Electromagnetic moments of the bound system of charged particles

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We consider a bound system of particles interacting via electromagnetic forces in an external electromagnetic field, including leading relativistic corrections. Each particle has a definite mass, charge, spin, and charge radius. We introduce suitable canonical transformations and a perturbation scheme to obtain a Hamiltonian which describes the global dynamics of the system. This enables the derivation of formulas for various electromagnetic moments, such as the magnetic dipole moment, the mean square charge radius, and the electric dipole polarizability.

I. INTRODUCTION

Let us consider a system of particles, like an atom, an ion, a molecule, or a nucleus, which forms a bound state. We are interested in the motion and global properties of this system in an external electromagnetic field. When relativistic corrections are included, the center of mass cannot be separated from internal degrees of freedom and this may cause appearance of additional corrections to electromagnetic moments. A typical problem is the magnetic moment of the system, for which the first correct description was presented by Hegstrom in [1]. Here we aim to present an approach, on the basis of previously obtained results, which allows one to obtain various electromagnetic moments including relativistic corrections, e.g. the charge radius and the electric dipole polarizability. Although we consider electromagnetic systems herein, the approach can be extended to a nonrelativistic system of strongly interacting particles, such as nuclei.

II. PERTURBATIVE APPROACH TO SEPARATION OF THE CENTER OF MASS MOTION

We assume that the Hamiltonian H for a system of particles can be decomposed as

$$H = H_{\rm S} + H_{\Pi} + \delta H, \tag{1}$$

where $H_{\rm S}$ is the Hamiltonian that involves only internal degrees of freedom. H_{Π} is the Hamiltonian for the global dynamics of the system, which involves center of mass and electromagnetic moments. δH is the remainder, which couples internal degrees of freedom to global motion. We will assume that the binding energy is much larger than the characteristic scale of energy in δH, so it makes sense to speak about a bound system. We will also assume that global motion is nonrelativistic. We aim to find an effective equation for the global motion that accounts for the coupling to internal degrees of freedom. The Schrödinger equation for the total system is

$$i\frac{\partial \psi}{\partial t} = (H - \mathcal{E}_{\rm S})\,\psi, \tag{2}$$

where the leading factor that comes from the binding energy $\mathcal{E}_{\rm S}$ was subtracted from the time dependence. The Hamiltonians $H_{\rm S}$ and H_{Π} involve different degrees of freedom of the system, so they commute

$$[H_{\rm S}, H_{\Pi}] = 0. \tag{3}$$

Moreover, it allows one to decompose the global wave function as follows

$$\psi = \psi_{\rm S}\psi_{\Pi} + \delta\psi, \tag{4}$$

where $\psi_{\rm S}$ is the wave function of the ground state of internal Hamiltonian $H_{\rm S}$ with corresponding energy $\mathcal{E}_{\rm S}$, namely

$$H_{\rm S}\psi_{\rm S} = \mathcal{E}_{\rm S}\psi_{\rm S}. \tag{5}$$

ψ_{Π} in Eq. (4) is the wave function describing the global dynamics of the system, so it depends only on global degrees of freedom. The last term in Eq. (4), $\delta\psi$, is a small correction that depends on all the variables, and results from the coupling of internal and external degrees of freedom. We will assume that

$$\langle\psi|\psi\rangle = 1 = \langle\psi_{\rm S}|\psi_{\rm S}\rangle_{\rm S}, \tag{6}$$
$$\langle\psi_{\rm S}|\delta\psi\rangle_{\rm S} = 0, \tag{7}$$
$$\langle\psi_{\rm S}|\delta H|\psi_{\rm S}\rangle_{\rm S} = 0, \tag{8}$$

where $\langle\ldots\rangle_S$ denotes the scalar product on internal degrees of freedom only. If the last condition (8) is not satisfied, one can always redefine H_{Π} to include $\langle\psi_{\rm S}|\delta H|\psi_{\rm S}\rangle_S$, and subtract this expectation value from δH. As a result, this condition does not reduce generality. Let us now project the Schrödinger equation (2) into $\psi_{\rm S}$, then using assumptions in (6) - (8) one obtains

$$i\frac{\partial\psi_{\Pi}}{\partial t} = H_{\Pi}\psi_{\Pi} + \langle\psi_{\rm S}|\delta H|\delta\psi\rangle_{\rm S}. \tag{9}$$

Eq. (2) with the wave function (4) can be rewritten in the form

$$\left(\mathcal{E}_{\rm S} - H_{\rm S} - H_{\Pi} + i\frac{\partial}{\partial t}\right)\delta\psi = \psi_S\left(H_{\Pi} - i\frac{\partial}{\partial t}\right)\psi_{\Pi} + \delta H\,(\psi_{\rm S}\psi_{\Pi} + \delta\psi) \tag{10}$$

and formally

$$\delta\psi = \frac{1}{[(\mathcal{E}_{\rm S} - H_{\rm S})' - H_{\Pi} + i\,\partial_t]}\delta H(\psi_{\rm S}\psi_{\Pi} + \delta\psi), \tag{11}$$

where prime denotes exclusion of the ground state from the resolvent, which is defined by the following series:

$$\delta\psi = \left[\frac{1}{(\mathcal{E}_S - H_S)'} + \frac{H_\Pi - i\,\partial_t}{(\mathcal{E}_S - H_S)'^2} + \ldots\right]\delta H\,(\psi_S\psi_\Pi + \delta\psi). \tag{12}$$

