigenvectors and add the corresponding eigenvalues. Indeed, let $\phi_n(R)$, $n = 1, 2, ...$, be a complete set of orthonormal eigenvectors of $H^{\text{EXT}}$:

$$H^{\text{EXT}} \phi_n(R) = E^{\text{EXT}}_n \phi_n(R),$$

(1.33)

where $E^{\text{EXT}}_n$ are the eigenvalues which are, of course, real since $H^{\text{EXT}}$ is a hermitian operator. Let $|\beta\rangle$ be the right eigenvectors of $\mathcal{M}$ to eigenvalues $E^{\text{INT}}(\beta)$, which can be complex:

$$\mathcal{M} |\beta\rangle = E^{\text{INT}}(\beta) |\beta\rangle, \quad (\beta = 1, 2, ..., N).$$

(1.34)
Then the eigenvectors $\Psi$ of $H_{\text{eff}}$ (1.30), (1.23) are

$$\Psi_{\beta,n}(R) = \phi_n(R) |\beta\rangle \equiv |\beta,n\rangle,$$  

(1.35)

with eigenvalues

$$E(\beta,n) = E_{a}^{\text{EXT}} + E_{\text{INT}}^{\beta}(n),$$  

(1.36)

i.e. we have

$$H_{\text{eff}} \Psi_{\beta,n}(R) = E(\beta,n) \Psi_{\beta,n}(R).$$  

(1.37)

Here we can assume without loss of generality that the electric field points in 3-direction:

$$\mathcal{E} = \mathcal{E} e_3.$$  

(1.38)

The eigenvalues and eigenvectors of the corresponding mass matrix

$$M = M_0 - D_3 \mathcal{E}$$  

(1.39)

were discussed extensively in [15]. For later use and to fix the notations we recall the main features here.

For an electric field (1.38) the mass matrix $M$ (1.39) commutes with the 3-component $\mathcal{F}_3$ of the total angular momentum operator:

$$[M, \mathcal{F}_3] = 0.$$  

(1.40)

We can diagonalize $M$ and $\mathcal{F}_3$ simultaneously. The right eigenvectors $|\alpha, F_3, \mathcal{E} e_3\rangle$ satisfy:

$$\mathcal{F}_3 |\alpha, F_3, \mathcal{E} e_3\rangle = F_3 |\alpha, F_3, \mathcal{E} e_3\rangle,$$

$$M |\alpha, F_3, \mathcal{E} e_3\rangle = E_{\text{INT}}^{\alpha}(\alpha, F_3, \mathcal{E} e_3) |\alpha, F_3, \mathcal{E} e_3\rangle;$$  

(1.41)

the left eigenvectors $(\alpha, \tilde{F}_3, \mathcal{E} e_3)$ satisfy:

$$(\alpha, \tilde{F}_3, \mathcal{E} e_3) \mathcal{F}_3 = (\alpha, F_3, \mathcal{E} e_3) F_3,$$

$$(\alpha, \tilde{F}_3, \mathcal{E} e_3) M = (\alpha, F_3, \mathcal{E} e_3) E_{\text{INT}}^{\alpha}(\alpha, F_3, \mathcal{E} e_3).$$  

(1.42)

Here we label the eigenvectors by $(\alpha, F_3)$ instead of $\beta$ as above, with $\alpha = 1, 2, ...$ numbering the eigenvectors to the same $F_3$. We will assume that there is no degeneracy of the complex energy levels for fixed $F_3$:

$$E_{\text{INT}}^{\alpha}(\alpha, F_3, \mathcal{E} e_3) \neq E_{\text{INT}}^{\alpha'}(\alpha', F_3, \mathcal{E} e_3) \text{ for } \alpha \neq \alpha'.$$  

(1.43)

This is true for all systems in external fields which we will consider. The condition (1.43) guarantees that the right eigenvectors (1.41) (left eigenvectors (1.42)) form a basis (the dual basis) in the $n = 2$ subspace where the normalization can be chosen such that

$$(\alpha, \tilde{F}_3, \mathcal{E} e_3 | \alpha', F_3', \mathcal{E} e_3) = \delta_{\alpha,\alpha'} \delta_{F_3,F_3'}.$$  

(1.44)

We introduce quasiprojectors (cf. (3.28) of [15]):

$$\Pi(\alpha, F_3, \mathcal{E} e_3) = |\alpha, F_3, \mathcal{E} e_3\rangle \langle \alpha, F_3, \mathcal{E} e_3|$$  

(1.45)
which satisfy
\[
\mathbb{P}(\alpha, F_3, \mathcal{E}e_3) \mathbb{P}(\alpha', F'_3, \mathcal{E}e_3) = \delta_{\alpha,\alpha'} \delta_{F_3,F'_3} \mathbb{P}(\alpha, F_3, \mathcal{E}e_3),
\]
\[
\text{Tr} \mathbb{P}(\alpha, F_3, \mathcal{E}e_3) = 1,
\]
but are not necessarily hermitian. We have
\[
\mathbb{1} = \sum_{\alpha,F_3} \mathbb{P}(\alpha, F_3, \mathcal{E}e_3),
\]
\[
\mathcal{M} = \sum_{\alpha,F_3} E^{\text{INT}}(\alpha, F_3, \mathcal{E}e_3) \mathbb{P}(\alpha, F_3, \mathcal{E}e_3),
\]
\[
F_3 = \sum_{\alpha,F_3} F_3 \mathbb{P}(\alpha, F_3, \mathcal{E}e_3).
\]
The total energies (1.36) are
\[
E(\alpha, F_3, \mathcal{E}e_3, n) = E^\text{EXT}_n + E^{\text{INT}}(\alpha, F_3, \mathcal{E}e_3).
\]

It was shown explicitly in Sect. 3.4 of [15] that the complex energy eigenvalues \(E^{\text{INT}}(\alpha, F_3, \mathcal{E}e_3)\) have no contributions linear in the P-violation parameters \(\delta_{1,2}\). This was derived by considering a reflection \(R\) on the 1-3-plane for the atom at rest. Now we have the atom in a box which need not be \(R\)-invariant. But for the constant electric field we have no coupling between the c.m. and the internal motions in our approximations. Thus even if the external field arrangement is not \(R\)-symmetric here, we still get no terms linear in \(\delta_{1,2}\) in the total energy eigenvalues \(E(\alpha, F_3, \mathcal{E}e_3, n)\) (1.50) for the constant external field.

In the following we will investigate situations where a non-trivial coupling between c.m. and internal motions is present. We will see that indeed for suitable external field arrangements having no reflection symmetry the total energy eigenvalues can get terms linear in the P-violation parameters \(\delta_{1,2}\).

### 1.3 General consequences of T-invariance

In this Section we will work out some general consequences of T-invariance for stable and unstable atomic systems in a static external electromagnetic field, described by the 4-potential \((A^\mu(x)) = (A(x), A^0(x))\). Let us start by considering the atomic system coupled to the radiation field at the level of quantum field theory (QFT). The Hamiltonian describing this system is
\[
H[A] = H_0(t) + H'[t, A],
\]
where \(H_0\), which includes the P-violating term \(H_{P^\mu}\), is the Hamiltonian for \(A^\mu = 0\), and \(H'\) is the interaction term with the external field. In terms of the fundamental lepton and quark fields the latter reads
\[
H'[t, A] = \int d^3x \, j_\mu(x, t) A^\mu(x),
\]
with \( j_\mu(x,t) \) the electromagnetic current operator. For static fields the total Hamiltonian is time-independent, as we know from Noether’s theorems. In the following we will work in the Schrödinger picture of quantum mechanics, identifying the Hamiltonians there with those of (1.51) at \( t = 0 \). Thus we set \( H_0 \equiv H_0(0) \) and \( H'[A] \equiv H'[0,A] \). We will now assume that another splitting of \( H \) can be made:

\[
H[A] = \tilde{H}_0[A] + H_{rad},
\]

where \( \tilde{H}_0[A] \) describes stable atomic systems in the external field \( A^\mu(x) \) and \( H_{rad} \) their coupling to the radiation field. This coupling will render the above systems except the lowest level unstable. Let \( |(0),\alpha,A \rangle \) be the eigenstates of \( \tilde{H}_0[A] \):

\[
\tilde{H}_0[A] |(0),\alpha,A \rangle = E_0(\alpha,A) |(0),\alpha,A \rangle, \quad (\alpha = 1, 2, \ldots),
\]

where \( E_0(\alpha,A) \) are real eigenvalues. In practice it turns out to be convenient to work with some suitable basis of orthonormal states

\[
|a,\tilde{n} \rangle \quad (a = 1, 2, \ldots; \tilde{n} = 1, 2, \ldots)
\]

for the eigenstates in (1.54). Below, the index \( a \) will be chosen to be related to the internal state of motion of the atom, \( \tilde{n} \) to the state of the c.m. motion. We denote by \( \mathcal{H} \) the Hilbert space spanned by the states (1.55).

With the inclusion of \( H_{rad} \) of (1.53) the states \( |a,\tilde{n} \rangle \) become in general unstable. Using the standard Wigner-Weisskopf procedure (cf. Sect. 3.2 of [15]) we find the effective Hamiltonian \( H_{eff} \) describing the time evolution of the undecayed states \( |a,\tilde{n} \rangle \) through the (approximate) solution of Schrödinger’s equation with the initial condition of having some combination of the states \( |a,\tilde{n} \rangle \) at time \( t = 0 \) (cf. (3.9) of [15]):

\[
\frac{i}{\partial t} |t \rangle = H[A] |t \rangle, \\
|t = 0 \rangle = \sum_{a,\tilde{n}} c_{a,\tilde{n}} |a,\tilde{n} \rangle.
\]

For \( t > 0 \) but neither too small nor too large times we get

\[
\langle a,\tilde{n} | \exp(-iH[A] \cdot t) | a',\tilde{n}' \rangle \simeq \langle a,\tilde{n} | \exp(-iH_{eff}[A] \cdot t) | a',\tilde{n}' \rangle.
\]

This represents the general definition of the effective Hamiltonian, which reduces to (1.20) in the non-relativistic limit.

We consider now time reversal (T) invariance. From QFT we learn that there exists an antiunitary operator \( V(T) \) which transforms the Hamiltonians as follows:

\[
(V(T) H'[A] V^{-1}(T))^\dagger = H'[A_T],
\]

\[
(V(T) H[A] V^{-1}(T))^\dagger = H[A_T],
\]

\[
(V(T) \tilde{H}_0[A] V^{-1}(T))^\dagger = \tilde{H}_0[A_T].
\]
Here $A_T$ denotes the T-transformed potential:

\[
A_T^0(x) = A^0(x), \\
A_T(x) = -A(x).
\] (1.61)

From (1.54) and (1.60) we find that $V(T)$ transforms the eigenstates $|\langle 0, \alpha, A \rangle \}$ of $\tilde{H}_0[A]$ into eigenstates $|\langle 0, \alpha, A_T \rangle \}$ of $\tilde{H}_0[A_T]$. Recall that $E_0(\alpha, A)$ are the eigenvalues of the hermitian operator $\tilde{H}_0[A]$ and thus real. We assume now that the space $\tilde{H}$ spanned by the basis vectors $|a, \tilde{n} \rangle$ in (1.55) is large enough to contain both the states $|\langle 0, \alpha, A \rangle \}$ and $|\langle 0, \alpha, A_T \rangle \}$. The action of $V(T)$ on the states $|a, \tilde{n} \rangle$ with chosen phase convention is then given by some matrix $\tilde{T}$ over $\tilde{H}$:

\[
V(T) |a, \tilde{n} \rangle = |a', \tilde{n}' \rangle \tilde{T}^{a'a',a\tilde{n}}. \] (1.62)

The antiunitarity of $V(T)$ implies:

\[
\tilde{T}^\dagger \tilde{T} = \mathbb{1}. \] (1.63)

The effective Hamiltonians $H_{\text{eff}}[A]$ (1.57) and $H_{\text{eff}}[A_T]$ can be identified with non-hermitian matrices over $\tilde{H}$

\[
H_{\text{eff}}[A] \equiv \left( \langle a, \tilde{n} | H_{\text{eff}}[A] | a', \tilde{n}' \rangle \right). \] (1.64)

From (1.57), (1.59) and (1.61) we now get as a consequence of T-invariance:

\[
\left( \tilde{T}^\dagger H_{\text{eff}}[A_T] \tilde{T} \right)^T = H_{\text{eff}}[A]. \] (1.65)

This is the generalization of (3.42) of [15] for atomic systems in arbitrary static external fields.

Let now $\{E(\alpha, A)\}$ be the spectrum of eigenvalues of $H_{\text{eff}}[A]$ and $\tilde{P}(\alpha, A)$ the quasiprojectors corresponding to $E(\alpha, A)$, $\alpha = 1, 2, ...$

\[
H_{\text{eff}}[A] = \sum_\alpha E(\alpha, A) \tilde{P}(\alpha, A). \] (1.66)

An argument using the resolvents of $H_{\text{eff}}[A]$ and $H_{\text{eff}}[A_T]$ analogous to (3.43) ff. of [13] shows that with a suitable numbering we have

\[
E(\alpha, A_T) = E(\alpha, A), \] (1.67)

\[
\left( \tilde{T}^\dagger \tilde{P}(\alpha, A_T) \tilde{T} \right)^T = \tilde{P}(\alpha, A). \] (1.68)

These equations embody the general consequences of T-invariance for the complex (real) eigenvalues and quasiprojectors (projectors) of unstable (stable) atomic states in static external fields.

Let us consider next a general improper rotation $R$ around some point $x^{(0)}$, which we choose without loss of generality as $x^{(0)} = 0$:

\[
R : x \to R \cdot x, \\
\det R = -1. \] (1.69)
For the external field we set:

\[ A^0_R(x) = A^0(R^{-1}x), \]
\[ A_R(x) = R \cdot A(R^{-1} \cdot x) \]  \hspace{1cm} (1.70)

The QFT-operator \( U(R) \) corresponding to \( R \) transforms the Hamiltonian (1.51) as follows:

\[ U(R) H[A, \delta_1, \delta_2] U^{-1}(R) = H[A_R, -\delta_1, -\delta_2], \]  \hspace{1cm} (1.71)

where we indicate now explicitly the dependence on the P-violation parameters \( \delta_1, \delta_2 \).

Assuming the space \( \tilde{\mathcal{H}} \) to be large enough to contain for a state also its \( U(R) \)-transform we can represent \( U(R) \) in \( \tilde{\mathcal{H}} \) by a matrix \( \tilde{R} \):

\[ U(R) |a, \tilde{n} \rangle = |a', \tilde{n}' \rangle \tilde{R}_{a\tilde{n}a', \tilde{n}'}, \]
\[ \tilde{R}^\dagger \tilde{R} = 1 \]  \hspace{1cm} (1.72)

For the effective Hamiltonian this leads to

\[ \tilde{R}^\dagger H_{\text{eff}}[A_R, -\delta_1, -\delta_2] \tilde{R} = H_{\text{eff}}[A, \delta_1, \delta_2]. \]  \hspace{1cm} (1.73)

Considering again the resolvents of \( H_{\text{eff}}[A, \delta_1, \delta_2] \) and \( H_{\text{eff}}[A_R, -\delta_1, -\delta_2] \) we find that the numbering of the spectra of complex energy eigenvalues can be chosen such that

\[ E(\alpha, A_R, -\delta_1, -\delta_2) = E(\alpha, A, \delta_1, \delta_2), \]  \hspace{1cm} (1.74)
\[ \tilde{R}^\dagger \tilde{\mathcal{P}}(\alpha, A_R, -\delta_1, -\delta_2) \tilde{R} = \tilde{\mathcal{P}}(\alpha, A, \delta_1, \delta_2). \]  \hspace{1cm} (1.75)

From (1.67) and (1.74) we find the following

**Theorem:** If the external field \( A \) has the property that the T-transformation for it is equivalent to some improper rotation \( R \)

\[ A_T = A_R, \]  \hspace{1cm} (1.76)

then

\[ E(\alpha, A, \delta_1, \delta_2) = E(\alpha, A, -\delta_1, -\delta_2). \]  \hspace{1cm} (1.77)

For the case that the energy level \( E(\alpha, A, \delta_1, \delta_2) \) is *not degenerate* for \( \delta_1 = \delta_2 = 0 \), this implies vanishing linear terms in \( \delta_1, \delta_2 \):

\[ \frac{\partial}{\partial \delta_j} E(\alpha, A, \delta_1, \delta_2) \bigg|_{\delta_1=\delta_2=0} = 0, \quad (j = 1, 2). \]  \hspace{1cm} (1.78)

As an example for the use of this theorem we consider a hydrogen atom at rest at \( x = 0 \) in static and spatially homogenous electric and magnetic fields \( \mathcal{E}, \mathcal{B} \). Let \( R \) be the reflection on the plane through \( x = 0 \) spanned by \( \mathcal{E} \) and \( \mathcal{B} \). We can write

\[ A^0(x) = -x \cdot \mathcal{E}, \]
\[ A(x) = -\frac{1}{2}x \times \mathcal{B}. \]  \hspace{1cm} (1.79)
which fulfills
\[ A^\mu(x) = A^\mu_R(x). \] (1.80)
Furthermore, for \( E \neq 0 \) and \( B \neq 0 \) there are in general no degeneracies of levels for \( \delta_1 = \delta_2 = 0 \). Thus we conclude that the energy eigenvalues of the stable and unstable levels of the hydrogen atom in a constant electric plus magnetic field have no terms linear in the P-violation parameters \( \delta_{1,2} \).

To illustrate the general T- and R-transformations we will now close this Section by discussing these for the non-relativistic effective Hamiltonian \([1.20] \). The space \( \tilde{\mathcal{H}} \) (cf. \([1.55] \) ff.) is then spanned by the vectors \( |\mathbf{R}; 2, a\rangle \) of \([1.13] \). We can choose a convenient orthonormal basis set of real functions \( \xi_{\tilde{n}}(\mathbf{R}) \) for the c.m. motion and set:
\[ |a, \tilde{n}\rangle = \xi_{\tilde{n}}(\mathbf{R}) |2, a\rangle. \] (1.81)
The T-transformation \([1.62] \) is represented by
\[ V(T) |a, \tilde{n}\rangle = \xi_{\tilde{n}}(\mathbf{R}) |2, a'\rangle \mathcal{T}_{a'a}, \] (1.82)
where \( \mathcal{T} \) is the matrix describing the T-transformation of the \( n = 2 \) atomic states (cf. \((3.33) \) of \([15] \)). Thus we find here
\[ \tilde{T}_{a'a', \tilde{n}' \tilde{n}} = \delta_{\tilde{n}' \tilde{n}} \mathcal{T}_{a'a}. \] (1.83)
It is now easy to verify \((1.63) \) explicitly for \( H_{\text{eff}}[A] \) of \((1.20) \). Thus, as it should be, the general results \((1.67), (1.68) \) hold in the non-relativistic limit.

Let us furthermore define the matrix \( \mathcal{R} \) of the R-transformation \((1.69) \) for the \( n = 2 \) states
\[ U(\mathbf{R}) |2, a\rangle = |2, a'\rangle \mathcal{R}_{a'a}. \] (1.84)
and \( (\mathcal{R}^t_{\tilde{n}' \tilde{n}}) \) by
\[ \xi_{\tilde{n}}(\mathbf{R}^{-1} \cdot \mathbf{R}) = \xi_{\tilde{n}'}(\mathbf{R}) \mathcal{R}^t_{\tilde{n}' \tilde{n}}. \] (1.85)
Then the matrix \( \tilde{\mathcal{R}} \) of \((1.72) \) is given by
\[ \tilde{\mathcal{R}}_{a'd', a\tilde{n}} = \mathcal{R}_{a'd'} \mathcal{R}_{a'a}. \] (1.86)
This is the matrix which is to be used in \((1.74) \) and \((1.75) \) in the non-relativistic limit.

In the following we will frequently make use of the general consequences of the T- and R-transformations spelled out in this Section.

### 2 Energy shifts for piecewise constant electric fields; exact calculation

We will now consider simple electric field arrangements which are neither parity- nor reflection-symmetric. We imagine a rectangular box which we subdivide into several segments, in each of which the \( \mathbf{E} \)-vector is pointing in a fixed direction, with its modulus also having in general different values. Within any of the segments the electric field

...
is assumed to be homogeneous, which results in a sudden variation at the interface, where the segments are connected to each other, and at the box surface which forms the boundary of the system. Of course, Maxwell’s equations require then charge distributions on the interfaces. Clearly it would be difficult to realize this experimentally, and we choose this situation only since it is simple to be analysed from the theoretical point of view. A more realistic experimental situation could be taken into account by including corrections to the sudden variation by means of perturbation theory in a small parameter describing e.g. the extension of the transition regions between the segments in relation to the total size of the segments.

Let the lengths of the edges of our rectangular box \( B \) be \( A_{1,2,3} \) in the 1,2,3-direction (Fig. 1):

\[
\text{box } B : \quad 0 \leq R_j \leq A_j, \quad (j = 1, 2, 3).
\]

In 1-direction we subdivide the box into segments numbered by \( \sigma \):

\[
\text{segment } S^{(\sigma)} : \quad R_1^{(\sigma-1)} \leq R_1 \leq R_1^{(\sigma)}, \quad 0 \leq R_j \leq A_j, \quad (j = 2, 3),
\]

where \( \sigma = 1, \ldots, \sigma_{\text{max}} \) and

\[
R^{(0)} \equiv 0 < R^{(1)}_1 < \ldots < R^{(\sigma_{\text{max}})}_1 \equiv A_1.
\]

This is illustrated in Fig. 1 for \( \sigma_{\text{max}} = 3 \). The electric field in \( S^{(\sigma)} \) is denoted by \( \mathbf{E}^{(\sigma)} \).

We will consider both neutral atoms and charged ions in such segmental boxes. The effective Hamiltonian \( H_{\text{eff}} \) reads now:

\[
H_{\text{eff}} = \frac{1}{2m} \mathbf{P}^2 + \mathbf{M}_0 - (q\mathbf{R} + \mathbf{D}) \cdot \sum_\sigma \mathbf{E}^{(\sigma)} \Theta(R_1^{(\sigma)} - R_1) \Theta(R_1 - R_1^{(\sigma-1)}),
\]

The problem is to solve the eigenvalue equation \( (1.23) \) with the boundary condition \( (1.29) \). There is a direct way to solve this problem by making an ansatz of linear combinations of constant field wave functions in each segment. Continuity conditions to be imposed on the wave function and its first derivative at the interfaces lead to a determinant equation from which the eigenenergies may be extracted. This technique will be outlined in the next paragraph and yields the minimum number of different segments, i.e. electric fields required to obtain P-odd effects. We will show that for boxes with 2 segments no energy shifts linear in the \( \delta_i \) \( (i = 1, 2) \) occur in our theoretical framework. However, for boxes with 3 segments such energy shifts \textit{do} occur as we will prove in Sect. \( \S \) using perturbation theory.

### 2.1 A neutral atom in a box with 2 segments

In this Section we consider a neutral atom in internal states of principal quantum number \( n = 2 \) in a box with two segments. The effective Hamiltonian \( (2.4) \) reads now:

\[
H_{\text{eff}} = \frac{1}{2m} \mathbf{P}^2 + \mathbf{M}_0 - \mathbf{D} \cdot \mathbf{E}(\mathbf{R}),
\]

where

\[
\mathbf{E}(\mathbf{R}) = E^{(1)}_1 \Theta(R_1^{(1)} - R_1) \Theta(R_1) + E^{(2)}_1 \Theta(A_1 - R_1) \Theta(R_1 - R_1^{(1)}).
\]
We have to solve (1.23) with the boundary condition (1.29):

\[ H_{\text{eff}} \Psi(R) = E \Psi(R), \]
\[ \Psi(R) = 0 \quad \text{for} \ R \in \partial B. \]  

(2.7)

(2.8)

The Hamiltonian (2.5) commutes with the part describing the motion in the 2- and 3-directions:

\[ H_{2,3} = \frac{1}{2m} \left( P_2^2 + P_3^2 \right). \]  

(2.9)

Here and in the following the boundary condition (2.8) is always understood to be imposed. Thus we can diagonalize \( H_{\text{eff}} \) and \( H_{2,3} \) simultaneously. The normalized eigenfunctions of \( H_{2,3} \) are

\[ \phi_{n_2,n_3}(R_2, R_3) = \frac{2}{\sqrt{A_2 A_3}} \sin \frac{n_2 \pi R_2}{A_2} \cdot \sin \frac{n_3 \pi R_3}{A_3}, \]  

(2.10)

\( \text{for} \quad (n_2 = 1, 2, 3, \ldots; n_3 = 1, 2, 3, \ldots) \). We have

\[ H_{2,3} \phi_{n_2,n_3}(R_2, R_3) = E_{2,3}(n_2, n_3) \phi_{n_2,n_3}(R_2, R_3), \]
\[ E_{2,3}(n_2, n_3) = \frac{1}{2m} \left[ \left( \frac{n_2 \pi}{A_2} \right)^2 + \left( \frac{n_3 \pi}{A_3} \right)^2 \right]. \]  

(2.11)

We can now make a product ansatz for the eigenfunctions of \( H_{\text{eff}} \) (2.5):

\[ \Psi(R) = \phi_{n_2,n_3}(R_2, R_3) \phi(R_1), \]
\[ \phi(R_1) = \begin{cases} \phi^{(1)}(R_1) & \text{for} \quad 0 \leq R_1 \leq R_1^{(1)}, \\ \phi^{(2)}(R_1) & \text{for} \quad R_1^{(1)} < R_1 < A_1, \end{cases} \]  

(2.12)

where \( \phi(R_1) \) has \( N \) components (cf. (1.17)), corresponding to the number of linearly independent \( n = 2 \) internal states.

