Electrodynamics of a compound system with relativistic corrections

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The electromagnetic interaction of a moving compound charged system with leading relativistic corrections is studied. An effective Hamiltonian is obtained by using a set of canonical transformations, and it is demonstrated that the coupling of the total motion to internal degrees of freedom is uniquely determined by Lorentz covariance. Several known results such as the Röntgen term and the interaction of the spin with the electric field are recovered, and new results for various relativistic and recoil corrections are obtained.

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In this paper we consider a system of N particles interacting electromagnetically. Each particle is characterized by mass m, charge e, spin $\vec{s}$, magnetic moment $\vec{\mu}=eg\vec{s}/(2m)$, and charge radius $\langle r^2\rangle$. We aim to derive an effective Hamiltonian of the compound system, starting from the Hamiltonians of the individual particles with their mutual interactions, including the electromagnetic field. This effective Hamiltonian will depend on global operators, such as total momentum, spin, on the electromagnetic field at the mass center, including its derivatives, and on internal degrees of freedom. The nonrelativistic Hamiltonian for a compound system has already been treated in the literature, for example, in [1,2]. It is known that the electric dipole coupling acquires a correction, the so called Röntgen term when the system moves [3,4]. Similarly, a spin of the moving body couples to the electric field [5] as a result of the Lorentz boost. In this work we rederive these known results and obtain an effective Hamiltonian including the leading relativistic correction. In order to carry out this derivation we assume that the electromagnetic field slowly changes within the dimension of the system, and perform a set of canonical transformations to decouple the total momentum from internal degrees of freedom as much as possible. It will be shown that most of the terms are determined by Lorentz covariance and gauge symmetry, and we therefore expect that this Hamiltonian should be valid also for nonelectromagnetically bound systems such as nuclei.

The initial Hamiltonian is a sum of one-particle terms H_a and two-particle interactions H_{ab} including relativistic corrections [6,7] (using natural units $\hbar=c=1$)

$$H=\sum_a H_a+\sum_{a>b} H_{ab}, \tag{1}$$

$$H_a=\frac{\vec{\pi}_a^2}{2m_a}+e_aA_a^0-\frac{e_a}{2m_a}g_a\vec{s}_a\cdot\vec{B}_a-\frac{e_a}{4m_a^2}(g_a-1)\times\vec{s}_a\cdot(\vec{E}_a\times\vec{\pi}_a-\vec{\pi}_a\times\vec{E}_a)-\frac{\vec{\pi}_a^4}{8m_a^3}-\frac{e_a}{6}\langle r_a^2\rangle\nabla\cdot\vec{E}_a, \tag{2}$$

$$\begin{aligned}H_{ab}=\frac{e_ae_b}{4\pi}\Bigg\{&\frac{1}{r_{ab}}-\frac{1}{2m_am_b}\pi_a^i\left(\frac{\delta^{ij}}{r_{ab}}+\frac{r_{ab}^ir_{ab}^j}{r_{ab}^3}\right)\pi_b^j\\&-\frac{2\pi}{3}\langle r_a^2+r_b^2\rangle\delta^3(r_{ab})+\frac{1}{2r_{ab}^3}\bigg[\frac{g_a}{m_am_b}\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_b\\&-\frac{g_b}{m_am_b}\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_a+\frac{(g_b-1)}{m_b^2}\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_b\\&-\frac{(g_a-1)}{m_a^2}\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_a\bigg]-\frac{2\pi g_ag_b}{3m_am_b}\delta^3(r_{ab})\vec{s}_a\cdot\vec{s}_b\\&+\frac{g_ag_b}{4m_am_b}\frac{s_a^is_b^j}{r_{ab}^3}\left(\delta^{ij}-\frac{3r_{ab}^ir_{ab}^j}{r_{ab}^2}\right)\Bigg\},\end{aligned} \tag{3}$$

where $\vec{\pi}=\vec{p}-eA(\vec{r})$ and $\langle r_a^2\rangle$ includes for convenience the Darwin term. We now introduce global variables, the center of mass $\vec{R}$ and the total momentum $\vec{\Pi}$ with $M=\Sigma_a m_a$, $e=\Sigma_a e_a$ as follows:

$$\vec{R}=\sum_a\frac{m_a}{M}\vec{r}_a, \tag{4}$$

$$\vec{\Pi}=\sum_a[\vec{p}_a-e_a\vec{A}(\vec{R})]=\vec{P}-e\vec{A}(\vec{R}), \tag{5}$$

and relative coordinates

$$\vec{x}_a=\vec{r}_a-\vec{R}, \tag{6}$$

$$\vec{q}_a=\vec{p}_a-\frac{m_a}{M}\vec{P}, \tag{7}$$

such that

$$[x_a^i,q_b^j]=i\delta^{ij}\left(\delta_{ab}-\frac{m_b}{M}\right), \tag{8}$$

$$[R^i,P^j]=i\delta^{ij}, \tag{9}$$

$$[x_a^i,P^j]=[R^i,q_a^j]=0. \tag{10}$$

We next perform a sequence of canonical transformations ϕ,

$$H' = e^{-i\phi} H e^{i\phi} + \partial_t \phi, \tag{11}$$

to transform the Hamiltonian to a form where the coupling of internal degrees of freedom to the total momentum is simplified, and can be interpreted in terms of Lorentz covariance. The first ϕ_1 is the Power-Zienau-Wooley transformation [2], which assumes that the characteristic wavelength of the electromagnetic field is larger than the size of the system

