Equation of motion for a bound system of charged particles

Krzysztof Pachucki [1] and Vladimir A. Yerokhin [2]

[1]*Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland*
[2]*Center for Advanced Studies, Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29, St. Petersburg 195251, Russia*

We consider a bound system of charged particles moving in an external electromagnetic field, including leading relativistic corrections. The difference from the point particle with a magnetic moment comes from the presence of polarizabilities. Due to the lack of separation of the total momentum from the internal degrees of freedom, the notion of polarizability of the bound state immersed in the continuum spectrum of the global motion is nontrivial. We introduce a bound-continuum perturbation theory and obtain a complete formula for the equation of motion for a polarizable bound system, such as atom, ion, or the nucleus. This formula may find applications when high precision is sought and small effects due polarizabilities are important.

I. INTRODUCTION

Let us consider a set of charged particles forming a bound system, like an atom, an ion, or a molecule. 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 causes the appearance of additional corrections to the electromagnetic moments and polarizabilities. A typical problem is the magnetic moment of the bound system, for which the first complete description was presented by Hegstrom in [1]. Here we rederive several results obtained in earlier works and obtain the complete $1/M$ corrections to known polarizabilities. Moreover, we derive polarizabilities that involve an additional field derivative and depend on a spin. Results are summarized in terms of a general Hamiltonian equation (45) and equations of motion (52) and (53), which include all the leading relativistic corrections. These results may find application when high precision is sought. For example, as has already been noticed by Thompson *et al.* [2], the cyclotron frequency is slightly changed due to the electric dipole polarizability, and this shift is actually measurable. What has not yet been noticed is that the coupling of the spin to the static electromagnetic field through spin dependent polarizabilities shifts the Larmor frequency, although this effect is presently below the experimental accuracy [3]. Perhaps the most important application will be for calculations of nuclear polarizabilities, which play a significant role in muonic atoms.

II. BOUND-CONTINUUM PERTURBATIVE APPROACH TO SEPARATION OF THE CENTER-OF-MASS MOTION

In the first step we shall present a perturbative scheme for a bound system immersed in the continuum spectrum of global motion, when internal and external degrees of freedom are coupled together due to the presence of an electromagnetic field. To the best of our knowledge, it was first introduced in Ref. [4], and here we develop it further. We assume that the

Hamiltonian H for a system of particles can be decomposed as

$$H = H_S + H_P, \tag{1}$$

where H_S is the Hamiltonian that involves only internal degrees of freedom and does not depend on an external electromagnetic field. H_P is the remainder, in which all dependence on the external field is placed.

When an atom or an ion moves in the external electromagnetic field, the internal degrees of freedom affect the center-of-mass motion and the spin precession. We here assume that the coupling of internal to global degrees of freedom is weak and does not affect significantly the internal state and the motion. In this case, the effects due to this coupling can be described perturbatively. In the following we formulate a systematic perturbative approach to account for all these effects. For this we assume that in the leading order our system is in the specified internal state ψ_S with the binding energy E_S

$$H_S \psi_S = E_S \psi_S. \tag{2}$$

The initial wave function ψ_Π describing the global motion of the system can be obtained as

$$\psi_\Pi = \langle \psi_S | \psi \rangle_S, \tag{3}$$

where $\langle \ldots \rangle_S$ denotes the matrix element in the subspace of internal degrees of freedom, and hence ψ_Π depends only on the global degrees of freedom. Let us note that the wave function ψ_Π is redefined in Eq. (14) to account for modifications of the internal state due to external perturbations. The total wave function can thus be decomposed as

$$\psi = \psi_S \psi_\Pi + \delta\psi. \tag{4}$$

Let us introduce a projection operator $P_\perp = I - |\psi_S\rangle\langle\psi_S|$; then

$$P_\perp \psi = \delta\psi. \tag{5}$$

The Schrödinger equation for the whole system is

$$i\frac{\partial \psi}{\partial t} = (H_S - E_S + H_P)\,\psi, \tag{6}$$

where the binding energy E_S was subtracted from the time dependence. Let us project the Schrödinger equation (2) into ψ_S and use Eq. (4):

$$\left(i\frac{\partial}{\partial t} - \langle\psi_S|H_P|\psi_S\rangle\right)\psi_\Pi = \langle\psi_S|H_P|\delta\psi\rangle_S. \tag{7}$$