Let us denote by \( |(\sigma), \beta \rangle \) the right eigenvectors of the mass matrices in the Sectors \( \sigma = 1, 2 \); corresponding to the internal, in general complex energy eigenvalues \( E_{\text{INT}}((\sigma), \beta) \):

\[ (\mathcal{M}_0 - D \cdot \mathcal{E}^{(\sigma)}) |(\sigma), \beta \rangle = E_{\text{INT}}((\sigma), \beta) |(\sigma), \beta \rangle, \quad (\beta = 1, \ldots, N). \]  

(2.13)

The corresponding left eigenvectors are denoted by \( \langle (\widetilde{\sigma}), \gamma | (\sigma), \beta \rangle \). We have

\[ \langle (\widetilde{\sigma}), \gamma | (\sigma), \beta \rangle = \delta_{\gamma \beta} \quad \text{for} \quad \sigma = 1, 2 \]  

(2.14)

(no summation over \( \sigma \)). Furthermore we define matrices \( U^{(1,2)} \) and \( U^{(2,1)} \) with matrix elements:

\[ U_{\gamma,\beta}^{(1,2)}(\delta_1, \delta_2) := \langle (\widetilde{1}), \gamma | (2), \beta \rangle, \]
\[ U_{\gamma,\beta}^{(2,1)}(\delta_1, \delta_2) := \langle (\widetilde{2}), \gamma | (1), \beta \rangle. \]  

(2.15)

We indicate explicitly the dependence of these matrices on the P-violation parameters \( \delta_{1,2} \). Of course, for the case of nuclear spin \( I = 0 \) there is no dependence on \( \delta_2 \). As we
discussed in Sect. 1.2, the complex energies $E^{NT}(\sigma, \beta)$ have no terms linear in $\delta_{1,2}$. We make now the following ansatz for $\phi^{(1,2)}(R_1)$ in (2.12):

$$
\phi^{(1)}(R_1) = \sum_\beta \zeta^{(1)}_\beta \sin \left[ Q^{(1)}_\beta R_1 \right] |(1), \beta),
$$

$$
\phi^{(2)}(R_1) = \sum_\beta \zeta^{(2)}_\beta \sin \left[ Q^{(2)}_\beta (R_1 - A_1) \right] |(2), \beta),
$$

(2.16)

where $Q^{(\sigma)}_\beta$ and $\zeta^{(\sigma)}_\beta$ are constants to be determined. With (2.14) and (2.16) we already satisfy the boundary condition (2.8). Let us now insert the ansatz (2.12), (2.16) in (2.21) and let $E$ be the sought eigenvalue of $H_{eff}$. We find that the $Q^{(\sigma)}_\beta$ in (2.16) are to be determined from

$$
\frac{1}{2m} \left( Q^{(\sigma)}_\beta \right)^2 = E - E_{2,3}(n_2, n_3) - E^{NT}(\sigma, \beta), \quad (\sigma = 1, 2; \beta = 1, ..., N).
$$

(2.17)

For definiteness, let $Q^{(\sigma)}_\beta$ be the root of (2.17) with positive real part and if this is zero, the one with positive imaginary part. Finally, the constants $\zeta^{(\sigma)}_\beta$ in (2.16) are determined by the transition conditions at the interface $R_1 = R_{1,1}$. There $\Psi(R)$ and $\partial\Psi(R)/\partial R_1 \equiv \partial_1 \Psi(R)$ must be continuous. These conditions lead to:

$$
\sum_\beta \zeta^{(1)}_\beta \sin \left[ Q^{(1)}_\beta R_1^{(1)} \right] |(1), \beta) = \sum_\beta \zeta^{(2)}_\beta \sin \left[ Q^{(2)}_\beta (R_1^{(1)} - A_1) \right] |(2), \beta),
$$

(2.18)

$$
\sum_\beta \zeta^{(1)}_\beta Q^{(1)}_\beta \cos \left[ Q^{(1)}_\beta R_1^{(1)} \right] |(1), \beta) = \sum_\beta \zeta^{(2)}_\beta Q^{(2)}_\beta \cos \left[ Q^{(2)}_\beta (R_1^{(1)} - A_1) \right] |(2), \beta).
$$

(2.19)

Multiplying (2.18) and (2.19) with $(\gamma, \gamma)$ and $(\gamma, \gamma)$, respectively, where $\gamma = 1, ..., N$, we get the following matrix equation:

$$
M_c(E, \delta_1, \delta_2) \cdot \zeta = 0,
$$

(2.20)

where

$$
M_c(E, \delta_1, \delta_2) = \left( \begin{array}{cc}
U^{(1,1)}(\delta_1, \delta_2) \cdot S^{(1)}(E, \delta_1, \delta_2) & -S^{(2)}(E, \delta_1, \delta_2) \\
C^{(1)}(E, \delta_1, \delta_2) & -U^{(1,2)}(\delta_1, \delta_2) \cdot C^{(2)}(E, \delta_1, \delta_2)
\end{array} \right),
$$

(2.21)

$$
\zeta = \left( \zeta^{(1)}_1, ..., \zeta^{(1)}_N, \zeta^{(2)}_1, ..., \zeta^{(2)}_N \right)^T.
$$

(2.22)

In (2.21) $S^{(\sigma)}$ and $C^{(\sigma)}$ ($\sigma = 1, 2$) are diagonal $N \times N$ matrices, with the diagonal elements given by

$$
S^{(1)}_{\beta, \beta}(E, \delta_1, \delta_2) = \sin \left[ Q^{(1)}_\beta R_1^{(1)} \right],
$$

$$
S^{(2)}_{\beta, \beta}(E, \delta_1, \delta_2) = \sin \left[ Q^{(2)}_\beta (R_1^{(1)} - A_1) \right],
$$

$$
C^{(1)}_{\beta, \beta}(E, \delta_1, \delta_2) = Q^{(1)}_\beta \cos \left[ Q^{(1)}_\beta R_1^{(1)} \right],
$$

$$
C^{(2)}_{\beta, \beta}(E, \delta_1, \delta_2) = Q^{(2)}_\beta \cos \left[ Q^{(2)}_\beta (R_1^{(1)} - A_1) \right].
$$

(2.23)
Note that in the matrices $S^{(\sigma)}, C^{(\sigma)}$ the dependence on the parameters $\delta_1, \delta_2$ enters only through the internal energy eigenvalues $E^{INT}(\sigma, \beta)$ (cf. (2.17)), which are even under the replacement $\delta_1, \delta_2 \rightarrow -\delta_1, \delta_2$. Therefore we have

$$S^{(\sigma)}(E, \delta_1, \delta_2) = S^{(\sigma)}(E, -\delta_1, -\delta_2),$$
$$C^{(\sigma)}(E, \delta_1, \delta_2) = C^{(\sigma)}(E, -\delta_1, -\delta_2), \quad (\sigma = 1, 2). \quad (2.24)$$

The condition for (2.20) having a nontrivial solution-vector $\zeta$ is:

$$\det M_c(E, \delta_1, \delta_2) = 0. \quad (2.25)$$

The roots of this equation give the complex energy eigenvalues of $H_{\text{eff}}$ (2.23). We want to see if these roots have terms linear in $\delta_1, \delta_2$.

### 2.1.1 Results for neutral atoms with $I = 0$

Let us first consider the case of a neutral hydrogen-like atom with vanishing nuclear spin. This is not realizable for conventional atoms but an atom consisting of a $\pi^+$ meson and an electron is a physical system to which our considerations apply. For this case the representations of $M_0$ and $D$ may be found in Appendix B of [12]. They are 8×8-matrices and thus the continuity conditions for the wave function and its derivative w.r.t. $R_1$ lead to a set of 16 linear equations (cf. (2.20)):

$$M_c(E, \delta_1) \cdot \zeta = 0 \quad (2.26)$$

From the determinant condition

$$\det M_c(E, \delta_1) = 0 \quad (2.27)$$

we get the energy eigenvalues. As we show in Appendix B, we can simplify the structure of $M_c$ considerably if we choose a suitable set of basis states having simple transformation properties under $T$ (time reversal) and $R$ (reflection on the 1–3-plane). We show in Appendix B that (2.27) is equivalent to an equation having no linear terms in $\delta_1$:

$$\det M'_c(E, \delta_1) = f_0(E) + \delta_1^2 f_2(E) + O(\delta_1^4) = 0 \quad (2.28)$$

Now we would like to use the implicit function theorem to calculate from (2.28) the dependence of the solutions $E$ on $\delta_1$.

However, we have to be careful. It turns out that for $\delta_1 = 0$ the energy levels are twofold degenerate, i.e. $f_0(E)$ has double zeroes. These degeneracies are even preserved to order $\delta_1$. We show all this in Appendix B, where we use the T-symmetry to derive that $\det M'_c = 0$ is equivalent to

$$\det M'^{\text{asym}}_c(E, \delta_1) = 0, \quad (2.29)$$

where $M'^{\text{asym}}_c = -(M'^{\text{asym}})_T$ is an antisymmetric matrix. Now, from a basic theorem of linear algebra (cf. Appendix B), the determinant of an antisymmetric matrix with even number of rows is always a square:

$$\det M'^{\text{asym}}_c(E, \delta_1) = [g(E, \delta_1)]^2. \quad (2.30)$$

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Therefore the solutions $E$ of (2.29) are twofold degenerate for any choice of $E^{(1)}, E^{(2)}$. Furthermore we find that

$$g(E, \delta_1) = g_0(E) + \delta_1^2 g_2(E) + O(\delta_1^4) \quad (2.31)$$

with $g_0(E)$ having only nondegenerate zeroes. The implicit function theorem implies then that the zeroes of $g(E, \delta_1)$ have no terms linear in $\delta_1$:

$$\frac{\partial E(\delta_1)}{\partial \delta_1} \bigg|_{\delta_1=0} = 0. \quad (2.32)$$

To conclude: Using the R and T symmetry relations we find that, for a box with two electric fields $E^{(1)}, E^{(2)}$, the complex eigenenergies of the atom have no terms linear in $\delta_1$.

### 2.1.2 Results for neutral atoms with $I = 1/2$

In this subsection we will consider the case of a neutral atom with $I = 1/2$, as e.g. $^1\text{H}$. The eigenenergies are again obtained from the condition

$$\det M_c(E, \delta_1, \delta_2) = 0 \quad (2.33)$$

for the continuity matrix $M_c$ given in (2.21). Now $M_c$ is a $32 \times 32$ matrix. Using the ± eigenstates as defined in Appendix A and their T and R symmetry relations we show in Appendix B that (2.33) is equivalent to

$$\det M'_c(E, \delta_1, \delta_2) = f_0(E) + \sum_{i,j} \delta_i \delta_j f_{2,ij}(E) + \text{terms of 4th order in } \delta_{1,2}. \quad (2.34)$$

Here $f_0(E)$ has (in general) no double zeroes and thus we can immediately conclude from the implicit function theorem that the energy eigenvalues, i.e. the solutions of (2.33), have no terms linear in $\delta_{1,2}$:

$$\frac{\partial E(\delta_1, \delta_2)}{\partial \delta_j} \bigg|_{\delta_1=\delta_2=0} = 0, \quad (2.35)$$

Thus, within our theoretical framework, we find that, for a $^1\text{H}$-atom in a box with 2 segments only there are no energy shifts linear in $\delta_{1,2}$.

### 2.2 A charged ion with nuclear spin $I = 0$ in a box with two segments

In the real world conventional one-electron atoms with vanishing nuclear spin are always electrically charged. Therefore we investigate now the modifications of the results of Section 2.1 due to the c.m. motion being influenced by the external electric field.

Let $q = e(Z - 1)$ be the charge of the ion. The effective Hamiltonian is given in (2.4) where we choose 2 segments, i.e. $\mathcal{E}(\mathbf{R})$ as in (2.6). In Sect. 2.1 the c.m. part of
the wave functions was built up by sines and cosines. Now, for a charged ion, we need the wave functions for a potential linear in the coordinate.

Let us consider first the general one-dimensional Schrödinger equation with a potential linear in the coordinate,

$$\left[ -\frac{\partial^2}{\partial R^2} - 2m(q \mathcal{E} R + E) \right] \psi(R) = 0. \quad (2.36)$$

The solutions of (2.36) are obtained with the help of the Airy functions defined by

$$\text{Ai}(z) = \frac{1}{3} \sqrt{z} \left( I_{-1/3}(\zeta) - I_{1/3}(\zeta) \right),$$

$$\text{Bi}(z) = \sqrt{\frac{2}{3}} \left( I_{-1/3}(\zeta) + I_{1/3}(\zeta) \right) \quad (2.37)$$

for $z > 0$ and

$$\text{Ai}(z) = \frac{1}{3} \sqrt{-z} \left( J_{-1/3}(\zeta) + J_{1/3}(\zeta) \right),$$

$$\text{Bi}(z) = \sqrt{\frac{2}{3}} \left( J_{-1/3}(\zeta) - J_{1/3}(\zeta) \right) \quad (2.38)$$

for $z < 0$, where $J_p$ ($I_p$) denote the (modified) Bessel functions,

$$\zeta := \frac{2}{3} m q \mathcal{E} / c^2, \quad c^2 = 2mq\mathcal{E}. \quad (2.39)$$

The general solution of (2.36) is then

$$\psi(R) = \xi_+ \psi_+(R, E, \mathcal{E}) - \xi_- \psi_-(R, E, \mathcal{E}), \quad (2.40)$$

where

$$\psi_+(R, E, \mathcal{E}) = \text{Ai}(R + 2mE/c^2),$$

$$\psi_-(R, E, \mathcal{E}) = \text{Bi}(R + 2mE/c^2) \quad (2.41)$$

and $\xi_\pm$ are constants. If we impose as boundary condition the vanishing of the wave function at $R = 0$ and $R = A$,

$$\psi(0) = \psi(A) = 0, \quad (2.42)$$

we get corresponding eigenenergies $E$ by solving the equation

$$\det \begin{pmatrix} \psi_+(0, E, \mathcal{E}) & \psi_-(0, E, \mathcal{E}) \\ \psi_+(A, E, \mathcal{E}) & \psi_-(A, E, \mathcal{E}) \end{pmatrix} = 0. \quad (2.43)$$

Let us number these eigenenergies by $E_m(A, \mathcal{E})$ and the corresponding normalized eigenfunctions (2.40) by $\phi_m(R, \mathcal{E})$, where $m = 1, 2, \ldots$. We can choose the functions $\phi_m(R, A, \mathcal{E})$ to be real and normalized:

$$\langle m, A, \mathcal{E} | m', A, \mathcal{E} \rangle = \int_0^A dR \phi_m(R, A, \mathcal{E}) \phi_{m'}(R, A, \mathcal{E}) = \delta_{m'm}. \quad (2.44)$$
Now we come to our problem of finding the eigenvalues of $H_{\text{eff}}$ (2.4) for a box with 2 segments. We make the following ansatz for the complete wave function $\Psi(R)$:

$$\Psi(R) = \begin{cases} 
\Psi^{(1)}(R) & \text{for } 0 \leq R_1 \leq R_1^{(1)}, \\
\Psi^{(2)}(R) & \text{for } R_1^{(1)} \leq R_1 \leq A_1,
\end{cases}$$

(2.45)

$$\Psi^{(\sigma)}(R) = \sum_{\beta, m_2, m_3} \zeta^{(\sigma)}_{\beta, m_2, m_3} \varphi_{m_2}(R_2, A_2, E^{(\sigma)}_2) \varphi_{m_3}(R_3, A_3, E^{(\sigma)}_3)$$

$$\times \left[ \zeta^{(\sigma)}_{+, \beta, m_2, m_3} \psi_+(R_1, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) - \zeta^{(\sigma)}_{-, \beta, m_2, m_3} \psi_-(R_1, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) \right] |(\sigma), \beta),$$

(2.46)

where we use the same notation as in Sect. 2.1, and we have with $E$ the sought energy eigenvalue of $H_{\text{eff}}$:

$$E^{(\sigma)}_{\beta, m_2, m_3} = E - E_{m_2} (A_2, E^{(\sigma)}_2) - E_{m_3} (A_3, E^{(\sigma)}_3) - E^{INT} (\sigma), \beta).$$

(2.47)

Furthermore, we set

$$\zeta^{(1)}_{\pm, \beta, m_2, m_3} = \psi_{\pm} (0, E^{(1)}_{\beta, m_2, m_3}, E^{(1)}_1),$$

$$\zeta^{(2)}_{\pm, \beta, m_2, m_3} = \psi_{\pm} (A_1, E^{(2)}_{\beta, m_2, m_3}, E^{(2)}_1).$$

(2.48)

This ansatz fulfills already the boundary conditions at the complete surface of the box. We still have to impose the continuity of $\Psi(R)$ and $\partial \Psi(R)/\partial R_1$ at the interface, i.e. at $R_1 = R_1^{(1)}$. This gives conditions analogous to (2.18), (2.19), which we can write as linear equation for the now infinite component vector $\zeta$:

$$M_c(E, \delta_1) \cdot \zeta = 0,$$

(2.49)

where

$$\zeta = \begin{pmatrix} \zeta^{(1)}_{+, \beta, m_2, m_3} \\
\zeta^{(2)}_{+, \beta, m_2, m_3} \end{pmatrix}^T,$$

$$\beta, \beta' = 1, ..., N; \; m_2, m'_{2} = 1, 2, ..., m_3, m'_{3} = 1, 2, ...$$

(2.50)

Explicitly we have:

$$M_c(E, \delta_1) = \begin{pmatrix} U^{(2,1)}(\delta_1) \Sigma^{(1)}(E, \delta_1) & -\Sigma^{(2)}(E, \delta_1) \\
\Sigma^{(1)}(E, \delta_1) & -U^{(1,2)}(\delta_1)\Sigma^{(2)}(E, \delta_1) \end{pmatrix},$$

(2.51)

$$U^{(\sigma, \alpha)}(\delta_1) = \left( (\delta_1, \alpha), (\sigma), (\beta), (m_2, A_2, E^{(\sigma)}_2)|m'_2, A_2, E^{(\sigma)}_2)(m_3, A_3, E^{(\sigma)}_3)|m'_3, A_3, E^{(\sigma)}_3) \right),$$

(2.52)

$$\Sigma^{(\sigma)}(E, \delta_1) = \left( \delta_{\alpha \beta} \zeta_{+, \beta, m_2, m_3}^{(\sigma)} \psi_+(R_1^{(1)}, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) - \zeta_{-, \beta, m_2, m_3}^{(\sigma)} \psi_-(R_1^{(1)}, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) \right) \delta_{m_2, m'_2} \delta_{m_3, m'_3},$$

(2.53)

$$C^{(\sigma)}(E, \delta_1) = \left( \delta_{\alpha \beta} \frac{\partial}{\partial R_1} \left[ \zeta_{+, \beta, m_2, m_3}^{(\sigma)} \psi_+(R_1, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) - \zeta_{-, \beta, m_2, m_3}^{(\sigma)} \psi_-(R_1, E^{(\sigma)}_{\beta, m_2, m_3}, E^{(\sigma)}_1) \right] \right) |_{R_1 = R_1^{(1)}} \delta_{m_2, m'_2} \delta_{m_3, m'_3}.$$

(2.54)
Now we choose as in Sect. 2.1.1 and Appendix B the $\pm$ basis states \[(B.6)\] for the internal motion of the ion. The matrices $U^{(r,s)}$ can then be split into submatrices $U^{(r,s)}_{r,s}$ ($r,s \in \{+, -\}$) as in \[(B.7), (B.8)\]. Of course, all these matrices are now infinite dimensional. It is easy to check that the matrices $U^{(r,s)}_{r,s}$ satisfy again the relations \[(B.10) - (B.12)\]. Thus for any finite truncation in the transverse modes, say

\[
m_2, m'_2 \leq K_2,
\]

\[
m_3, m'_3 \leq K_3,
\]

(2.55)

we can immediately take over the methods of Sect. 2.1.1 and conclude that there are no shifts in the eigenenergies $E$ which are linear in $\delta_1$.

Of course, we would now like to take the limit $K_2, K_3 \to \infty$. We will not give a rigorous mathematical treatment of this limit but discuss it in physical terms. Suppose we have an eigenenergy $E$. Then we see from \[(2.47)\] that the energies $E^{(r)}_{\beta,m_2,m_3}$ will be more and more negative for higher and higher transverse energies $E_{m_2}, E_{m_3}$, i.e. for $m_2, m_3 \to \infty$. But for large negative $E^{(r)}_{\beta,m_2,m_3}$ the Airy functions \[(2.37), (2.38)\] will be exponentially decreasing or increasing. Clearly, the corresponding contribution in $\Psi^{(r)}(R)$ \[(2.46)\] must in essence be exponentially decreasing when going away from the interface or surface of the box, and this decrease will be the faster the more negative $E^{(r)}_{\beta,m_2,m_3}$ is.

We can write the energy eigenvalue $E$ as

\[
E = \frac{\langle \Psi | H_{\text{eff}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}.
\]

(2.56)

Choosing now some large enough $K_2, K_3$, we see that the contribution from the high transverse modes with $m_2 > K_2, m_3 > K_3$ will in essence come from the interface and/or the surfaces and can be made arbitrarily small in the integrals \[(2.56)\]. Here it is important that $H_{\text{eff}}$ contains no parts with high frequency in any direction. Thus we estimate that the limit $K_2, K_3 \to \infty$ should be harmless.

In conclusion: In this Section we found that, within the framework of our calculations, there are no energy shifts linear in the P-violation parameter $\delta_1$ also for a charged ion with nuclear spin $I = 0$ in a box with two segments.

3 Energy shifts from perturbation theory for atoms in a box with three segments

In Sections 2.1 and 2.2 we considered boxes with two segments, but did not find any P-violating energy shifts. This is somewhat surprising, since the setup with two electric field vectors together with the fixed direction marked by the external geometry does form a chiral situation. But apparently, this is not sufficient to have energy shifts revealing parity violation.

The above results require another segment to be added and to consider a situation where one can form a nontrivial trihedral out of the electric field vectors alone. For the simplest case of neutral atoms with $I = 0$, this adds another 16 rows and columns to $M_c$ \[(2.21), (B.13)\], as now continuity conditions have to be imposed at two interfaces.
and the wave function $\phi_c^{(2)}$ of the middle segment consists of sine and cosine terms. The result is a determinant equation for a nontrivial $32 \times 32$-matrix, which we have not analysed, since it is rather complicated. Instead, we turn in this Section to simpler calculations based on Rayleigh-Schrödinger perturbation theory.

Let us consider a box with three segments (Fig. 1) where the electric fields are

$$\mathcal{E}^{(\sigma)} = \mathcal{E}e_3 + \mathcal{E}'^{(\sigma)}, \quad (\sigma = 1, 2, 3).$$

We assume that the electric field in 3-direction, $\mathcal{E}e_3$ is dominant:

$$|\mathcal{E}'^{(\sigma)}| \ll |\mathcal{E}|, \quad (\sigma = 1, 2, 3).$$

We will then write down a perturbation expansion with respect to the terms induced in $H_{\text{eff}}$ (2.4) by the fields $\mathcal{E}'^{(\sigma)}$. Indeed, let us write $H_{\text{eff}}$ as follows:

$$H_{\text{eff}} = H_{\text{eff}, 0} + H_{\text{eff}, 1},$$

where

$$H_{\text{eff}, 0} = \frac{1}{2m} \mathbf{p}^2 + M_0 - (qR_3 + D_3)\mathcal{E},$$

$$H_{\text{eff}, 1} = -(q \mathbf{R} + D) \cdot \sum_{\sigma=1}^{3} \mathcal{E}'^{(\sigma)} \Theta(R_1^{(\sigma)} - R_1) \Theta(R_1 - R_1^{(\sigma-1)}).$$

Denoting by $\mathbf{R}$ the reflection on the 1–3-plane $x_2 = A_2/2$, we see that $H_{\text{eff}, 0}$ is R symmetric whereas $H_{\text{eff}, 1}$ in general is not. Thus we expect from the results of Sect. 1.3 that the eigenenergies of $H_{\text{eff}, 0}$ will not have linear terms in $\delta_{1,2}$ but that such terms will be generated upon inclusion of $H_{\text{eff}, 1}$ with a suitable arrangement of fields $\mathcal{E}'^{(\sigma)}$.