δH is assumed to be a small correction, so we neglect $\delta\psi$ on the right hand side of Eq. (12)

$$\delta\psi = \frac{1}{[(\mathcal{E}_S - H_S)' - H_\Pi + i\,\partial_t]}\delta H\,\psi_S\psi_\Pi. \tag{13}$$

H_Π and the characteristic time scale of δH is much smaller then the excitation energy of H_S, so we use Eq. (12) and neglect the higher order terms

$$\delta\psi = \frac{1}{(\mathcal{E}_S - H_S)'}\delta H\,\psi_S\psi_\Pi + \ldots \tag{14}$$

Finally, the equation for ψ_Π becomes

$$i\frac{\partial\psi_\Pi}{\partial t} = H_{\text{eff}}\,\psi_\Pi, \tag{15}$$

$$H_{\text{eff}} = H_\Pi + \langle\psi_S|\delta H\frac{1}{(\mathcal{E}_S - H_S)'}\delta H|\psi_S\rangle_S + \ldots$$

which can be rewriten in the more convenient form

$$H_{\text{eff}} = \langle\psi_S|H - \mathcal{E}_S|\psi_S\rangle_S + \langle\psi_S|H\frac{1}{(\mathcal{E}_S - H_S)'}H|\psi_S\rangle_S + \ldots \tag{16}$$

In the actual calculations we perform additional canonical transformations to avoid the higher order terms denoted by dots in the above.

III. HAMILTONIAN FOR THE COMPOUND SYSTEM

We consider now a system of N charged particles placed in the external electromagnetic field, including the leading relativistic corrections. We assume that the magnetic field is homogenous, and for the electric field we keep the first derivatives to account for the charge radius. We would like to separate the center-of-mass motion and obtain general formulae for electromagnetic moments, such as the magnetic dipole moment μ, the charge radius, and the electric dipole polarizabiliy. Our approach is based on Refs. [2, 3], where relativistic effects are included perturbatively, while the wave function is nonrelativistic and includes the spin. The initial Hamiltonian is a sum of one-particle terms H_a and two-particle interactions H_{ab} including relativistic corrections [4, 5] (using natural units $\hbar = c = 1$)

$$H = \sum_a H_a + \sum_{a>b,b} H_{ab}, \tag{17}$$

with

$$H_a = \frac{\vec{\pi}_a^2}{2\,m_a} + e_a\,A_a^0 - \frac{e_a}{2\,m_a}\,g_a\,\vec{s}_a\cdot\vec{B}_a - \frac{e_a}{4\,m_a^2}\,(g_a - 1)\,\vec{s}_a\cdot\left(\vec{E}_a\times\vec{\pi}_a - \vec{\pi}_a\times\vec{E}_a\right)$$

$$- \frac{\vec{\pi}_a^4}{8\,m_a^3} - \frac{e_a}{6}\,r_{Ea}^2\,\nabla\cdot\vec{E}_a + \frac{e_a}{8\,m_a^3}\left[4\,\vec{\pi}_a^2\,\vec{s}_a\cdot\vec{B}_a + (g_a - 2)\left\{\vec{\pi}_a\cdot\vec{B}_a\,,\,\vec{\pi}_a\cdot\vec{s}_a\right\}\right], \tag{18}$$

$$H_{ab} = \frac{e_a\,e_b}{4\,\pi}\left\{\frac{1}{r_{ab}} - \frac{1}{2\,m_a\,m_b}\,\pi_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)\pi_b^j - \frac{2\,\pi}{3}\,(r_{Ea}^2 + r_{Eb}^2)\,\delta^3(r_{ab})\right.$$

$$+ \frac{1}{2\,r_{ab}^3}\left[\frac{g_a}{m_a\,m_b}\,\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_b - \frac{g_b}{m_a\,m_b}\,\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_a + \frac{(g_b - 1)}{m_b^2}\,\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_b\right.$$

$$\left.\left. - \frac{(g_a - 1)}{m_a^2}\,\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_a\right] - \frac{2\,\pi\,g_a\,g_b}{3\,m_a\,m_b}\,\delta^3(r_{ab})\,\vec{s}_a\cdot\vec{s}_b + \frac{g_a\,g_b}{4\,m_a\,m_b}\,\frac{s_a^i\,s_b^j}{r_{ab}^3}\left(\delta^{ij} - \frac{3\,r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right)\right\}, \tag{19}$$

where $\vec{\pi} = \vec{p} - e\,A(\vec{r})$. r_{Ea}^2 is the mean square charge radius of a particle a and it includes for convenience the Darwin term, so for the point $s = 1/2$ particle $r_E^2 = 3/(4\,m^2)$. We now introduce global variables, the center of mass $\vec{R}$, and the total momentum $\vec{\Pi}$