$\delta\psi$ in the right-hand side is to be determined perturbatively as follows. One projects the Schrödinger equation (6) into the subspace orthogonal to ψ_S with $P_\perp$

$$i\frac{\partial}{\partial t}\delta\psi = P_\perp(H_S - E_S + H_P)(\psi_S\,\psi_\Pi + \delta\psi), \tag{8}$$

and solves the resulting equation, assuming $H_S - E_S$ is large in comparison to H_P; then

$$\delta\psi = \frac{1}{(E_S - H_S)'}\left[H_P\,\psi_S\,\psi_\Pi - \left(i\frac{\partial}{\partial t} - H_P\right)\delta\psi\right]. \tag{9}$$

Another convenient form of the solution is

$$\delta\psi = \frac{1}{\left[(E_S - H_S)' + P_\perp\left(i\frac{\partial}{\partial t} - H_P\right)P_\perp\right]}H_P\,\psi_S\,\psi_\Pi. \tag{10}$$

The replacement of Eq. (10) into Eq. (7) gives

$$\left\{i\frac{\partial}{\partial t} - \langle\psi_S|H_P|\psi_S\rangle - \langle\psi_S|H_P\frac{1}{\left[(E_S - H_S)' + P_\perp\left(i\frac{\partial}{\partial t} - H_P\right)P_\perp\right]}H_P|\psi_S\rangle\right\}\psi_\Pi = 0. \tag{11}$$

Up to this point, our considerations have been exact, with no approximations involved. We now introduce a perturbative expansion, assuming the second term in the denominator to be small as compared to the first one to obtain

$$\left\{i\frac{\partial}{\partial t} - \langle H_P\rangle_S - \langle\psi_S|H_P\frac{1}{(E_S - H_S)'}H_P + H_P\frac{1}{(E_S - H_S)'}\left(H_P - i\frac{\partial}{\partial t}\right)\frac{1}{(E_S - H_S)'}H_P + \cdots|\psi_S\rangle\right\}\psi_\Pi = 0. \tag{12}$$

The neglected terms denoted by dots include higher powers in the derivatives over time. They are of the order of the ratio of the external field frequency to the excitation energy of the internal state, which we assume to be small. Other neglected terms involve the ratio of the spatial field derivatives over the mass M and terms involving three powers of the external field, they are also assumed to be small. The above equation, neglecting these higher-order terms, is now transformed as follows:

$$\langle\psi_S|H_P\frac{\left(i\frac{\partial}{\partial t} - \langle H_P\rangle_S\right)}{[(E_S - H_S)']^2}H_P|\psi_S\rangle = \frac{1}{2}\left\{\langle\psi_S|H_P\frac{1}{[(E_S - H_S)']^2}H_P|\psi_S\rangle, \left(i\frac{\partial}{\partial t} - \langle H_P\rangle_S\right)\right\} + \frac{1}{2}\langle\psi_S|\left[H_P, i\frac{\partial}{\partial t} - \langle H_P\rangle_S\right]$$

$$\times \frac{1}{[(E_S - H_S)']^2}H_P|\psi_S\rangle + \frac{1}{2}\langle\psi_S|H_P\frac{1}{[(E_S - H_S)']^2}\left[i\frac{\partial}{\partial t} - \langle H_P\rangle_S, H_P\right]|\psi_S\rangle. \tag{13}$$

The first term in the above can be eliminated by the redefinition ψ_Π, namely $\psi_\Pi = e^\lambda\,\tilde{\psi}_\Pi$, with

$$\lambda = -\frac{1}{2}\langle\psi_S|H_P\frac{1}{[(E_S - H_S)']^2}H_P|\psi_S\rangle. \tag{14}$$

This brings the equation of motion to the more familiar form

$$\left(i\frac{\partial}{\partial t} - H_\Pi\right)\tilde{\psi}_\Pi = 0, \tag{15}$$

with

$$H_\Pi = \langle\psi_S|H_P + H_P\frac{1}{(E_S - H_S)'}H_P + H_P\frac{1}{(E_S - H_S)'}(H_P - \langle H_P\rangle_S)\frac{1}{(E_S - H_S)'}H_P$$

$$- \frac{1}{2}\left[H_P, i\frac{\partial}{\partial t} - \langle H_P\rangle_S\right]\frac{1}{[(E_S - H_S)']^2}H_P - \frac{1}{2}H_P\frac{1}{[(E_S - H_S)']^2}\left[i\frac{\partial}{\partial t} - \langle H_P\rangle_S, H_P\right]|\psi_S\rangle. \tag{16}$$

