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Retarded Boson–Fermion interaction in atomic systems

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Abstract. The retarded interaction between an electron and a spin-0 nucleus, that has been derived from electro–dynamical perturbation theory is discussed here. A brief account of the derivation is given. The retarded form is correct through order v^2/c^2. Use of the relative coordinates leads to an effective one-electron operator that can be used through all orders of perturbation theory. A few unitary transformations give rise to the interaction that is valid in the non-relativistic limit.

Keywords. Boson; Fermion; retarded interaction; electro-dynamical perturbation theory.

1. Introduction

Recently, we investigated the relativistic dynamics of the electron(s) and a spin-1/2 nucleus in an atom in the presence of a uniform magnetic field.[1–3] We used the projected form of the electron–nuclear retarded interaction from quantum electro-dynamics[4] and derived a relativistic Hamiltonian H_{atom} for phenomenology.

The nuclei of different elements, however, can have different spins. In particular, many important atoms such as C^{12} and O^{16} have spin-0 nuclei that effectively act as bosons. It is always possible to question the validity of the traditional Hamiltonian operator for an atom with a spin-0 nucleus. One normally considers only the Coulomb interaction between the nucleus and the electrons. In ref. 5 we have explicitly derived, from quantum electro–dynamics (QED), the retarded interaction between one Dirac particle and one Klein–Gordon particle in the absence of a magnetic field. The aim of this paper is to report this development in simpler terms.

The importance of this progress is as follows. In our previous work, the two spin-1/2 particle treatment[1] was generalized to the case of an all-spin-1/2-fermion atom in ref. 3. Similarly, the treatment in ref. 5 can be generalized to the case of a neutral many-electron atom with a spin-0 nucleus (or a molecule with spin-0 and spin-1/2 nuclei).

The QED Hamiltonian is written down, and it is shown in §2 how an effective Hamiltonian operator can be obtained for a phenomenological treatment from the QED perturbation theory. The retardation effect arises from the finite speed of light, and the fact that a virtual photon is always in transit. By separating the center of mass motion, a wave equation that looks like the effective equation for only one spin-1/2 fermion is derived in §3. The retardation effect can now be calculated to all orders. Separation of the positive-energy part of the wave equation is achieved by a set of unitary transformations in §4, from which the non-relativistic limit is easily obtained. A few important points are discussed in §5.

2. To the phenomenological Hamiltonian

We take the first particle as a Dirac fermion and the second one as a Klein–Gordon boson. What we have in mind is an atom made up from one electron and a spin-0 nucleus. The corresponding relativistic Hamiltonian operators are

$$h_D(\mathbf{1}) = c\alpha_1 \cdot \pi_{\mathbf{1}} + \beta_1 m_1 c^2 - \frac{e_1}{c} A_0(\mathbf{r}_1), \tag{1}$$

that is, the Dirac Hamiltonian (for the electron), and

$$h_{KG}(2) = \frac{\pi_2^2}{2m_2}(\tau_{23} + i\tau_{22}) + m_2 c^2 \tau_{23}, \tag{2}$$

the Klein–Gordon Hamiltonian (for the nucleus), both being valid for wave equations that are first-order in time. The mechanical momentum operators are written as

$$\pi_i = \mathbf{p}_i - \frac{e_i}{c}\mathbf{A}(\mathbf{r}_i),$$

for $i = 1, 2$. The τ_i's are the Pauli spin matrices.

It is possible to combine the two corresponding wave equations in terms of independent time vari-

ables in a covariant formalism. Thereafter, the application of an equal time constraint leads to the Hamiltonian in coordinate representation, $H = h_D(\mathbf{r}_1) + h_{KG}(\mathbf{r}_2)$.[6] Furthermore, $A_0(r_1)$ may be viewed as arising from the presence of the second particle.[5] The last step, of course, spoils the covariance, but gives rise to a meaningful Hamiltonian for phenomenology.