The idea is now to calculate $\delta_{1,2}$-linear contributions to the eigenenergies $E$ of $H_{\text{eff}}$ in perturbation theory based on the separation (3.3). The eigenvectors as well as the eigenvalues $E^{(0)}$ of $H_{\text{eff}, 0}$ may be determined numerically in a simple way and the series of higher corrections to $E^{(0)}$ contains just matrix elements of $H_{\text{eff}, 1}$ w.r.t. these eigenvectors.

### 3.1 Results for a neutral atom with $I = 0$

Let us again consider first a neutral atom with nuclear spin $I = 0$. The eigenvectors of $H_{\text{eff}, 0}$ are then easily written down, using the results of Sect. 1.2

$$|\alpha, F_3, \mathcal{E}e_3, n\rangle := \phi_n(\mathbf{R})|\alpha, F_3, \mathcal{E}e_3\rangle,$$

$$\phi_n(\mathbf{R}) = \sqrt{2} \prod_{i=1}^{3} \sin \left( \frac{n_i \pi R_i}{A_i} \right).$$

The corresponding eigenvalues $E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n = (n_1, n_2, n_3))$ satisfy

$$H_{\text{eff}, 0}|\alpha, F_3, \mathcal{E}e_3, n\rangle = E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n)|\alpha, F_3, \mathcal{E}e_3, n\rangle,$$

$$E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n) = \frac{1}{2m} \sum_{i=1}^{3} \left( \frac{n_i \pi}{A_i} \right)^2 + E^{INT}(\alpha, F_3, \mathcal{E}e_3).$$
We know from the results of Sections 3.3 and 3.4 of [15] that \( E^{INT}(\alpha, F_3, \mathcal{E}e_3) \) has no terms linear in \( \delta \) and that these energy eigenvalues for \( F_3 \) and \(-F_3\) are degenerate. These statements are then also true for \( E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n) \), i.e. we have

\[
E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n) = E^{(0)}(\alpha, -F_3, \mathcal{E}e_3, n),
\]  

(3.9)

and, neglecting terms of order \( \delta_1^2, E^{(0)}(\alpha, F_3, \mathcal{E}e_3, n) \) is independent of \( \delta_1 \).

Now we go from \( H_{\text{eff},0} \) to \( H_{\text{eff},1} \) considering \( H_{\text{eff},1} \) as a perturbation. The twofold degeneracy (3.9) of the zero order energies forces us to use degenerate perturbation theory (cf. [30], [28], [29]). Also we have to remember that our effective Hamiltonian is non-hermitian. As stated in Section 1.1, we will always assume in the general discussion that all non-hermitian matrices occurring are diagonalizable (For our specific numerical examples this assumption holds, as we see from the explicit calculations). Then the standard degenerate perturbation theory treatment for hermitian matrices of [30], [28], [29] can be taken over for our case, the only difference being that projectors have to be replaced by quasiprojectors.

Consider now the perturbation of the degenerate energy level characterized by \((\alpha, |F_3|, \mathcal{E}e_3, n) \equiv \bar{\alpha},\)

\[
E^{(0)}_{\bar{\alpha}} \equiv E^{(0)}(\alpha, |F_3|, \mathcal{E}e_3, n) = E^{(0)}(\alpha, -|F_3|, \mathcal{E}e_3, n).
\]  

(3.10)

The corresponding right eigenvectors of \( H_{\text{eff},0} \)

\[
|\bar{\alpha}, \pm \rangle \equiv |\alpha, \pm|F_3|, \mathcal{E}e_3, n\rangle
\]  

(3.11)

span a space \( \mathcal{R}^{(0)}_{\bar{\alpha}} \). According to the methods of Kato and Bloch (cf. [30]-[29]) the perturbed eigenvalues can be obtained by solving an eigenvalue problem in \( \mathcal{R}^{(0)}_{\bar{\alpha}} \). Using first Kato’s method (cf. [27]) we define the following matrices:

\[
\mathbb{P}^{(0)}_{\bar{\alpha}} = \sum_{m=\pm} |\bar{\alpha}, m\rangle \langle \bar{\alpha}, m|,
\]

(3.12)

\[
\mathbb{Q}^{(0)}_{\bar{\alpha}} = 1 - \mathbb{P}^{(0)}_{\bar{\alpha}},
\]

(3.13)

\[
\mathbb{Q}^{(0)}_{\bar{\alpha}, k} = \frac{\mathbb{P}^{(0)}_{\bar{\alpha}}}{\epsilon^k} \sum_{\beta \neq \bar{\alpha}} (E^{(0)}_{\bar{\alpha}} - E^{(0)}_{\beta})^k, \quad (k = 1, 2, ...);
\]

\[
S_{\bar{\alpha}, 0} = -\mathbb{P}^{(0)}_{\bar{\alpha}},
\]

\[
S_{\bar{\alpha}, k} = \frac{\mathbb{Q}^{(0)}_{\bar{\alpha}}}{\epsilon^k}, \quad \text{for} \quad k = 1, 2, ...
\]

(3.14)

Here the \( \mathbb{P}^{(0)}_{\bar{\alpha}}, \beta \neq \bar{\alpha}, \) denote the quasiprojectors on all the other degenerate eigen-subspaces of \( H_{\text{eff},0} \), corresponding to the eigenvalues \( E^{(0)}_{\beta} \). We define furthermore the operators:

\[
(k_1, ..., k_{n+1}) := S_{\bar{\alpha}, k_1} H_{\text{eff}, 1} S_{\bar{\alpha}, k_2} \cdots H_{\text{eff}, 1} S_{\bar{\alpha}, k_{n+1}},
\]

(3.15)

where the \( k_j \) are non-negative integers. We note the relation

\[
(k_1, ..., k_n, k_{n+1} + l_1, l_2, ..., l_{m+1}) = [1 - \delta_{0,k_{n+1}} - \delta_{0,l_1}](k_1, ..., k_n, k_{n+1} + l_1, l_2, ..., l_{m+1}).
\]

(3.16)
With the help of the operators (3.15) we define two further matrices over \( \mathcal{R}_\alpha^{(0)} \) as follows:

\[
\hat{K}_\alpha = \mathbb{I}^{(0)} + \sum_{n=2}^{\infty} A^{(n)},
\]

\[
\hat{H}_\alpha = E_\alpha^{(0)} \hat{K}_\alpha + \sum_{n=1}^{\infty} B^{(n)},
\]

(3.17)

where

\[
A^{(n)} = -\sum_{(n)} (0, k_1, ..., k_{n-1}, 0),
\]

\[
B^{(n)} = \sum_{(n-1)} (0, k_1, ..., k_{n-1}, 0),
\]

(3.18)

and

\[
\sum_{(p)} (0, k_1, ..., k_{n-1}, 0)
\]

(3.19)

denotes the sum over all non-negative integers \( k_1, ..., k_{n-1} \) satisfying \( k_1 + ... + k_{n-1} = p \).

In Kato’s method the eigenvalues \( E_\alpha \) of \( H_{\text{eff}} = H_{\text{eff},0} + H_{\text{eff},1} \) are obtained as solutions of the following eigenvalue problem in \( \mathcal{R}_\alpha^{(0)} \):

\[
(\hat{H}_\alpha - E_\alpha \hat{K}_\alpha) | \rangle = 0,
\]

(3.21)

where \( | \rangle \in \mathcal{R}_\alpha^{(0)} \).

We show now that both, \( \hat{K}_\alpha \) and \( \hat{H}_\alpha \) are matrices over \( \mathcal{R}_\alpha^{(0)} \) which are multiples of the 2\( \times \)2 unit matrix there. Indeed, let us first consider the matrix elements of \( \hat{K}_\alpha \):

\[
\hat{K}_\alpha | \tilde{\alpha}, m \rangle = | \tilde{\alpha}, m' \rangle (\hat{K}_\alpha)_{m'm},
\]

(\( \hat{K}_\alpha \)_{m'm} = (\tilde{\alpha}, m' | \hat{K}_\alpha | \tilde{\alpha}, m)).

(3.22)

From T-invariance we get, using (A.2), (A.3) and (A.12) of Appendix A and that \( \phi_n(\mathbf{R}) \) in (3.6) is a real function:

\[
(T^\dagger(0, k_1, ..., k_{n-1}, 0)T)^T = (0, k_{n-1}, ..., k_1, 0),
\]

(3.23)

\[
(T^\dagger \hat{K}_\alpha T)^T = \hat{K}_\alpha,
\]

(3.24)

\[
(\tilde{\alpha}, m' | \hat{K}_\alpha | \tilde{\alpha}, m) = (\tilde{\alpha}, m' | T^\dagger \hat{K}_\alpha T | \tilde{\alpha}, m) = (-1)^{2F+(m+m')}F_n(|\tilde{\alpha}, m' | \hat{K}_\alpha | \tilde{\alpha}, m),
\]

(3.25)

Note that the matrix \( T \) acts on the internal atomic state vectors only, but the transposition has to be taken including the c.m. part of the state vectors. In (3.25) \( F \) and \( |F_3| = -F, ..., F \) are half-integers. Therefore we get:

\[
(\tilde{\alpha}, + | \hat{K}_\alpha | \tilde{\alpha}, +) = (\tilde{\alpha}, + | \hat{K}_\alpha | \tilde{\alpha}, +),
\]

(3.26)
i.e. \( \hat{K}_\alpha \) is proportional to the unit matrix in \( \mathcal{R}_\alpha^{(0)} \). The proof that also \( \hat{H}_\alpha \) is a multiple of the unit matrix in \( \mathcal{R}_\alpha^{(0)} \) is analogous. As a result we see that the twofold degeneracy of the eigenvalue (3.10) is maintained to all orders in the perturbation theory.

The actual calculation of the perturbed eigenvalues is best done with the help of Bloch’s method \(^\text{29}\) which gives a smaller number of terms which have to be calculated in each order. Let us define the matrix \( \hat{\mathcal{H}}_\alpha \) by

\[
\hat{\mathcal{H}}_\alpha \hat{K}_\alpha = \hat{\mathcal{H}}_\alpha, \\
\hat{\mathcal{H}}_\alpha \mathcal{P}_\alpha^{(0)} = \hat{\mathcal{H}}_\alpha.
\]

(3.27)

One finds the following expansion for \( \hat{\mathcal{H}}_\alpha \):

\[
\hat{\mathcal{H}}_\alpha = E_\alpha^{(0)} \mathcal{P}_\alpha^{(0)} + \sum_{n=1}^{\infty} C^{(n)},
\]

(3.28)

where

\[
C^{(1)} = (0, 0), \\
C^{(n)} = \sum'_{(n-1)} (0, k_1, ..., k_{n-1}, 0), \quad (n \geq 2).
\]

(3.29)

Here \( \sum'_{(n-1)} \) denotes the sum as in (3.19), (3.20), with the additional requirement

\[
k_1 + ... + k_m \geq m \quad \text{for} \quad m = 1, ..., n - 1.
\]

(3.30)

Clearly, the eigenvalue problem (3.21) is equivalent to

\[
(\hat{\mathcal{H}}_\alpha - E_\alpha)| \rangle = 0,
\]

(3.31)

with \( | \rangle \in \mathcal{R}_\alpha^{(0)} \). Furthermore \( \hat{\mathcal{H}}_\alpha \) is a multiple of the unit matrix in \( \mathcal{R}_\alpha^{(0)} \), as we see from (3.27). Thus we find

\[
E_\alpha = \frac{1}{2} \text{Tr} \hat{\mathcal{H}}_\alpha = E_\alpha^{(0)} + \sum_{n=1}^{\infty} E_\alpha^{(n)}, \\
E_\alpha^{(n)} = \sum'_{(n-1)} \frac{1}{2} \text{Tr} (0, k_1, ..., k_{n-1}, 0), \quad (n = 1, 2, ...).
\]

(3.32)

The first three correction terms read:

\[
E_\alpha^{(1)} = \frac{1}{2} \text{Tr} (0, 0), \\
E_\alpha^{(2)} = \frac{1}{2} \text{Tr} (0, 1, 0), \\
E_\alpha^{(3)} = \frac{1}{2} \text{Tr} \{ (0, 1, 1, 0) + (0, 2, 0, 0) \}.
\]

(3.33)

Using (3.10) and arguments analogous to (3.22) ff. we can write \( E_\alpha^{(3)} \) as follows:

\[
E_\alpha^{(3)} = \frac{1}{2} \text{Tr} (0, 1, 1, 0) - \left[ \frac{3}{2} \text{Tr} (0, 2, 0) \right] \left[ \frac{1}{2} \text{Tr} (0, 0) \right].
\]

(3.34)
Now we consider a reflection $R$ on the 1–3-plane $R_2 = A_2/2$ (cf. Fig. 1):

$$R : \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \rightarrow \begin{pmatrix} x_1 \\ A_2 - x_2 \\ x_3 \end{pmatrix}.$$ (3.35)

The reflected field $E_R^{(\sigma)}$ has its 1- and 3-components unchanged, the 2-component changes sign (cf. (1.70)). According to Sect. 1.1 we want to calculate the following energy difference (cf. (1.25) with $E_p \rightarrow E_R$)

$$\Delta E_\alpha = E_\alpha(E) - E_\alpha(E_R)$$ (3.36)

which is a parity-odd observable. From (3.4), (3.5) we see that for our neutral atom ($q = 0$) we have

$$H_{\text{eff},0}(E_R, \delta_1) = H_{\text{eff},0}(E, \delta_1),$$

$$H_{\text{eff},0}(E_R, -\delta_1) = \overline{R} H_{\text{eff},0}(E, -\delta_1) \overline{R}^\dagger,$$ (3.37)

$$H_{\text{eff},1}(E') = -\sum_{\sigma=1}^3 E''^{(\sigma)} D \cdot \Theta(R_1^{(\sigma)} - R_1) \Theta(R_1 - R_1^{(\sigma-1)}),$$

$$H_{\text{eff},1}(E'_R) = \overline{R} H_{\text{eff},1}(E') \overline{R}^\dagger.$$ (3.38)

Here $\overline{R}$ is the operator representing the reflection $R$ as defined in (1.72). From the $R$-transformation of the states (3.6) as given in (A.13) we get the following:

$$(0, k_1, ..., k_{n-1}, 0)|E_R, \delta_1\rangle = \overline{R}(0, k_1, ..., k_{n-1}, 0)|E, -\delta_1\rangle \overline{R}^\dagger,$$ (3.39)

$$\hat{H}_\alpha(E_R, \delta_1) = \overline{R} \hat{H}_\alpha(E, -\delta_1) \overline{R}^\dagger,$$ (3.40)

$$\Delta E_\alpha = \frac{1}{2} \text{Tr} \left[ \hat{H}_\alpha(E, \delta_1) - \hat{H}_\alpha(E_R, \delta_1) \right]$$

$$= \frac{1}{2} \text{Tr} \left[ \hat{H}_\alpha(E, \delta_1) - \hat{H}_\alpha(E, -\delta_1) \right].$$ (3.41)

Let us now have a closer look at the traces occurring in (3.32). We define the spherical components of the dipole operator $D$ and the fields $E'^{(\sigma)}$ as usual:

$$D_{\pm} = \mp \frac{1}{\sqrt{2}} (D_1 \pm i D_2),$$

$$D_0 = D_3$$ (3.42)

and analogously $E''^{(\sigma)}$ ($m = \pm, 0; \sigma = 1, 2, 3$). Under the reflection $R$ (3.35) we have

$$\overline{R}^\dagger D_m \overline{R} = (-1)^m D_{-m}.$$ (3.43)

From (3.13) and (3.38) we get

$$\frac{1}{2} \text{Tr} (0, k_1, ..., k_{n-1}, 0)$$

$$= \sum_{\sigma,m} \left( D_{m_1}^{(\sigma_1)} k_1, D_{m_2}^{(\sigma_2)}, ..., k_{n-1}, D_{m_n}^{(\sigma_n)} \right) \delta_1 \cdot (-1)^{m_1+...+m_n} E^{(\sigma_1)}_{m_1} \cdot E^{(\sigma_n)}_{-m_n},$$ (3.44)
where we set
\[
\left(D^{(\sigma_1)}_{m_1}, k_1, D^{(\sigma_2)}_{m_2}, k_2, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{\delta_1}
= (-1)^{n-1/2} \text{Tr} \left\{ S_{\alpha,0} D_{m_1} \Theta(R^{(\sigma_1)} - R_1) \Theta(R_1 - R^{(\sigma_1^{-1})}) \times S_{\alpha,k_1} \cdots S_{\alpha,k_{n-1}} D_{m_n} \Theta(R^{(\sigma_n)} - R_1) \Theta(R_1 - R^{(\sigma_n^{-1})}) S_{\alpha,0} \right\}.
\] (3.45)

The point is now to realize that these expressions are invariant under rotations around the 3-axis performed in the internal space only. This is clear from the factorization of the states (3.6) into the internal and the c.m. motion parts and the definitions (3.14), (3.43) and leads to the following results:

\[
\left(D^{(\sigma_1)}_{m_1}, k_1, D^{(\sigma_2)}_{m_2}, k_2, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{\delta_1} = 0
\quad \text{for } \sum_{j=1}^{n} m_j \neq 0.
\] (3.46)

The time reversal transformation \(T\) gives (cf. (3.38) of [15] and (3.23)):

\[
\left(D^{(\sigma_1)}_{m_1}, k_1, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{\delta_1} = \left(D^{(\sigma_n)}_{m_n}, k_{n-1}, \ldots, k_1, D^{(\sigma_1)}_{m_1}\right)_{\delta_1}.
\] (3.47)

For \(n = 2\) we get a further relation from \(T\). Due to the factorization of the states (3.6) into the internal and c.m. parts we have

\[
\left(D^{(\sigma_1)}_{m_1}, k_1, D^{(\sigma_2)}_{m_2}\right)_{\delta_1} = \left(D^{(\sigma_1)}_{m_2}, k_1, D^{(\sigma_2)}_{m_1}\right)_{\delta_1},
\] (3.48)

as is proved easily using (3.38) and (3.47) of [15] and (3.14), (3.43).

The reflection (3.35) gives

\[
\mathcal{E}^{(\sigma)}_{\text{Rm}} = (-1)^m \mathcal{E}^{(-\sigma)}_{-\text{m}},
\] (3.49)

\[
\left(D^{(\sigma_1)}_{m_1}, k_1, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{\delta_1} = (-1)^{\sum_{j=1}^{n} m_j} \left(D^{(\sigma_1)}_{m_1}, k_1, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{-\delta_1}.
\] (3.50)

With these relations we get for \(\Delta E_{\alpha}\) (3.36), (3.41):

\[
\Delta E_{\alpha} = \sum_{n=1}^{\infty} \Delta E^{(n)}_{\alpha},
\]

\[
\Delta E^{(n)}_{\alpha} = \sum_{(n-1)}^{\prime} \sum_{\sigma,m} \frac{1}{2} \left[ \left(D^{(\sigma_1)}_{m_1}, k_1, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{\delta_1} - \left(D^{(\sigma_1)}_{m_1}, k_1, \ldots, k_{n-1}, D^{(\sigma_n)}_{m_n}\right)_{-\delta_1} \right]
\times \left[ (-1)^{\sum_{j=1}^{n} m_j} \mathcal{E}^{(\sigma_1)}_{m_1} \cdots \mathcal{E}^{(\sigma_n)}_{m_n} - \mathcal{E}^{(-\sigma_1)}_{m_1} \cdots \mathcal{E}^{(-\sigma_n)}_{m_n} \right],
\] (3.51)

where only the terms with \(\sum m_j = 0\) are non-zero (cf. (3.46)). In (3.51) the energy shifts \(\Delta E^{(n)}_{\alpha}\) are written in a way to exhibit explicitly that they are odd functions of \(\delta_1\) and proportional to parity-odd combinations of the electric field components \(\mathcal{E}^{(\sigma)}_{m}\).
Explicitly we get from (3.51) for the lowest $n$-values:

$$
\Delta E^{(1)}_{\vec{a}} = \frac{1}{2} \text{Tr} (0, 0)_{\delta_1} - \frac{1}{2} \text{Tr} (0, 0)_{-\delta_1}
$$

$$
= \sum_{\sigma} \frac{1}{2} \left[ \left( D^{(\sigma)}_0 \right)_{\delta_1} - \left( D^{(\sigma)}_0 \right)_{-\delta_1} \right] [\mathcal{E}^{(\sigma)}_0 - \mathcal{E}^{(\sigma)}_{\delta_1}]
$$

$$
= 0,
$$

(3.52)

$$
\Delta E^{(2)}_{\vec{a}} = \frac{1}{2} \text{Tr} (0, 1, 0)_{\delta_1} - \frac{1}{2} \text{Tr} (0, 1, 0)_{-\delta_1}
$$

$$
= \frac{1}{2} \sum_{\sigma} \left[ \left( D^{(\sigma)}_{+1}, 1, D^{(\sigma)}_{-2} \right)_{\delta_1} - \left( D^{(\sigma)}_{+1}, 1, D^{(\sigma)}_{-2} \right)_{-\delta_1} \right]
$$

$$
- \left( D^{(\sigma)}_{-1}, 1, D^{(\sigma)}_{+2} \right)_{\delta_1} + \left( D^{(\sigma)}_{-1}, 1, D^{(\sigma)}_{+2} \right)_{-\delta_1} [\mathcal{E}^{(\sigma)}_{-1} \mathcal{E}^{(\sigma)}_{+2} - \mathcal{E}^{(\sigma)}_{-1} \mathcal{E}^{(\sigma)}_{+2}]
$$

$$
= 0,
$$

(3.53)

where we used (3.48). In a similar way we find

$$
\text{Tr} (0, 2, 0)_{\delta_1} - \text{Tr} (0, 2, 0)_{-\delta_1} = 0.
$$

(3.54)

The first non-vanishing result is the term with $n = 3$. We get from (3.34):

$$
\Delta E^{(3)}_{\vec{a}} = \frac{1}{2} \text{Tr} (0, 1, 0)_{\delta_1} - \frac{1}{2} \text{Tr} (0, 1, 0)_{-\delta_1}
$$

$$
- \frac{1}{2} \text{Tr} (0, 2, 0)_{\delta_1} + \frac{1}{2} \text{Tr} (0, 2, 0)_{-\delta_1} \frac{1}{2} \text{Tr} (0, 0)_{-\delta_1}.
$$

(3.55)

From (3.52) and (3.54) we find that the 3rd and 4th terms on the r.h.s. cancel. Thus we finally obtain:

$$
\Delta E^{(3)}_{\vec{a}} = \sum_{\sigma, m} \frac{1}{2} \left[ \left( D^{(\sigma)}_{m_1}, 1, D^{(\sigma)}_{m_2}, 1, D^{(\sigma)}_{m_3} \right)_{\delta_1} - \left( D^{(\sigma)}_{m_1}, 1, D^{(\sigma)}_{m_2}, 1, D^{(\sigma)}_{m_3} \right)_{-\delta_1} \right]
$$

$$
\times \left[ (-1)^{m_1+m_2+m_3} \mathcal{E}^{(\sigma)}_{m_1} \mathcal{E}^{(\sigma)}_{m_2} \mathcal{E}^{(\sigma)}_{m_3} - \mathcal{E}^{(\sigma)}_{m_1} \mathcal{E}^{(\sigma)}_{m_2} \mathcal{E}^{(\sigma)}_{m_3} \right].
$$

(3.56)

To show that this term is actually non-zero, let us consider the example where the perturbation is absent in Section $\sigma = 2$:

$$
\mathcal{E}^{(2)} = 0.
$$

(3.57)

We then get from (3.58):

$$
\Delta E^{(3)}_{\vec{a}} = \delta_1 \left[ c^{(3)}_{\vec{a}} e_3 \cdot \mathcal{E}^{(1)} - c^{(3)}_{\vec{a}} e_3 \cdot \mathcal{E}^{(3)} \right] \frac{1}{\gamma^2} \left( e_3 \cdot \left( \mathcal{E}^{(1)} \times \mathcal{E}^{(3)} \right) \right),
$$

(3.58)

where we set for $\sigma = 1, 3$:

$$
\delta_1 c^{(\sigma)}_{\vec{a}} = -2i \varepsilon^3 \cdot \left\{ (D^{(\sigma)}_+, 1, D^{(\sigma)}_0, 1, D^{(\sigma)}_-)_{\delta_1} + (D^{(\sigma)}_0, 1, D^{(\sigma)}_+, 1, D^{(\sigma)}_-)_{\delta_1} \right\}
$$

$$
+ (D^{(\sigma)}_+, 1, D^{(\sigma)}_-, 1, D^{(\sigma)}_0)_{\delta_1} - (\delta_1 \rightarrow -\delta_1) \right\},
$$

(3.59)

$$(\tau = 3 \text{ for } \sigma = 1; \tau = 1 \text{ for } \sigma = 3).$$

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To give some numbers we consider a box (Fig. 1) of dimension
\[ A_1 = A_2 = A_3 = 8\text{nm} \quad (3.60) \]
and segment lengths (cf. (2.2)):
\[ R^{(1)}_1 = 0.4 \cdot A_1, \quad R^{(2)}_1 = 0.6 \cdot A_1. \quad (3.61) \]

In Fig. 2a we plot the real parts of the corresponding unperturbed eigenenergies \( E^{(0)}_{\bar{\alpha}} \) for our “hydrogen” atom with \( I = 0 \) as function of the electric field \( \mathcal{E} \). We note that the transverse parts of the wave functions, characterized by the integers \( n_2, n_3 \) (cf. (3.6)) do not mix under perturbations by \( H_{\text{eff},1} \) (3.5) for our case here \( (q = 0) \).