$$\vec{R} = \sum_a \frac{m_a}{M}\,\vec{r}_a, \tag{20}$$

$$\vec{\Pi} = \sum_a [\vec{p}_a - e_a\,\vec{A}(\vec{R})] = \vec{P} - e\,\vec{A}(\vec{R}), \tag{21}$$

where $M = \sum_a m_a$ and $e = \sum_a e_a$, and relative coordinates

$$\vec{x}_a = \vec{r}_a - \vec{R}, \tag{22}$$

$$\vec{q}_a = \vec{p}_a - \frac{m_a}{M}\,\vec{P}, \tag{23}$$

such that

$$\left[x_a^i \, , q_b^j\right] \;=\; i\,\delta^{ij}\left(\delta_{ab} - \frac{m_b}{M}\right), \qquad (24)$$

$$\left[R^i \, , P^j\right] \;=\; i\,\delta^{ij}, \qquad (25)$$

$$\left[x_a^i \, , P^j\right] \;=\; \left[R^i \, , q_a^j\right] = 0. \qquad (26)$$

Next, we perform a canonical transformation ϕ

$$H' = e^{-i\,\phi}\,H\,e^{i\,\phi} + \partial_t\phi, \qquad (27)$$

which assumes that the characteristic wavelength of the electromagnetic field is larger than the size of the system, as follows:

$$\phi \;=\; \sum_a e_a \int_0^1 du\, \vec{x}_a \cdot \vec{A}\big(\vec{R} + u\,\vec{x}_a\big)$$

$$= \sum_a e_a \left[x_a^i\, A^i + \frac{1}{2!}\, x_a^i\, x_a^j\, A_{,j}^i + \dots\right]. \qquad (28)$$

The scalar potential is transformed to

$$\sum_a e_a\, A_a^0 + \partial_t\phi = e\, A^0 - D^i\, E^i - \frac{1}{2!}\, D^{ij}\, E_{,j}^i, \qquad (29)$$

where

$$D^i \;=\; \sum_a e_a\, x_a^i, \qquad (30)$$

$$D^{ij} \;=\; \sum_a e_a\, x_a^i\, x_a^j, \qquad (31)$$

and $A^0 \equiv A^0(\vec{R}), \vec{E} \equiv \vec{E}(\vec{R})$, similarly $\vec{B} \equiv \vec{B}(\vec{R})$. The kinetic momentum is transformed to

$$e^{-i\,\phi}\,\pi_a^j\,e^{i\,\phi} = \tilde{\pi}_a^j + \frac{m_a}{M}\,\Pi^j, \qquad (32)$$

where

$$\tilde{\pi}_a = \vec{q}_a + \frac{1}{2}\left(e_a\,\vec{x}_a + \frac{m_a}{M}\,\vec{D}\right) \times \vec{B}, \qquad (33)$$

and the kinetic energy is

$$e^{-i\,\phi}\sum_a \frac{\pi_a^2}{2\,m_a}\,e^{i\,\phi} = \frac{\Pi^2}{2M} + \frac{\vec{\Pi}}{M}\cdot\vec{D}\times\vec{B} + \sum_a \frac{\tilde{\pi}_a^2}{2\,m_a}. \qquad (34)$$

Finally, the transformed Hamiltonian takes the form

$$H' = H_{BP} + H_{\partial E} + H_{\Pi}, \qquad (35)$$

where

$$\begin{aligned}
H_{BP} \;=\; & \sum_a \Bigg\{ \frac{\tilde{\pi}_a^2}{2\,m_a} - \frac{\tilde{\pi}_a^4}{8\,m_a^3} - \frac{e_a}{2\,m_a}\, g_a\, \vec{s}_a \cdot \vec{B} + \frac{e_a}{8\,m_a^3}\left[4\,\tilde{\pi}_a^2\,\vec{s}_a\cdot\vec{B} + (g_a - 2)\left\{\tilde{\pi}_a\cdot\vec{B}\,,\,\tilde{\pi}_a\cdot\vec{s}_a\right\}\right] \\
& - \frac{e_a\,(g_a - 1)}{2\,m_a^2}\,\vec{s}_a\times\vec{E}\cdot\tilde{\pi}_a \Bigg\} + \sum_{a>b,b} \frac{e_a\, e_b}{4\,\pi}\Bigg\{\frac{1}{r_{ab}} - \frac{1}{2\,m_a\,m_b}\,\tilde{\pi}_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3}\right)\tilde{\pi}_b^j \\
& - \frac{2\,\pi}{3}\left(r_{Ea}^2 + r_{Eb}^2\right)\delta^3(r_{ab}) - \frac{2\,\pi\, g_a\, g_b}{3\,m_a\,m_b}\,\vec{s}_a\cdot\vec{s}_b\,\delta^3(r_{ab}) + \frac{g_a\, g_b}{4\,m_a\,m_b}\,\frac{s_a^i\, s_b^j}{r_{ab}^3}\left(\delta^{ij} - 3\,\frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^2}\right) \\
& + \frac{1}{2\,r_{ab}^3}\Bigg[\frac{g_a}{m_a\,m_b}\,\vec{s}_a\cdot\vec{r}_{ab}\times\tilde{\pi}_b - \frac{g_b}{m_a\,m_b}\,\vec{s}_b\cdot\vec{r}_{ab}\times\tilde{\pi}_a + \frac{(g_b - 1)}{m_b^2}\,\vec{s}_b\cdot\vec{r}_{ab}\times\tilde{\pi}_b \\
& - \frac{(g_a - 1)}{m_a^2}\,\vec{s}_a\cdot\vec{r}_{ab}\times\tilde{\pi}_a\Bigg)\Bigg]\Bigg\}, \qquad (36)
\end{aligned}$$