$$\phi_1 = \sum_a e_a \int_0^1 du \vec{x}_a \cdot \vec{A}(\vec{R} + u\vec{x}_a) = \sum_a e_a \left[x_a^i A^i + \frac{1}{2!} x_a^i x_a^j A^i_{,j} + \frac{1}{3!} x_1^i x_a^j x_a^k A^i_{,jk} + \cdots \right]. \tag{12}$$

The scalar potential is transformed to

$$\sum_a e_a A_a^0 + \partial_t \phi_1 = eA^0 - \sum_a e_a \left(x_a^i E^i + \frac{1}{2!} x_a^i x_a^j E^i_{,j} + \frac{1}{3!} x_a^i x_a^j x_a^k E^i_{,jk} \right) = eA^0 - D^i E^i - \frac{1}{2!} D^{ij} E^i_{,j} - \frac{1}{3!} D^{ijk} E^i_{,jk}, \tag{13}$$

where $A^0 \equiv A^0(\vec{R})$, $\vec{E} \equiv \vec{E}(\vec{R})$, similarly $\vec{B} \equiv \vec{B}(\vec{R})$, and the last equation defines the symbol D. The kinetic momentum is transformed to

$$e^{-i\phi_1} \pi_a^j e^{i\phi_1} = q_a^j + \frac{e_a}{2} (\vec{x}_a \times \vec{B})^j + \frac{e_a}{3} x_a^i x_a^k \epsilon^{jil} B^l_{,k} + \frac{m_a}{M} \left[\Pi^j + \frac{1}{2} (\vec{D} \times \vec{B})^j + \frac{1}{6} D^{ik} \epsilon^{jil} B^l_{,k} \right], \tag{14}$$

and the kinetic energy to

$$e^{-i\phi_1} \sum_a \pi_a^2 e^{i\phi_1} = \frac{\Pi^2}{2M} + \sum_a \frac{q_a^2}{2m_a} + \frac{1}{2} \left\{ \frac{\Pi^j}{M}, (\vec{D} \times \vec{B})^j + \frac{1}{2} D^{ik} \epsilon^{jil} B^l_{,k} \right\} - \sum_a \frac{e_a}{2m_a} \vec{l}_a \cdot \vec{B} - \sum_a \frac{e_a}{6m_a} (l_a^l x_a^k + x_a^k l_a^l) B^l_{,k} + \frac{3}{8M} (\vec{D} \times \vec{B})^2 + \sum_a \frac{e_a^2}{8m_a} (\vec{x}_a \times \vec{B})^2, \tag{15}$$

where $\vec{l}_a = \vec{x}_a \times \vec{q}_a$. While $\vec{l}_a$ is not an angular momentum operator, the sum $\Sigma_a \vec{l}_a$ obeys angular momentum commutation relations and can be interpreted as the total orbital angular momentum. The transformed Hamiltonian, denoted by H_1, can now be obtained by using Eqs. (4)–(7) and (13)–(15),