The corresponding operator of field theory can be written as

$$\hat{H} = \hat{H}^0 + \hat{H}'. \tag{3}$$

The zeroth order operator includes the field-free terms, the radiation Hamiltonian, Coulomb interaction, and for the sake of convenience, the diamagnetic interaction:

$$\hat{H}^0 = (\hat{H}_D^0 + \hat{H}_C) + (\hat{H}_{KG}^0 + \hat{H}_{KG2,\mathrm{int}}) + \hat{H}_{\mathrm{rad}}. \tag{4}$$

The perturbation consists of only the paramagnetic interaction terms,

$$\hat{H}' = \hat{H}_{D,\mathrm{int}} + \hat{H}_{KG1,\mathrm{int}}. \tag{5}$$

The paramagnetic interaction terms that are linear in vector potential start contributing at the second order in perturbation theory. The diamagnetic term contributes to all orders including the first order. The effect of the diamagnetic contribution is mainly a self-energy correction, and after a re-normalization procedure leaves only the higher-level corrections to energy. The paramagnetic and diamagnetic terms start contributing together only from the third order with results at order v^4/c^4.

In the absence of any other external (electric or magnetic) field, the various operators involved above are given by

$$\hat{H}_D^0 = \int d^3r\ \psi^\dagger(\mathbf{r})\, h_D^0(\mathbf{r})\ \psi(\mathbf{r}),$$

$$\hat{H}_C = e_1 e_2 \int d^3r_1 \int d^3r_2\ \frac{\hat{\rho}_D^0(\mathbf{r}_1)\hat{\rho}_{KG}^0(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|},$$

$$\hat{H}_{D,\mathrm{int}} = -\frac{e_1}{c} \int d^3r\, \hat{\mathbf{j}}_D^0(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t),$$

$$\hat{H}_{KG}^0 = \int d^3r\ \phi^\dagger(\mathbf{r})\tau_{23} h_{KG}^0(\mathbf{r})\ \phi(\mathbf{r}),$$

$$\hat{H}_{KG1,\mathrm{int}} = -\frac{e_2}{c} \int d^3r\, \hat{\mathbf{j}}_{KG}^0(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t),$$

$$\hat{H}_{KG2,\mathrm{int}} = \frac{e_2^2}{2m_2c^2} \int d^3r\ :\phi^\dagger(\mathbf{r}) (\tau_{23} + i\tau_{22})\phi(\mathbf{r}):\mathrm{A}(\mathbf{r},t)^2, \tag{6}$$

and

$$\hat{H}_{\mathrm{rad}} = \frac{1}{V}\sum_{\mathbf{k}\lambda}\left(\hat{N}_{\mathbf{k}\lambda} + \frac{1}{2}\right)\hbar\omega_{\mathbf{k}}\ .$$

Here, $\hat{N}_{\mathbf{k}\lambda}$ is the number operator for photons with wave vector $\mathbf{k}$ and polarization λ, $\hat{N}_{\mathbf{k}\lambda} = A_{\mathbf{k}\lambda}^\dagger A_{\mathbf{k}\lambda}$, and the field-theoretical density and current operators are as follows:

$$\hat{\rho}_D^0(\mathbf{r}) = :\psi^\dagger(\mathbf{r})\psi(\mathbf{r}):,$$

$$\hat{\rho}_{\mathrm{KG}}^0(\mathbf{r}) = :\phi^\dagger(\mathbf{r})\tau_3\phi(\mathbf{r}):,$$

$$\hat{\mathbf{j}}_D^0(\mathbf{r}) = \mathrm{c}:\psi^\dagger(\mathbf{r})\boldsymbol{\alpha}_1\psi(\mathbf{r}):, \tag{7}$$

and

$$\hat{\mathbf{j}}_{KG}^0(\mathbf{r}) = \frac{1}{2m_2}\,[:\phi^\dagger(\mathbf{r})\tau_{23}(\tau_{23} + i\tau_{22})\mathbf{p}_2\phi(\mathbf{r}): + :(\mathbf{p}_2\ \phi(\mathbf{r}))^\dagger(\tau_{23} - i\tau_{22})\tau_{23}\phi(\mathbf{r}):].$$

The field operators ψ and ϕ are defined in the free particle picture. The vector potential is written as