$$H_{\partial E} \;=\; -\sum_a \frac{e_a}{6}\, r_{Ea}^2\, \nabla\vec{E} - \frac{1}{2!}\, D^{ij}\, E_{,j}^i - \sum_a \frac{e_a\,(g_a - 1)}{4\,m_a^2}\,\epsilon^{ikl}\left\{s_a^i\, E_{,j}^k\, x_a^j\,,\,\tilde{\pi}_a^l\right\}, \qquad (37)$$

$$\begin{aligned}
H_{\Pi} \;=\; & \frac{\vec{\Pi}^2}{2\,M} + e\, A^0 - \vec{D}\cdot\vec{E} + \vec{D}\cdot\vec{B}\times\frac{\vec{\Pi}}{M} - \frac{1}{8\,M^3}\,\Pi^4 - \frac{1}{2\,M^3}\,\Pi^2\,\vec{\Pi}\cdot\vec{D}\times\vec{B} \\
& + \Pi^i\, Q_{ij}\, \Pi^j + \frac{1}{2}\left\{\Pi^i\,,\,Q_i\right\}, \qquad (38)
\end{aligned}$$

$$Q^{ij} = -\frac{\delta^{ij}}{2\,M^2}\left(\sum_a \frac{\tilde{\pi}_a^2}{2\,m_a} + \sum_{a>b,b}\frac{e_a\,e_b}{4\,\pi\,r_{ab}}\right) - \frac{1}{2\,M^2}\left(\sum_a \frac{\tilde{\pi}_a^i\,\tilde{\pi}_a^j}{m_a} + \sum_{a>b,b}\frac{e_a\,e_b}{4\,\pi}\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)$$
$$+\sum_a \frac{e_a}{4\,M^2\,m_a}\left[2\,\delta^{ij}\,\vec{s}_a\cdot\vec{B} + (g_a-2)\,B^i\,s_a^j\right], \tag{39}$$

$$Q^i = \sum_a \frac{e_a}{4\,M\,m_a^2}\left[4\,\tilde{\pi}_a^i\,\vec{s}_a\cdot\vec{B} + (g_a-2)\,B^i\,\pi_a\cdot\vec{s}_a + (g_a-2)\,s_a^i\,\tilde{\pi}_a\cdot\vec{B}\right]$$
$$+\sum_{a\neq b,b}\frac{e_a\,e_b}{4\,\pi}\left[\frac{1}{2\,M\,m_a\,r_{ab}^3}\,(\vec{s}_a\times\vec{r}_{ab})^i - \frac{1}{2\,M\,m_b}\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)\tilde{\pi}_b^j\right]$$
$$-\sum_a \frac{e_a\,(g_a-1)}{2\,m_a\,M}\,(\vec{s}_a\times\vec{E})^i - \sum_a \frac{1}{4\,M\,m_a^2}\,\{\tilde{\pi}_a^2,\,\tilde{\pi}_a^i\}. \tag{40}$$

In order to simplify the derivation of the effective Hamiltonian H_{eff} in Eq. (16), we perform the next canonical transformation ϕ. In this case it should be noted that the Q_0^i operator

$$Q_0^i = Q^i\Big|_{\vec{E}=\vec{B}=0}$$
$$= \frac{1}{2\,M}\sum_{a\neq b,b}\frac{e_a\,e_b}{4\,\pi}\left[\frac{1}{m_a\,r_{ab}^3}\,(\vec{s}_a\times\vec{r}_{ab})^i \tag{41}\right.$$
$$\left.-\frac{1}{m_b}\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)q_b^j\right] - \sum_a \frac{1}{2\,M\,m_a^2}\,\vec{q}_a^2\,q_a^i$$

can be expressed as a commutator

$$\vec{Q}_0 = i\,[H_S,\,\vec{T}], \tag{42}$$

where

$$\vec{T} = \frac{1}{2M}\sum_a\left(\frac{\vec{s}_a\times\vec{q}_a}{m_a} - \frac{q_a^j\,\vec{x}_a\,q_a^j}{m_a} - \sum_{b\neq a}\frac{e_a\,e_b}{4\,\pi}\frac{\vec{x}_a}{r_{ab}}\right) \tag{43}$$

and H_S is the nonrelativistic Hamiltonian of the bound system

$$H_S = \sum_a \frac{\vec{q}_a^2}{2\,m_a} + \sum_{a>b,b}\frac{e_a\,e_b}{4\,\pi\,r_{ab}}. \tag{44}$$