$$\begin{aligned} H_1 = {} & \frac{\Pi^2}{2M} + \sum_a \frac{q_a^2}{2m_a} + \frac{1}{2} \left\{ \frac{\Pi^j}{M}, (\vec{D} \times \vec{B})^j + \frac{1}{2} D^{ik} \epsilon^{jil} B^l_{,k} \right\} - \sum_a \frac{1}{8m_a^3} \left(\vec{q}_a + \frac{m_a}{M} \vec{\Pi} \right)^4 + eA^0 - D^i E^i - \frac{1}{2!} D^{ij} E^i_{,j} - \frac{1}{3!} D^{ijk} E^i_{,jk} \\ & + \frac{3}{8M} (\vec{D} \times \vec{B})^2 + \sum_a \frac{e_a^2}{8m_a} (\vec{x}_a \times \vec{B})^2 - \sum_a \frac{e_a}{2m_a} \vec{l}_a \cdot \vec{B} - \sum_a \frac{e_a}{6m_a} (l_a^l x_a^k + x_a^k l_a^l) B^l_{,k} - \sum_a \frac{e_a g_a}{2m_a} s_a^j (B^j + x_a^i B^j_{,i}) \\ & - \sum_a \frac{e_a (g_a - 1)}{4m_a^2} \left\{ \vec{s}_a \times \vec{E}, \vec{q}_a + \frac{m_a}{M} \vec{\Pi} \right\} + \sum_{a>b} \frac{e_a e_b}{4\pi} \left[\frac{1}{x_{ab}} - \frac{2\pi}{3} \langle r_a^2 + r_b^2 \rangle \delta^3(r_{ab}) - \frac{1}{2m_a m_b} \left(q_a^i + \frac{m_a}{M} \Pi^i \right) \left(\frac{\delta^{ij}}{x_{ab}} + \frac{x_{ab}^i x_{ab}^j}{x_{ab}^3} \right) \right. \\ & \times \left(q_b^j + \frac{m_b}{M} \Pi^j \right) + \frac{g_a}{2x_{ab}^3 m_a m_b} \vec{s}_a \cdot \vec{x}_{ab} \times \left(\vec{q}_b + \frac{m_b}{M} \vec{\Pi} \right) - \frac{g_b}{2x_{ab}^3 m_a m_b} \vec{s}_b \cdot \vec{x}_{ab} \times \left(\vec{q}_a + \frac{m_a}{M} \vec{\Pi} \right) \\ & \left. + \frac{(g_b - 1)}{2x_{ab}^3 m_b^2} \vec{s}_b \cdot \vec{x}_{ab} \times \left(\vec{q}_b + \frac{m_b}{M} \vec{\Pi} \right) - \frac{(g_a - 1)}{2x_{ab}^3 m_a^2} \vec{s}_a \cdot \vec{x}_{ab} \times \left(\vec{q}_a + \frac{m_a}{M} \vec{\Pi} \right) - \frac{2\pi g_a g_b}{3m_a m_b} \delta^3(x_{ab}) \vec{s}_a \cdot \vec{s}_b + \frac{g_a g_b}{4m_a m_b} \frac{s_a^i s_b^j}{x_{ab}^3} \left(\delta^{ij} - \frac{3x_{ab}^i x_{ab}^j}{x_{ab}^2} \right) \right], \end{aligned} \tag{16}$$

where all fields $\vec{A}$, $\vec{E}$, and $\vec{B}$ are at the point $\vec{R}$, and we have neglected many higher order terms, such as the $\vec{E} \times \vec{B}$ term and relativistic corrections to magnetic interactions, and left only leading relativistic corrections. Let us now consider terms involving powers of $\vec{\Pi}$. The highest power term

$$-\sum_a \frac{1}{8m_a^3} \left(\frac{m_a}{M} \vec{\Pi} \right)^4 = -\frac{\vec{\Pi}^4}{8M^3} \tag{17}$$

is the relativistic correction to the kinetic energy of the whole system. The term $\vec{\Pi}\vec{\Pi}^2$ vanishes identically because $\Sigma_a \vec{q}_a = 0$. The quadratic terms are

$$\frac{\Pi^2}{2M}-\frac{\Pi^i\Pi^j}{2M^2}\left[\sum_{a>b}\frac{e_ae_b}{4\pi}\left(\frac{\delta^{ij}}{x_{ab}}+\frac{x^i_{ab}x^j_{ab}}{x^3_{ab}}\right)+\sum_a\frac{(\delta^{ij}q_a^2+2q^i_aq^j_a)}{2m_a}\right]$$
$$=\frac{\Pi^2}{2M}\left[1-\frac{1}{M}\left(\sum_a\frac{q_a^2}{2m_a}+\sum_{a>b}\frac{e_ae_b}{4\pi x_{ab}}\right)\right]$$
$$-\frac{\Pi^i\Pi^j}{2M^2}\left[\sum_{a>b}\frac{e_ae_b}{4\pi}\frac{x^i_{ab}x^j_{ab}}{x^3_{ab}}+\sum_a\frac{q^i_aq^j_a}{m_a}\right]. \quad (18)$$

While the first term in the above has an obvious physical interpretation, with the internal energy being added to the mass of the system, the second term is eliminated by using the canonical transformation ϕ_2,

$$\phi_2=\frac{\Pi^i\Pi^j}{8M^2}\sum_a(x^i_aq^j_a+x^j_aq^i_a+q^i_ax^j_a+q^j_ax^i_a). \quad (19)$$

This transformation, according to Eq. (11) generates the contribution δ_2H, which shall be added to the total Hamiltonian of the system

$$\delta_2H=i[H_0,\phi_2]+\partial_t\phi_2$$
$$=\frac{\Pi^i\Pi^j}{2M^2}\left[\sum_{a>b}\frac{e_ae_b}{4\pi}\frac{x^i_{ab}x^j_{ab}}{x^3_{ab}}+\sum_a\frac{q^i_aq^j_a}{m_a}+E^iD^j\right]$$
$$+\frac{e}{8M^2}(E^i\Pi^j+\Pi^iE^j)\sum_a(x^i_aq^j_a+x^j_aq^i_a+q^i_ax^j_a+q^j_ax^i_a), \quad (20)$$

where

$$H_0=\sum_a\frac{q_a^2}{2m_a}+\sum_{a>b}\frac{e_ae_b}{4\pi x_{ab}}+eA^0-\vec{D}\cdot\vec{E}, \quad (21)$$

and we neglect $[\Pi^j,E^i](\ldots)$, which is a higher order correction. The second term in Eq. (20) will be combined with the fourth term in Eq. (33) and further transformed in Eqs. (37) and (38). Let us now summarize the transformations performed so far by presenting the total Hamiltonian H_2 of the system