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{k},\boldsymbol{\lambda}}(A_{\mathbf{k}\lambda}\lambda e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathrm{k}}t)} + A_{\mathbf{k}\lambda}^\dagger\kappa^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathrm{k}}t)}) \tag{8}$$

where Ω is the volume. Using these expressions, the operators $\hat{H}_{D,\mathrm{int}}$ and $\hat{H}_{KG1,\mathrm{int}}$ can be explicitly written as

$$\hat{H}_{D,\mathrm{int}} = -e_1\sum_{\mathbf{k},\boldsymbol{\lambda}}\int d^3r_2 :\psi^\dagger(\mathbf{r}_1) \left[A_{\mathbf{k}\lambda}\alpha_1\cdot\lambda\frac{e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega_{\mathrm{k}}t)}}{\sqrt{\Omega}} + A_{\mathbf{k}\lambda}^\dagger\alpha_1\cdot\lambda^*\frac{e^{-i(\mathbf{k}\cdot\mathbf{r}_1-\omega_k t)}}{\sqrt{\Omega}}\right]\psi(\mathbf{r}_1): \tag{9}$$

and

$$\hat{H}_{KG1,\mathrm{int}} = -\frac{e_2}{m_2 c}\sum_{\mathbf{k}\lambda}\int d^3 r_2 : \phi^{\dagger}(\mathbf{r}_2)\tau_{23}(\tau_{23} + i\tau_{22})$$

$$\times\left[A_{\mathbf{k}\lambda}\frac{e^{i(\mathbf{k}\cdot\mathbf{r}_2-\omega_k t)}}{\sqrt{\Omega}} + A^{\dagger}_{\mathbf{k}\lambda}\frac{e^{-i(\mathbf{k}\cdot\mathbf{r}_2-\omega_k t)}}{\sqrt{\Omega}}\right](p_{2\lambda}\phi(\mathbf{r}_2)) : \tag{10}$$

while one adopts $\lambda = \lambda^*$. Furthermore, the transverse gauge ($\mathbf{k}\cdot\lambda = 0$) is chosen for the subsequent calculations.

The first order contribution to energy vanishes. The second order contribution is found from the D–KG1 and KG1–D interactions, that is,

$$E_i^{(2)} = \sum_n \sum_{\substack{\mathbf{k}\lambda \\ (n,\{N'\})\neq(i,\{N\})}} \sum_{N'} \frac{\langle\psi_i^{(0)}; N_{\mathbf{k}\lambda} \mid \hat{H}_{\mathrm{D,int}} \mid \psi_n^{(0)}; N'_{\mathbf{k}\lambda}\rangle}{E_i^{(0)} - E_n^{(0)} - ck(N'_{\mathbf{k}\lambda} - N_{\mathbf{k}\lambda})}$$

$$\times$$

$$\langle\psi_i^{(0)}; N_{\mathbf{k}\lambda} \mid \hat{H}_{\mathrm{KG1,int}} \mid \psi_n^{(0)}; N'_{\mathbf{k}\lambda}\rangle$$

$$+\sum_n \sum_{\substack{\mathbf{k}\lambda \\ (n,\{N'\})\neq(i,\{N\})}} \sum_{N'} \frac{\langle\psi_n^{(0)}; N'_{\mathbf{k}\lambda} \mid \hat{H}_{\mathrm{D,int}} \mid \psi_i^{(0)}; N_{\mathbf{k}\lambda}\rangle}{E_i^{(0)} - E_n^{(0)} - ck(N'_{\mathbf{k}\lambda} - N_{\mathbf{k}\lambda})}. \tag{11}$$

The D–D and KG1–KG1 contributions give the self-energy for the Dirac and the Klein–Gordon particles respectively. These can be removed by a re-normalization technique.

Using the relations and identities

$$\sum_{\lambda}\alpha_{1\lambda}\mathbf{p}_{2\lambda} = \alpha_1\cdot\mathbf{p}_2 - \alpha_1\cdot\hat{\mathbf{k}}\ \mathbf{p}_2\cdot\hat{\mathbf{k}}, \tag{12}$$

$$e^{i\mathbf{k}\cdot\mathbf{r}}\alpha_1\cdot\mathbf{k} = -i\alpha_1\cdot(\nabla e^{i\mathbf{k}\cdot\mathbf{r}}), \tag{13}$$

$$\mathbf{p}_2\cdot\hat{\mathbf{k}} = -\frac{k^3}{2}\mathbf{p}_2\cdot\left(\nabla_k\frac{1}{k^2}\right), \tag{14}$$

and

$$\alpha_1\cdot(\nabla\hat{\mathbf{r}}\cdot\mathbf{p}_2) = \frac{\alpha_1\cdot\mathbf{p}_2}{r} - \frac{\alpha_1\cdot\hat{\mathbf{r}}\ \ \hat{\mathbf{r}}\cdot\mathbf{p}_2}{r}, \tag{15}$$

the second order contribution to energy can be brought to a simple form using which one can write the effective QED Hamiltonian operator

$$\hat{H}_{\mathrm{eff}} = \hat{H}^0 + (\hat{H}^{(2)}_{D,KG1} + \hat{H}^{(2)}_{KG1,D}). \tag{16}$$