This is the general equation valid for a wide range of bound systems immersed into slowly varying external fields, including nuclei. Let us now consider a simple case of the nonrelativistic bound system of charged particles

$$H_S = \sum_a \frac{\vec{q}_a^2}{2\,m_a} + \sum_{a>b,b}\frac{e_a\,e_b}{4\,\pi\,r_{ab}}, \tag{17}$$

$$H_P = \frac{\vec{\Pi}^2}{2\,M} + e\,A^0 - \vec{d}\cdot\vec{E}'. \tag{18}$$

where $\vec{d}$ is the dipole moment operator, $\vec{E}'$ is the electric field as seen by the moving bound system

$$\vec{E}' = \vec{E} + \left(\frac{\vec{\Pi}}{M} \times \vec{B}\right)_{\mathrm{sym}}, \tag{19}$$

and where

$$(\vec{\Pi} \times \vec{B})^i_{\mathrm{sym}} = \tfrac{1}{2}\,\epsilon^{ijk}\,\{\Pi^j, B^k\}. \tag{20}$$

With these nonrelativistic H_S and H_P Hamiltonians, H_Π takes the following form:

$$H_\Pi = \frac{\vec{\Pi}^2}{2M} + e\,A^0 + E'^i\,E'^j\,\langle\psi_S|d^i\,\frac{1}{(E_S - H_S)'}\,d^j|\psi_S\rangle$$

$$+ \frac{1}{2}\left\{\left[E^i, -i\frac{\partial}{\partial t} + \frac{\Pi^2}{2M}\right]E^j + E^i\left[-i\frac{\partial}{\partial t} + \frac{\Pi^2}{2M}, E^j\right]\right\}\langle\psi_S|d^i\,\frac{1}{[(E_S - H_S)']^2}\,d^j|\psi_S\rangle \tag{21}$$

$$= \frac{\vec{\Pi}^2}{2M} + e\,A^0 + \frac{1}{2}\left[\{E'^i, E'^j\} + \frac{i\,\epsilon^{ijk}}{M}\,B^l\,E^l_{,k}\right]\langle\psi_S|d^i\,\frac{1}{E_S - H_S}\,d^j|\psi_S\rangle$$

$$+ \frac{1}{2}\left[\frac{1}{M}\,E^i_{,k}\,E^j_{,k} + i\,(\dot{E}^i E^j - E^i \dot{E}^j) + \frac{1}{2M}\,(E^i \Pi^2 E^j - E^j \Pi^2 E^i)\right]\langle\psi_S|d^i\,\frac{1}{[E_S - H_S]^2}\,d^j|\psi_S\rangle. \tag{22}$$

The antisymmetric in the i, j part corresponds to the vector polarizability and leads to an additional spin precession.

In the second example we add to H_P the following term:

$$\delta H_P = i\,\vec{\Pi}\,[\vec{t}, H_S], \tag{23}$$

with some arbitrary Hermitian operator $\vec{t}$. Such a term appears after separation of the center-of-mass motion for the bound system of relativistic particles [5], and we demonstrate here how to deal with it. The resulting correction to H_Π is

$$\delta H_\Pi = \langle\psi_S|H_P\,\frac{1}{(E_S - H_S)'}\,\delta H_P + H_P\,\frac{1}{[(E_S - H_S)']^2}\left[e\,A^0 + \frac{\Pi^2}{2M} - i\frac{\partial}{\partial t}, \delta H_P\right]|\psi_S\rangle$$

$$+ \langle\psi_S|\delta H_P\,\frac{1}{(E_S - H_S)'}\,H_P + \left[\delta H_P, e\,A^0 + \frac{\Pi^2}{2M} - i\frac{\partial}{\partial t}\right]\frac{1}{[(E_S - H_S)']^2}\,H_P|\psi_S\rangle. \tag{24}$$