$$H_2=H_{\rm IN}+H_\Pi+H_{\rm MM}-\vec{D}\cdot\vec{E}-\frac{1}{2}\left(D^{ij}-\frac{\delta^{ij}}{3}D^{kk}\right)E^i_{,j}$$
$$-\frac{1}{6}D^{ijk}E^i_{,jk}+\frac{\Pi^i\Pi^j}{2M^2}E^iD^j+\sum_a\left\{-\frac{e_a}{2m_a}(\vec{l}_a+g_a\vec{s}_a)\cdot\vec{B}\right.$$
$$+\frac{e_a}{2m_a^2}(g_a-1)\vec{s}_a\cdot\vec{q}_a\times\vec{E}-\frac{e_a}{6m_a}(l^j_ax^i_a+x^i_al^j_a)B^j_{,i}$$
$$\left.-\frac{e_a}{2m_a}g_ax^i_as^j_aB^j_{,i}\right\}+\frac{1}{2}\left\{\frac{\Pi^j}{M},(\vec{D}\times\vec{B})^j+\frac{1}{2}D^{ik}\epsilon^{jil}B^l_{,k}\right.$$
$$+\frac{1}{2}\sum_{a\neq b}\frac{e_ae_b}{4\pi}\left[\left(\frac{\vec{s}_a}{m_a}\times\frac{\vec{x}_{ab}}{x^3_{ab}}\right)^j-\left(\frac{\delta^{ij}}{x_{ab}}+\frac{x^i_{ab}x^j_{ab}}{x^3_{ab}}\right)\frac{q^i_a}{m_a}\right]$$
$$+\sum_a\left[-\frac{q_a^2}{2m_a^2}q^j_a-\frac{e_a}{2m_a}(g_a-1)(\vec{s}_a\times\vec{E})^j\right.$$
$$\left.\left.+\frac{eE^i}{4M}(x^i_aq^j_a+x^j_aq^i_a+q^i_ax^j_a+q^j_ax^i_a)\right]\right\}, \quad (22)$$

where

$$H_{\rm IN}=\sum_{a>b}\frac{e_ae_b}{4\pi}\left\{\frac{1}{x_{ab}}-\frac{1}{2m_am_b}q^i_a\left(\frac{\delta^{ij}}{x_{ab}}+\frac{x^i_{ab}x^j_{ab}}{x^3_{ab}}\right)q^j_b-\frac{2\pi}{3}\langle r_a^2\right.$$
$$+r_b^2\rangle\delta^3(r_{ab})+\frac{1}{2x^3_{ab}}\left[\frac{g_a}{m_am_b}\vec{s}_a\cdot\vec{x}_{ab}\times\vec{q}_b-\frac{g_b}{m_am_b}\vec{s}_b\cdot\vec{x}_{ab}\right.$$
$$\left.\times\vec{q}_a+\frac{(g_b-1)}{m_b^2}\vec{s}_b\cdot\vec{x}_{ab}\times\vec{q}_b-\frac{(g_a-1)}{m_a^2}\vec{s}_a\cdot\vec{x}_{ab}\times\vec{q}_a\right]$$
$$\left.-\frac{2\pi g_ag_b}{3m_am_b}\delta^3(x_{ab})\vec{s}_a\cdot\vec{s}_b+\frac{g_ag_b}{4m_am_b}\frac{s^i_as^j_b}{x^3_{ab}}\left(\delta^{ij}-\frac{3x^i_{ab}x^j_{ab}}{x^2_{ab}}\right)\right\}$$
$$+\sum_a\left(\frac{\vec{q}_a^{\,2}}{2m_a}-\frac{\vec{q}_a^{\,4}}{8m_a^3}\right), \quad (23)$$

$$H_\Pi=\frac{\vec{\Pi}^2}{2M}\left[1-\frac{1}{M}\left(\sum_a\frac{\vec{q}_a^{\,2}}{2m_a}+\sum_{a>b}\frac{e_ae_b}{4\pi x_{ab}}\right)\right]$$
$$-\frac{\vec{\Pi}^4}{8M^3}+eA^0-\frac{e}{6}\langle R^2\rangle\vec{\nabla}\vec{E}, \quad (24)$$

$$H_{\rm MM}=\frac{3}{8M}(\vec{D}\times\vec{B})^2+\sum_a\frac{e_a^2}{8m_a}(\vec{x}_a\times\vec{B})^2, \quad (25)$$

and the charge radius $\langle R^2\rangle$ is

$$e\langle R^2\rangle=\sum_ae_a[\langle r_a^2\rangle+\langle x_a^2\rangle]+\cdots, \quad (26)$$

where by dots we denote omitted higher order terms. We shall transform now the terms with a single power of $\vec{\Pi}$ and start with spin dependent terms. The canonical transformation ϕ_3 is

$$\phi_3=-\sum_a\frac{\vec{s}_a}{2m_a}\times\vec{q}_a\cdot\frac{\vec{\Pi}}{M}, \quad (27)$$