Thus we consider only the levels with the lowest transverse energies corresponding to \( n_2 = n_3 = 1 \). For the Lamb shift \( L \) and the \( 2P_{3/2} - 2P_{1/2} \) energy difference \( \Delta \) as well as the widths \( \Gamma_S, \Gamma_P \) we take the values from real hydrogen (cf. Table III of [15]). The zero of the energy scale is put at the energy of the \( 2P_{1/2} \) level in vacuo.

Now we introduce the perturbation in the electric field
\[
\mathcal{E}'^{(1)} = \begin{pmatrix} \mathcal{E}' \\ 0 \end{pmatrix}, \quad \mathcal{E}'^{(2)} = 0, \quad \mathcal{E}'^{(3)} = \begin{pmatrix} 0 \\ \eta \mathcal{E}' \end{pmatrix}. \quad (3.62)
\]

This leads to an energy shift \( E^{(0)}_{\bar{\alpha}} \rightarrow E'_{\bar{\alpha}} \) as calculated in (3.32) and to a P-violating energy difference \( \Delta E'_{\bar{\alpha}} \). This is given to lowest nontrivial order in (3.58), from which we see that \( \Delta E'^{(3)}_{\bar{\alpha}} \) is proportional to \( \eta \mathcal{E}'^3 \) and thus changes sign if we change the chirality of the field arrangement (\( \eta \rightarrow -\eta \)):
\[
\Delta E'^{(3)}_{\bar{\alpha}} = \delta_1 c^{(1)}_{\bar{\alpha}} \eta \left( \frac{\mathcal{E}'}{\mathcal{E}} \right)^3. \quad (3.63)
\]

We plot the real and imaginary parts of the coefficient \( c^{(1)}_{\bar{\alpha}} \) for the state \( \bar{\alpha} = (2S_{1/2}, |F_3| = 1/2, n_1 = 1, n_2 = 1, n_3 = 1) \) in Fig. 3. Of course, we would like to make \( |\Delta E'^{(3)}_{\bar{\alpha}}| \) as big as possible by increasing \( \mathcal{E}' \). However, there are limits to this in our calculation. The perturbation treatment is only reliable as long as the energy shifts induced by the perturbation are small compared to the spacing of the unperturbed levels. Thus, we can at best trust our calculation for values of \( |\mathcal{E}'| \leq \mathcal{E}'_{\text{max}} \) which we estimate from the requirement that the first plus second order energy shift is equal to the minimum of the unperturbed energy differences:
\[
|E^{(1)}_{\bar{\alpha}}(\pm \mathcal{E}'_{\text{max}})| + |E^{(2)}_{\bar{\alpha}}(\pm \mathcal{E}'_{\text{max}})| = \min_{\beta \neq \bar{\alpha}} |E^{(0)}_{\beta} - E^{(0)}_{\bar{\alpha}}|. \quad (3.64)
\]

Here we choose the plus or minus sign according to which gives the lower value for \( \mathcal{E}'_{\text{max}} \). We plot \( \mathcal{E}'_{\text{max}} \) in Fig. 4 for the level \( \bar{\alpha} = (2S_{1/2}, |F_3| = 1/2, n_1 = 1, n_2 = 1, n_3 = 1) \). The P-violating energy and lifetime shifts for \( \mathcal{E}' = \mathcal{E}'_{\text{max}} \) are then shown in Fig. 5. From this calculation we can thus establish theoretically for our “hydrogen” atom with \( I = 0 \) a P-violating energy shift of the order of
\[
\Re \Delta E'^{(3)}_{\bar{\alpha}} / h \simeq \delta_1 \cdot 5 \cdot 10^3 \text{Hz} = -2.46 \cdot 10^{-9} \text{Hz}. \quad (3.65)
\]
Since $\delta_1$ is of the order $10^{-11}...10^{-12}$ (cf. (3.20), (3.21) of [15]), this is an extremely small energy shift. Fortunately there is — at least in theory — a way to enhance the effect dramatically. In fact, we will show now how to obtain energy shifts not of order $\delta_1$ but of order $\sqrt{\delta_1}$.

Consider Figure 2a. There is a crossing between the levels $\bar{\alpha} = (2S_1/2, |F_3| = 1/2; n = (1,1,1))$ and $\bar{\beta} = (2P_1/2, |F_3| = 1/2; n = (2,1,1))$ in the real parts at an electric field strength $E \simeq 500$ V/cm. Correspondingly, the maximally allowed perturbation field strength $E'_{\text{max}}$ is at a minimum at $E \simeq 500$ V/cm as can be seen in Fig. 4. This can be easily understood from (3.64) and the fact that $|\Im E_{\bar{\alpha}}(0)/h| \simeq 16$ MHz and $|\Im E_{\bar{\beta}}(0)/h| \simeq 38$ MHz are by two orders of magnitude smaller than $|\Re E_{\bar{\alpha},\bar{\beta}}(0)/h| \simeq 1.6$ GHz (cf. Figs. 2a, 2b). Then, the r.h.s. of (3.64) becomes very small at the zero of the real part $\Re (E_{\bar{\beta}}(0) - E_{\bar{\alpha}}(0))$ and so does $E'_{\text{max}}$. However, this only means that our calculation as done so far is limited. In fact, the P-violating energy and lifetime shifts at such a crossing of levels may nevertheless have a maximum. We will show this in the following using again degenerate perturbation theory treating all the crossing levels together.

We consider a configuration with a crossing of levels in both the real and the imaginary parts at the same field strength:

$$\Re \left( E_{\bar{\beta}}^{(0)}(\mathcal{E}_3) - E_{\bar{\alpha}}^{(0)}(\mathcal{E}_3) \right) = 0, \quad (3.66)$$
$$\Im \left( E_{\bar{\beta}}^{(0)}(\mathcal{E}_3) - E_{\bar{\alpha}}^{(0)}(\mathcal{E}_3) \right) = 0. \quad (3.67)$$

We find (cf. Fig. 2b) that (3.67) is fulfilled at

$$\mathcal{E}_{\text{res}} \simeq 1024 \text{ V/cm} \quad (3.68)$$

for $\alpha = 2S_{1/2}, \beta = 2P_{1/2}$. If one now adjusts the box lengths to

$$A_1 = 5.84 \text{ nm}, \quad A_2 = A_3 = 8 \text{ nm}, \quad (3.69)$$

then (3.66) is satisfied for $\bar{\alpha} = (2S_{1/2}, |F_3| = 1/2; n_1 = 1), \bar{\beta} = (2P_{1/2}, |F_3| = 1/2; n_1 = 2)$ and so is (3.67) as there are no contributions to the imaginary part of the energy from the c.m. motion. Note that (3.66) could also be fulfilled by adjusting $A_2, A_3$, but the differences between energy levels with different c.m. quantum numbers $n_2, n_3$ will not appear for neutral atoms as energy denominators in the perturbation series, since the perturbation fields $\mathcal{E}^{(\sigma)}$ are chosen not to vary along the 2- and 3-directions. Then, due to orthogonality, only matrix elements

$$(\alpha, F_3; (n_1, n_2, n_3)| H_{\text{eff},1}| \beta, F_3'; (n_1', n_2, n_3))$$

are diagonal in $n_2, n_3$ are nonzero.

In order to calculate a reliable value for the P-violating energy shifts, we use degenerate perturbation theory in the 4-dimensional subspace spanned by the states

$$|\bar{\alpha}, \pm \rangle := |2S_{1/2}, \pm |F_3|, \mathcal{E}_{\text{res}} e_3; (1,1,1)), \quad |\bar{\beta}, \pm \rangle := |2P_{1/2}, \pm |F_3|, \mathcal{E}_{\text{res}} e_3; (2,1,1)), \quad (3.70)$$
where \(|F_3| = 1/2\). In analogy to (3.12), (3.14) we define the matrices:

\[
P^{(0)}_{(\bar{\alpha}\bar{\beta})} := \sum_{m=\pm} \left[ |\bar{\alpha},m\rangle(\bar{\alpha},m| + |\bar{\beta},m\rangle(\bar{\beta},m| \right],
\]

(3.71)

\[
Q^{(0)}_{(\bar{\alpha}\bar{\beta})} := 1 - P^{(0)}_{(\bar{\alpha}\bar{\beta})},
\]

(3.72)

\[
\frac{Q^{(0)}_{(\bar{\alpha}\bar{\beta})}}{e^k} := \sum_{\gamma \neq \bar{\alpha}} \left( E^{(0)}_{\gamma} - E^{(0)}_{\bar{\alpha}} \right)^k, \quad (k = 1, 2, ...)
\]

(3.73)

\[
S_{(\bar{\alpha}\bar{\beta}),0} := -P^{(0)}_{(\bar{\alpha}\bar{\beta})},
\]

\[
S_{(\bar{\alpha}\bar{\beta}),k} := \frac{Q^{(0)}_{(\bar{\alpha}\bar{\beta})}}{e^k}, \quad \text{for} \quad k = 1, 2, ...
\]

(3.74)

(Remember that in (3.73) \(E^{(0)}_{\bar{\alpha}} = E^{(0)}_{\bar{\beta}} \neq E^{(0)}_{\gamma}\)). Using these matrices we define, similarly to (3.15), the operators

\[
(k_1, ..., k_{n+1}) := S_{(\bar{\alpha}\bar{\beta}),k_1} H_{\text{eff},1} S_{(\bar{\alpha}\bar{\beta}),k_2} \cdots H_{\text{eff},1} S_{(\bar{\alpha}\bar{\beta}),k_{n+1}}.
\]

(3.75)

In the following we will show that all energy levels remain at least twofold degenerate to all orders of perturbative theory also in this case. We define

\[
\hat{K}_{(\bar{\alpha}\bar{\beta})} := P^{(0)}_{(\bar{\alpha}\bar{\beta})} + \sum_{n=2}^{\infty} A^{(n)},
\]

(3.76)

\[
\hat{H}_{(\bar{\alpha}\bar{\beta})} := E^{(0)}_{\bar{\alpha}} K_{(\bar{\alpha}\bar{\beta})} + \sum_{n=1}^{\infty} B^{(n)},
\]

(3.77)

with \(A^{(n)}, B^{(n)}\) defined as in (3.18), but in terms of the operators (3.73).

Instead of discussing now Kato’s eigenvalue problem (3.21) we will now introduce and use a modified version of Bloch’s method [29]. We define a matrix \(\tilde{H}_{(\bar{\alpha}\bar{\beta})}\) by the conditions (see Appendix [C]):

\[
(K_{(\bar{\alpha}\bar{\beta})})^{1/2} \tilde{H}_{(\bar{\alpha}\bar{\beta})}(K_{(\bar{\alpha}\bar{\beta})})^{1/2} = \tilde{H}_{(\bar{\alpha}\bar{\beta})},
\]

\[
\tilde{H}_{(\bar{\alpha}\bar{\beta})} P^{(0)}_{(\bar{\alpha}\bar{\beta})} = \tilde{H}_{(\bar{\alpha}\bar{\beta})},
\]

\[
P^{(0)}_{(\bar{\alpha}\bar{\beta})} \tilde{H}_{(\bar{\alpha}\bar{\beta})} = \tilde{H}_{(\bar{\alpha}\bar{\beta})}.
\]

(3.78)

Bloch’s operator \(\tilde{H}_{(\bar{\alpha}\bar{\beta})}\) defined as in (3.27) with \(\bar{\alpha} \rightarrow (\bar{\alpha}\bar{\beta})\) is in general non-hermitian even if \(\hat{H}_{(\bar{\alpha}\bar{\beta})}\) and \(\hat{K}_{(\bar{\alpha}\bar{\beta})}\) are hermitian. In contrast, \(\tilde{H}_{(\bar{\alpha}\bar{\beta})}\) is hermitian if \(\hat{H}_{(\bar{\alpha}\bar{\beta})}\) and \(\hat{K}_{(\bar{\alpha}\bar{\beta})}\) are hermitian, which would be the case for stable states, i.e. \(\Gamma_S = \Gamma_P = 0\). We will need this property of \(\tilde{H}_{(\bar{\alpha}\bar{\beta})}\) later when we want to check, that our effect proportional to \(\sqrt{\delta_{11}}\) vanishes for the case of stable states. We assume that the perturbation expansion of \(\tilde{H}_{(\bar{\alpha}\bar{\beta})}\) is well defined and converges (cf. Appendix [C] for the conditions for this to be the case). The eigenvalue problem (3.21) is then equivalent to the following standard diagonalization problem:

\[
(\tilde{H}_{(\bar{\alpha}\bar{\beta})} - E) \mid \psi \rangle = 0,
\]

(3.79)
where \( |\rangle \in \mathcal{R}_{\alpha\beta}^{(a)} \).

Now we will show, that the eigenvalue problem factorizes and leaves a twofold degeneracy of the eigenenergies. We define the \( 2 \times 2 \) matrices:

\[
\tilde{H}_{\gamma'\gamma} := \begin{pmatrix} \tilde{H}_{\alpha\alpha} - E & \tilde{H}_{\alpha\beta} \\ \tilde{H}_{\beta\alpha} & \tilde{H}_{\beta\beta} - E \end{pmatrix}
\]

where \( \gamma', \gamma \in \{\alpha, \beta\} \); \( m', m \in \{+1, -1\} \). Now the secular matrix reads:

\[
S(E) := \begin{pmatrix} \tilde{H}_{\alpha\alpha} - E & \tilde{H}_{\alpha\beta} \\ \tilde{H}_{\beta\alpha} & \tilde{H}_{\beta\beta} - E \end{pmatrix}
\]

By simple manipulations we obtain that

\[
\det S(E) = \det S'(E) \left[ \det \tilde{H}_{\alpha\beta} \det \tilde{H}_{\beta\alpha} \right]^{-1},
\]

where

\[
S'(E) := \begin{pmatrix} \tilde{H}_{\alpha\alpha} - E & \tilde{H}_{\alpha\beta} \\ \tilde{H}_{\alpha\beta} & \tilde{H}_{\beta\beta} - E \end{pmatrix}.
\]

Using T-invariance we show in Appendix C that \( \tilde{H}_{\alpha\alpha}, \tilde{H}_{\beta\beta} \) and \( \tilde{H}_{\alpha\beta} \tilde{H}_{\beta\alpha} \) are all multiples of the \( 2 \times 2 \) unit matrix.

Then it follows from (3.82), (3.83) that

\[
\det S(E) = \left( (a - E)(b - E) - c \right)^2,
\]

where

\[
a := \frac{1}{2} \text{Tr} \tilde{H}_{\alpha\alpha}, \\
b := \frac{1}{2} \text{Tr} \tilde{H}_{\beta\beta}, \\
c := \frac{1}{2} \text{Tr} (\tilde{H}_{\alpha\beta} \tilde{H}_{\beta\alpha}).
\]

Thus \( \det S(E) \) is a perfect square, all eigenvalues \( E \) are twofold degenerate and \( \det S(E) = 0 \) if and only if

\[
(a - E)(b - E) - c = 0.
\]

This is a quadratic equation for \( E \) which has the solutions

\[
E_{\alpha\beta,\pm} := \frac{1}{2} \left[ a + b \pm \sqrt{(a - b)^2 + 4c} \right]
\]

\[
= \frac{1}{2} \left[ a + b \pm \sqrt{[-i(a - b) + 2\sqrt{c}][i(a - b) + 2\sqrt{c}]} \right].
\]

The complex numbers \( a, b, c \) can be expanded in \( \delta_1 \):

\[
a = a_0 + \delta_1 a_1 + ...
\]

\[
b = b_0 + \delta_1 b_1 + ...
\]

\[
c = c_0 + \delta_1 c_1 + ...
\]
and thus we get for the eigenenergies (3.87):

\[ E_{\bar{\alpha}\bar{\beta},\pm} = \frac{1}{2} \left[ a_0 + b_0 + \delta_1 (a_1 + b_1) + \mathcal{O}(\delta_1^2) \right] \]

\[ \pm \left\{ -i(a_0 - b_0) + 2\sqrt{c_0} \right\}\left\{ i(a_0 - b_0) + 2\sqrt{c_0} \right\} \]

\[ + \delta_1 \left[ 2(a_0 - b_0)(a_1 - b_1) + 4c_1 \right] + \mathcal{O}(\delta_1^2) \}^{1/2} \]  

(3.89)

Now it is clear that in the case

\[ (a_0 - b_0)^2 + 4c_0 \neq 0 \]  

(3.90)

we will get at best P-violating energy shifts linear in \( \delta_1 \). If, however,

\[ i(a_0 - b_0) + 2\sqrt{c_0} = 0 \]  

(3.91)

or

\[ -i(a_0 - b_0) + 2\sqrt{c_0} = 0 \]  

(3.92)

and together with (3.91) or (3.92):

\[ 2(a_0 - b_0)(a_1 - b_1) + 4c_1 \neq 0, \]  

(3.93)

we will obtain

\[ E_{\bar{\alpha}\bar{\beta},\pm} = \frac{1}{2} \left[ a_0 + b_0 \pm \sqrt{\delta_1} \left\{ 2(a_0 - b_0)(a_1 - b_1) + 4c_1 \right\}^{1/2} \right. \]

\[ + \mathcal{O}(\delta_1) \]. \]  

(3.94)

This is a P-violating splitting which can be distinguished from a P-conserving one as it changes its phase by a factor of \( i \) under a change of sign of \( \delta_1 \) or a reversal of the handedness of the external field arrangement which changes the signs of \( a_1, b_1, c_1 \). In other words: we have to search for a degeneracy of two complex energy levels (3.87) in an external electric field with non-zero handedness in the absence of P-violation, i.e. for \( \delta_1 = 0 \). Then the small P-violation effects proportional to \( \delta_1 \) in the matrix elements can produce an energy shift of order \( \sqrt{\delta_1} \).

Note, that this is clearly an effect which results from the non-hermiticity of \( \tilde{H}_{(\bar{\alpha}\bar{\beta})} \), i.e., which is only possible for unstable states. For the case of stable states, \( \tilde{H}_{(\bar{\alpha}\bar{\beta})} \) is hermitian (cf. (3.78)) and therefore we get for the submatrices (3.80)

\[ \tilde{H}_{\bar{\alpha}\bar{\alpha}} = \tilde{H}^{\dagger}_{\bar{\alpha}\bar{\alpha}}, \quad \tilde{H}_{\bar{\beta}\bar{\beta}} = \tilde{H}^{\dagger}_{\bar{\beta}\bar{\beta}}, \quad \tilde{H}_{\bar{\alpha}\bar{\beta}} = \tilde{H}^{\dagger}_{\bar{\beta}\bar{\alpha}}. \]  

(3.95)

From (3.83) we find then that \( a, b, c \) and likewise \( a_0, b_0, c_0 \), and \( a_1, b_1, c_1 \) are real and

\[ c \geq 0, \quad c_0 \geq 0; \]

\[ c_1 = 0 \quad \text{if} \quad c_0 = 0. \]  

(3.96)

Now the condition (3.91) is equivalent to (3.92) and leads to \( a_0 = b_0 \) and \( c_0 = 0 \) which implies through (3.96) also \( c_1 = 0 \). Therefore, (3.93) cannot be fulfilled simultaneously
with \((3.91)\) or, equivalently, \((3.92)\) for the case of stable states, and there will be no energy shifts proportional to \(\sqrt{\delta_1}\) for them.

On the contrary, if \(a, b\) and \(c\) are complex numbers, which is the case for unstable states, one can in general fulfill \((3.91)\) or \((3.92)\) together with \((3.93)\). We will show by the results of a numerical investigation, that this is indeed the case. We choose the following general configuration of three perturbation fields:

\[
E^{(r)}_{\sigma} = \eta^{(r)}_{\sigma} E^{(r)}; \quad (\sigma = 1, 2, 3),
\]

\[(3.97)\]

In Appendix D we give a proof that for sufficiently small \(E^{(r)}\) there exist indeed “resonance” values for the vectors \(\eta^{(r)}_{\sigma}\) where energy shifts proportional to \(\sqrt{\delta_1}\) occur. As an example we choose \(E^{(r)} = 3\) V/cm. Then the calculation to first order in \(E^{(r)}\) gives the following resonance values:

\[
\eta^{(1)}_{res,-} = \begin{pmatrix} 1 \\ 0 \\ -61.31 \end{pmatrix}, \quad \eta^{(2)}_{res,-} = \begin{pmatrix} 0 \\ 0 \\ 574.93 \end{pmatrix}, \quad \eta^{(3)}_{res,-} = \begin{pmatrix} 0 \\ 1 \\ -63.31 \end{pmatrix},
\]

\[(3.98)\]

where \((3.92)\) and \((3.93)\) are fulfilled. Higher orders in \(E^{(r)}\) can only shift these values slightly.

In Figs. 6a and b we plot the decadic logarithms of the moduli of the real and imaginary parts of the \(P\)-violating energy shift (cf. \((3.94)\))

\[
E_{\alpha \beta,+}(\{E^{(r)}_{\sigma}\}) - E_{\alpha \beta,+}(\{E^{(r)}_{\rho}\})
\]

\[(3.99)\]

for our “hydrogen” in a field configuration given by \((3.61)\), \((3.68)\) and \((3.98)\) vs. the deviation \(\eta^{(2)}_{\beta} - \eta^{(2)}_{\beta,res,-}\) of \(\eta^{(2)}_{\beta}\) from the resonance value \(\eta^{(2)}_{\beta,res,-} = 574.93\) for which the \(P\)-even splitting of levels is removed, revealing an enhancement of the \(P\)-violating splitting of the order of \(1/\sqrt{\delta_1}\). The width of the peak is proportional to \(\sqrt{\delta_1}\) and found to be \(\Delta \eta^{(2)}_{\beta} \simeq 0.4 \cdot 10^{-4}\), corresponding to \(E' \Delta \eta^{(2)}_{\beta} = 1.2 \cdot 10^{-4}\) V/cm. Note, however, that in Fig. 6a the differences of the real parts of the energies of the levels are at maximum of the order of \(10^{-2}\) Hz whereas the lifetime of the levels is calculated to be \(0.29 \cdot 10^{-8}\) s. This corresponds to a line width \(\Delta E/h = 5.44 \cdot 10^7\) Hz. Thus it is certainly not an easy task to detect frequency shifts of order \(10^{-2}\) Hz in such broad lines. But our calculation is only meant to provide an illustration how energy shifts proportional to \(\sqrt{\delta_1}\) can be obtained. Certainly, for a realistic experimental situation one would try to optimize such an effect.

### 3.2 Results for an ion with \(I = 0\)

In this section we will discuss the modifications one has to include for the physically relevant case of ions without nuclear spin, as \(\frac{4}{2}\)He\(^+\). As we have already discussed in Section 2.2 one has to introduce Airy functions instead of sines and cosines for the c.m.
wave functions. We write the (right) eigenstates of $H_{\text{eff},0}$ as

$$\begin{align*}
|\alpha, F_3, \mathcal{E} e_3, n \rangle & := |\alpha, F_3, \mathcal{E} e_3 \rangle \cdot \phi_n(R), \\
\phi_n(R) & := N_{n3} [\psi_+(R_3, E_{n3}, \mathcal{E}) - \xi_{n3} \psi_-(R_3, E_{n3}, \mathcal{E})] \\
& \times \prod_{i=1}^{2} \sqrt{\frac{2}{A_i}} \sin \left( \frac{n_i \pi R_i}{A_i} \right),
\end{align*}$$

(3.100)

where the Airy functions $\psi_\pm$ are defined as in (2.37), (2.38), (2.40) f. The eigenenergies $E_{n3}$ corresponding to the Airy modes, which are numbered by $n_3$, are obtained by solving a determinant equation analogous to (2.43), the coefficients $\xi_{n3}$ and the normalization $N_{n3}$ follow from (2.40) and (2.44), respectively. Using the eigenstates (3.100) one computes the perturbation series in an analogous manner as described in (3.12)–(3.20) for Kato’s and (3.27)–(3.30) for Bloch’s method. Note that the perturbation $H_{\text{eff},1}$ (3.5) to the effective Hamiltonian $H_{\text{eff},0}$ now contains the additional term

$$- q R 3 \sum_{\sigma=1}^{3} \mathcal{E}^{i(\sigma)} \Theta(R_1^{i(\sigma)} - R_1) \Theta(R_1 - R_1^{(\sigma-1)}),$$

(3.101)

which was absent in the $q = 0$ case. Therefore, the terms of order $n = 1, 2, \ldots$ of the series (3.17), (3.18), (3.29) have the following structure (symbolically)

$$A^{(n)} \propto \left( (q R + D)^n \right)$$

(3.102)

and similarly for $B^{(n)}$, $C^{(n)}$.