Consequently, we assume that

$$\phi = -\vec{T}\cdot\vec{\Pi} \tag{45}$$

and obtain a new Hamiltonian H''

$$H'' = e^{-i\phi}\,H'\,e^{i\phi} + \partial_t\phi \tag{46}$$
$$= H' + \delta H,$$

where

$$\delta H = -i\left[H_S + \frac{\Pi^2}{2\,M} + e\,A^0 - \vec{D}\cdot\left(\vec{E} + \frac{\vec{\Pi}}{M}\times\vec{B}\right)\right.$$
$$\left.-i\,\partial_t,\,\vec{T}\cdot\vec{\Pi}\right]. \tag{47}$$

We will limit the effective Hamiltonian to terms that are independent, linear in electromagnetic field strength, and quadratic in electric field, thus neglecting the higher order terms in Eq. (16), so

$$H_{\text{eff}} = \langle\psi_S|H'' - H_{BP}\Big|_{\vec{E}=\vec{B}=0}|\psi_S\rangle \tag{48}$$
$$+\langle\psi_S|H''\frac{1}{(\mathcal{E}_S - H_S)'}H''|\psi_S\rangle$$

The expectation value of δH on ψ_S is

$$\langle\delta H\rangle = i\left\langle\left[\vec{D}\cdot\left(\vec{E} + \frac{\vec{\Pi}}{M}\times\vec{B}\right),\,\vec{T}\cdot\vec{\Pi}\right]\right\rangle$$
$$= -\frac{\epsilon^{ijk}}{4\,M}\left\{\left(\vec{E} + \frac{\vec{\Pi}}{M}\times\vec{B}\right)^i,\,\Pi^j\right\}$$
$$\times\sum_a\left\langle\left(\frac{e_a}{m_a} - \frac{e}{M}\right)(s_a^k + l_a^k)\right\rangle$$
$$-\frac{1}{6}\langle\vec{D}\cdot\vec{T} + \vec{T}\cdot\vec{D}\rangle\vec{\nabla}\cdot\vec{E} \tag{49}$$

The resulting effective Hamiltonian from Eq. (48), after re-arrangement, details of which are presented in the following sections, becomes

$$H_{\text{eff}} = e\,A^0 + \frac{\Pi^2}{2\,M}\left(1 - \frac{\mathcal{E}_S}{M}\right) - \frac{\Pi^4}{8\,M^3} - \frac{e}{6}\,R^2\,\nabla\cdot\vec{E} \tag{50}$$
$$-\frac{e}{2\,M}\,(g+\delta g)\,\vec{S}\cdot\vec{B} + \frac{e}{2\,M^2}\,(g-1)\,\vec{S}\cdot\vec{\Pi}\times\vec{E}$$
$$+\frac{e}{2\,M^3}\left[\Pi^2\,\vec{S}\cdot\vec{B} + \frac{(g-2)}{2}\,\vec{S}\cdot\vec{\Pi}\,\vec{B}\cdot\vec{\Pi}\right] - \frac{\alpha_E}{2}\,\vec{E}^2$$

where $\vec{S}$ is a global spin operator, and formulas for R^2, g, δg, and α_E are presented in the following sections.

A. Mean square charge radius

The mean square charge radius is defined as a coefficient at $\nabla \vec{E}$, see Eq. (50). It is present in $H_{\partial E}$

$$H_{\partial E} = -\sum_a \frac{e_a}{6} \nabla \vec{E} \left[r_{Ea}^2 + x_a^2 + \frac{(g_a - 1)}{m_a^2} \vec{x}_a \times \vec{q}_a \cdot \vec{s}_a \right] \tag{51}$$

and also in δH

$$\langle \delta H \rangle = -\frac{1}{6} \nabla \vec{E} \langle \vec{T} \cdot \vec{D} + \vec{D} \cdot \vec{T} \rangle. \tag{52}$$

For the total mean square charge radius R^2 of the system, we obtain

$$e R^2 = \sum_a e_a \left[r_{Ea}^2 + \langle x_a^2 \rangle + \frac{(g_a - 1)}{m_a^2} \langle \vec{x}_a \times \vec{q}_a \cdot \vec{s}_a \rangle + 2 \langle \vec{x}_a \cdot \vec{T} \rangle \right]. \tag{53}$$

The first two terms are widely known, the third one was recently discovered by Flambaum et al. [6], and the last term is new. It would be interesting to calculate them for deuteron, for which the the charge radius is well known from atomic isotope shift measurements [7]. However, in the presence of strong interactions the formula for R^2 may change, and this should be verified using the effective chiral perturbation theory.