The commutator in the above is

$$\left[e\,A^0 + \frac{\Pi^2}{2M} - i\frac{\partial}{\partial t}, i\,\vec{t}\,\vec{\Pi}\right] = \left(\vec{E} + \frac{\vec{\Pi}}{M} \times \vec{B}\right)_{\mathrm{sym}}\vec{t} = \vec{E}'\,\vec{t} \tag{25}$$

and δH_Π becomes

$$\delta H_\Pi = \langle i[\vec{d}\,\vec{E}', \vec{t}\,\vec{\Pi}]\rangle + \langle\psi_S|\vec{d}\,\vec{E}'\,\frac{1}{(E_S - H_S)'}\,\vec{t}\,\vec{E}'|\psi_S\rangle + \langle\psi_S|\vec{t}\,\vec{E}'\,\frac{1}{(E_S - H_S)'}\,\vec{d}\,\vec{E}'|\psi_S\rangle. \tag{26}$$

Alternatively, this result can be obtained by a unitary transformation of the original Hamiltonian, as follows:

$$H' = e^{-i\phi}\,H\,e^{i\phi} + \partial_t\phi = H + i\,[H - i\,\partial_t, \phi], \tag{27}$$

with

$$\phi = -\vec{t}\,\vec{\Pi}. \tag{28}$$

The resulting new Hamiltonian

$$H' = H_S - E_S + H_P - \vec{t}\,\vec{E}' + i[\vec{d}\,\vec{E}', \vec{t}\,\vec{\Pi}] \tag{29}$$

leads to the same H_Π, although in a much more straightforward way. This demonstrates the internal consistency of the bound-continuum perturbative formalism. In the next section we apply it to the most general Hamiltonian of a bound system and derive formulas for polarizabilities.

III. HAMILTONIAN FOR A BOUND SYSTEM INTERACTING WITH AN ELECTROMAGNETIC FIELD

Let us assume that the electric and magnetic potentials have linear and quadratic components, and the field strengths are time independent. The general Hamiltonian was derived from the first principles in Refs. [4,5] by a sequence of unitary

transformations of $H = \sum_a H_a + \sum_{a>b} H_{ab}$, where H_a is a one particle Hamiltonian with relativistic corrections and H_{ab} is a two-body Hamiltonian with Coulomb interactions and relativistic corrections,

$$
H = H_S + \frac{\vec{\Pi}^2}{2M}\left(1 - \frac{H_S}{M}\right) - \frac{\Pi^4}{8M^3} + eA^0 - (\vec{d} + \delta\vec{d})\cdot\vec{E} - \vec{d}\cdot\left(\frac{\vec{\Pi}}{M}\times\vec{B}\right)_{\text{sym}} - \frac{1}{2}(d^{ij} + \delta d^{ij})E^i_{,j} - \frac{1}{2}\mu^{ij}B^j_{,i}
$$

$$
- (\vec{\mu} + \delta\vec{\mu})\cdot\vec{B} + \left(\vec{\mu} - \frac{e}{2M}\vec{S}\right)\left(\frac{\vec{\Pi}}{M}\times\vec{E}\right)_{\text{sym}} + \frac{3}{8M}(\vec{d}\times\vec{B})^2 + \frac{1}{8}B^iB^j(\delta^{ij}d'^{kk} - d'^{ij}) - \frac{e}{2M}E^iE^jd^{ij}, \quad (30)
$$

where $E^i_{,j} = \partial E^i/\partial R^j$, and we have introduced the following global variables: the center of mass $\vec{R}$ and the total momentum $\vec{\Pi}$

$$
\vec{R} = \sum_a \frac{m_a}{M}\vec{r}_a, \quad (31)
$$

$$
\vec{\Pi} = \sum_a [\vec{p}_a - e_a\vec{A}(\vec{R})] = \vec{P} - e\vec{A}(\vec{R}), \quad (32)
$$

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

$$
\vec{x}_a = \vec{r}_a - \vec{R}, \quad (33)
$$

$$
\vec{q}_a = \vec{p}_a - \frac{m_a}{M}\vec{P}, \quad (34)
$$

such that

$$
[x^i_a, q^j_b] = i\,\delta^{ij}\left(\delta_{ab} - \frac{m_b}{M}\right), \quad (35)
$$

$$
[R^i, P^j] = i\,\delta^{ij}, \quad (36)
$$

$$
[x^i_a, P^j] = [R^i, q^j_a] = 0. \quad (37)
$$

The above Hamiltonian includes the following electromagnetic moments:

$$
\mu^i = \sum_a \frac{e_a}{2m_a}(l^i_a + g_a s^i_a), \quad (38)
$$

$$
\mu^{ij} = \sum_a \frac{e_a}{m_a}\left[g_a x^i_a s^i_a + \frac{1}{3}(l^j_a x^i_a + x^i_a l^j_a)\right], \quad (39)
$$

$$
S^i = \sum_a l^i_a + s^i_a, \quad (40)
$$

$$
d^i = \sum_a e_a x^i_a, \quad (41)
$$

$$
d^{ij} = \sum_a e_a x^i_a x^j_a, \quad (42)
$$

$$
d'^{ij} = \sum_a \frac{e^2_a}{m_a}x^i_a x^j_a, \quad (43)
$$

and relativistic corrections to them [4]

$$
\delta\vec{d} = -\frac{e}{2M}\sum_a\left(\frac{q^j_a \vec{x}_a q^j_a}{m_a} + \sum_{b\neq a}\frac{e_a e_b}{4\pi}\frac{\vec{x}_a}{r_{ab}}\right). \quad (44)
$$

$\delta\vec{\mu}$ is given in Refs. [1,4] and we neglect δd^{ij} the relativistic correction to the electric quadrupole operator. Moreover, the electromagnetic fields in Eq. (30) and below are at the mass center $\vec{R}$.

Using the bound-continuum perturbative approach, namely Eq. (16), H in Eq. (30) gives the following effective Hamiltonian H_Π for the motion in the external static electromagnetic field:

$$
H_\Pi = eA^0 + \frac{\Pi^2}{2M} - \frac{\Pi^4}{8M^3} - \frac{eg}{2M}\vec{S}\cdot\vec{B}
$$

$$
+ \frac{e(g-1)}{2M^2}\vec{S}\cdot\vec{\Pi}\times\vec{E} - \frac{Q}{6}(S^i S^j)^{(2)}E^i_{,j}
$$

$$
- \frac{\alpha^{ij}_E}{4}\{E'^i, E'^j\} - \frac{\alpha^{ij}_M}{2}B^i B^j
$$

$$
- \frac{\alpha^{ijk}_{VM}}{4}B^i(E^j_{,k} + E^k_{,j}) - \frac{\alpha^{ijk}_{VE}}{4}E^i(B^j_{,k} + B^k_{,j}), \quad (45)
$$

where the mass M of the system includes now the total binding energy, the g factor is defined by

$$
\langle\vec{\mu}\rangle \equiv \frac{e}{2M}g\vec{S}, \quad (46)
$$

the quadrupole moment Q is

$$
\langle 3d^{ij} - d^{kk}\delta^{ij}\rangle = Q(S^i S^j)^{(2)}, \quad (47)
$$

and where

$$
\alpha^{ij}_E = 2\left\langle(d^i + \delta d^i)\frac{1}{H_S - E_S}(d^j + \delta d^j)\right\rangle + \frac{e}{M}\langle d^{ij}\rangle, \quad (48)
$$

$$
\alpha^{ij}_M = 2\left\langle\mu^i\frac{1}{H_S - E_S}\mu^j\right\rangle - \frac{3}{4M}\langle\vec{d}^2\delta^{ij} - d^i d^j\rangle
$$

$$
- \frac{1}{4}\langle d'^{kk}\delta^{ij} - d'^{ij}\rangle, \quad (49)
$$

$$
\alpha^{ijk}_{VM} = -i\frac{\delta^{ij}}{M}\epsilon^{mnk}\left\langle d^m\frac{1}{H_S - E_S}d^n\right\rangle
$$

$$
+ \left\langle\mu^i\frac{1}{H_S - E_S}d^{jk} + \text{H.c.}\right\rangle, \quad (50)
$$

$$
\alpha^{ijk}_{VE} = \left\langle d^i\frac{1}{H_S - E_S}\mu^{jk} + \text{H.c.}\right\rangle, \quad (51)
$$

and we neglect the electric quadrupole polarizability. The first part of the Hamiltonian in Eq. (45) is very much unique, the coupling of spin to the electromagnetic field is fully described by a BMT equation [6], and the result obtained here is in agreement with the small momentum expansion of this equation. The second part of H_Π involves intrinsic polarizabilities, which solely depend on the internal Hamiltonian H_S.