Since matrix elements of (3.101) w.r.t. the states (3.100) are diagonal in the internal quantum numbers $(\alpha, F_3)$, $\delta_1$-linear P-violating contributions to the series can only arise from matrix elements of $\mathcal{D}$. Therefore, up to the third order, $n \leq 3$, there will be no P-violating contributions to the energy shifts $\Delta E^{(n)}_{\bar{\alpha}}$ (cf. (3.52) ff.) involving matrix elements of (3.101). This follows from our result that such contributions appear only for $n \geq 3$ in the $q = 0$ case. Hence, the expressions (3.52), (3.53), (3.58) f. for the P-violating energy shifts $\Delta E^{(i)}_{\bar{\alpha}}$ up to $n = 3$ remain valid for ions with $I = 0$.

However, when one calculates the maximally allowed perturbation field strength $\mathcal{E}_{\text{max}}'$ using (3.64), the contributions from the matrix elements of (3.101) to the P-conserving energy shifts $E^{(1)}_{\bar{\alpha}}, E^{(2)}_{\bar{\alpha}}$ have to be taken into consideration.

We will now present results for $^4_2\text{He}^+$-ions in a box of lengths:

$$A_1 = A_2 = A_3 = 1\text{nm}. \quad (3.103)$$

Note that compared to the case of our “hydrogen” (cf. (3.60)) we rescaled the $A_i$ by a factor

$$Z^{-2}(Z + N)^{-1/2} = 1/8 \quad (3.104)$$

for $^4_2\text{He}^+$ ($Z = N = 2$) in order to obtain an approximate scaling factor of $Z^4$ for the c.m. energies. For $\mathcal{E}' = 0$ the contribution of the c.m.-mode in $i$-direction reads

$$E_{ni} = \frac{n_i^2 \pi^2}{2 m A_i^2}, \quad (3.105)$$
As the mass of the nucleus of a light atom may be approximated by \((Z + N)\) times the mass of the proton, we obtain the desired scaling factor \(Z^4\) for the c.m. energies (3.105), if we multiply the widths \(A_i\) of the box used for hydrogen with (3.104):

\[
\frac{n_i^2 \pi^2 Z^4 [Z + N]}{2 (Z + N) m A_i^2} = Z^4 E_{n_i} \quad (i = 1, 2, 3; \ n_i = 1, 2, \ldots).
\] 

(3.106)

As it was mentioned in section 3.2 of [15], one obtains “reduced \(Z = 1\)” problems from the general \(Z\) case if one multiplies all electric field strengths of the \(Z = 1\) case by \(Z^5\). In the following we will choose such rescaled fields in addition to the rescaled box widths and observe, that all energies will approximately be larger by a factor of \(Z^4 = 16\) compared to the results for “hydrogen”.

In Fig. 7 we plot the lowest levels of the c.m. motion in 3-direction vs. the electric field strength \(E\), which are the solutions to (2.43), the eigenenergies of the Airy states. As the zero of the energy scale we choose the “minimum” of the energy in 3-direction,

\[
E_{3,\text{min}} := \begin{cases} 
0 & \text{for } E \leq 0, \\
-q A_3 E & \text{for } E > 0.
\end{cases}
\] 

(3.107)

For \(E = 0\) the quadratic dependence on \(n_3\) corresponding to the sine-/cosine modes is recovered.

The Lamb shift \(L\) and the energy difference \(\Delta\) as well as the widths \(\Gamma_S, \Gamma_P\) for \(^4\text{He}^+\) are given in Table II of [15]. In the following we again restrict ourselves to levels with the lowest c.m. energies corresponding to \(n_i = 1, i = 1, \ldots, 3\).

We plot \(\mathcal{E}'_{\text{max}}\) in Fig. 8 for the level \(\bar{\alpha} = (2S_{1/2}, |F_3| = \frac{1}{2}, n = (1, 1, 1))\). In Figs. 9a, b we show the P-violating (a) energy shifts and (b) shifts of the decay width for \(\mathcal{E}' = \mathcal{E}'_{\text{max}}\). We have chosen the same configuration of the perturbation fields as in (3.61), (3.62) with \(\eta = 1\). From our calculation we obtain a theoretical energy shift of the order of

\[
\Re \Delta E^{(3)}_{\bar{\alpha}}/h \simeq \delta_1 \cdot 1.2 \cdot 10^5 \text{ Hz} = 1.36 \cdot 10^{-6} \text{ Hz},
\] 

(3.108)

which is larger by a factor of \(550 \gtrsim Z^4 \delta_1(2, 2)/\delta_1(1, 0)\) compared to the result (3.63) for the “hydrogen atom” with \(I = 0\).

As one can expect there is the same possibility as in the \(q = 0\) case to obtain P-violating energy shifts of the order of \(\sqrt{\delta_1}\).

The calculation is the same as described in Section 3.1, (3.66)–(3.97), and Appendix D, (D.1)–(D.8) and (D.13) f., except that it now involves the states (3.100) and the additional piece (3.101) to \(H_{\text{eff}}\). The secular matrix may be block-diagonalized in the same way as in (3.80)–(3.84) because (3.101) is diagonal in the internal quantum numbers \((\gamma, m)\).

We have chosen the crossing of the levels \(\bar{\alpha} = (2S_{1/2}, n = (1, 1, 1)), \ \bar{\beta} = (2P_{1/2}, n = (2, 1, 1)), \ (3.66), \ (3.67),\) which occurs at:

\[
\mathcal{E}_{\text{res}} = Z^5 \cdot 30.11 \text{ kV/cm}
\] 

(3.109)

for \(A_1 = 0.76 \text{ nm}, A_2 = A_3 = 1 \text{ nm}\).
For the case of a $^4\text{He}^+$ ion in a box described by (3.61), (3.109), (3.110), we choose again perturbing fields as in (3.97). We show in Appendix D that for $E' = 96 \text{ V/cm}$.

\begin{equation}
E' = 96 \text{ V/cm}.
\end{equation}

the resonance values for $\eta^{(\sigma)}$ to first order in $E'$ are

\begin{align}
\eta^{(1)}_{\text{res},-} &= \begin{pmatrix} 1 \\ 0 \\ -47.37 \end{pmatrix}, \\
\eta^{(2)}_{\text{res},-} &= \begin{pmatrix} 0 \\ 0 \\ 356.97 \end{pmatrix}, \\
\eta^{(3)}_{\text{res},-} &= \begin{pmatrix} 0 \\ 1 \\ -49.73 \end{pmatrix}.
\end{align}

(3.112)

Here again the analogues of (3.92) and (3.93) are satisfied.

In Fig. 10a and b we plot the decadic logarithms of the moduli of the real and twice the imaginary parts of the P-violating energy shift

\begin{equation}
E_{\alpha \bar{\beta},+} (\{E'^{(\sigma)}\}) - E_{\alpha \bar{\beta},+} (\{E_{\text{r}}^{(\sigma)}\})
\end{equation}

for $^4\text{He}^+$ in a field configuration given by (3.109) and (3.112) f. vs. the deviation $\eta_{3}^{(2)} - \eta_{3,\text{res},-}^{(2)}$ from the resonance value $\eta_{3,\text{res},-}^{(2)} = 356.97$ for which the P-even splitting of levels is removed, revealing an enhancement of the P-violating splitting of the order of $1/\sqrt{\delta_1}$. The width of the peak is proportional to $\sqrt{\delta_1}$ and found to be $\Delta \eta_{3}^{(2)} = 10^{-3}$ ($E' \Delta \eta_{3}^{(2)} = 9.6 \cdot 10^{-2} \text{ V/cm}$). In Fig. 10a the differences of the real parts of the energies of the levels are now at maximum of the order of 1 Hz. The lifetime of the levels is calculated to be $0.19 \cdot 10^{-9} \text{ s}$, which corresponds to a line width $\Delta E/h = 8.60 \cdot 10^{8} \text{ Hz}$. As before it will not be easy to detect frequency shifts of order 1 Hz in such broad lines. Also this calculation is only meant to show that energy shifts proportional to $\sqrt{\delta_1}$ can in principle be obtained also for ions and it illustrates how $q \neq 0$ affects the numerical solutions.

### 3.3 Results for a neutral atom with $I = 1/2$

Let us now turn to the case of a neutral atom with $I = 1/2$, i.e. $^1\text{H}$. As discussed in Appendix A, the eigenstates of $H_{\text{eff},0}(E_3) (3.14)$ are twofold degenerate in $F_3 = \pm |F_3|$ for fixed $l, j, F$, if $F_3 \neq 0$:

\begin{equation}
E^{(0)}(\alpha, F_3, E_3, n) = E^{(0)}(\alpha, -F_3, E_3, n),
\end{equation}

(3.114)

where $\alpha = (2, l, j, F)$, but there is no degeneracy between the levels of different $F$, but equal $|F_3|$. Hence, for the calculation of perturbative corrections to levels with $|F_3| \neq 0$, the same method involving degenerate perturbation theory applies as it is described for the $I = 0$ case in Section 3.1. As far as the $|F_3| = 0$ levels are concerned, simple non-degenerate perturbation theory will be sufficient.

Let us concentrate first on the question, if the $F_3$ degeneracy of the $|F_3| \neq 0$ states is in general broken by the perturbation fields $E'^{(\sigma)}$. Our results of Chapter 2.1.1 indicate that this will be the case.
Consider the degenerate energy levels characterized by \( \bar{\alpha} = (\alpha, |F_3|, \mathcal{E}_3, n), |F_3| \neq 0 \). The corresponding right eigenstates of \( H_{\text{eff},0} \) (equation 3.4 with \( q = 0 \)),

\[
|\bar{\alpha}, \pm \rangle := |\alpha, \pm |F_3|, \mathcal{E}_3, n\rangle,
\]

span a two-dimensional space \( \mathcal{R}_{\bar{\alpha}}^{(0)} \). Now we turn to \( H_{\text{eff},1} \) (equation 3.5 with \( q = 0 \)) and use the same notation for the perturbation theory treatment as in (3.12)–(3.21).

From T-invariance we obtain again the relation (3.25). However, now \( F \) and \( |F_3| \) are integers and we get

\[
(\tilde{\bar{\alpha}}, + |\tilde{\bar{K}}_\alpha |\tilde{\bar{\alpha}}, +) = (\tilde{\bar{\alpha}}, - |\tilde{\bar{K}}_\alpha |\tilde{\bar{\alpha}}, -),
\]

and self-identities for the off-diagonal elements, which therefore need not to be zero. The analogous relations apply to the matrix elements of \( \tilde{H}_\alpha \).

For both, the general analysis and for actual calculations we use our modified Bloch method defining \( \tilde{H}_\alpha \) in analogy to (3.78) (cf. Appendix C). Then, in order to solve the eigenvalue problem analogous to (3.79), one has to solve the secular equation

\[
\det (\tilde{H}_\alpha - E_\alpha) = 0,
\]

where

\[
\tilde{H}_\alpha = \left( (\tilde{\bar{\alpha}}, m' |\tilde{H}_\alpha |\tilde{\bar{\alpha}}, m) \right) \equiv (\tilde{H}_{\bar{\alpha},m'm}).
\]

From T-invariance we find, similarly to (3.116):

\[
\tilde{H}_{\bar{\alpha},++} = \tilde{H}_{\bar{\alpha},--}.
\]

The solutions of (3.117) are:

\[
E_{\bar{\alpha},\pm} = \tilde{H}_{\bar{\alpha},++} \pm \left[ \tilde{H}_{\bar{\alpha},+-} - \tilde{H}_{\bar{\alpha},-+} \right]^{1/2}.
\]

Thus, in general the twofold degeneracy of the levels of \( H_{\text{eff},0} \) for \( |F_3| \neq 0 \) is broken by the perturbation.

Let us now consider the perturbation expansion of \( \tilde{H}_\alpha \) according to (C.8) of Appendix C

\[
\tilde{H}_\alpha = E_{\alpha}^{(0)} \mathbb{1}_{\alpha}^{(0)} + \sum_{n=1}^{\infty} \tilde{C}^{(n)}.
\]

For the diagonal elements \( \tilde{H}_{\bar{\alpha},mm} \) the same arguments apply which are given in Section 5.1 ((3.42)–(3.56)) for the trace of \( \tilde{H}_\alpha \). In this way we see that there will be no \( \delta_{1,2}\)-linear contributions to \( \tilde{H}_{\bar{\alpha},mm} \) below the third order.

As far as the off-diagonal elements \( \tilde{H}_{\bar{\alpha},m'm}, m' \neq m \) are concerned, they are non-zero only above the first order. Indeed, for the first order term in (3.121) we have:

\[
(\tilde{\bar{\alpha}}, m' |\tilde{C}^{(1)} |\tilde{\bar{\alpha}}, m) = (\tilde{\bar{\alpha}}, m' |H_{\text{eff},1} |\tilde{\bar{\alpha}}, m).
\]

For \( m' \neq m \) this matrix element vanishes due to the same argument which led to (3.46) and the fact that the difference \( \Delta F_3 \) in \( F_3 \) between the degenerate unperturbed states
(3.114) satisfies $|\Delta F_3| = |m - m'||F_3| \geq 2$ and that the dipole operator (3.42) cannot change $F_3$ by more than one unit.

We consider now in detail the following configuration of perturbing fields:

$$\mathcal{E}^{(\sigma)} := \eta^{(\sigma)} \cdot \mathcal{E}', \quad (\sigma = 1, 2, 3),$$

(3.123)

where the dimensionless vectors $\eta^{(\sigma)}$ are left arbitrary for the moment. For the expansion of $\tilde{H}_{\tilde{\alpha},m'm}$ we have then from (3.121):

$$\tilde{H}_{\tilde{\alpha},m'm} = E^{(0)}_{\tilde{\alpha}} \delta_{m'm} + \sum_{n=1}^{\infty} (\tilde{\alpha}, m'| \tilde{C}^{(n)} | \tilde{\alpha}, m),$$

(3.124)

with

$$(\tilde{\alpha}, m'| \tilde{C}^{(n)} | \tilde{\alpha}, m) = \left(c^{(n,0)}_{\tilde{\alpha},m'm} + \sum_{i=1}^{2} \delta_i c^{(n,i)}_{\tilde{\alpha},m'm} \right) \mathcal{E}^m + \mathcal{O}(\delta^2_{1,2})$$

$$m', m \in \{+1, -1\}, n \geq 1.$$  

(3.125)

From the discussion above we find

$$c^{(n,i)}_{\tilde{\alpha},m'm} = 0 \quad \text{for} \quad n \leq 2; \quad i = 1, 2, \quad \text{if} \quad m' = m;$$

$$c^{(1,i)}_{\tilde{\alpha},m'm} = 0 \quad \text{for} \quad i = 0, 1, 2, \quad \text{if} \quad m' \neq m.$$  

(3.126)

Using these relations we can easily convince ourselves that a consistent evaluation of $E_{\tilde{\alpha},\pm} (3.120)$ up to order $\mathcal{E}'^2$ requires only the knowledge of the coefficients $c^{(n,i)}_{\tilde{\alpha},m'm}$ for $n \leq 2$. We get then:

$$E_{\tilde{\alpha},\pm} = E^{(0)}_{\tilde{\alpha}} + \sum_{n=1}^{2} c^{(n,0)}_{\tilde{\alpha},++} \mathcal{E}^m$$

$$\pm \left(\left[c^{(2,0)}_{\tilde{\alpha},+-} + \sum_{i=1}^{2} \delta_i c^{(2,i)}_{\tilde{\alpha},+-} \right] \left[c^{(2,0)}_{\tilde{\alpha},-+} + \sum_{i=1}^{2} \delta_i c^{(2,i)}_{\tilde{\alpha},-+} \right] \right)^{1/2} \mathcal{E}'^2 + \mathcal{O}(\mathcal{E}'^3).$$  

(3.127)

In the general case where all coefficients $c^{(n,i)}_{\tilde{\alpha},m'm}$ appearing in (3.127) differ from zero, one therefore gets for the level shifts:

$$E_{\tilde{\alpha},\pm} = E^{(0)}_{\tilde{\alpha}} + E^{(1,0)}_{\tilde{\alpha}} + E^{(2,0)}_{\tilde{\alpha}}$$

$$\pm \frac{1}{2} \left(\Delta E^{(2,0)}_{\tilde{\alpha}} + \sum_{i=1}^{2} \delta_i \Delta E^{(2,i)}_{\tilde{\alpha}} + \mathcal{O}(\delta^2_{1,2}) \right) + \mathcal{O}(\mathcal{E}'^3).$$  

(3.128)

In $E^{(n,i)}_{\tilde{\alpha}}, \Delta E^{(n,i)}_{\tilde{\alpha}}$ $n$ denotes the order in $\mathcal{E}'$, $i = 0$ the order zero in $\delta_{1,2}$ and $i = 1, 2$ the order one in $\delta_1, \delta_2$ respectively. We see that here linear terms in $\delta_{1,2}$ occur already at order $\mathcal{E}'^2$.

To give some numbers we choose an electric field configuration (3.123) with

$$\eta_{3}^{(\sigma)} = 0; \quad \text{for} \quad \sigma = 1, 3 \quad \text{and} \quad \eta^{(2)} = 0.$$  

(3.129)
Then the first order level shift vanishes, $E^{(1,0)}_\alpha = 0$ and we have

$$E_{\alpha,\pm} = E^{(0)}_\alpha + \sum_{\sigma,\tau} \left\{ \tilde{c}_{\alpha,1}^{\sigma\tau} (\eta_1^{(\sigma)} \eta_1^{(\tau)} + \eta_2^{(\sigma)} \eta_2^{(\tau)}) \right\}$$

$$+ \left[ \sum_{\rho,\kappa} \left( \tilde{c}_{\alpha,2}^{\sigma\tau\rho\kappa} (\eta_1^{(\sigma)} \eta_1^{(\tau)} - \eta_2^{(\sigma)} \eta_2^{(\tau)}) (\eta_1^{(\rho)} \eta_1^{(\kappa)} - \eta_2^{(\rho)} \eta_2^{(\kappa)}) ight. \right.$$

$$+ \left. \left. \left( \tilde{c}_{\alpha,3}^{\sigma\tau\rho\kappa} (\eta_1^{(\sigma)} \eta_2^{(\tau)} + \eta_2^{(\sigma)} \eta_1^{(\tau)}) (\eta_1^{(\rho)} \eta_2^{(\kappa)} + \eta_2^{(\rho)} \eta_1^{(\kappa)}) \right) \right\} \right]^{1/2} \mathcal{E}^2$$

$$+ \mathcal{O}(\mathcal{E}^3), \quad (3.130)$$

where the $\tilde{c}_{\alpha,i}, \tilde{c}_{\alpha,i}$ are complex numbers which depend on $\mathcal{E}$. The sums over $\sigma, \tau, \rho, \kappa$ run over the segment numbers 1,3. In order to compute the P-violating energy shift for the levels $\alpha = (\alpha, |F_3| = 1, n = (1, 1, 1))$ for $\alpha = n|j|F \in \{2S_{1/2}1, 2P_{1/2}1, 2P_{3/2}1, 2P_{3/2}2\}$, we take the values for $L, \Delta, \Gamma_s, \Gamma_p$ and the hyperfine splittings $\bar{A}_1, \bar{A}_2, \bar{A}_3$ from Table III of [15] and chose the following configuration:\footnote{In this paper we use the notation $A_i, i = 1, 2, 3$ for the cartesian lengths of the box, which are not to be confused with the hfs-splittings which we denote here by $\bar{A}_i, i = 1, 2, 3$.}

$$A_1 = A_2 = A_3 = 8 \text{ nm}, \quad (3.131)$$

$$R_1^{(1)}/A_1 = 0.45, \quad R_1^{(2)}/A_1 = 0.55. \quad (3.132)$$

As one can see from (3.131), the $\delta_{1,2}$-linear contributions vanish if $\eta_1^{(\sigma)} = 0$ or $\eta_2^{(\sigma)} = 0; \sigma = 1, 3$; or if $\eta_1^{(\sigma)} = \eta_2^{(4-\sigma)} = 0, \sigma = 1, 3$ and $\eta_2^{(\sigma)} = \pm \eta_1^{(4-\sigma)}$. We choose

$$\eta^{(1)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \eta^{(2)} = 0, \quad \eta^{(3)} = \begin{pmatrix} 0 \\ 0.5 \\ 0 \end{pmatrix} \quad (3.133)$$

in order to maximize the P-violating effect. In Table I we give numbers for the P-conserving as well as the P-violating contributions to $E_{\alpha,\pm}$ for different levels $\alpha$ at different electric fields $\mathcal{E}$. From the analogue of (3.64), we found the maximally allowed perturbation field strengths and used these to compute the results in Table I.

We establish thus theoretically a P-violating energy shift of the order of

$$\Re \left( E(\mathcal{E}, \{\mathcal{E}^{(\sigma)}\}) - E(\mathcal{E}, \{\mathcal{E}^{(\sigma)}_R\}) \right)/h = \left( 1.2 \delta_1 - 20.2 \delta_2 + \mathcal{O}(|\mathcal{E}'/\mathcal{E}|^3) \right) \text{ kHz}$$

$$= -2.56 \cdot 10^{-8} \text{ Hz},$$

$$2\Im \left( E(\mathcal{E}, \{\mathcal{E}^{(\sigma)}\}) - E(\mathcal{E}, \{\mathcal{E}^{(\sigma)}_R\}) \right)/h = \left( -1.1 \delta_1 + 16.3 \delta_2 + \mathcal{O}(|\mathcal{E}'/\mathcal{E}|^3) \right) \text{ 10}^4 \text{ s}^{-1}$$

$$= 2.08 \cdot 10^{-7} \text{ s}^{-1} \quad (3.134)$$

for $\alpha = 2S_{1/2}1$ where the numerical values for $\delta_{1,2}$ are taken from Table III of [15]. We observe that the nuclear spin dependent term $\propto \delta_2$ of the energy shift is enhanced by a factor of $\sim 17 \text{ w.r.t.} \text{ the spin independent one. As was already noted in [15],}$
an enhancement of the terms proportional to $\delta_2$ over the ones proportional to $\delta_1$ is expected to be a general feature of P-violating effects for $^1H$ (cf. (6.39), (6.40) of [13]). Numerically an energy shift (3.134) is, of course, very small and presumably not easily measured.

Let us now consider the possibility of P-violating energy shifts of the order of $\sqrt{\delta_{1,2}}$. From (3.120) we can easily see how this can be achieved. Let us expand $\tilde{H}_{\alpha,m'}$ in $\delta_{1,2}$:

$$\tilde{H}_{\alpha,m'} = \tilde{H}_{\alpha,m'}^{(0)} + \delta_1 \tilde{H}_{\alpha,m'}^{(1)} + \delta_2 \tilde{H}_{\alpha,m'}^{(2)} + O(\delta_1^2, \delta_1 \delta_2, \delta_2^2).$$

(3.135)

For unstable states as we are considering here $\tilde{H}_{\alpha}$ is a non-hermitian matrix and we can have

$$\tilde{H}_{\alpha,+\pm}^{(0)} = 0,$$

(3.136)

$$\tilde{H}_{\alpha,+\pm}^{(1)} \neq 0, \quad i = 1, 2,$$

(3.137)

$$\tilde{H}_{\alpha,-++}^{(0)} \neq 0.$$  

(3.138)

In this situation the level shifts (3.120) read:

$$\tilde{E}_{\alpha,\pm} = \tilde{H}_{\alpha,+\pm}^{(0)}$$

$$\pm \left[ \left( \delta_1 \tilde{H}_{\alpha,+\pm}^{(1)} + \delta_2 \tilde{H}_{\alpha,+\pm}^{(2)} \right) \tilde{H}_{\alpha,-++}^{(0)} \right]^{1/2} + O(\delta_1^2, \delta_1 \delta_2).$$

(3.139)

Without P-violation, i.e. for $\delta_1 = \delta_2 = 0$, the levels would be degenerate.

Note that we need not to have a crossing of the energies and lifetimes of the unperturbed states in order to achieve a degeneracy of levels for nonzero handedness of the external fields. As the degeneracy of the $\pm |F_3|$ levels gets broken by electric field perturbations anyway, it suffices to suppress this breaking by a convenient choice of $\eta^{(\sigma)}$, $\sigma = 1, 2, 3$ at any field $\mathcal{E}$. Hence, we can choose a convenient zero order field strength of e.g. $\mathcal{E} = 200$ V/cm.