The additional part in the effective QED Hamiltonian operator is given by

$$\hat{H}^{(2)}_{D,KG1} + \hat{H}^{(2)}_{KG1,D} = -\frac{e_1 e_2}{2m_2 c}\int \mathrm{d}^3 r_1\ \mathrm{d}^3 r_2\ : \psi^{\dagger}(\mathbf{r}_1)$$

$$[:\phi^{\dagger}(\mathbf{r}_2)\times\tfrac{1}{r}(\alpha_1\cdot\mathbf{p}_2 + \hat{\mathbf{r}}\cdot\alpha_1\ \hat{\mathbf{r}}\cdot\mathbf{p}_2)$$

$$\tau_{23}(\tau_{23} + i\tau_{22})\phi(\mathbf{r}_2):]\psi(\mathbf{r}_1): \tag{17}$$

where we have used the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. The vector $\hat{\mathbf{r}}$ is the unit vector in the direction of r. The effective operator is correct through order v^2/c^2. A comparison with (11) and the calculations that followed reveal that the additional interaction arises from the emission of a virtual photon from one of the particles and its subsequent absorption by the other particle, while the virtual photon has the finite speed c.

The first-order Klein–Gordon wave function is normalized as

$$\int d^3 r\ \psi^{(1)\dagger}_{KG}(\mathbf{r})\tau_{23}\psi^{(1)}_{KG}(\mathbf{r}) = 1. \tag{18}$$

Therefore, the QED Hamiltonian correct through order (v^2/c^2) can be written as

$$\hat{H}_{\mathrm{reduced}} = \int d^3 r_1 \int d^3 r_2 : \psi^{\dagger}(\mathbf{r}_1)$$

$$\left[:\phi^{\dagger}(\mathbf{r}_2)\tau_{23}\times\left\{h_D^0(1) + h_{KG}^0(2) + \frac{e_1 e_2}{r} + H^{(1)}_{\mathrm{ret}}\right\}\phi(\mathbf{r}_2):\right]$$

$$\psi(\mathbf{r}_1): + \hat{H}^{\mathrm{int}}_{KG2} + \hat{H}_{\mathrm{rad}}. \tag{19}$$

This shows that the effective phenomenological Hamiltonian is

$$H^{(1)}_{\mathrm{eff}} = h_D^0(1)\tau_{23} + \tau_{23}h_{KG}^0(2) + \frac{e_1 e_2}{r}\tau_{23} + H^{(1)}_{\mathrm{ret}} \tag{20}$$

where the retarded part of interaction is given by

$$H^{(1)}_{\mathrm{ret}} = -\frac{e_1 e_2}{2m_2 c}\frac{1}{r}[\alpha_1\cdot\mathbf{p}_2 + \hat{\mathbf{r}}\cdot\alpha_1\ \hat{\mathbf{r}}\cdot\mathbf{p}_2](\tau_{23} + i\tau_{22}). \tag{21}$$

These operators correspond to the first-order Klein–Gordon wave function $\psi^{(1)}_{\mathbf{p}_2}(\mathbf{r}_2)$ that is a two-component column vector.

The normalized first-order Klein–Gordon wave function $\psi^{(1)}_{\mathbf{p}_2}(\mathbf{r}_2)$ is related to the second-order function by

$$\psi^{(1)}_{\mathbf{p}_2}(\mathbf{r}_2) = V\psi^{(2)}_{\mathbf{p}_2}(\mathbf{r}_2) \equiv \left(\frac{m_2c^2}{4H^0_{KG}(2)}\right)^{1/2} (\tau_{21}+\tau_{23})\begin{pmatrix} 1 \\ H^0_{KG}(2)/m_2c^2 \end{pmatrix}\psi^{(2)}_{\mathbf{p}_2}(\mathbf{r}_2). \quad (22)$$