and it leads to the contribution denoted by δ_3H,

$$\delta_3H=i[H_0,\phi_3]+\partial_t\phi_3=-\sum_a\frac{e_a}{2m_a}\vec{s}_a\cdot\vec{E}\times\frac{\vec{\Pi}}{M}+\sum_a\frac{e}{2M}\vec{s}_a\cdot\vec{E}$$
$$\times\frac{\vec{\Pi}}{M}+\sum_a\frac{e}{2M}\vec{s}_a\cdot\vec{E}\times\frac{\vec{q}_a}{m_a}-\frac{1}{2}\sum_{a\neq b}\frac{e_ae_b}{4\pi}\frac{\vec{s}_a}{m_a}\cdot\frac{\vec{x}_{ab}}{x^3_{ab}}\times\frac{\vec{\Pi}}{M}, \quad (28)$$

where we have neglected $[\Pi^i,E^j]$ times some operators. These terms are relativistic corrections to the finite size and the quadrupole moment, which we neglect here from the beginning. The first and the fourth terms in the above cancel out with corresponding terms in H_2 in Eq. (22), the second term when combined with orbital angular momentum will give total spin, and the third term together with the similar term in H_2 in Eq. (22) is canceled by the next transformation ϕ_4,

$$\phi_4 = -\sum_a \left[\frac{e_a}{2m_a}(g_a-1) - \frac{e}{2M}\right]\vec{s}_a \times \vec{x}_a \cdot \vec{E}. \tag{29}$$

It gives the following contribution to the Hamiltonian:

$$\delta_4 H = i[H_0,\phi_4] + \partial_t \phi_4 = -\sum_a \left[\frac{e_a}{2m_a}(g_a-1) - \frac{e}{2M}\right]\vec{s}_a \times \frac{\vec{q}_a}{m_a}\cdot\vec{E} - \sum_a \left[\frac{e_a}{2m_a}(g_a-1) - \frac{e}{2M}\right]\vec{s}_a \times \vec{x}_a \cdot \partial_t \vec{E}. \tag{30}$$

The next canonical transformation ϕ_5 is used to remove the following terms from H_2:

$$-\frac{\Pi^j}{M}\left[\sum_a \frac{q_a^2}{2m_a^2}q_a^j + \frac{1}{2}\sum_{a\neq b}\frac{e_a e_b}{4\pi}\left(\frac{\delta^{ij}}{x_{ab}} + \frac{x_{ab}^i x_{ab}^j}{x_{ab}^3}\right)\frac{q_a^i}{m_a}\right], \tag{31}$$

and is of the form

$$\phi_5 = \frac{1}{2}\left(\sum_a \frac{q_a^j x_a^i q_a^j}{m_a} + \sum_{a\neq b}\frac{x_a^i}{x_{ab}}\frac{e_a e_b}{4\pi}\right)\frac{\Pi^i}{M}. \tag{32}$$

Calculation of the commutator with H_0 is more tedious, and as before we neglect terms involving the commutator $[E^i,\Pi^j](\ldots)$, since they are relativistic corrections to the finite size and the quadrupole moment. The result is

$$\begin{aligned}\delta_5 H &= i[H_0,\phi_5] + \partial_t\phi_5\\ &= \sum_a \frac{q_a^2}{2m_a^2}q_a\cdot\frac{\vec{\Pi}}{M} + \frac{1}{2}\sum_{a\neq b}\frac{e_a e_b}{4\pi}\frac{\Pi^i}{M}\left(\frac{\delta^{ij}}{x_{ab}} + \frac{x_{ab}^i x_{ab}^j}{x_{ab}^3}\right)\frac{q_a^j}{m_a}\\ &\quad - \frac{1}{2M}\vec{E}\times\vec{\Pi}\sum_a\left(\frac{e_a}{m_a} - \frac{e}{M}\right)\vec{l}_a\\ &\quad + \frac{1}{4M}E^k\Pi^i\sum_a\left(\frac{e_a}{m_a} - \frac{e}{M}\right)(x_a^i q_a^k + x_a^k q_a^i + q_a^k x_a^i + q_a^i x_a^k)\\ &\quad + \frac{eE^i}{2M}\left(\sum_a \frac{1}{m_a}q_a^j x_a^i q_a^j + \sum_{a\neq b}\frac{e_a e_b}{4\pi}\frac{x_a^i}{x_{ab}}\right).\end{aligned} \tag{33}$$

The first two terms in the above cancel those in Eq. (31), the third term is left intact, and the fourth and the fifth are subjects of further transformations. Before applying them, let us summarize the obtained results in terms of H_5.