(3.140)

The condition (3.136) reads now (cf. (3.124)–(3.126)):

$$\tilde{H}_{\alpha,+\pm}^{(0)} = \sum_{n=2}^{\infty} c_{\alpha,+\pm}^{(n,0)} \mathcal{E}^n$$

$$= c_{\alpha,+\pm}^{(2,0)} \mathcal{E}^2 + c_{\alpha,+\pm}^{(3,0)} \mathcal{E}^3 + ...$$

$$= 0.$$  

(3.141)

To order $\mathcal{E}^2$ we can easily solve this equation. We found a solution to

$$c_{\alpha,+\pm}^{(2,0)} = 0$$

(3.142)

to be

$$\eta^{(1)} = \begin{pmatrix} 3.91 \\ 0.0764 \\ 0 \end{pmatrix}, \quad \eta^{(2)} = 0, \quad \eta^{(3)} = \begin{pmatrix} 3.91 \\ -0.328 \\ 0 \end{pmatrix},$$

(3.143)
where we chose the box geometry as in (3.131), (3.132). Note that to order $\mathcal{E}'^2$ the magic condition (3.142) does not depend on $\mathcal{E}'$ and we get P-violating energy shifts proportional to $\sqrt{\delta_{1,2}}$ for all $\mathcal{E}'$. However, the requirement of applicability of perturbation theory (cf. (3.64)) gives here as maximally allowed value

$$\mathcal{E}'_{\text{max}} = 8.3 \text{ V/cm.} \quad (3.144)$$

The reason for this relatively small number is that the r.h.s. of (3.64) is now of the order of the hfs splitting, which, at $\mathcal{E} = 200 \text{ V/cm}$, is by two orders of magnitude smaller than the differences between levels for nuclear spin $I = 0$. Thus, choosing for instance $\mathcal{E}' = 5 \text{ V/cm} < \mathcal{E}'_{\text{max}}$ we are safely in the region where we can apply perturbation theory.

Using now the implicit function theorem in a way analogous to (D.7) ff. of Appendix D we establish that a solution to (3.141) exists to all orders in $\mathcal{E}'$ for sufficiently small $\mathcal{E}'$. In other words: For such small enough field strength $\mathcal{E}'$ higher order terms in the perturbation expansion (3.144) will only displace the “resonance” position slightly but cannot change the qualitative features. Thus we establish theoretically the existence of P-violating energy shifts proportional to $\sqrt{\delta_{1,2}}$.

The signal to look for in an experiment is the difference of the eigenenergies $E_{\bar{\alpha},\pm} (3.139)$ for the perturbation fields $\mathcal{E}'^{(\alpha)}$ and the reflected ones $\mathcal{E}'_{\text{R}}^{(\alpha)}$,

$$\mathcal{E}'_{\text{R}}^{(\alpha)} = \eta^{(\alpha)} \cdot \mathcal{E}', \quad (3.145)$$

where $\eta^{(\alpha)}$ are the same vectors as in (3.143) but with the opposite sign of the 2-components.

In Figs. 11 a, b we plot the real and imaginary parts of these energy differences

$$E_{\bar{\alpha},\pm} (\{\mathcal{E}'^{(\alpha)}\}) - E_{\bar{\alpha},\pm} (\{\mathcal{E}'_{\text{R}}^{(\alpha)}\}) \quad (3.146)$$

for $\mathcal{E}' = 5 \text{ V/cm}$ versus the deviation of $\mathcal{E}'^{(3)}$ from the resonance value $\mathcal{E}'_{2,\text{res}} = -1.64 \text{ V/cm}$. Numbers for other values of $\mathcal{E}'$ are easily obtained from Figs. 11 a, b, since (in our approximation) these energy differences are proportional to $\mathcal{E}'^2$. The width of the peak is proportional to $\sqrt{\delta_i}$ and found to be $2.6 \cdot 10^{-12} \text{ V/cm}$. The differences of the real parts of the energies shown in Figs. 11a, b are at maximum of the order of $10^{-5} \text{ Hz}$ whereas the lifetime of the levels is found to be $4.13 \cdot 10^{-8} \text{ s}$. This corresponds to a line width $\Delta \mathcal{E}/h = 3.86 \cdot 10^6 \text{ Hz}$. Again we note that detecting frequency shifts of order $10^{-5} \text{ Hz}$ in such broad lines is certainly not easy. However, our example shows, how energy shifts proportional to $\sqrt{\delta_{1,2}}$ can be obtained for atoms with $I = 1/2$. In Figs. 11 a, b we observe the rise of the signal by a factor $\sim 1/\sqrt{\delta_2} \sim 10^6$ at the resonance value. We are sure that for a realistic experimental situation one can optimize such effects. But it remains to be seen what values of $\Delta \mathcal{E}$ one can then obtain.
4 Conclusions

In this article we have investigated parity violation in hydrogen-like atoms due to Z-boson exchange between the lepton and the quarks in the nucleus. In particular we have considered the consequences of this P-violating neutral current interaction for the eigenenergies of the atoms which are moving in inhomogeneous external electric and magnetic fields in finite regions of space.

In this first part we have discussed the general formalism to treat a non-relativistic atom in an external field arrangement. We derived the consequences of T-invariance for the eigenenergies of the atoms. In general these eigenenergies arise from an interplay of the internal and the c.m. motion of the atom. We have shown that for an atom confined to a finite region of space where we have a homogeneous electric field the eigenenergies get no P-violating contribution. Then we studied configurations of an external electric field within a rectangular box, where the field is homogeneous throughout different segments of the box and shows sudden variations at the interfaces of these segments. In part II we will study configurations where the field varies adiabatically along a certain direction in space.

We studied hydrogen like atoms in states of principal quantum number \( n = 2 \) in detail. First we considered boxes with two segments only, where the two electric field vectors together with the vector which is normal to the interface form a chirally non-symmetric configuration which could in principle be sufficient to exhibit P-violating effects. However, we showed, that for this geometry there are no P-violating energy shifts due to the T-symmetry at least in our scheme of approximations. Thus we found that a box with a minimum of three segments is needed if the electric field varies along one direction of the rectangular box only.

We studied then explicitly hydrogen-like atoms with vanishing nuclear spin \( I = 0 \) like \( ^{4}\text{He}^+ \) and with nuclear spin \( I = 1/2 \) like \( ^{1}\text{H} \) in a box with three segments using the methods of Rayleigh Schrödinger perturbation theory. We indeed found P-violating contributions to the eigenenergies of the systems for field configurations carrying nonzero chirality. This opens the possibility of determining the parameters of the neutral current P-violation in atoms by frequency measurements.

We found energy shifts linear in the P-violation parameters \( \delta_i \) \((i = 1, 2)\), where \( \delta_i \approx 10^{-12} \) are the mixing amplitudes between \( S \) and \( P \) levels due to the nuclear spin independent and dependent P-violating contributions to the Hamiltonian divided by the Lamb shift determining the order of magnitude of P-odd effects. Such energy shifts were found to be of the order of \( 10^{-5} \ldots 10^{-9} \) Hz for boxes of \( \sim 5\text{-}10\) nm size. To measure these extremely small effects would require an accuracy which only in the context of the hydrogen 21 cm-line-measurements, cf. [7], has been reached so far.

There is some similarity of the energy shifts linear in the P-violation parameters for the systems we considered with the P-violating energy difference between the two enantiomers of chiral molecules. Such energy differences are studied theoretically e.g. in [34, 35]. But we emphasize that our physical systems are very different from chiral...
molecules and also the physics of our P-odd energy shifts is quite different from that in chiral molecules. In chiral molecules the P-odd energy difference occurs with no external field due to a P-violating distortion of the electronic wave functions in the chiral arrangement of the nuclei. The c.m. motion of the molecule is irrelevant for this. In our case we consider simple atomic systems where questions of “spontaneous” occurrence of handed molecules, maybe due to a spontaneous symmetry breaking \[36\] do not occur. We get P-odd energy shifts only in the presence of external fields. The interplay of the c.m. and internal motions of the atom is crucial. Since we have only one nucleus and one electron around it our energy shifts certainly do not occur due to the movement of the electron in a chiral lattice of nuclei. As will be seen even more clearly in part II of this work our energy shifts arise in essence through P-violating rotations of the atom as a whole in the external field (cf. also \[15\]). Through the boundary conditions for stationary states such rotations lead to P-odd energy shifts. However, we can make a somewhat loose connection between P-odd energy shifts in chiral molecules and our results in the following way. We start from our situation of an atom in a box with a chiral electric field and — in a “Gedankenexperiment” — imagine to make the box smaller and smaller until it has atomic dimensions, and the field stronger, of the order of atomic fields. Then it will no longer make sense to talk of the motion of an atom in an external field. Instead we have an electron and a nucleus interacting and moving in a common external field. If, in addition, we fix the position of the nucleus we arrive at a situation similar to the single centre approximation, which is used in calculations of the P-odd energy shifts in chiral molecules \[34\]. There one considers single orbitals of electrons being exposed to the potential of one of the nuclei (single centre) and in addition to a chiral external electric field which summarizes the effects of the other nuclei. Again we see that chiral molecules and the situations we considered represent very different limiting cases in the above “Gedankenexperiment”.

We found that there are possibilities to enhance the P-odd effects in the energy levels dramatically, by many orders of magnitude. At a crossing of two levels of unstable states, i.e. complex energy levels in an electric field with nonzero handedness the P-violating energy shifts can become proportional to \(\sqrt{\delta_{1,2}}\), \(i = 1, 2\). The comparison of these levels with the levels for the field configuration of opposite handedness shows a drastic difference: Under a reversal of the handedness the P-violating shift gets multiplied by a phase factor \(i\). This means, that the shifts in the real and imaginary parts of the complex eigenenergies are exchanged. We emphasize that such energy shifts \(\propto \sqrt{\delta_{1,2}}\) only appear for unstable states.

Numerically we found the following results. For the case of a “hydrogen” atom with nuclear spin \(I = 0\) we obtained P-violating energy shifts proportional to \(\sqrt{\delta_1}\) of \(\Delta E/h \simeq 10^{-2}\) Hz. For \(\text{^4He}^+\) we found the same kind of shifts with \(\Delta E/h \simeq 1\) Hz. Considering the real atom \(^{1}\text{H}\) with nuclear spin \(I = 1/2\), we found energy shifts proportional to \(\sqrt{\delta_{1,2}}\) of the order of \(\Delta E/h \simeq 10^{-5}\) Hz. These shifts are considerably smaller than the results of the calculation neglecting the nuclear spin of \(^{1}\text{H}\) because the narrow hfs-splitting restricted the reliability of our perturbative calculation to smaller electric field strengths. An improved calculation should overcome these restrictions.
and could lead to much larger effects. In any case, our results show, that at the (would be) crossing points of the (P-conserving) complex energy levels, there remains a P-violating splitting and the change of this energy difference with the reversal of the field’s handedness is enhanced greatly compared to the shifts away from the crossings.

Finally we note that for the case of hydrogen discussed here all our energy shifts are much more sensitive to the parameter $\delta_2$ than to $\delta_1$ (cf. (1.10)–(1.12)). The reason for this is the same as given in Sects. 6.1 and 6.2 of [15]. Thus a measurement of our effects could lead to a determination of the nuclear spin-dependent weak charge $Q^{(2)}_W$ (1.11) which depends on the contribution of s-quarks to the proton spin. In this way parity violation in atoms could give information concerning the “spin crisis” of the nucleons.

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Appendix

A Representations of n=2 matrices and states

In this appendix we discuss the non-hermitian mass matrix $M$ (1.39) and the dipole operator $D$ as well as the matrix representations of the T and R transformations for atoms with nuclei of $I = 0$ and 1/2 transforming like the $\alpha$-particle and the nucleon, respectively. In addition we present the T- and R-transformation properties for the eigenvectors of the mass matrix. Here T is the time reversal operation and R denotes the reflection on the 1–3-plane. R can be considered as a product of a parity operation followed by a rotation by $\pi$ around the 2-axis:

$$R : x_1 \rightarrow -x_2, x_2 \rightarrow -x_1, x_3 \rightarrow x_3,$$

$$R = e^{i\pi F_2} \cdot P.$$  \hfill (A.1)

All our conventions for the states etc. are as in [15]. The matrices representing T and R are denoted by $T$ and $R$, respectively (cf. (3.33) and (3.58) of [15].)

The T- and R-transformation properties of $M$, of the quasiprojectors $P_I$ and the eigenvalues $E$ (cf. Sect. 1.2; we drop the index INT for internal here) are given in Sects. 3.3, 3.4, and Appendix B of [15]. We have from T

$$E(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2) = E(\alpha, -F_3, \mathcal{E} e_3, \delta_1, \delta_2),$$  \hfill (A.2)

$$(T^\dagger P(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2) T)^T = P(\alpha, -F_3, \mathcal{E} e_3, \delta_1, \delta_2)$$  \hfill (A.3)

and from R:

$$E(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2) = E(\alpha, -F_3, \mathcal{E} e_3, -\delta_1, -\delta_2),$$  \hfill (A.4)

$$(R^\dagger P(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2) R)^T = P(\alpha, -F_3, \mathcal{E} e_3, -\delta_1, -\delta_2).$$  \hfill (A.5)

Since $T = -R$ for $I = 0$ and $T = R$ for $I = 1/2$, we get from (A.2) to (A.5), combining the T- and R-transformations:

$$E(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2) = E(\alpha, F_3, \mathcal{E} e_3, -\delta_1, -\delta_2),$$  \hfill (A.6)

$$(P(\alpha, F_3, \mathcal{E} e_3, \delta_1, \delta_2))^T = P(\alpha, F_3, \mathcal{E} e_3, -\delta_1, -\delta_2).$$  \hfill (A.7)

From the above relations for the quasiprojectors we turn now to the T- and R-transformation properties for the right and left eigenvectors of $M$. Consider first the case of vanishing electric field, $\mathcal{E} = 0$. The corresponding eigenstates of $M_0$ are given up to order $\delta_{1,2}$ in App. B, Tables B.IV and B.VIII of [15]. For their T-transformation we have

$$\left(T^\dagger 2\hat{l}, j, F, F_3, 0\mathcal{E} e_3, \delta_1, \delta_2\right)^T = (-1)^{F+F_3+l}(2\hat{l}, j, F, -F_3, 0\mathcal{E} e_3, \delta_1, \delta_2),$$

$$\left(2\hat{l}, j, F, F_3, 0\mathcal{E} e_3, \delta_1, \delta_2\right)^T T = (-1)^{F+F_3+l}(2\hat{l}, j, F, -F_3, 0\mathcal{E} e_3, \delta_1, \delta_2).$$  \hfill (A.8)
Here \( l = 0, 1, 2, \ldots \) or in spectroscopic notation \( S, P, \ldots \) denotes the orbital angular momentum quantum number and the hat indicates the perturbation by the P-violating Hamiltonian. Similarly we find for their R transformation

\[
\mathcal{R}|2\hat{l}, j, F, F_3, 0\mathbf{e}_3, \delta_1, \delta_2 \rangle = (-1)^{F + F_3 + l}|2\hat{l}, j, F, -F_3, 0\mathbf{e}_3, -\delta_1, -\delta_2 \rangle,
\]

\[
(2\hat{l}, j, F, F_3, 0\mathbf{e}_3, \delta_1, \delta_2)|\mathcal{R}^\dagger = (-1)^{F + F_3 + l}(2\hat{l}, j, F, -F_3, 0\mathbf{e}_3, -\delta_1, -\delta_2| \quad (A.9)
\]

By an argument similar to the one given below one can see that with a suitable normalization of the states eqs. (A.8) and (A.9) are valid not only up to order \( \delta_{1,2} \) but to all orders in \( \delta_{1,2} \).

We will now define the eigenstates of \( \mathcal{M} \) for \( \mathcal{E} \neq 0 \) using the methods explained in App. C of [15]. We set

\[
|\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2 \rangle = \mathcal{P}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) \mathcal{N}^{-1/2}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2),
\]

\[
(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) = (\alpha, F_3, 0\mathbf{e}_3, \delta_1, \delta_2) \mathcal{P}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) \mathcal{N}^{-1/2}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2),
\]

\[
(A.10)
\]

where

\[
\mathcal{N}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) = \text{Tr} \left[ \mathcal{P}(\alpha, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) \mathcal{P}(\alpha, F_3, 0\mathbf{e}_3, \delta_1, \delta_2) \right] \quad (A.11)
\]

and \( \alpha \) stands for \( (2\hat{l}, j, F) \). For \( \mathcal{E} \neq 0 \) these quantum numbers are not conserved and therefore indicate here the values for the corresponding state at \( \mathcal{E} = 0 \). From (A.3) and (A.8) we now obtain immediately:

\[
\mathcal{N}(2\hat{l}, j, F, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) = \mathcal{N}(2\hat{l}, j, F, -F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2),
\]

\[
\left( (2\hat{l}, j, F, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) \right)^T = (-1)^{F + F_3 + l}(2\hat{l}, j, F, -F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2),
\]

\[
(A.12)
\]

Similarly we get from (A.5) and (A.9):

\[
\mathcal{N}(2\hat{l}, j, F, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) = \mathcal{N}(2\hat{l}, j, F, -F_3, \mathcal{E}\mathbf{e}_3, -\delta_1, -\delta_2),
\]

\[
\mathcal{R}|2\hat{l}, j, F, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2 \rangle = (-1)^{F + F_3 + l}|2\hat{l}, j, F, -F_3, \mathcal{E}\mathbf{e}_3, -\delta_1, -\delta_2 \rangle,
\]

\[
(2\hat{l}, j, F, F_3, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2)|\mathcal{R}^\dagger = (-1)^{F + F_3 + l}(2\hat{l}, j, F, -F_3, \mathcal{E}\mathbf{e}_3, -\delta_1, -\delta_2| \quad (A.13)
\]

Up to now we have worked with the basis states (1.41) which are simultaneous eigenstates of \( \mathcal{M} \) (1.39) and \( F_3 \). Alternatively, we may use the basis set of (left and right) eigenstates of \( \mathcal{M} \), which, for \( |F_3| \neq 0 \), are defined as follows:

\[
|\alpha, |F_3|, \pm, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2 \rangle := \frac{1}{\sqrt{2}} \left[ |\alpha, |F_3|, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2 \rangle \pm (-1)^{1/2-I} \mathcal{R}|\alpha, |F_3|, \mathcal{E}\mathbf{e}_3, -\delta_1, -\delta_2 \rangle \right],
\]

\[
(\alpha, |F_3|, \pm, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2) := \frac{1}{\sqrt{2}} \left[ (\alpha, |F_3|, \mathcal{E}\mathbf{e}_3, \delta_1, \delta_2 \rangle \pm (-1)^{1/2-I}(\alpha, |F_3|, \mathcal{E}\mathbf{e}_3, -\delta_1, -\delta_2| \mathcal{R} \right],
\]

\[
(A.14)
\]
For $F_3 = 0$ which occurs only for $I = 1/2$ we label the states as defined in (1.10) with $+(-)$ if $F + l$ is even (odd). In (1.14) $R$ denotes the reflection (1.1) on the 1–3-plane. For $\delta_1 = \delta_2 = 0$ the states (1.14) are simultaneous eigenstates of $\mathcal{M}$ (1.39) and $\mathcal{R}$.

As one can easily check, the definition of the relative phases between the two linearly combined $F_3$-eigenstates as well as the normalizations are chosen in such a way that the orthonormality relations

\[
(\alpha, |F_3\rangle, r, e_{3}, \delta_1, \delta_2 | \beta, |F_3\rangle, r', e_{3}, \delta_1, \delta_2) = \delta_{\alpha\beta}\delta|F_3\rangle|F_3\rangle\delta_{rr'},
\]

(A.15)

with \(r, r' \in \{+, -\}\), are fulfilled. The transformation under $T$, $R$, $R \circ T$ of the states for the case $I = 0$ is given by

\[
T : \quad \left(\mathcal{T}|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1\right)^T = \mp i (\alpha, |F_3\rangle, \mp, e_{3}, \delta_1),
\]

(A.16)

\[
R : \quad \mathcal{R}^\dagger|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1\rangle = \pm i (\alpha, |F_3\rangle, \mp, e_{3}, -\delta_1),
\]

(A.17)

\[
R \circ T : \quad \left(|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1\right)^T = \pm i (\alpha, |F_3\rangle, \mp, e_{3}, -\delta_1),
\]

(A.18)

and for the case $I = 1/2$ by

\[
T : \quad \left(\mathcal{T}|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1, \delta_2\right)^T = \pm (\alpha, |F_3\rangle, \pm, e_{3}, \delta_1, \delta_2),
\]

(A.19)

\[
R : \quad \mathcal{R}^\dagger|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1, \delta_2\rangle = \pm (\alpha, |F_3\rangle, \mp, e_{3}, -\delta_1, -\delta_2),
\]

(A.20)

\[
R \circ T : \quad \left(|\alpha, |F_3\rangle, \pm, e_{3}, \delta_1, \delta_2\right)^T = \pm (\alpha, |F_3\rangle, \mp, e_{3}, -\delta_1, -\delta_2),
\]

(A.21)

We note that for given $\alpha = (2\hat{l}, j, F)$ and $|F_3\rangle \neq 0$ the corresponding $+$ and $-$ states are linearly independent and eigenstates of $\mathcal{M}$ to the same complex energy eigenvalue. For $\alpha = (2\hat{l}, j, F)$ and $F_3 = 0$ we have only the $+(-)$ state for $l + F$ even (odd) as explained above, and there is no energy degeneracy.

**B  The continuity matrix $M_c$**

In this appendix we give details of the calculation which leads to the results of Section 2.1. We consider first, as in Sect. 2.1.1, a neutral atom with an $I = 0$ nucleus.

Let us have a closer look at the eigenstates $|\sigma, \beta\rangle$ of the internal motion (cf. (2.13)).

In Sect. 1.2 we have recalled the properties of the right and left eigenvectors of the mass matrix (1.39) for an external electric field in 3-direction. Let us now consider
For the eigenvectors defined by (2.13) we can then set
\[
|\sigma', \beta, \delta_1, \delta_2\rangle := |\alpha, F_3, \mathcal{E}^{(\sigma)} e_3; \delta_1, \delta_2\rangle,
\]
where \( \beta \) is a shorthand notation for \( (\alpha, F_3) \), and we indicate explicitly the dependence on \( \delta_{1,2} \). The corresponding left eigenvectors are
\[
((\sigma'), \tilde{\beta}, \delta_1, \delta_2).
\]
By a proper rotation \( R_0 \) we can bring the pair of vectors \( \mathcal{E}^{(1)} \) and \( \mathcal{E}^{(2)} \) into the 1-3-plane. By further suitable rotations around the 2-axis by angles \( \theta^{(1)} \) or \( \theta^{(2)} \) we can make either \( \mathcal{E}^{(1)} \) or \( \mathcal{E}^{(2)} \) to point along the positive 3-axis. With \( F_i \) \( (i = 1, 2, 3) \) the generators of rotations around the coordinate axes this is formally expressed as follows:
\[
\exp[i\theta^{(1)}F_2] \cdot R_0 : \mathcal{E}^{(1)} \to |\mathcal{E}^{(1)} e_3, \\
\exp[i\theta^{(2)}F_2] \cdot R_0 : \mathcal{E}^{(2)} \to |\mathcal{E}^{(2)} e_3.
\]
For the eigenvectors defined by (2.13) we can then set
\[
|\sigma, \beta, \delta_1, \delta_2\rangle = \mathcal{D}(R_0^{-1}) \cdot \exp[-i\theta^{(\sigma)}E_2] |\sigma', \beta, \delta_1, \delta_2\rangle, \quad (\sigma = 1, 2),
\]
and correspondingly
\[
((\sigma), \tilde{\beta}, \delta_1, \delta_2) = ((\sigma'), \tilde{\beta}, \delta_1, \delta_2) \cdot \exp[i\theta^{(\sigma)}E_2] \cdot \mathcal{D}(R_0), \quad (\sigma = 1, 2).
\]
Here \( \mathcal{D} \) are the representation matrices of the rotation group in the space of the \( n = 2 \) atomic states. From (B.3), (B.4) we can write the matrices (2.15) as:
\[
U^{\sigma,\tau}_{\gamma,\beta}(\delta_1, \delta_2) = ((\sigma'), \tilde{\gamma}, \delta_1, \delta_2) \exp[i(\theta^{(\sigma)} - \theta^{(\tau)}) E_2] |(\sigma'), \beta, \delta_1, \delta_2\rangle,
\]
\( (1 \leq \sigma, \tau \leq 2) \).
Thus we have expressed \( U^{\sigma,\tau}_{\gamma,\beta} \) by the eigenstates (B.1) for electric fields pointing in 3-direction and the relative angle \( \theta^{(\sigma)} - \theta^{(\tau)} \) between the fields \( \mathcal{E}^{(\sigma)} \) and \( \mathcal{E}^{(\tau)} \).