The Hamiltonian for the more familiar Klein–Gordon equation that is second-order in time is written as

$$H^0_{KG} = (m_2^2c^4 + c^2p_2^2)^{1/2}. \quad (23)$$

We find $V^\dagger\tau_{23}V = 1$ consistent with the same density condition, $\psi^{(1)\dagger}\tau_{23}\psi^{(1)} = \psi^{(2)\dagger}\psi^{(2)}$. Also, $V^\dagger\tau_{22}V = 0$ and $V^\dagger V = (H^{0\,2}_{KG} + m_2^2c^4)/2m_2c^2H^0_{KG}$ such that $H^{(2)}_{\text{eff}} = V^\dagger H^{(1)}_{\text{eff}}V$. It now needs only a few steps of calculation to find the effective phenomenological Hamiltonian for the usage of the second-order Klein–Gordon picture,

$$H^{(2)}_{\text{eff}} = h^0_D(1) + \tau_{23}H^0_{KG}(2) + \frac{e_1e_2}{r} + H^{(2)}_{\text{ret}}. \quad (24)$$

The matrix τ_{23} accounts for positive as well as negative-energy states of the nucleus. Moreover, the retardation term now appears to be simpler, that is,

$$H^{(2)}_{\text{ret}} = -\frac{e_1e_2}{2m_2c}\frac{1}{r}[\alpha_1\cdot\mathbf{p}_2 + \hat{\mathbf{r}}\cdot\alpha_1\,\hat{\mathbf{r}}\cdot\mathbf{p}_2]. \quad (25)$$

It is similar to the Breit interaction that is valid for two spin-1/2 particles,[7] as if one has replaced α_2 in the Breit operator by $\mathbf{p}_2/m_2c$ for an one-component treatment of the second fermion. However, $H^{(2)}_{\text{ret}}$ is for a fermion–boson system. For a two spin-0 boson system, if one carries out a treatment that is similar to that described above, one would obtain a $\mathbf{p}_1/m_1$–$\mathbf{p}_2/m_2$ interaction. This indicates that the retarded parts of the electro-dynamical interaction for all three types of two-particle systems (two-fermion, boson–fermion and two spin-zero bosons) are basically equivalent to each other as these arise from the fundamental mechanics that a virtual photon of finite speed c is exchanged between the two particles.

3. Phenomenological Hamiltonian in relative coordinates

It is usual to describe a two-particle system in relative coordinates. This is so as the internal energetics that manipulates itself in terms of spectral features remains invariant in inertial frames. The center of mass motion reveals itself only in the form of a Doppler shift of the invariant spectrum.

The center of mass coordinates are defined by $\mathbf{R}_{\text{cm}} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ corresponding to the center of mass momentum operator $\mathbf{P}_{\text{cm}} = (\mathbf{p}_1 + \mathbf{p}_2)$ that commutes with both $H^{(1)}_{\text{eff}}$ and $H^{(2)}_{\text{eff}}$. Another effective Hamiltonian can be obtained by replacing $\mathbf{P}_{\text{cm}}$ in $H^{(1)}_{\text{eff}}$ and $H^{(2)}_{\text{eff}}$ by its eigenvalue $\mathbf{P}_{\text{cm}}$. The relative coordinates $\mathbf{r}$ has been defined earlier, and the corresponding relative momentum operator is $\mathbf{p} = (m_2\mathbf{p}_1 - m_1\mathbf{p}_2)/(m_1 + m_2)$. The relative motion is obtained from the condition $P_{\text{cm}} = 0$. A consequence of this condition is that $\mathbf{p}_1$ and $\mathbf{p}_2$ appearing in the effective Hamiltonians $H^{(1)}_{\text{eff}}$ and $H^{(2)}_{\text{eff}}$ are to be replaced by $\mathbf{p}$ and $-\mathbf{p}$, respectively. In particular, we get

$$H^{(2)}_{\text{ret}} = +\frac{e_1e_2}{2m_2c}\frac{1}{r}[\alpha_1\cdot\mathbf{p} + \hat{\mathbf{r}}\cdot\alpha_1\,\hat{\mathbf{r}}\cdot\mathbf{p}]. \quad (26)$$

Retaining only the normal (positive-energy) sector of the Klein–Gordon particle in (24), one obtains an effective Hamiltonian for the single spin-1/2 entity,

$$H_{\text{eff}} = (c\alpha_1\cdot\mathbf{p} + m_1c^2\beta_1) + (m_2^2c^4 + c^2p^2)^{1/2} + \frac{e_1e_2}{r} + \frac{e_1e_2}{2m_2c}\frac{1}{r}[a_1\cdot\mathbf{p} + \hat{\mathbf{r}}\cdot\alpha_1\,\hat{\mathbf{r}}\cdot\mathbf{p}]. \quad (27)$$