$$\begin{aligned}H_5 &= H_{\rm IN} + H_\Pi + H_{M1} + H_{\rm MM} - \vec{D}\cdot\vec{E} + \frac{\Pi^i\Pi^j}{2M^2}E^i D^j\\ &\quad + \frac{eE^i}{2M}\sum_{a\neq b}\frac{x_a^i}{x_{ab}}\frac{e_a e_b}{4\pi} + \frac{1}{2}\left\{\frac{\Pi^j}{M},(\vec{D}\times\vec{B})^j + \frac{1}{2}D^{ik}\epsilon^{jil}B^l_{,k}\right.\\ &\quad \left. + E^i\sum_a\frac{e_a}{4m_a}(x_a^i q_a^j + x_a^j q_a^i + q_a^i x_a^j + q_a^j x_a^i)\right\}\\ &\quad - \sum_a\left\{-\frac{eE^i}{2M}\frac{1}{m_a}q_a^j x_a^i q_a^j + \frac{e_a}{2}(x_a^i x_a^j - x_a^2\delta^{ij}/3)E^i_{,j}\right.\\ &\quad + \frac{e_a}{30}x_a^2(x_a^i E^i_{,jj} + 2x_a^j E^i_{,ij}) + \left[\frac{e_a}{2m_a}(g_a-1) - \frac{e}{2M}\right]\vec{s}_a\\ &\quad \left.\times\vec{x}_a\cdot\partial_t\vec{E} + \frac{e_a}{6m_a}(l_a^j x_a^i + x_a^i l_a^j)B^j_{,i} + \frac{e_a}{2m_a}g_a x_a^i s_a^j B^j_{,i}\right\},\end{aligned} \tag{34}$$

where

$$H_{M1} = -\sum_a \frac{e_a}{2m_a}(\vec{l}_a + g_a\vec{s}_a)\cdot\vec{B} + \sum_a\left[\frac{e_a}{2m_a}(\vec{l}_a + g_a\vec{s}_a) - \frac{e}{2M}(\vec{l}_a + \vec{s}_a)\right]\frac{1}{2M}(\vec{\Pi}\times\vec{E} - \vec{E}\times\vec{\Pi}). \tag{35}$$

We used in Eq. (34) the following tensor decomposition:

$$x^i x^j x^k = (x^i x^j x^k)^{(3)} + \frac{x^2}{5}(\delta^{ij}x^k + \delta^{ik}x^j + \delta^{jk}x^i), \tag{36}$$

and neglected the electric octupole interaction. It is worth noting that the Hamiltonian in Eq. (35) includes the interaction of the total spin with the electromagnetic field, in a similar way [see Eq. (50)] as in Eq. (2).

The transformation ϕ_6 is used to bring the last term involving $\vec{\Pi}$ to the more familiar form

$$\phi_6 = -\frac{1}{4M}(E^j\Pi^i + \Pi^i E^j)\sum_a e_a x_a^i x_a^j. \tag{37}$$

The corresponding contribution to the Hamiltonian is

$$\begin{aligned}\delta_6 H &= i[H_0,\phi_6] + \partial_t\phi_6\\ &= -\frac{1}{4M}(\partial_t E^j\Pi^i + \Pi^i\partial_t E^j)\sum_a e_a x_a^i x_a^j - \frac{e}{2M}E^i E^j\sum_a e_a x_a^i x_a^j\\ &\quad - \frac{1}{8M}(E^j\Pi^i + \Pi^i E^j)\sum_a\frac{e_a}{m_a}(x_a^i q_a^j + x_a^j q_a^i + q_a^i x_a^j + q_a^j x_a^i).\end{aligned} \tag{38}$$

The last term cancels out with the corresponding one in H_5 and the first term will have interpretation of the velocity correction to $E2$ transition. The next, ϕ_7, is used to transform two terms containing $eE^i/(2M)$ in H_5,

$$\phi_7 = \frac{eE^i}{4M}\sum_a(x_a^j q_a^i x_a^j - x_a^i q_a^j x_a^j - x_a^j q_a^j x_a^i), \tag{39}$$

and gives

$$\begin{aligned}\delta_7 H &= i[H_0,\phi_7] + \partial_t\phi_7 = \frac{e\partial_t E^i}{4M}\sum_a(x_a^j q_a^i x_a^j - x_a^i q_a^j x_a^j - x_a^j q_a^j x_a^i)\\ &\quad - \frac{e}{4}E^i E^j\sum_a\frac{m_a}{M}\left(\frac{e_a}{m_a} - \frac{e}{M}\right)(2x_a^i x_a^j - \delta^{ij}x_a^2)\\ &\quad - \frac{eE^i}{2M}\sum_a\frac{1}{m_a}q_a^j x_a^i q_a^j - \frac{eE^i}{4M}\sum_{a\neq b}\frac{e_a e_b}{4\pi}\frac{x_a^i}{x_{ab}}.\end{aligned} \tag{40}$$

The first term in Eq. (40) is combined with the second term in the result of the last transformation ϕ_8,

$$\phi_8 = \frac{e\partial_t E^i}{12M}\sum_a m_a x_a^i x_a^2, \tag{41}$$

which is

$$\begin{aligned}\delta_8 H &= i[H_0,\phi_8] + \partial_t\phi_8\\ &= \frac{e\partial_t^2 E^i}{12M}\sum_a m_a x_a^i x_a^2 + \frac{e\partial_t E^i}{12M}\sum_a (x_a^j q_a^i x_a^j + x_a^i q_a^j x_a^j + x_a^j q_a^j x_a^i),\end{aligned} \tag{42}$$

to obtain

$$\frac{e\partial_t\vec{E}}{6M}\sum_a (\vec{l}_a\times\vec{x}_a - \vec{x}_a\times\vec{l}_a). \tag{43}$$