We will now show that (2.27) is equivalent to an equation having no linear terms in \( \delta_1 \) (2.28). In order to achieve this we choose the states defined in (A.14) of Appendix A as a basis. In the notation \( |n\hat{l}, F, |F_3, r, \mathcal{E} e_3, \delta_1\rangle \equiv |n\hat{l}_{F}, |F_3, r, \mathcal{E} e_3, \delta_1\rangle, \quad (r = \pm), \) for \( I = 0, j = F \), as explained in (A.10) ff. of Appendix A, we write the basis of right eigenvectors as:
\[
|2\hat{S}_{1/2}, 1 \frac{1}{2}, r, |\mathcal{E}^{(\sigma)} e_3, \delta_1\rangle,
|2\hat{P}_{1/2}, 1 \frac{1}{2}, r, |\mathcal{E}^{(\sigma)} e_3, \delta_1\rangle,
|2\hat{P}_{3/2}, 1 \frac{1}{2}, r, |\mathcal{E}^{(\sigma)} e_3, \delta_1\rangle,
|2\hat{P}_{3/2}, 2 \frac{1}{2}, r, |\mathcal{E}^{(\sigma)} e_3, \delta_1\rangle,
\]
\( (r = \pm, \sigma = 1, 2) \) (B.6)
and the analogous set for the left eigenvectors. We now write \(|(\sigma, \alpha, r, \delta_1)\), \(\alpha = 1, 2, 3, 4\), as shorthand for the states (B.6) and define the following \(4 \times 4\) matrices (cf. (B.5)):

\[
\begin{align*}
(U^{(\sigma, \tau)_{\pm \pm}}(\delta_1))_{\alpha \beta} & := (\sigma', \alpha, \pm, \delta_1 | e^{i(\sigma-\tau)E_1} | (\tau'), \beta, \pm, \delta_1), \\
(U^{(\sigma, \tau)_{\pm \mp}}(\delta_1))_{\alpha \beta} & := (\sigma', \alpha, \pm, \delta_1 | e^{i(\sigma-\tau)E_1} | (\tau'), \beta, \mp, \delta_1),
\end{align*}
\]

where \(\sigma, \tau \in \{1, 2\}\) and

\[
\theta = \theta^{(2)} - \theta^{(1)}
\]

is the relative angle between the fields \(E^{(2)}\) and \(E^{(1)}\). From the transformation properties of \(F_2\) and of the states (B.6) under \(R\) (cf. (A.18)) we find

\[
U^{(\sigma, \tau)}_{r s}(\delta_1) = r \cdot s \cdot U^{(\sigma, \tau)}_{r s}(\delta_1)
\]

and from the \(R \circ T\) transformation (A.18) we get

\[
[U^{(\sigma, \tau)}_{(r, \sigma)}(\delta_1)]^T = U^{(\tau, \sigma)}_{(r, \sigma)}(-\delta_1).
\]

Therefore, as a consequence of the \(T\)-transformation, the \(U\)-matrices obey

\[
[U^{(\sigma, \tau)}_{(r, \sigma)}(\delta_1)]^T = r \cdot s \cdot U^{(\sigma, \tau)}_{(r, \sigma)}(-\delta_1).
\]

From (B.10) we see that \(U^{(\sigma, \tau)}_{\pm \pm}\) in (B.7) is even, \(U^{(\sigma, \tau)}_{\pm \mp}\) in (B.8) is odd under \(\delta_1 \rightarrow -\delta_1\).

Let us furthermore define \(4 \times 4\) matrices \(S^{(\sigma)}\), \(C^{(\sigma)}\) as in (2.23). Note that the values \(Q^{(\sigma)}_{\beta}\) defined in (2.17) are the same for the + and − states. Putting everything together we find for \(M_c(E, \delta_1)\), in the basis of the ± states and with a suitable arrangement of rows and columns:

\[
M_c(E, \delta_1) = M'_c(E, \delta_1) \cdot M''_c(E, \delta_1),
\]

where

\[
M'_c = \begin{pmatrix}
U^{(2,1)_{++}} & Tg^{(2)} & U^{(2,1)_{+-}} & 0 \\
0 & U^{(1,2)_{++}} & 0 & U^{(1,2)_{+-}} \\
0 & 0 & U^{(1,2)_{+-}} & 0 \\
0 & 0 & 0 & U^{(1,2)_{--}}
\end{pmatrix},
\]

\[
Tg^{(2)} = S^{(2)} \cdot C^{(2)-1},
\]

\[
C^{(1)} = C^{(1)} \cdot S^{(1)-1},
\]

\[
M''_c(E, \delta_1) = \begin{pmatrix}
S^{(1)} & 0 & 0 & 0 \\
0 & -C^{(2)} & 0 & 0 \\
0 & 0 & S^{(1)} & 0 \\
0 & 0 & 0 & -C^{(2)}
\end{pmatrix}.
\]

From (B.13) we get

\[
\det M_c(E, \delta_1) = \det M'_c(E, \delta_1) \cdot \det M''_c(E, \delta_1).
\]
For general fields \( \mathcal{E}^{(1)}, \mathcal{E}^{(2)} \) we have \( \det M'' \neq 0 \) and therefore \( \det M_c(E, \delta_1) = 0 \) implies \( \det M'_c(E, \delta_1) = 0 \) and vice versa. Now we know that in \( M'_c(B.14) \) the submatrices \( U^{(r,s)} \pm \delta \) are independent of, and the \( U^{(r,s)} \pm \delta \) are linear in \( \delta_1 \), neglecting terms of order \( \delta_1^2 \). Thus we have

\[
\det M'_c(E, \delta_1) = \det \begin{pmatrix} A & \delta_1 D \\ \delta_1 C & B \end{pmatrix} = \det(CAC^{-1}B - \delta_1^2 CD), \quad \text{(B.18)}
\]

where \( A, \ldots, D \) are square matrices depending on \( E \) but not on \( \delta_1 \). Therefore we can write the equation determining \( E \) as in (2.28).

Now we will discuss the properties of the matrix \( M'_c(B.14) \) and give the proofs of (2.29)–(2.31).

After rearranging rows and columns of \( M'_c \) and multiplying some columns with \((-1)\), we find

\[
\det M'_c(E, \delta_1) = \det M'_c \text{ asym}(E, \delta_1), \quad \text{(B.19)}
\]

\[
M'_c \text{ asym} := \begin{pmatrix}
0 & -U^{(2,1)+} & L^{(2,1)+} & Tg^{(2)} \\
-U^{(1,2)-} & 0 & C_l^{(1)} & U^{(1,2)+} \\
-U^{(1,2)-} & -C_l^{(1)} & 0 & U^{(1,2)+} \\
-Tg^{(2)} & -U^{(2,1)+} & U^{(2,1)+} & 0 \\
\end{pmatrix}. \quad \text{(B.20)}
\]

Using now the \( T \) relations (B.11) and the definitions (2.23), (B.15) of the matrices \( Tg^{(r)}, C_l^{(r)} \), it follows immediately that the above matrix is antisymmetric. Note that \( M'_c \text{ asym} \) is a 16\( \times \)16-matrix.

A basic theorem of linear algebra — that the determinant of an antisymmetric matrix \( M \) with an even number of rows is a square — may be applied now. In order to prove this theorem, one writes the matrix \( M = -M'\), assuming \( M \neq 0 \) (after possibly necessary rearrangements of rows and columns) as

\[
M = \begin{pmatrix} A & B \\ -B^T & C \end{pmatrix}, \quad \text{with} \quad A := \begin{pmatrix} 0 & a \\ -a & 0 \end{pmatrix}, \quad a \neq 0, \quad \text{(B.21)}
\]

being a 2\( \times \)2 matrix and \( C = -C^T \) antisymmetric. Then, with

\[
\det M = \det \left\{ \begin{pmatrix} 1 & 0 & 0 & 1 \\ B^T & A^{-1} & 0 & 0 \\ \end{pmatrix} M \begin{pmatrix} 1 & -A^{-1}B \\ 0 & 1 \end{pmatrix} \right\} = \det \begin{pmatrix} A & 0 \\ 0 & C + B^T A^{-1} B \end{pmatrix}, \quad \text{(B.22)}
\]

it follows that \( \det M = a^2 \det M' \), with \( M' = C + B^T A^{-1} B \) being antisymmetric. The theorem now follows by mathematical induction over the number of rows of \( M \).

Applying this theorem to \( M'_c \text{ asym} \text{(B.20)} \) and using (B.28) we find:

\[
\det M_c(E, \delta_1) = \det M'_c \text{ asym}(E, \delta_1) = [g(E, \delta_1)]^2 = f_0(E) + \delta_1^2 f_2(E) + O(\delta_1^4), \quad \text{(B.23)}
\]

\[
g(E, \delta_1) = g_0(E) + \delta_1^2 g_2(E) + O(\delta_1^4). \quad \text{(B.24)}
\]
From (B.23) we see that the energy eigenvalues $E$ are at least twofold degenerate for all fields $\mathcal{E}^{(1)}, \mathcal{E}^{(2)}$ up to order $\delta_1$ (Terms of higher order in $\delta_1$ have been neglected in previous stages of the calculations). We know that for $\mathcal{E}^{(1)} = \mathcal{E}^{(2)}$ there is at most a twofold degeneracy, thus, apart from possible special values of $\mathcal{E}^{(1)}, \mathcal{E}^{(2)}$ the degeneracy will not be bigger than twofold. It follows that for generic values of $\mathcal{E}^{(1)}, \mathcal{E}^{(2)}$ $g_0(E)$ will have only non-degenerate zeroes. The energy eigenvalues are now obtained from
\begin{equation}
 g(E, \delta_1) = 0 \tag{B.25}
\end{equation}
and using the implicit function theorem we find from (B.24) that the solutions $E = E(\delta_1)$ of (B.25) have no terms linear in $\delta_1$:
\begin{equation}
 \frac{\partial E(\delta_1)}{\partial \delta_1} \bigg|_{\delta_1=0} = 0. \tag{B.26}
\end{equation}
This completes the proof of the assertions made in Sect. 2.1.1 for the case of nuclear spin $I = 0$.

Finally we have to deal with the case $I = 1/2$ and to prove that (2.33) is equivalent to (2.34) (cf. Sect. 2.1.2). Using the $\pm$ eigenstates as defined in (A.14) and the subsequent text of Appendix A we introduce matrices $U^{(\sigma, r)s}(\delta_1, \delta_2)$ ($r, s \in \{+, -\}$), as in (B.7), (B.8), for which the transformation properties under $R$, $R \circ T$ and $T$ analogous to (B.10)–(B.12) now read:
\begin{align*}
 R : & \quad U^{(\sigma, r)s}(\delta_1, \delta_2) = r \cdot s \cdot U^{(\sigma, r)s}(-\delta_1, -\delta_2), \tag{B.27} \\
 R \circ T : & \quad [U^{(\sigma, r)s}(\delta_1, \delta_2)]^T = U^{(r, \sigma)s r}(-\delta_1, -\delta_2), \tag{B.28} \\
 T : & \quad [U^{(\sigma, r)s}(\delta_1, \delta_2)]^T = r \cdot s \cdot U^{(r, \sigma)s r}(\delta_1, \delta_2). \tag{B.29}
\end{align*}
From (B.27) we see again that $U^{(\sigma, r)s}$ is symmetric (antisymmetric) under $(\delta_1, \delta_2) \to (-\delta_1, -\delta_2)$ for $r = s$ ($r \neq s$). The matrix $M_c$ factorizes as follows:
\begin{equation}
 M_c(E, \delta_1, \delta_2) = M'_c(E, \delta_1, \delta_2) \cdot M''_c(E, \delta_1, \delta_2), \tag{B.30}
\end{equation}
with
\begin{align*}
 M'_c &= \begin{pmatrix}
 U^{(1,2)++} & Tg^{(2)+} & U^{(1,2)+-} & 0 \\
 0 & U^{(1,2)+-} & 0 & Tg^{(2)-} \\
 0 & 0 & U^{(1,2)+-} & 0 \\
 0 & 0 & 0 & U^{(1,2)+-}
\end{pmatrix}, \tag{B.31} \\
 M''_c &= \begin{pmatrix}
 S^{(1)+} & 0 & 0 & 0 \\
 0 & -C^{(2)+} & 0 & 0 \\
 0 & 0 & S^{(1)+} & 0 \\
 0 & 0 & 0 & -C^{(2)+}
\end{pmatrix}, \tag{B.32}
\end{align*}
\begin{align*}
 Tg^{(2)r} &= S^{(2)r}(C^{(2)r})^{-1}, \\
 Ct^{(1)r} &= C^{(1)r}(S^{(1)r})^{-1},
\end{align*}
\begin{equation}
 r \in \{+, -\}. \tag{B.33}
\end{equation}
Here $S^{(2)r}, C^{(1)r}$ are the diagonal matrices as defined in (2.23) for the $r = +, -$ states. Now the important difference to the $I = 0$ case is that for $I = 1/2$ the $r = +$ and $r = -$ sectors are not simply related since the $F_3 = 0$ states with $r = \pm$ are not energy degenerate (cf. Appendix A). Thus the corresponding values $Q_\beta$ in (2.23) are different and also $S^{(2)+} \neq S^{(2)-}, C^{(1)+} \neq C^{(1)-}$.

We can draw the following conclusions for the eigenenergies $E$ obtained from

$$\det M'_c(E, \delta_1, \delta_2) = 0. \quad (B.34)$$

For $\delta_1 = \delta_2 = 0$ the matrix $M'_c$ is block-diagonal since

$$U^{(2,1)\pm\mp}(0, 0) = U^{(1,2)\pm\mp}(0, 0) = 0. \quad (B.35)$$

But for general fields $\mathcal{E}^{(1)}, \mathcal{E}^{(2)}$ this does not lead to an energy degeneracy, since the $++$ and $-$ blocks of $M'_c$ have different determinants due to the non-degeneracy of the $F_3 = 0$ plus and minus states. For $\delta_1, \delta_2$ unequal zero, we see from (B.31) that we can apply the same arguments as in (B.18) and (2.28) in order to obtain (2.34).

### C  A modified version of Bloch’s method for degenerate perturbation theory

In order to calculate eigenvalues and eigenvectors of a time independent operator $\hat{O}$ in a perturbative approach, where $\hat{O}$ is a sum

$$\hat{O} = \hat{O}_0 + \lambda \hat{O}_1 \quad (C.1)$$

of an operator $\hat{O}_0$, whose eigenvalues and (orthonormalized, complete set of) eigenvectors are known, and a perturbation $\lambda \hat{O}_1$ with a small parameter $\lambda$, one uses time independent perturbation theory to calculate perturbative corrections to these eigenvalues and eigenvectors. If (some of) the unperturbed eigenvectors of $\hat{O}_0$ have the same eigenvalues, which e.g. is the case in most of our problems, one has to use degenerate perturbation theory (cf. e.g. [30]). For this case of degeneracies, several methods have been given to write down the explicit perturbative expansion of the eigenvalues of $\hat{O}$. In Chap. 3 we have used both Kato’s (cf. (3.17)–(3.21)) and Bloch’s (cf. (3.27)–(3.31)) method. The advantage of Bloch’s method is that by modifying $\hat{H}$ (cf. (3.27)) one obtains an eigenvalue problem (3.31), where the sought eigenvalue $E$ is multiplied only by a unit operator. This eventually yields simpler expressions (compare (3.28) ff. with (3.17) ff.). However, if $\hat{H}$ and $\hat{K}$ are hermitian $\hat{H}$ in general is not because of the asymmetric multiplication with $\hat{K}$ in (3.27):

$$\hat{H} \hat{K} = \hat{H}. \quad (C.2)$$

---

3 Since the discussion here is general we drop the indeces $\bar{\alpha}$ or $(\bar{\alpha}\bar{\beta})$ on the operators $\hat{H}, \hat{K}$, as well as on the eigenvalues $E$, which in the main text are used to indicate the subspace of unperturbed states in which the diagonalization takes place.
In order to obtain both, an eigenvalue problem of the form (3.31) and hermiticity, we introduce a modified version of Bloch’s method (cf. (3.78) f.), which we describe in more detail in this appendix.

The method is similar to the well-known treatment of small oscillations in classical mechanics, where the equations of motion, after a Fourier transformation, lead to the eigenvalue problem

\[
(V - \omega_k^2 T) \cdot a_k = 0.
\]

Here \( V = (V_{ij}) \) and \( T = (T_{ij}) \) are the second order coefficients of the expansion of the potential and the kinetic energy about the minimum of the potential w.r.t. small displacements of the generalized coordinates. The elements of the eigenvectors \( a_k \) give the Fourier coefficients of the transformed solutions of the equations of motion with eigenfrequencies \( \omega_k \) (cf. e.g. [31]).

If \( T \) is hermitian and positive, it possesses a hermitian and positive inverse \( T^{-1} \) and square root \( T^{1/2} \) with \( (T^{1/2})^2 = T \). Then (C.3) is equivalent to

\[
(T^{-1/2}VT^{-1/2} - \omega_k^2) \cdot a'_k = 0,
\]

with \( a'_k = T^{1/2}a_k \). Therefore it suffices to find a set of eigenvectors \( a'_k \) of \( \tilde{U} = T^{-1/2}VT^{-1/2} - \omega_k^2 \).

We extend this method to our case of the (in general) non-hermitian matrices \( \hat{H} \) and \( \hat{K} \) (the analogues of \( V \) and \( T \) respectively) and define a matrix \( \tilde{H} \) by

\[
\hat{K}^{1/2}\tilde{H}\hat{K}^{1/2} = \hat{H},
\]

\[
\tilde{H} \mathbb{P}^{(0)} = \tilde{H},
\]

\[
\mathbb{P}^{(0)}\tilde{H} = \tilde{H}.
\]

Our eigenvalue problem (3.21) which is similar to (C.3) is then equivalent to (3.79):

\[
(\tilde{H} - E)|\rangle = 0,
\]

where \(|\rangle\in \mathcal{R}^{(0)}\).

From the expansions of \( \hat{K} \) and \( \hat{H} \), (3.17) ff., we find the expansion of \( \hat{K}^{-1/2} \), the inverse of \( \hat{K}^{1/2} \) in the space \( \mathcal{R}^{(0)} \). This inverse exists for sufficiently small \( \mathcal{E}' \), since \( \hat{K} \) is then arbitrarily close to \( \mathbb{P}^{(0)} \) which acts as the unit matrix over \( \mathcal{R}^{(0)} \) (cf. (3.17)). Up to fourth order in \( \mathcal{E}' \) we get:

\[
\hat{K}^{-1/2} = \mathbb{P}^{(0)} + \frac{1}{2}(0, 2, 0)
\]

\[
+ \frac{1}{2} [(0, 1, 2, 0) + (0, 2, 1, 0) + (0, 3, 0, 0) + (0, 0, 3, 0)]
\]

\[
+ \frac{1}{2} \sum_{(4)} (0, k_1, k_2, k_3, 0) - \frac{3}{8}(0, 2, 0, 2, 0)
\]

\[
+ O(\mathcal{E}'^5).
\]

From (3.17) f. and (C.7) we calculate the expansion of \( \tilde{H} \) as

\[
\tilde{H} = \hat{K}^{-1/2}\tilde{H}\hat{K}^{-1/2}
\]

\[
= E^{(0)} \mathbb{P}^{(0)} + \hat{K}^{-1/2} \left( \sum_{n=1}^{\infty} B^{(n)} \right) \hat{K}^{-1/2}
\]

\[
= E^{(0)} \mathbb{P}^{(0)} + \sum_{n=1}^{\infty} \tilde{C}^{(n)},
\]

(3.8)
with the terms of order \( n = 1, 2, 3, 4 \):
\[
\begin{align*}
\tilde{C}^{(1)} &= (0, 0), \\
\tilde{C}^{(2)} &= (0, 1, 0), \\
\tilde{C}^{(3)} &= (0, 1, 1, 0) + \frac{1}{2} \left[(0, 2, 0, 0) + (0, 0, 2, 0)\right], \\
\tilde{C}^{(4)} &= (0, 1, 1, 1, 0) + \frac{1}{2} \left[(0, 0, 1, 2, 0) + (0, 1, 2, 0, 0) + (0, 2, 0, 1, 0) + (0, 0, 2, 1, 0) + (0, 1, 0, 2, 0) + (0, 0, 0, 3, 0) + (0, 3, 0, 0, 0)\right].
\end{align*}
\] (C.9)

Finally we will discuss the T-invariance properties of Kato’s eigenvalue problem and show that the matrices \( \tilde{H}_{\alpha\alpha}, \tilde{H}_{\beta\beta} \) and \( \tilde{H}_{\alpha\beta}\tilde{H}_{\beta\alpha} \) obtained by our modified version of Bloch’s method (cf. (3.80), (3.83) and Section 3.1) are all multiples of the 2×2 unit matrix.

Let us consider first Kato’s operator \( \hat{K} \). The matrix elements of \( \hat{K}_{(\tilde{\alpha}\tilde{\beta})} \) read:
\[
(\hat{K}_{(\tilde{\alpha}\tilde{\beta})})_{(\gamma', m'), (\tilde{\gamma}, m)} = (\tilde{\gamma}', m' | \hat{K}_{(\tilde{\alpha}\tilde{\beta})} | \tilde{\gamma}, m),
\] (C.10)
where \( \tilde{\gamma}', \tilde{\gamma} \in \{\tilde{\alpha}, \tilde{\beta}\}; m', m \in \{+1, -1\} \). For the diagonal block matrices with \( \tilde{\gamma}' = \tilde{\gamma} \), the same T-invariance arguments as in (3.23)–(3.25) apply, which yield that they are multiples of the unit matrices in \( \mathcal{R}_{(\alpha)}^{(0)}, \mathcal{R}_{(\beta)}^{(0)} \), cf. (3.26). As far as the off-diagonal matrices \( \tilde{\gamma}' \neq \tilde{\gamma} \) are concerned, it follows from (C.12) that
\[
(\tilde{\gamma}', m' | \hat{K}_{(\tilde{\alpha}\tilde{\beta})} | \tilde{\gamma}, m) = (-1)^{F' + F' + F + (m' + m)|F_3|}(\tilde{\gamma}, -m | \hat{K}_{(\tilde{\alpha}\tilde{\beta})} | \tilde{\gamma}', -m').
\] (C.11)

Analogous relations apply for the matrix elements of \( \hat{H}_{(\tilde{\alpha}\tilde{\beta})} \).

We can now explicitly check that e.g. \( \tilde{H}_{\alpha\beta}\tilde{H}_{\beta\alpha} \) is a multiple of the 2×2 unit matrix. From (C.11) and the analogous relation for \( \hat{H}_{(\tilde{\alpha}\tilde{\beta})} \), together with (3.78), we get:
\[
(\tilde{\alpha}, m | \tilde{H}_{\alpha\beta}\tilde{H}_{\beta\alpha} | \tilde{\alpha}, m'') = \sum_{m' = \pm 1} (\tilde{\alpha}, m | \tilde{H}_{(\tilde{\alpha}\tilde{\beta})} | \tilde{\beta}, m') (\tilde{\beta}, m' | \tilde{H}_{(\tilde{\alpha}\tilde{\beta})} | \tilde{\alpha}, m'')
\times (-1)^{2(F' + F'' + m'|F_3| + (m' + m'')|F_3|)}
\]
(C.12)
Since \( 2(F' + m'|F_3|) \) is even, it follows that \( 2F + (m + m'')|F_3| \) is even/odd for \( m'' = m / m'' = -m \), respectively. Because we sum over \( m' \) in (C.12) this completes the proof. To show that \( \tilde{H}_{\alpha\beta}\tilde{H}_{\beta\alpha} - E \) is also a multiple of the unit matrix, we still have to use the analogue of (3.23) for \( \tilde{H}_{\beta\beta} \).