Both the operators h^0_{KG} and H^0_{KG} can have positive as well as negative energy eigenvalues. Therefore, use of the effective Hamiltonian $H^{(1)}_{\text{eff}}$ (or $H^{(2)}_{\text{eff}}$) by treating the operator $H^{(1)}_{\text{ret}}$ (or $H^{(2)}_{\text{ret}}$) from (21) [or (25)] as a perturbation will lead to what is known as the continuum dissolution or the infinite degeneracy problem at second and higher orders. It becomes imperative that the effect of these retardation terms must be evaluated in any of the two ways: (i) by treating these interactions in a projected form, or (ii) by evaluating only the first-order correction to energy. The situation changes drastically when one uses the single spin-1/2 effective Hamiltonian given by (27). The interaction $H^{(2)}_{\text{ret}}$ in (26) just modifies of the Coulomb potential that now appears in (27) as an external potential, and it can be used through all orders in perturbation theory or in a self-consistent-

field calculation as the equation involved is effectively for a single particle. The infinite degeneracy is no longer possible since only the normal sector of the bosonic Hamiltonian has been retained. However, $H_{\rm ret}^{(2)}$ contains retardation effects of order (v^2/c^2) only, and the calculated effect of retardation will be correct only through this order.

4. To the non-relativistic limit

Chemistry is basically a subject dealing with interactions in the electro–magnetic regime. Most of the chemical systems are weakly relativistic, and most of the chemical effects are in the non-relativistic limit with only a few exceptions. X-ray spectroscopy is one such deviation. The nuclear spin magnetic moment, that gives rise to NMR, is another. The retarded interaction is of order v^2/c^2. Moreover, it contains one nuclear mass in the denominator instead of one electron mass, thus being much smaller than the so-called external potential (electron–nuclear Coulombic interaction). The effect of the electron–nuclear retarded interaction would be small, but nevertheless visible because of the advances in atomic spectroscopy during the last few decades. It is, therefore, natural to inspect this effect in the non-relativistic limit.

The effective Hamiltonian $H_{\rm eff}$ has the Klein–Gordon component in an explicitly separated form, and one needs to separate only the positive-mass and negative-mass components of the Dirac particle. This is to be achieved by removing the odd operator $\boldsymbol{\alpha}_1$ by a series of unitary transformations. We use three successive unitary operators,

$$U^{(1)} = \cos\eta_1 + \frac{\boldsymbol{\gamma}_1 \cdot \mathbf{p}_1}{\xi_1}\sin\eta_1 \tag{28}$$

where

$$\xi_1 = |\,\alpha_1 \cdot \mathbf{p}_1\,| \text{ and } \eta_1 = -\frac{1}{2}\tan^{-1}\left(\frac{\xi_1}{m_1 c}\right)$$

$$W^{(1)} = \exp\left[-\frac{i\hbar e_1}{4m_1^2 c^3}\alpha_1 \cdot \boldsymbol{E}_1\right] \tag{29}$$

where

$$\boldsymbol{E}_1 = -\frac{1}{e_1}(\boldsymbol{\nabla}_1 R_e)$$

and

$$W^{(2)} = \exp\left[-\frac{1}{2m_1 c^2}\beta_1 R_o\right] \tag{30}$$

where R_e and R_o stand for the even and odd parts of the retarded interaction, respectively. Use of these three unitary transformations yields the Hamiltonian

$$\begin{aligned} H_{\rm sep} &= W^{(2)^{-1}} W^{(1)^{-1}} U^{(1)^{-1}} \tilde{H}_{\rm eff}^{(2)}\; U^{(1)} W^{(1)} W^{(2)} \\ &= \beta_1 H_{KG}^0(1) + \tau_{23} H_{KG}^0(2) + \frac{e_1 e_2}{r} \\ &\quad - \frac{\pi e_1 e_2 \hbar^2}{2m_1^2 c^2}\delta^3(\mathbf{r}) - \frac{e_1 e_2 \hbar}{4m_1^2 c^2}\sigma_1 \cdot \frac{\mathbf{r}}{r^3} \times \mathbf{p}_1 \\ &\quad - \frac{e_1 e_2}{2m_1 m_2 c^2}\beta_1\left[-\hbar\sigma_1 \cdot \frac{\mathbf{r}}{r^3} \times \mathbf{p}_2 + \frac{1}{r}\mathbf{p}_1 \cdot \mathbf{p}_2\right. \\ &\quad \left. + \mathbf{r}\left(\frac{\mathbf{r}}{r^3} \cdot \mathbf{p}_2\right) \cdot \mathbf{p}_1\right] + \mathbf{O}(v^3/c^3), \end{aligned} \tag{31}$$

that is in a separated form through order v^2/c^2. The last term (that contains a sum within a square bracket) arises from the retardation of interaction.