B. Electric dipole polarizability

The energy shift Eqs. (48) due to the electric dipole polarizability Eq. (50) is

$$-\frac{\alpha_E}{2} \vec{E}^2 = \langle \psi_S | (\vec{D} + \delta \vec{D}) \cdot \vec{E} \frac{1}{\mathcal{E}_S - H_S} (\vec{D} + \delta \vec{D}) \cdot \vec{E} | \psi_S \rangle \tag{54}$$

so one obtains for α_E

$$\alpha_E = \frac{2}{3} \langle \psi_S | (\vec{D} + \delta \vec{D}) \frac{1}{H_S - \mathcal{E}_S} (\vec{D} + \delta \vec{D}) | \psi_S \rangle. \tag{55}$$

The relativistic correction to the electric dipole operator $\delta \vec{D}$ comes from Eq. (47)

$$-\delta \vec{D} \cdot \vec{E} = -i \left[e A^0 - i \partial_t , \vec{T} \cdot \vec{\Pi} \right], \tag{56}$$

so

$$\delta \vec{D} = e \vec{T}, \tag{57}$$

and $\vec{T}$ is defined in Eq. (43). In all the previous calculations of the electric dipole polarizability of nuclei, the contribution coming from δD was missing. This correction is particularly important for muonic atoms, where nuclear polarizability effects are large.

C. Kinetic energy

When the electromagnetic field is neglected, the expectation value of $H'' - \mathcal{E}_S$ is

$$H_{\text{eff}} = \frac{\Pi^2}{2 M} - \frac{\Pi^4}{8 M^3} + \Pi^i \Pi^j \langle Q_0^{ij} \rangle, \tag{58}$$

where

$$\begin{aligned} Q_0^{ij} &= Q^{ij}\Big|_{\vec{E}=\vec{B}=0} \\ &= -\frac{\delta^{ij}}{2 M^2} \left(\sum_a \frac{\vec{q}_a^2}{2 m_a} + \sum_{a>b,b} \frac{e_a e_b}{4 \pi r_{ab}} \right) \\ &\quad -\frac{1}{2 M^2} \left(\sum_a \frac{q_a^i q_a^j}{m_a} + \sum_{a>b,b} \frac{e_a e_b}{4 \pi} \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right). \end{aligned} \tag{59}$$

The expectation value of the second term vanishes, while that of the first term is $\mathcal{E}_S$, so

$$\begin{aligned} H_{\text{eff}} &= \frac{\Pi^2}{2 M} \left(1 - \frac{\mathcal{E}_S}{M} \right) - \frac{\Pi^4}{8 M^3} \\ &\approx \frac{\Pi^2}{2 (M + \mathcal{E}_S)} - \frac{\Pi^4}{8 (M + \mathcal{E}_S)^3}. \end{aligned} \tag{60}$$

H_{eff} is a kinetic energy with the total mass being the sum of individual masses and the binding energy, as it should be. This is in agreement with Eq. (50).

D. Spin in the external homogenous electric field

Hereinafter we assume that the electric and the magnetic fields are homogenous. The magnetic moment μ of the compound system is defined as

$$\vec{\mu} = \left\langle \sum_a \frac{e_a}{2 m_a} (\vec{l}_a + g_a \vec{s}_a) \right\rangle \equiv \frac{e}{2 M} g \vec{S}, \tag{61}$$

where the last equation defines the g-factor, and $\vec{l}_a = \vec{x}_a \times \vec{q}_a$ and $\vec{S} = \sum_a (\vec{l}_a + \vec{s}_a)$. The coupling of the static magnetic moment to the magnetic field is

$$H_{\text{eff}} = -\vec{\mu} \cdot \vec{B}. \tag{62}$$

When the system moves, the magnetic moment couples to the electric field as follows

$$H_{\text{eff}} = \frac{\vec{\Pi} \times \vec{E}}{2 M} \cdot \sum_a \left\langle \frac{e_a (g_a - 1)}{m_a} \vec{s}_a \right\rangle + \delta H, \tag{63}$$

where

$$\delta H = \frac{\vec{\Pi} \times \vec{E}}{2 M} \cdot \sum_a \left\langle \left(\frac{e_a}{m_a} - \frac{e}{M} \right) (\vec{s}_a + \vec{l}_a) \right\rangle. \tag{64}$$

After combining both terms

$$
\begin{aligned}
H_{\text{eff}} &= \frac{\vec{\Pi} \times \vec{E}}{2\,M} \cdot \sum_a \left\langle \frac{e_a}{m_a}\left(g_a\,\vec{s}_a + \vec{l}_a\right) - \frac{e}{M}\left(\vec{l}_a + \vec{s}_a\right) \right\rangle \\
&= \frac{e}{2\,M^2}\,(g-1)\,\vec{S} \cdot \vec{\Pi} \times \vec{E}
\end{aligned}
\tag{65}
$$

the coupling of the moving spin to the electric field coincides with that in Eq. (50).

E. Spin in the external homogenous magnetic field

Corrections of order $O(\vec{\Pi}^2)$ to the coupling of the spin to the magnetic field are

$$
H_{\text{eff}} = \Pi^i\,\langle Q_B^{ij}\rangle\,\Pi^j + \delta H,
\tag{66}
$$

where the part of Q^{ij} that is linear in $\vec{B}$ is

$$
\begin{aligned}
\langle Q_B^{ij}\rangle &= \frac{1}{2\,M^2}\sum_a \frac{e_a}{2\,m_a}\left\langle \delta^{ij}\,\vec{x}_a \times \vec{q}_a \cdot \vec{B} - (\vec{x}_a \times \vec{B})^i\,q_a^j \right.\\
&\quad \left. -q_a^i\,(\vec{x}_a \times \vec{B})^j + \left(2\delta^{ij}\,\vec{s}_a \cdot \vec{B} + (g_a - 2)B^i\,s_a^j\right) \right\rangle\\
&= \frac{1}{2\,M^2}\sum_a \frac{e_a}{2\,m_a}\left\langle 2\,\delta^{ij}\,(\vec{l}_a + \vec{s}_a)\cdot\vec{B} - B^i\,l_a^j \right.\\
&\quad \left. +(g_a - 2)\,B^i\,s_a^j \right\rangle,
\end{aligned}
\tag{67}
$$

where we used the expectation value identity

$$
\langle x_a^i\,q_a^j\rangle = \frac{1}{2}\,\langle x_a^i\,q_a^j - x_a^j\,q_a^i\rangle.
\tag{68}
$$