IV. APPLICATIONS

The resulting equations of motion are

$$
\frac{d\vec{\Pi}}{dt} = i[H_\Pi, \vec{\Pi}] + \frac{\partial\vec{\Pi}}{\partial t}, \quad (52)
$$

$$\frac{d\vec{S}}{dt} = i\,[H_\Pi,\ \vec{S}]. \tag{53}$$

The first observation is the presence of the spin-dependent force in the homogeneous electromagnetic field, namely

$$\vec{F} = -\frac{e^2\,(g-1)}{2\,M^2}\,\vec{B} \times (\vec{E} \times \vec{S}). \tag{54}$$

Being suppressed by $\mu\,B/M$ with respect to the Lorentz force, it is a very small force and we are not aware of any experiment that demonstrates its presence.

The case of a charged particle in a Penning trap has been analyzed in detail in Ref. [7], but without polarizabilities. The interesting effect due to the scalar electric dipole polarizability, which has already been observed [2], is the shift of the cyclotron frequency ω_C. Let us assume a nonrelativistic spinless system, for which the Hamiltonian is

$$H_\Pi = e\,A^0 + \frac{\Pi^2}{2\,M} - \frac{\alpha_E}{2}\,\vec{E}' \cdot \vec{E}'. \tag{55}$$

In a classical picture the ion stays in the region where $\vec{E}$ vanishes in the minimum of the electromagnetic (axially symmetric) potential A^0, so

$$\begin{aligned}
H_\Pi &= \frac{\Pi^2}{2\,M} - \frac{\alpha_E}{2\,M^2}\,(\vec{\Pi} \times \vec{B})^2 \\
&= \frac{P_z^2}{2\,M} + \frac{\Pi_x^2 + \Pi_y^2}{2\,M}\left(1 - \frac{\alpha_E\,B^2}{2\,M^2}\right) \\
&= \frac{P_z^2}{2\,M} + \frac{\Pi_x^2 + \Pi_y^2}{2\,M_\perp},
\end{aligned} \tag{56}$$

where $M_\perp = M + \alpha_E\,B^2/(2\,M)$. As a result, the cyclotron frequency $\omega_C = e\,B/M_\perp$ is slightly shifted by the polarizability α_E [2].

The magnetic polarizability is usually calculated neglecting $1/M$ corrections because it is very small. Nonetheless we will derive the closed formula for the leading recoil correction, because it affects the accurate determination of the refractive index of He [8]. Our result for the scalar magnetic polarizability

$$\alpha_M = \frac{2}{3}\left\langle \mu^i\,\frac{1}{H-E}\,\mu^i \right\rangle - \frac{\langle d^i\,d^i \rangle}{2\,M} - \frac{\langle d''^i \rangle}{6} \tag{57}$$

includes $1/M$ effects exactly. After expanding this formula in the electron-nuclear mass ratio, one obtains

$$\alpha_M = -\frac{e^2}{6\,m}\left\langle \sum_a \vec{r}_a^2 \right\rangle - \frac{e^2}{6\,M}\sum_{a,b}\langle \vec{r}_a\,\vec{r}_b \rangle + O\!\left(\frac{m}{M}\right)^2, \tag{58}$$

in agreement with Ref. [9] for the particular case of the helium atom.

Coming back to the Penning trap, the vector polarizability α_{VM} in Eq. (50) depends on the spin, and thus contributes to the Larmor frequency. This frequency is accurately measured in the determination of the bound electron g factor, where ion is placed [10] in the homogeneous magnetic field $\vec{B} = (0, 0, B)$ and the quadrupole electric field

$$e\,A^0 = U_0\left(z^2 - \frac{x^2 + y^2}{2}\right), \tag{59}$$

where $e < 0$ is the electron charge. For an ion with a spinless nucleus the corresponding shift of an energy level is

$$\delta E_{VM} = \left\langle \vec{\mu} \cdot \vec{B}\,\frac{1}{E-H}\,\frac{1}{2}\,d^{ij}\,E^i_{,j} \right\rangle + \text{H.c.} \tag{60}$$

This correction may get an enhancement if there is an excited state with a small energy difference from the reference state. This is the case for boronlike ions, where the first excited $2P_{3/2}$ state is close to the ground $2P_{1/2}$ state, specifically, for boronlike argon Ar^{13+} measured in Ref. [3] at the 10^{-9} accuracy level.