At this point we are finished with canonical transformations and summarize results in terms of the total Hamiltonian $H \equiv H_8$,

$$H = H_{\rm IN} + H_\Pi + H_{E1} + H_{M1} + H_{E2} + H_{\rm EE} + H_{\rm MM}, \tag{44}$$

where

$$\begin{aligned}H_{E1} = &-\vec{D}\cdot\left[\vec{E} + \frac{1}{2M}(\vec{\Pi}\times\vec{B} - \vec{B}\times\vec{\Pi}) - \frac{\vec{\Pi}}{2M}\left(\frac{\vec{\Pi}}{M}\cdot\vec{E}\right)\right]\\ &+ \frac{e}{6M}\sum_a (\vec{l}_a\times\vec{x}_a - \vec{x}_a\times\vec{l}_a)\cdot\partial_t\vec{E} - \sum_a \frac{e_a}{30}x_a^2(x_a^i E^i_{,jj}\\ &+ 2x_a^j E^i_{,ij}) - \sum_a \frac{e_a}{2m_a}g_a x_a^i s_a^j B^j_{,i} - \sum_a \frac{e_a}{6m_a}(l_a^j x_a^i + x_a^i l_a^j)B^j_{,i}\\ &+ \frac{eE^i}{4M}\sum_{a\neq b}\frac{e_a e_b}{4\pi}\frac{x_a^i}{x_{ab}} - \sum_a\left[\frac{e_a}{2m_a}(g_a - 1) - \frac{e}{2M}\right]\vec{s}_a\\ &\times\vec{x}_a\cdot\partial_t\vec{E} + \frac{e}{12M}\sum_a m_a x_a^2\vec{x}_a\cdot\partial_t^2\vec{E},\end{aligned} \tag{45}$$

$$\begin{aligned}H_{E2} = &-\frac{1}{2}\sum_a e_a(x_a^i x_a^j - x_a^2\delta^{ij}/3)\\ &\times\left[E^i_{,j} + \frac{1}{2M}\{\Pi^k, \delta^{jk}\partial_t E^j + \epsilon^{ikl}B^l_{,j}\}\right],\end{aligned} \tag{46}$$

$$H_{EE} = -\frac{e}{4M}\vec{E}^2\sum_a e_a\vec{x}_a^2 + \frac{e^2}{4M^2}E^iE^j\sum_a m_a(2x_a^i x_a^j - \delta^{ij}x_a^2), \tag{47}$$

and the term $\vec{\Pi}\cdot(\nabla\times\vec{B} - \partial_t\vec{E})\Sigma_a e_a\vec{x}_a^2/(6M)$, which vanishes outside the sources of the electromagnetic field, is neglected. We have split this Hamiltonian into parts, which have a separate physical interpretation. $H_{\rm IN}$ in Eq. (23) is the internal Hamiltonian of the system. H_Π in Eq. (24) is the kinetic and potential energy of the total system, for convenience including the finite size correction. H_{E1}, H_{M1}, H_{E2} are interaction Hamiltonians for $E1$, $M1$, and $E2$ transitions respectively.

H_{E1} in Eq. (45) includes a number of relativistic corrections, the so-called Röntgen term [3,4] and other velocity dependent terms. These terms have an interpretation of the velocity correction to the electric dipole interaction, namely,

$$\begin{aligned}&\frac{\vec{\Pi}^2}{2M}\left[1 - \frac{1}{M}\left(\sum_a\frac{\vec{q}_a^2}{2m_a} + \sum_{a>b}\frac{e_a e_b}{4\pi x_{ab}}\right)\right]\\ &\quad - \vec{D}\cdot\left[\vec{E} + \frac{\vec{\Pi}}{M}\times\vec{B} - \frac{\vec{\Pi}}{2M}\left(\frac{\vec{\Pi}}{M}\cdot\vec{E}\right)\right]\\ &\quad = \frac{\vec{\Pi}^2}{2M}\left[1 - \frac{1}{M}\left(\sum_a\frac{\vec{q}_a^2}{2m_a} + \sum_{a>b}\frac{e_a e_b}{4\pi x_{ab}} - \vec{D}\cdot\vec{E}\right)\right] - \vec{D}\cdot\vec{E}',\end{aligned} \tag{48}$$

where

$$\vec{E}' = \vec{E} + \frac{\vec{\Pi}}{M}\times\vec{B} + \frac{1}{2M^2}\vec{\Pi}^2\vec{E} - \frac{1}{2M^2}\vec{\Pi}(\vec{\Pi}\cdot\vec{E}) \tag{49}$$

is the Lorentz boost transformation of the electric field $\vec{E}$ up to quadratic terms in the velocity $\vec{\Pi}/M$. H_{E1} includes also the term $\frac{eE^i}{4M}\Sigma_{a\neq b}\frac{e_a e_b}{4\pi}\frac{x_a^i}{x_{ab}}$ for which we could not find a physical interpretation, and this term is the only place where the coupling of the compound system to the electromagnetic field depends on internal interactions between elements of this system. We have not been able to eliminate this term by a further canonical transformation.