The non-relativistic limit is obtained from $H_{\rm sep}$ by substituting unity for β_1. The Hamiltonian in the non-relativistic limit can be written as

$$H_{\rm nonrel} = (m_1 + m_2)c^2 + H_{\rm Sch} + H_{\rm rel} + H_{\rm corr}. \tag{32}$$

For a neutral system, $e_1 = -e_2 = e$, and one finds

$$\begin{aligned} H_{\rm Sch} &= \frac{p^2}{2\mu} - \frac{e^2}{r}, \\ H_{\rm rel} &= -\frac{p^4}{8\mu^3 c^2} + \frac{\pi e^2 \hbar^2}{2m_1^2 c^2}\delta^3(\mathbf{r}) + \frac{e^2}{2\mu^2 c^2}\mathbf{S}_1 \cdot \frac{\mathbf{r}}{r^3} \times \mathbf{p}, \\ H_{\rm corr} &= \frac{3p^4}{8m_1 m_2 \mu c^2} - \frac{e^2}{2m_1 m_2 c^2}\left[\frac{1}{r}p^2 + \mathbf{r}\left(\frac{\mathbf{r} \cdot \mathbf{p}}{r^3}\right) \cdot \mathbf{p}\right] \\ &\quad - \frac{e^2}{2m_2^2 c^2}\mathbf{S}_1 \cdot \frac{\mathbf{r}}{r^3} \times \mathbf{p} \end{aligned} \tag{33}$$

where μ is the reduced mass. Out of these, the retardation contribution is

$$-\frac{e^2}{2m_1m_2c^2}\left[\frac{1}{r}p^2+\mathbf{r}\left(\frac{\mathbf{r}\cdot\mathbf{p}}{r^3}\right)\cdot\mathbf{p}-2\mathbf{S}_1\cdot\frac{\mathbf{r}}{r^3}\times\mathbf{p}\right]. \quad (34)$$

The rest account for (i) the kinetic energy and kinetic energy corrections for the electron and the nucleus, (ii) the Coulomb energy of interaction between the two particles, and (iii) the Darwin energy and the spin-orbit interaction energy only for the electron. This sums up the non-relativistic limit for the dynamics of individual particles and their non-retarded interaction.

5. Discussion

When the system is placed in a non-zero uniform magnetic field, the total pseudo-momentum commutes with the effective Hamiltonian. The components of the total pseudo-momentum, however, commute with each other only when the total charge is zero. Therefore, the relative motion can be precisely defined only for a neutral atom when it is placed in an external magnetic field.

The Hamiltonian H_{nonrel} is essentially the same as the non-relativistic limit Hamiltonian for two fermions. It is almost identical with that given by (64) of ref. 1 for zero magnetic field ($B = 0$), and (17) of ref. 8 in the absence of intrinsic magnetic moments ($\mu_1 = 0$, $\mu_2 = 0$) and nuclear spin ($I = 0$). The only difference is the absence of the Darwin term and the spin-orbit coupling for the second particle at order (v^2/c^2), which is normal for a spin-0 boson.

The leading terms in retardation corrections to energy are of order $(m_e/m_n)\alpha^2Z^4(\alpha^2m_ec^2)$ where α is the fine structure constant and Z is the atomic number. As $(m_pZ/m_n) < 1$ where m_p is the proton mass for all atoms except H^1, the ratio of the retardation correction to the orbital energy is at most of order $2{\cdot}9Z^2 \times 10^{-8}$ in atomic units. The calculation of retardation correction becomes meaningless for molecules unless the orbital energy is calculated correctly through 8 digits. Numerical calculations on atoms can generate results near the Dirac–Fock limit.[9] Analytical calculations can also do it, but they require a very large basis set.[10–13] The retardation effects will be important for the finer features of an atomic system such as Lamb shift that starts at order $\alpha^3Z^4(\alpha^2m_ec^2)$. This has been discussed in detail for a one-electron ion in ref. 5.

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