We calculate this effect as described in the Appendix, representing the corresponding correction to the g factor as

$$\delta g_{VM} = 2\,U_0\,\mathcal{R}, \tag{61}$$

where U_0 is the parameter of the quadrupole electric field in the trap (59) and $\mathcal{R}$ is the atomic part. The parameter U_0 can be expressed in terms of the measured axial frequency ν_z of the ion in the trap

$$U_0 = \frac{1}{2\,Q}\,\frac{M}{m}\,\frac{(2\,\pi\,\hbar\,\nu_z)^2}{(m\,c^2)^2}, \tag{62}$$

where Q is the charge number of the ion, M is the ion mass, and m is the electron mass.

The obtained result for the ground $2P_{1/2}$ state of $^{197}Ar^{13+}$ is

$$\delta g_{VM} = 1.7 \times 10^{-17}, \tag{63}$$

which is much below the present experimental accuracy [3]. It is interesting that the effect is strongly Z dependent and increases for smaller Z. For example, for boronlike carbon it is about four orders of magnitude larger (see the Appendix) but still too small to be of experimental interest at present.

The last example is the relativistic correction to the electric dipole polarizability for a system with nonvanishing charge. The neutral case $e = 0$ has been investigated in detail, in particular for the helium atom [8], for which all relativistic corrections to the electric dipole polarizability come from the internal Hamiltonian, and there are no corrections to the electric dipole moment operator. However, in the case $e \neq 0$ there are additional corrections, specifically

$$\delta\alpha_E = \frac{4}{3}\left\langle \vec{d}\,\frac{1}{H-E}\,\delta\vec{d} \right\rangle + \frac{e}{3\,M}\left\langle \sum_a e_a x_a^2 \right\rangle, \tag{64}$$

where $\vec{d}$ is the electric dipole operator with respect to the mass center, $\delta\vec{d}$ is defined in Eq. (44), and the last term can be interpreted as the mean-square charge radius. $\delta\alpha_E$ is a small correction in the case of ions, but it can be significant in the case of nuclei. Because this formula has been obtained for purely electromagnetic systems, it may not be valid for a nucleus, but it indicates the existence of corrections to polarizabilities, which come from the separation of internal and global degrees of freedom. Such corrections may play a role in muonic atoms, where significant discrepancies have been observed [11], particularly for the hyperfine splitting [12].

V. SUMMARY

In this work we have formulated a perturbation theory that allows the systematic derivation of the properties of a bound charged system in the external electromagnetic field. It is found that for slowly changing electromagnetic fields, the perturbation theory provides the equation of motion for a point particle with magnetic dipole and electric quadrupole moments, and additionally includes different types of polarizabilities. It is an obvious fact, but it has not yet been shown with including relativistic corrections. We have derived formulas for dipole polarizabilities including finite nuclear mass effects and new types of polarizabilities, which include one more derivative in the electromagnetic field. Several examples demonstrate the potential applications of the derived formulas.

APPENDIX: CORRECTION TO THE ATOMIC g FACTOR DUE TO QUADRUPOLE ELECTRIC FIELD

In this section, we perform a relativistic calculation of the correction to the g factor induced by the quadrupole electric field in the Penning trap. Within the independent-electron approximation, the leading contribution to the g factor of an alkali-metal-like atom (one electron v beyond the closed shells) is given by

$$
\begin{aligned}
g &= \frac{1}{\mu_0 B_z \mu_v} \delta E \\
&= \frac{1}{\mu_0 B_z \mu_v} \langle v | (-e/2) B_z [\vec{r} \times \vec{\alpha}]_z | v \rangle \\
&= \langle v | \frac{1}{\mu_v} [\vec{r} \times \vec{\alpha}]_z | v \rangle,
\end{aligned}
\tag{A1}
$$

where $\mu_0 = |e|/2$ is the Bohr magneton, $e < 0$ is the electric charge, B is assumed to be directed along the z axis, and μ_v is the momentum projection of the valence state v.