H_{M1} in Eq. (35) involves coupling of spin and angular momentum to the electromagnetic field. The expectation value of the second term is

$$\begin{aligned}&\sum_a\left\langle\frac{e_a}{2m_a}(\vec{l}_a + g_a\vec{s}_a) - \frac{e}{2M}(\vec{l}_a + \vec{s}_a)\right\rangle\frac{1}{2M}(\vec{\Pi}\times\vec{E} - \vec{E}\times\vec{\Pi})\\ &\quad = \frac{e}{2M}(g-1)\frac{\vec{S}}{2M}\cdot(\vec{\Pi}\times\vec{E} - \vec{E}\times\vec{\Pi}),\end{aligned} \tag{50}$$

where the total spin $\vec{S}$ is

$$\vec{S} = \sum_a(\vec{s}_a + \vec{l}_a), \tag{51}$$

and the factor g is defined by

$$\frac{eg}{2M}\vec{S} \equiv \left\langle\sum_a\frac{e_a}{2m_a}(\vec{l}_a + g_a\vec{s}_a)\right\rangle. \tag{52}$$

It has been demonstrated in [5] that the presence of the term in Eq. (50), which has the same form for any spin, is required by Lorentz covariance.

H_{E2} in Eq. (46) is the electric quadrupole coupling to the electromagnetic field and includes the correction due to the nonvanishing velocity of the system. H_{EE} in Eq. (47) is an additional contribution to the electric polarizability, which vanishes for the neutral system, and $H_{\rm MM}$ in Eq. (25) is the known magnetic susceptibility [8].

All the corrections to the electromagnetic interaction, which involve the total mass of the system (in the denominator), are small for atomic systems. Nevertheless they are non-negligible when confronted with precise measurements; for example, nuclear recoil corrections to the g factor of atomic systems. They have been obtained by Hegstrom in [9], and in our notation his leading terms are

$$\delta H = -\frac{e}{2m_e}\left[\left(1-\frac{m_e}{m_N}\right)\vec{L}+g\vec{S}\right]\cdot\vec{B}-\frac{e}{2m_N}\sum_{j\neq k} i\vec{r}_j\times\vec{\nabla}_k, \tag{53}$$

where m_e, m_N are the electron and the nucleus mass, and $\vec{L}$, $\vec{S}$ are the total angular momentum and the spin of all electrons. One can show that the expression obtained here,

$$\delta H = -\sum_a \frac{e_a}{2m_a}(\vec{l}_a+g_a\vec{s}_a)\cdot\vec{B}, \tag{54}$$

is equivalent to the result in Eq. (53) for the case of a spinless nucleus. Another possible application of the obtained Hamiltonian is the calculation of forbidden radiative molecular transition rates, such as ortho para in H_2. This transition has been considered by Raich and Good in [10], although we think their calculations are not complete. This is because they have not included higher order couplings to the electromagnetic field. Namely, the part of our Hamiltonian, which is responsible for this transition, is

$$\begin{aligned}\delta H = &-\sum_A e_A\vec{x}_A\cdot\vec{E}-\sum_b e_b\vec{x}_b\cdot\vec{E}-\sum_A\frac{e_A}{2m_A}[g_A x_A^i s_A^j B^j_{,i}\\&+(g_A-1)\vec{s}_A\times\vec{x}_A\cdot\partial_t\vec{E}]+\sum_{A,b}\frac{e_A e_b}{4\pi}\frac{1}{2x_{Ab}^3}\\&\times\left(\frac{g_A}{m_A m_b}\vec{s}_A\cdot\vec{x}_{Ab}\times\vec{p}_b-\frac{(g_A-1)}{m_A^2}\vec{s}_A\cdot\vec{x}_{Ab}\times\vec{p}_A\right).\end{aligned} \tag{55}$$

A, b are indices of nuclei and electrons, respectively. This transition can go directly via the third term, which has been omitted in Ref. [10], or by a hyperfine perturbation of the electronic state: the third term, followed by the electric dipole interaction: the first term of Eq. (55).

Recoil corrections, which are small for atoms and molecules, become important for atomic nuclei. They are uniquely determined by Lorentz covariance, and do not depend on internal interactions within the system, with only one exception. Therefore we might expect a very similar Hamiltonian for a nonelectromagnetically bound, but still nonrelativistic system, such as a nucleus. It would be interesting to verify this, and to perform similar calculations for nuclear systems using χ-effective perturbation theory [11,12] and to obtain precise values for the charge radius, polarizabilities, or the magnetic moment, which can be confronted with those obtained from atomic spectroscopy.

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