### D General proof of the existence of \( \sqrt{\delta_1} \)-resonances

In this appendix we give a proof that for sufficiently small \( \mathcal{E}' \) there exist “resonance” values for the vectors \( \eta^{(\omega)} \) where energy shifts proportional to \( \sqrt{\delta_1} \) occur (cf. (3.95)–(3.97)).
Let us again first consider the case of a “hydrogen” atom with nuclear spin $I = 0$. We expand $a$ and $b$ \( B.88 \) in powers of $\mathcal{E}'$ up to second order and $c$, which has the dimension of $a^2, b^2$, up to third order, where $\delta_1$-linear contributions of lowest order in $\mathcal{E}'$ show up. This gives

\[
\begin{align*}
    a &= a_0^{(0)} + a_0^{(1)} \mathcal{E}' + a_0^{(2)} \mathcal{E}'^2 + O(\mathcal{E}'^3), \\
    b &= b_0^{(0)} + b_0^{(1)} \mathcal{E}' + b_0^{(2)} \mathcal{E}'^2 + O(\mathcal{E}'^3), \\
    c &= c_0^{(0)} + c_0^{(1)} \mathcal{E}' + c_0^{(2)} \mathcal{E}'^2 + (c_0^{(3)} + \delta_1 c_1^{(3)}) \mathcal{E}'^3 + O(\mathcal{E}'^4). 
\end{align*}
\]

All coefficients $a_i^{(n)}, b_i^{(n)}, c_i^{(n)}, i = 0, 1; n = 0, 1, 2, \ldots$, depend still on the $\eta^{(s)}$ and of course on the unperturbed configuration parameters \( (3.61), (3.68), (3.69) \), but not on $\mathcal{E}'$. From the definition \( (3.78) \) of $\tilde{H}(\alpha\beta)$ together with \( (3.76) \) and \( (3.77) \) it follows, that (cf. \( B.85 \))

\[
\begin{align*}
    a_0^{(0)} &= E_\alpha^{(0)}, \\
    b_0^{(0)} &= E_\beta^{(0)}, \\
    c_0^{(0)} &= c_0^{(1)} = 0. 
\end{align*}
\]

The series for $c$ in \( D.1 \) implies

\[
\sqrt{c} = \sqrt{c_0^{(2)} \mathcal{E}'} + \frac{c_0^{(3)} + \delta_1 c_1^{(3)}}{2\sqrt{c_0^{(2)}}} \mathcal{E}'^2 + O(\mathcal{E}'^3). \tag{D.3}
\]

As one can see, the third order term of $c$ is needed in order to obtain a consistent expansion of $\pm i(a - b) + 2\sqrt{c}$ up to second order in $\mathcal{E}'$. Since we $E_\alpha^{(0)} = E_\beta^{(0)}$ \( (3.66), (3.67) \), the lowest order contribution to the radicand in \( B.87 \) will be $\propto \mathcal{E}'^2$. Therefore we can write the l.h.s. of \( B.91 \), \( B.92 \) as follows:

\[
\pm i(a_0 - b_0) + 2\sqrt{c_0} =: \mathcal{E}' \cdot F_\pm(\{\eta^{(s)}\}, \mathcal{E}') = \left[ \pm i(a_0^{(1)} - b_0^{(1)}) + 2\sqrt{c_0^{(2)}} + O(\mathcal{E}') \right] \mathcal{E}'. \tag{D.4}
\]

Suppose now a set of perturbation fields \( B.97 \) can be found satisfying \( B.91 \) or \( B.92 \) at order $\mathcal{E}'$, i.e.

\[
\begin{align*}
    F_+(\{\eta^{(s)}\}, \mathcal{E}' = 0) &= 0 \quad \text{for} \quad \eta^{(s)} = \eta^{(s)}_{\text{res},+}, \tag{D.5} \\
    F_-(\{\eta^{(s)}\}, \mathcal{E}' = 0) &= 0 \quad \text{for} \quad \eta^{(s)} = \eta^{(s)}_{\text{res},-}, \tag{D.6}
\end{align*}
\]

where also \( B.93 \) holds. Considering e.g. \( D.5 \) we can then apply the implicit function theorem in order to show that a solution to \( B.91 \), i.e.

\[
F_+(\{\eta^{(s)}\}, \mathcal{E}') = 0 \tag{D.7}
\]

for some values $\eta^{(s)} = \eta^{(s)}_{\text{res},+}$ exists to all orders in $\mathcal{E}'$ for sufficiently small $\mathcal{E}'$.

Now the condition that the implicit function theorem may be used is that (a) $F_+$ is a continuous function and that (b) the functional determinant

\[
\frac{\mathcal{D} F_+}{\mathcal{D}(\eta^{(s)}_i, \eta^{(s)}_j)} := \begin{vmatrix}
\frac{\partial F_+}{\partial \eta^{(s)}_i} & \frac{\partial F_+}{\partial \eta^{(s)}_j} \\
\frac{\partial F_+}{\partial \eta^{(s)}_j} & \frac{\partial F_+}{\partial \eta^{(s)}_j}
\end{vmatrix}_{\mathcal{E}'=0, \eta^{(s)}_i = \eta^{(s)}_{\text{res},+}, \eta^{(s)}_j = \eta^{(s)}_{\text{res},+}} \neq 0 \tag{D.8}
\]

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with respect to some pair of coefficients \( \eta^{(e)}_1 \neq \eta^{(e)}_2 \) does not vanish at the zero of \( F_+ (\mathcal{E}' = 0) \) which is determined by (D.3). Similar statements hold for \( F_- \). We emphasize that we can in this way give a general existence proof of P-violating energy shifts proportional to \( \sqrt{\delta_1} \) using only the lowest relevant orders of perturbation theory.

For the case of our “hydrogen” atom in an unperturbed configuration described by (3.61), (3.68), (3.69), the perturbation field configurations satisfy (D.14) with either:

\[
\eta^{(1)}_{\text{res}, \pm} = \begin{pmatrix} \eta_1^{(1)} \\ \eta_2^{(1)} \\ \pm 77.08 \tilde{\eta} \end{pmatrix}, \quad \eta^{(2)}_{\text{res}, \pm} = \begin{pmatrix} 0 \\ 0 \\ \mp 480.58 \tilde{\eta} \end{pmatrix}, \quad \eta^{(3)}_{\text{res}, \pm} = \begin{pmatrix} \eta_1^{(3)} \\ \eta_2^{(3)} \\ \pm 77.30 \tilde{\eta} \end{pmatrix}, \quad (D.9)
\]

where

\[
\tilde{\eta} := \sqrt{(\eta_1^{(1)} - \eta_3^{(3)})^2 + (\eta_2^{(2)} - \eta_3^{(3)})^2}.
\]

In general, there will be a continuous set of solutions of (D.5), (D.6). In order to simplify the calculation, we have chosen our solutions such that they also satisfy

\[
\mathcal{R}(a_0^{(3)} - b_0^{(2)}) = 0.
\]

The functional determinant (D.8) with respect to \( \eta_3^{(1)} - \eta_3^{(3)} \) and \( \eta_3^{(1)} + \eta_3^{(3)} \) evaluates to

\[
\frac{\mathcal{D} F_\pm}{\mathcal{D} (\eta_3^{(1)} - \eta_3^{(3)}, \eta_3^{(1)} + \eta_3^{(3)})} = \mp 2.63 \cdot 10^{-5} (\text{MHz h V}^{-1} \text{cm})^2.
\]

This completes the proof, that to any order in \( \mathcal{E}' \), there exist non-trivial solutions of (3.91) and (3.92). In general one expects, that for such a solution also (3.93) holds. We will now give explicit solutions of (3.91), (3.92) to second order in \( \mathcal{E}' \), which yield a P-violating energy shift proportional to \( \sqrt{\delta_1} \).

We expand the two P-even factors of the radicand in (3.87), i.e. \( \pm i(a_0 - b_0) + 2\sqrt{c_0} \) up to second order in \( \mathcal{E}' \) (cf. (D.1), (D.3)):

\[
\pm i(a_0 - b_0) + 2\sqrt{c_0} =: \mathcal{E}' \cdot \left[ F_\pm^{(0)}(\{\eta^{(e)}\}) + F_\pm^{(1)}(\{\eta^{(e)}\}) \mathcal{E}' + \mathcal{O}(\mathcal{E}'^2) \right]
= \left[ \pm i(a_0^{(1)} - b_0^{(1)}) + 2\sqrt{c_0^{(2)}} \right] \mathcal{E}'
+ \left[ \pm i(a_0^{(2)} - b_0^{(2)}) + c_0^{(3)}/\sqrt{c_0^{(2)}} \right] \mathcal{E}'^2
+ \mathcal{O}(\mathcal{E}'^3).
\]

Here \( F_\pm^{(0)}(\{\eta^{(e)}\}) \equiv F_\pm(\{\eta^{(e)}\}, \mathcal{E}' = 0) \) and \( F_\pm^{(1)}(\{\eta^{(e)}\}) \) are the zero and first order coefficients of the expansion of \( F_\pm (\mathcal{D.4}) \) in terms of \( \mathcal{E}' \). Now, for \( \mathcal{E}' \neq 0 \) and to second order in \( \mathcal{E}' \), (3.91) and (3.92) imply

\[
F_\pm^{(0)}(\{\eta^{(e)}\}) + F_\pm^{(1)}(\{\eta^{(e)}\}) \cdot \mathcal{E}' = 0.
\]

Again, for our “hydrogen” atom in an unperturbed configuration described by (3.61), (3.68), (3.69), the perturbation field configuration (3.62) satisfies (D.14) with either:

\[
\eta^{(1)}_{\text{res}, \pm} = \begin{pmatrix} 1 \\ 0 \\ 117.00 \end{pmatrix}, \quad \eta^{(2)}_{\text{res}, \pm} = \begin{pmatrix} 0 \\ 0 \\ -702.30 \end{pmatrix}, \quad \eta^{(3)}_{\text{res}, \pm} = \begin{pmatrix} 0 \\ 1 \\ 117.21 \end{pmatrix} \quad (D.15)
\]
for 
\[ E' = 0.3 \text{ V/cm} \quad \text{(D.16)} \]
or
\[
\begin{pmatrix}
1 \\
0 \\
-61.31
\end{pmatrix}, \quad \begin{pmatrix}
0 \\
0 \\
574.93
\end{pmatrix}, \quad \begin{pmatrix}
0 \\
1 \\
-63.31
\end{pmatrix},
\]
for
\[ E' = 3 \text{ V/cm}. \quad \text{(D.18)} \]

Note that the perturbation fields (D.16), (D.18) have been chosen in a way that they fulfill the condition \(|E'| < E'_{max}\), where \(E'_{max}\) is obtained by an argument as in (3.64) adapted for our case here. This gives an estimate of the maximum for which the perturbation series is reliable. \(E'_{max}\) is found to be
\[
E'_{max,+} = 9 \text{ V/cm}, \quad E'_{max,-} = 12 \text{ V/cm} \quad \text{(D.19)}
\]
for the “+”- and “−”-solutions (D.15) and (D.17) respectively. Within these limits, we looked for solutions which for simplicity we required to satisfy:
\[
\Re \left( a^{(1)}_0 - b^{(1)}_0 + E' \left( a^{(2)}_0 - b^{(2)}_0 \right) \right) = 0. \quad \text{(D.20)}
\]
This led to further restrictions on \(E'\), and the values given in (D.16), (D.18) represent approximately the maximal ones compatible with (D.20). Then for the “+”-solution (D.15) \(E'\) turned out to be an order of magnitude smaller than for the “−”-solution (D.17).

To finish we turn to the case of an ion with \(I = 0\). For the case of a \(^4\He^+\) ion in a box described by (3.61), (3.109), (3.110), the following perturbation field configurations satisfy (D.3), (D.6):

\[
\begin{align*}
\hat{\eta}_{res,±}^{(1)} &= \begin{pmatrix}
\hat{\eta}_1^{(1)} \\
\hat{\eta}_2^{(1)}
\end{pmatrix}, \\
&\quad \begin{pmatrix}
0.02 \hat{\eta}_1 \mp (62.02 \mp 0.11) \sqrt{\hat{\eta}_1^2 + \hat{\eta}_2^2}
\end{pmatrix}, \\
\hat{\eta}_{res,±}^{(2)} &= \begin{pmatrix}
0 \\
0
\end{pmatrix}, \\
&\quad \begin{pmatrix}
-0.06 \hat{\eta}_1 \pm 445.77 \sqrt{\hat{\eta}_1^2 + \hat{\eta}_2^2}
\end{pmatrix}, \\
\hat{\eta}_{res,±}^{(3)} &= \begin{pmatrix}
\hat{\eta}_1^{(3)} \\
\hat{\eta}_2^{(3)}
\end{pmatrix}, \\
&\quad \begin{pmatrix}
0.02 \hat{\eta}_1 \mp (62.02 \pm 0.11) \sqrt{\hat{\eta}_1^2 + \hat{\eta}_2^2}
\end{pmatrix}
\end{align*}
\]

where
\[
\hat{\eta}_1 := \eta_1^{(1)} - \eta_1^{(3)}, \\
\hat{\eta}_2 := \eta_2^{(1)} - \eta_2^{(3)}. \quad \text{(D.22)}
\]
In general, as for \( q = 0 \), there will be continuous sets of solutions of (D.5), (D.6). In order to simplify the calculation, we have again chosen our solutions such, that they also satisfy (D.11).

The functional determinants (D.8) with respect to \( \eta^{(1)}_3 - \eta^{(3)}_3 \) and \( \eta^{(1)}_3 + \eta^{(3)}_3 \) evaluate to

\[
\frac{\mathcal{D}F_\pm}{\mathcal{D}(\eta^{(1)}_3 - \eta^{(3)}_3, \eta^{(1)}_3 + \eta^{(3)}_3)} = \mp 4.70 \cdot 10^{-8} \left( \text{MHz} \cdot \text{h} \cdot \text{V}^{-1} \cdot \text{cm} \right)^2. \tag{D.23}
\]

This completes the proof for \( ^4\text{He}^+ \), that to any order in \( \mathcal{E}' \), there exist non-trivial solutions of (3.91), (3.92) (cf. the discussion concerning the implicit function theorem in 3.1). For such a solution one in general expects, that (3.93) holds as well. As in the previous section, we will now give explicit solutions of (3.91), (3.92) to second order in \( \mathcal{E}' \), which yield P-violating energy shifts proportional to \( \sqrt{\delta_1} \) (3.94). We proceed as in (D.13) f. The following perturbation field configurations satisfy (D.14):

\[
\eta^{(1)}_{\text{res,}+} = \begin{pmatrix} 1 \\ 0 \\ 94.45 \end{pmatrix}, \quad \eta^{(2)}_{\text{res,}+} = \begin{pmatrix} 0 \\ 0 \\ -653.30 \end{pmatrix}, \quad \eta^{(3)}_{\text{res,}+} = \begin{pmatrix} 0 \\ 1 \\ 94.62 \end{pmatrix} \tag{D.24}
\]

for \( \mathcal{E}' = 9.6 \text{ V/cm} \) \tag{D.25}

and

\[
\eta^{(1)}_{\text{res,}-} = \begin{pmatrix} 1 \\ 0 \\ -47.37 \end{pmatrix}, \quad \eta^{(2)}_{\text{res,}-} = \begin{pmatrix} 0 \\ 0 \\ 356.97 \end{pmatrix}, \quad \eta^{(3)}_{\text{res,}-} = \begin{pmatrix} 0 \\ 1 \\ -49.73 \end{pmatrix} \tag{D.26}
\]

for

\[
\mathcal{E}' = 96 \text{ V/cm}. \tag{D.27}
\]

As in the \( q = 0 \) case the perturbation fields (D.25), (D.27) satisfy the condition \( |\mathcal{E}'| < \mathcal{E}'_{\text{max}} \), where \( \mathcal{E}'_{\text{max}} \) is given by (3.64) and is an estimate of the maximum for which the perturbation series can be used. \( \mathcal{E}'_{\text{max}} \) is found to be

\[
\mathcal{E}'_{\text{max,}+} = 192 \text{ V/cm}, \quad \mathcal{E}'_{\text{max,}-} = 320 \text{ V/cm} \tag{D.28}
\]

for the “+”- and “−”-solutions (D.24) and (D.26) respectively. Within these limits, (D.25) and (D.27) are chosen such that solutions exist, which for simplicity we again chose to be restricted to those which satisfy (D.20).
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Table Captions

TABLE I. The P-conserving as well as the P-violating perturbative contributions to the eigenenergies $E_{\bar{\alpha}}, \pm$ (3.128) ff. up to 2nd order perturbation theory for different levels $\bar{\alpha} = (\alpha, |F_3|; n = (1, 1, 1))$ of $^1\text{H}$ at different electric fields $E$ for the corresponding maximally allowed perturbation field strengths $E'_{\text{max}}$.

Figure Captions

FIG. 1. Sketch of the electric field configuration in a box divided into three segments (1)–(3). The electric field is homogeneous within every segment and varies suddenly along the 1-direction.

FIG. 2 a,b. The energy levels $E^{(\alpha)} = E^{(\alpha)}(\alpha, |F_3|, \mathcal{E} e_3; n)$ (3.10) for a “hydrogen” atom with $I = 0$ in an external electric field $\mathcal{E} e_3$ and $n = (n_1, n_2, n_3)$. The real parts for $\alpha = 2S_{1/2}$ and $2P_{1/2}$ and $n_2 = n_3 = 1$ are shown in a, the decay widths (twice the negative of the imaginary parts in units of $s^{-1}$) for $\alpha = 2S_{1/2}$, $2P_{1/2}$ and $2P_{3/2}$ in b. In our calculation the imaginary parts are independent of $n$.

FIG. 3. The real and imaginary parts of the P-violating energy-difference $\Delta E^{(\alpha)}_\alpha : \mathcal{E}^3/(\eta \mathcal{E}^3 \delta_1 h)$ (cf. (3.63)) as a function of $\mathcal{E}$ for the state $\bar{\alpha} = (\alpha, |F_3|; n) = (2S_{1/2}, 1/2; (1, 1, 1))$ within a range of $\mathcal{E}$, where extrema due to a level crossing occur (cf. Fig. 2a).

FIG. 4. The field strength value $E'_{\text{max}}$ characterizing the limit of applicability of our perturbative treatment (cf. (3.64)) as a function of the field strength $\mathcal{E}$ for the same level $\bar{\alpha}$ as in Fig. 3.

FIG. 5 a,b. The P-violating energy shift $\Delta E^{(\alpha)}_\alpha$ (3.63) for $\mathcal{E}' = E'_{\text{max}}$. The real part is plotted in a, twice the imaginary part in b.

FIG. 6 a,b. The decadic logarithms of the probabilities of (a) the real and (b) twice the imaginary parts of the P-violating energy-difference $E_{\bar{\alpha} \bar{\beta},+}((\mathcal{E}'^{(\alpha)})) - E_{\bar{\alpha} \bar{\beta},+}((\mathcal{E}'^{(\bar{\alpha})}))$ (5.99) for our “hydrogen” vs. the deviation $\eta_{\bar{\beta}}^{(2)} - \eta_{\bar{\beta}, \text{res},-}^{(2)}$ from the resonance value $\eta_{\bar{\beta}, \text{res},-}^{(2)} = 574.9$ for which the P-even splitting of levels is removed, revealing a P-violating splitting of the order of $\sqrt{\delta_1}$.

FIG. 7. The lowest energy levels of the c.m. motion of a $^3\text{He}^+$ ion moving in one dimension in a linearly rising electric field potential of a field strength $\mathcal{E}$ within an interval of length $A = 1$ nm. These are the eigenenergies of the Airy states (cf. (2.43)). For $\mathcal{E} = 0$ they show the quadratic behaviour of the eigenenergies of sinus states (cf. (2.11)).

FIG. 8. The field strength value $E'_{\text{max}}$ characterizing the limit of applicability of our perturbative treatment of $^3\text{He}^+$ as a function of the field strength $\mathcal{E}$ for the level $\bar{\alpha} = (2S_{1/2}, 1/2; (1, 1, 1))$.

FIG. 9 a,b. The P-violating energy shift $\Delta E^{(\alpha)}_\alpha$ in $^3\text{He}^+$ for $\mathcal{E}' = E'_{\text{max}}$ for the same level $\bar{\alpha}$ as in Fig. 8. The real part is plotted in a, the imaginary part in b.

FIG. 10 a,b. The decadic logarithms of the moduli of (a) the real and (b) twice the imaginary parts of the P-violating energy-difference $E_{\bar{\alpha} \bar{\beta},+}((\mathcal{E}'^{(\alpha)})) - E_{\bar{\alpha} \bar{\beta},+}((\mathcal{E}'^{(\bar{\alpha})}))$ (5.113) for
\( ^4\text{He}^+ \) vs. the deviation \( \eta_3^{(3)} - \eta_{3,\text{res},-} \) of \( \eta_3^{(3)} \) from the resonance value \( \eta_{3,\text{res},-} = 525.4 \) for which the P-even splitting of levels is removed in 2nd order perturbation theory, revealing a P-violating splitting of the order of \( \sqrt{\delta_1} \).

**Fig. 11 a,b.** The decadic logarithm of the moduli squared of (a) the real and (b) twice the imaginary parts of the P-violating energy-difference \( E_{\bar{\alpha},\pm}(\{E_{\pm}^{(s)}\}) - E_{\bar{\alpha},\pm}(\{E_{\pm}^{(s)}\}) \) (3.146) for \( ^1\text{H} \) vs. the deviation \( \mathcal{E}_2^{(3)} - \mathcal{E}_{2,\text{res}}^{(3)} \) of \( \mathcal{E}_2^{(3)} \) from the resonance value \( \mathcal{E}_{2,\text{res}}^{(3)} = -1.64 \text{ V/cm} \) for which the P-even splitting of levels is removed in 2nd order perturbation theory, revealing a P-violating splitting of the order of \( \sqrt{\delta_2} \).
| $\alpha, |F_3|$ | $\mathcal{E}$ | $\mathcal{E}_{\max}$ | $E_{\alpha}^{(2,0)}/h$ | $\Delta E_{\alpha}^{(2,0)}/h$ | $\Delta E_{\alpha}^{(2,1)}/h$ | $\Delta E_{\alpha}^{(2,2)}/h$ |
|---|---|---|---|---|---|---|
| [V/cm] | [V/cm] | [MHz] | [MHz] | [MHz] | [10^4 Hz] | [10^4 Hz] |
| Re | Im | Re | Im | Re | Im |
| $2S_{\frac{1}{2}}^1, 1$ | 340 | 84 | -13 | -0.89 | 0.091 | 0.082 | 0.12 | -0.085 | -2.0 | 1.3 |
| $2P_{\frac{1}{2}}^1, 1$ | 380 | 228 | -44 | 0.57 | 0.34 | 0.0026 | -0.027 | 0.0045 | -0.70 | -0.041 |
| $2P_{\frac{3}{2}}^1, 1$ | 370 | 284 | -15 | 3.5 | 6.5 | -1.5 | 25 | 1.0 | -450 | -14 |
| $2P_{\frac{3}{2}}^2, 1$ | 350 | 206 | 3.9 | 1.9 | 0.20 | -0.064 | 80 | -12 | -1250 | 240 |

Figure 1
Figure 2a

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} = (2S_{1/2,1/2}; 3) \]

\[ (\alpha, |F_3|; n_1) = (2S_{1/2,1/2}; 3) \]

\[ (2S_{1/2,1/2}; 2) \]

\[ (2P_{1/2,1/2}; 3) \]

\[ (2S_{1/2,1/2}; 1) \]

\[ (2P_{1/2,1/2}; 2) \]

\[ (2P_{1/2,1/2}; 1) \]

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Im \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Im \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ (\alpha, |F_3|) = (2S_{1/2,1/2}; 3) \]

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Im \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

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\[ \Im \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Re \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]

\[ \Im \frac{E_{\alpha}^{(0)}}{\hbar} \left[ 10^4 \text{MHz} \right] \]
\[
\Delta E_3^\gamma \left( \frac{\epsilon_3^2}{\sqrt{\epsilon_3^3 \cdot \delta_1 \cdot h}} \right) [\text{MHz}]
\]
\[
\tilde{\alpha} = (2S_\frac{1}{2}, |F_3| = \frac{1}{2}; n = (1, 1, 1))
\]
\[ \bar{\alpha} = (2S_{\frac{1}{2}}, |F_3| = \frac{1}{2}; \mathbf{n} = (1, 1, 1)) \]

**Figure 5a**

**Figure 5b**
\[
\eta_3^{(2)} \cdot \eta_{3,\text{res,--}}
\]

Figure 6a

\[
\lg |\Re(E_{\alpha\beta} + (\mathcal{E}^{(e)}) - E_{\alpha\beta} + (\mathcal{E}^{(e)}_R))| / (\hbar \cdot \text{Hz})
\]

Figure 6b

\[
\lg |\Im(E_{\alpha\beta} + (\mathcal{E}^{(e)}) - E_{\alpha\beta} + (\mathcal{E}^{(e)}_R))| / (\hbar \cdot \text{s}^{-1})
\]

\[
\eta_3^{(2)} \cdot \eta_{3,\text{res,--}}
\]
\( \frac{(E_{n3} - E_{3,\text{min}})}{\hbar} \) [10^4 MHz]

\( \frac{E}{Z^5} \) [V/cm]

\( \bar{\alpha} = (2S_{1}^4, |F_3| = \frac{1}{2}; n = (1, 1, 1)) \)
\(\bar{\alpha} = (2S\frac{1}{2}, |F_3| = \frac{1}{2}; \mathbf{n} = (1, 1, 1))\)

\(\frac{E}{Z^5} [\text{V/cm}]\)

Figure 9a

\(\Re\Delta E_\phi(\bar{\alpha})/(\delta_1 \cdot \bar{h}) [\text{kHz}]\)

\(\bar{\alpha} = (2S\frac{1}{2}, |F_3| = \frac{1}{2}; \mathbf{n} = (1, 1, 1))\)

\(\frac{23\Delta E_\phi(\bar{\alpha})}{|\delta_1 \cdot \bar{h}|} [10^3 \text{s}^{-1}]\)

\(\bar{\alpha} = (2S\frac{1}{2}, |F_3| = \frac{1}{2}; \mathbf{n} = (1, 1, 1))\)

\(\frac{E}{Z^5} [\text{V/cm}]\)

Figure 9b
\[ \eta_3^{(2)} - \eta_{3,\text{res},-} \]

\[ \eta_3^{(2)} - \eta_{3,\text{res},-} \]
Figure 11a

\[ \log |\Re (E_{\alpha, \pm} (E_R^{\psi}) - E_{\alpha, \pm} (E_R^{\psi})) / (\hbar Hz)| \]

\[ \mathcal{E}^{(3)}_2 - \mathcal{E}^{(3)}_{2, res} \text{ [V/cm]} \]

Figure 11b

\[ \log |\Im (E_{\alpha, \pm} (E_R^{\psi}) - E_{\alpha, \pm} (E_R^{\psi})) / (\hbar s^{-1})| \]

\[ \mathcal{E}^{(3)}_2 - \mathcal{E}^{(3)}_{2, res} \text{ [V/cm]} \]