The electrostatic quadrupole potential in the Penning trap is [10]

$$
e \Phi(r) = U_0 \left(z^2 - \frac{x^2 + y^2}{2} \right) = U_0 \sqrt{\frac{4\pi}{5}} r^2 Y_{20}(\vec{r}), \quad (A2)
$$

where Y_{lm} is the spherical harmonics. The correction to the g factor due to Φ appears as a second-order perturbative correction. Fixing the momentum projection of the valence state as $\mu_v = 1/2$, we obtain

$$
\delta g = 2 U_0 \sum_{n \neq v} \frac{1}{\varepsilon_v - \varepsilon_n} \langle v \, 1/2 | 2 \, [\vec{r} \times \vec{\alpha}]_z | n \, 1/2 \rangle
$$
$$
\times \langle n \, 1/2 | \sqrt{\frac{4\pi}{5}} r^2 Y_{20}(\vec{r}) | v \, 1/2 \rangle.
\tag{A3}
$$

This correction is enhanced for B-like ions because of large mixing between the $2p_{1/2}$ and $2p_{3/2}$ states. In this case, we

keep only the term with the smallest denominator in the sum over n, obtaining

$$
\delta g = 2 U_0 \frac{1}{\varepsilon_v - \varepsilon_{v'}} \langle v \, 1/2 | 2 \, [\vec{r} \times \vec{\alpha}]_z | v' \, 1/2 \rangle
$$
$$
\times \langle v' \, 1/2 | \sqrt{\frac{4\pi}{5}} r^2 Y_{20}(\vec{r}) | v \, 1/2 \rangle,
\tag{A4}
$$

where $v = 2p_{1/2}$ and $v' = 2p_{3/2}$. Performing angular integrations, we get

$$
\mathcal{R} \equiv \langle v \, 1/2 | 2 \, [\vec{r} \times \vec{\alpha}]_z | v' \, 1/2 \rangle \, \langle v' \, 1/2 | \sqrt{\frac{4\pi}{5}} r^2 Y_{20}(\vec{r}) | v \, 1/2 \rangle
$$
$$
= -\frac{4}{15} \left[\int_0^\infty dr \, r^3 \, (g_v f_{v'} + f_v g_{v'}) \right]
$$
$$
\times \left[\int_0^\infty dr \, r^4 \, (g_v g_{v'} + f_v f_{v'}) \right].
\tag{A5}
$$

With the hydrogenic wave functions, we obtain

$$
\mathcal{R} = \frac{8}{(Z\alpha)^2} - \frac{47}{10} + O((Z\alpha)^2)
\tag{A6}
$$

and

$$
\delta g = 2 U_0 \left[-\frac{256}{(Z\alpha)^6} + \frac{1552}{5(Z\alpha)^4} + \cdots \right].
\tag{A7}
$$

We present more accurate results for two specific cases of B-like argon and carbon. Calculating radial integrals with wave functions obtained with the localized Dirac-Fock potential, we get $\mathcal{R} = 615 \pm 8\%$ for argon and $\mathcal{R} = 1.3 \times 10^4 \pm 60\%$ for carbon, where the uncertainty estimates the residual electron-correlation effects. Using the experimental values of the $2p_{3/2} - 2p_{1/2}$ energy splitting (0.206 458 Ry for argon and 0.000 578 Ry for carbon), we arrive at (in relativistic units)

$$
\delta g(\mathrm{Ar}^{13+}) = 2 U_0 \, [-1.12 \times 10^8] \pm 8\%,
\tag{A8}
$$

$$
\delta g(\mathrm{C}^+) = 2 U_0 \, [-8.7 \times 10^{11}] \pm 60\%.
\tag{A9}
$$

The parameter U_0 characterizes the trapping potential and is specific for each experiment. We obtain the value of U_0 in the experiment on B-like argon [10] from the reported value of the axial frequency ν_z of the ion in the trap as

$$
U_0 = \frac{M}{2 Q} (2 \pi \nu_z)^2,
\tag{A10}
$$

where Q is the charge number of the ion. Since all the calculations have been performed with the electron mass $m = 1$, it should be converted to dimensionless units as follows:

$$
U_0 = \frac{1}{2 Q} \frac{M}{m} \frac{(2 \pi \hbar \nu_z)^2}{(m c^2)^2}.
\tag{A11}
$$

Using physical constants

$$
\hbar = 6.582 \times 10^{-16} \text{ eV s},
\tag{A12}
$$

$$
m c^2 = 0.511 \times 10^6 \text{ eV},
\tag{A13}
$$

parameters of the ion $Q = 13$, $M/m = 72833.97$, and the measured axial frequency [3] $\nu_z = 650$ kHz, we arrive at

$$
U_0(^{40}\mathrm{Ar}^{13+}) = 7.752 \times 10^{-26}.
\tag{A14}
$$

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