The contribution from the additional canonical transformation Eq. (49) is

$$
\delta H = -\frac{\vec{\Pi}\times\vec{B}}{2M^2}\sum_a\left\langle \left(\frac{e_a}{m_a} - \frac{e}{M}\right)\vec{\Pi}\times(\vec{s}_a + \vec{l}_a) \right\rangle
\tag{69}
$$

The total $O(\vec{\Pi}^2)$ interaction takes the form

$$
H_{\text{eff}} = \frac{e}{2\,M^3}\left[\Pi^2\,\vec{S}\cdot\vec{B} + \frac{(g-2)}{2}\,\vec{S}\cdot\vec{\Pi}\,\vec{B}\cdot\vec{\Pi}\right]
\tag{70}
$$

and coincides with that in Eq. (50).

IV. MAGNETIC MOMENT

The relativistic corrections to the magnetic moment of bound states with arbitrary particle masses have already been considered in the literature [1, 3, 8] and very recently in [10]. Here we rederive the general formula for the arbitrary state, obtain the known result for the magnetic moment of hydrogen-like ions in the S state, and confirm and obtain a more accurate result for positronium ion Ps$^-$ in the ground state. Consider the relativistic interaction with the magnetic field resulting from H_{BP} in Eq. (36), and neglect the terms quadratic in $\vec{B}$.

$$
\begin{aligned}
\delta H &= -\sum_a \frac{e_a}{2\,m_a}\,g_a\,\vec{s}_a\cdot\vec{B} + \sum_a \frac{1}{4\,m_a^3}\left[q_a^2\,\vec{D}_a\times\vec{q}_a\cdot\vec{B} + 2\,e_a\,q_a^2\,\vec{s}_a\cdot\vec{B} + e_a\,(g_a-2)\,\vec{q}_a\cdot\vec{s}_a\,\vec{q}_a\cdot\vec{B}\right]\\
&\quad + \sum_{a\neq b,b}\frac{e_a\,e_b}{4\,\pi}\left[-\frac{1}{4\,m_a\,m_b}\,q_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)(\vec{D}_b\times\vec{B})^j\right.\\
&\quad \left.+\frac{1}{4\,r_{ab}^3}\frac{g_a}{m_a\,m_b}\,(\vec{s}_a\times\vec{r}_{ab})\cdot(\vec{D}_b\times\vec{B}) - \frac{1}{4\,r_{ab}^3}\frac{(g_a-1)}{m_a^2}\,(\vec{s}_a\times\vec{r}_{ab})\cdot(\vec{D}_a\times\vec{B})\right],
\end{aligned}
\tag{71}
$$

where

$$
\vec{D}_a = e_a\,\vec{x}_a + \frac{m_a}{M}\,\vec{D}.
\tag{72}
$$

Eq. (71) agrees with the former result of Hegstrom [1], and is essentially the same as that in Ref. [3]. For S-states, only the spin dependent terms in (71) contribute, so

$$
\begin{aligned}
\delta H &= -\sum_a \frac{e_a}{2m_a}\,\vec{s}_a\cdot\vec{B}\left\{g_a - \frac{\vec{q}_a^2}{m_a^2}\left(\frac{2}{3} + \frac{g_a}{6}\right)\right.\\
&\quad \left.+\frac{1}{3}\sum_{b\neq a}\frac{e_b}{4\pi}\frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\left[\frac{g_a}{m_b}\vec{D}_b - \frac{g_a-1}{m_a}\vec{D}_a\right]\right\}.
\end{aligned}
\tag{73}
$$

First we will consider the hydrogen-like ion. It is a system consisting of one electron of mass m and charge $-e$, and the nucleus of charge Ze and mass m_N. We neglect the spin of

the nucleus, so the Hamiltonian is

$$\delta H = \frac{e}{2m}\vec{s}\cdot\vec{B}\left\{g_e - \frac{\vec{q}^2}{m^2}\left(\frac{2}{3}+\frac{g_e}{6}\right) + \frac{Z\alpha}{3\,M\,r_{eN}}\right.$$
$$\times\left[g_e\left(-Z\frac{M}{m_N}+(Z-1)\frac{m_N}{M}\right)\right.$$
$$\left.\left.+(g_e-1)\left(\frac{M}{m}+(Z-1)\frac{m}{M}\right)\right]\right\}. \quad (74)$$

The correction δg is given by the expectation value of the Hamiltonian on the hydrogen-like system state $\phi = \phi_{nlm_l}$, where n,l,m_l are respective quantum numbers

$$\langle\delta H\rangle = \frac{e}{2m}\vec{s}\cdot\vec{B}(g_e+\delta g), \quad (75)$$

where

$$\delta g = -\frac{(Z\,\alpha)^2}{3\,n^2\,(1+x)^2}\left[-\frac{g_e}{2}+4-\frac{1}{1+x}\right.$$
$$\left.+Z\,x^2\left(g_e+\frac{1}{1+x}\right)\right] \quad (76)$$

and $x = m/m_N$, in agreement with Refs. [3, 8].

In the case of the positronium ion Ps$^-$ in the ground state, the spin comes only from the positron, since two electrons are in the singlet state. Hence from the beginning we neglect terms proportional to electron spin, and assume that indices $1, 2$ refer to electrons, while index 3 refers to the positron.

$$\delta H = -\frac{e}{2m}\vec{s}_3\cdot\vec{B}\left\{g_e - \frac{\vec{q}_3^2}{m^2}\left(\frac{2}{3}+\frac{g_e}{6}\right)\right. \quad (77)$$
$$-\frac{\alpha}{9m}\left[\frac{5}{3}\left(\frac{1}{r_{13}}+\frac{\vec{r}_{13}\cdot\vec{r}_{23}}{r_{13}^3}\right)+g_e\frac{\vec{r}_{13}\cdot(\vec{r}_{12}-\vec{r}_{23})}{r_{13}^3}\right.$$
$$\left.\left.+\frac{5}{3}\left(\frac{1}{r_{23}}+\frac{\vec{r}_{13}\cdot\vec{r}_{23}}{r_{23}^3}\right)-g_e\frac{\vec{r}_{23}\cdot(\vec{r}_{12}+\vec{r}_{13})}{r_{23}^3}\right]\right\}$$

As previously, we find a correction to the magnetic moment of Ps$^-$ from the expectation value of the Hamiltonian (77).

$$\langle\delta H\rangle = -\frac{e}{2m}\vec{s}_3\cdot\vec{B}\,g_{\text{Ps}^-}. \quad (78)$$

Of note, g_{Ps^-} is defined differently from the g-factor in Eq. (61). Following this definition and Eq. (77) g_{Ps^-} is

$$g_{\text{Ps}^-} = g_e + \alpha^2\,\delta g, \quad (79)$$
$$\delta g = -\left\langle\vec{p}_3^2\left(\frac{2}{3}+\frac{g_e}{6}\right)+\frac{1}{r_{13}}\left(\frac{10}{27}+\frac{2}{9}g_e\right)\right.$$
$$\left.+\frac{\vec{r}_{13}\cdot\vec{r}_{23}}{r_{13}^3}\left(\frac{10}{27}-\frac{4}{9}g_e\right)\right\rangle, \quad (80)$$

where for convenience we used in the last equation atomic units, so above matrix elements are dimensionless. Table I

presents expectation value of operators in the ground state of Ps$^-$ calculated numerically, where the uncertainty for our total g-factor g_{Ps^-} is estimated by $2\,\alpha^4\,\delta g$. Our value for δg is in agreement with the one obtained in [10] $-0.51(1)$, but is significantly more accurate and includes the leading QED effects. Surprisingly we do not agree with the corresponding formula obtained in [10], which is much different and not equivalent to that of ours in Eq. (80), and also we disagree with their total g-factor $g_{\text{Ps}^-} = 2.004\,61(1)$.

TABLE I: Expectation values of operators in (80) on the ground state of Ps$^-$ in atomic units, fundamental constants are from Ref. [9]

Energy	$-0.262\,005\,070$
$\langle\vec{p}_3^2\rangle$	$0.257\,532\,962$
$\langle\frac{1}{r_{13}}\rangle$	$0.339\,821\,023$
$\langle\frac{\vec{r}_{13}\cdot\vec{r}_{23}}{r_{13}^3}\rangle$	$0.046\,478\,421$
δg	$-0.510\,551\,028(1)$
g_e	$2.002\,319\,304$
g_{Ps^-}	$2.002\,292\,117(3)$

V. SUMMARY

We have presented an approach to derive an effective Hamiltonian that governs the dynamics of the whole bound system from individual Hamiltonians of its ingredients, including leading relativistic corrections. This approach is based on our two former works [2, 3], and in comparison to them it is much simpler. We derived a formula for the charge radius, which can be used for systems such as nuclei. Besides the known terms, it includes new terms which until now have not been taken into account in the calculation of nuclear charge radii. Similarly, the electric dipole polarizability includes corrections to the electric dipole moment δD that have been omitted in all previous calculations of the nuclear polarizability. The obtained formula for the magnetic moment is in agreement with that obtained previously [1, 3, 8] and we improve the result published recently for the positronium ion [10]. The presented approach can also be used for nuclei, to calculate their electromagnetic moment, but this requires incorporation of strong interactions via the chiral perturbation theory. It is especially important in view of very accurate results for nuclear charge radii differences between isotopes obtained from atomic spectroscopy [7, 11].

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