Description of Takashi Itoh's 'Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics'

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The effective quantum mechanical Hamiltonian for a multielectron atom was derived in 1965 by Takashi Itoh. Itoh derived the Hamiltonian by treating the multielectron atom as a system of electrons in a static electromagnetic field moving at velocities small compared to the speed of light [1].

I. INTRODUCTION

This paper will describe Takashi Itoh's derivation of the effective quantum mechanical Hamiltonian for a system of electrons in a static electromagnetic field. Itoh derived the Hamiltonian from quantum electrodynamics assuming that the velocities of the electrons were much smaller than the speed of light. The resulting multiple-term Hamiltonian provides a good approximation of the Hamiltonian for a multielectron atom.

In Itoh's paper "Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics," [1] the Hamiltonian is derived for a system of n electrons in a static external electromagnetic field. The terms in Itoh's Hamiltonian each involve the interaction of the electrons with four space-time fields. Two of these fields are the scalar potential, $\Phi(\vec{r},t)$, and the vector potential, $\vec{A}(\vec{r},t)$, which describe the electromagnetic field. The other two fields are the electric field, $\vec{E}(\vec{r},t)$, and the magnetic field, $\vec{B}(\vec{r},t)$. These fields are related by Maxwell's equations:

$$\vec{E} = -\nabla\Phi \tag{1}$$

$$\vec{B} = \nabla\times\vec{A} \tag{2}$$

In order to deal with electron-field interactions and electron-electron interactions separately, the four fields can be decomposed into an extrinsic part and an intrinsic part:

$$\Phi(\vec{r},t) \rightarrow \Phi_{ext}(\vec{r},t) + \Phi_{int}(\vec{r},t) \tag{3}$$

$$\vec{A}(\vec{r},t) \rightarrow \vec{A}_{ext}(\vec{r},t) + \vec{A}_{int}(\vec{r},t) \tag{4}$$

$$\vec{E}(\vec{r},t) \rightarrow \vec{E}_{ext}(\vec{r},t) + \vec{E}_{int}(\vec{r},t) \tag{5}$$

$$\vec{B}(\vec{r},t) \rightarrow \vec{B}_{ext}(\vec{r},t) + \vec{B}_{int}(\vec{r},t) \tag{6}$$

The extrinsic part of each field is the contribution of the static external electromagnetic field, and the intrinsic part of the the fields is the contribution of the electromagnetic fields produced by the electrons. Thus, the electron-field interactions describe the interaction of the electrons with the extrinsic part of the fields; and the electron-electron interactions describe the interaction of the electrons with the intrinsic part of the fields. The complete Hamiltonian is a summation of each electron's interactions with the intrinsic and extrinsic parts of the fields. This paper will provide a physical and mathematical description of the resulting Hamiltonian.

II. DERIVATION

A. Electron-Field Interactions

The first term to consider in the Hamiltonian is the relativistic energy of each electron. For a single electron, this energy can be expressed as:

$$E_e = \sqrt{(m_e c^2) + (pc)^2} \tag{7}$$

$$E_e = m_e c^2\sqrt{1+(\frac{pc}{m_e c^2})^2} \tag{8}$$

where m_e is the mass of an electron, p is the electron's momentum, and c is the speed of light. Using the binomial expansion, this expression can be written as:

$$E_e = m_e c^2[1+\frac{1}{2}(\frac{pc}{m_e c^2})^2 - \frac{1}{8}(\frac{pc}{m_e c^2})^4 + ...] \tag{9}$$

By distributing the factor of $m_e c^2$ and ignoring the higher order terms, the relativistic energy can be given by the first three terms in the expansion:

$$E_0 = m_e c^2 \tag{10}$$

$$E_1 = \frac{p^2}{2m_e} \tag{11}$$

$$E_2 = -\frac{p^4}{8m_e^3 c^3} \tag{12}$$

where p^2 is $(\vec{p}\cdot\vec{p})$ and p^4 is $(\vec{p}\cdot\vec{p})^2$. The first term, E_0, is the rest energy of the electron; the second term, E_1, is the electron's kinetic energy; and the last term, E_2,

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is the first order relativistic correction to the kinetic energy. These terms describe the energy of a single electron moving with momentum p in free space.

In a static electromagnetic field, a moving electron will interact with the magnetic field via the Lorenz force $F_B = q\vec{v} \times \vec{B}$. Using the principle of minimal electromagnetic coupling, this interaction can be derived from the electron's free kinetic energy using the guage transformation $\vec{p} \rightarrow \vec{p} - (\frac{q}{c})\vec{A}_{ext}$, where q is the charge of the particle (in this case -e). Using this quage transformation, the energy E_1 becomes:

$$E_1 = \frac{p^2}{2m_e} + \frac{e^2}{2m_e c^2}\vec{A}_{ext}\cdot\vec{A}_{ext} + \frac{e}{c}\frac{\vec{p}\cdot\vec{A}_{ext} + \vec{A}_{ext}\cdot\vec{p}}{2m_e} \quad (13)$$

The electron will also interact with the external electric field via the Coloumb interaction $F_E = q\vec{E}$. The energy of this interaction is given by:

$$E_E = -e\Phi_{ext} \quad (14)$$

For a system of n electrons, the Hamiltonian is the sum of the each individual electron's interactions with the external field. Therefore:

$$\begin{aligned}\hat{H} &= \sum_j^n \frac{p_j^2}{2m_e} - \sum_j^n \frac{p_j^4}{8m_e^3c^3} + \sum_j^n \frac{e}{m_e c}\vec{p_j}\cdot\vec{A}_{ext}(\vec{r_j}) \\ &+ \sum_j^n \frac{e^2}{2m_e c^2}\vec{A}_{ext}(\vec{r_j})^2 - \sum_j^n e\Phi_{ext}(\vec{r_j}) \quad (15)\end{aligned}$$

In addition to these terms, there is a contribution from the interaction of the electron's spin angular momentum and the external magnetic field. Classically, the Hamiltonian of an electron in an external magnetic field is $\hat{H} = -\mu\cdot\vec{B}_{ext}$, where μ is the electron's magnetic moment. In quantum mechanics, $\mu = -\frac{g_e e}{2m_e c}\vec{S}$, where g_e is the Dirac magnetic moment ($g_e \simeq 2$) and $\vec{S}$ is the spin magnetic moment of the electron. Thus, the contribution of the spin-magnetic field coupling to the Hamiltonian is given by:

$$\hat{H} = \sum_j^n \frac{e}{m_e c}\vec{S}_j\cdot\vec{B}_{ext}(\vec{r}_j) \quad (16)$$

Because the electron is moving, the magnetic field that the electron "sees" or interacts with is the external magnetic field with a correction term for relativistic effects (time dilation,etc.). An electron moving in an external magnetic field $\vec{B}_{ext}$ will see an effective magnetic field:

$$\vec{B}_{eff} = \gamma(\vec{B}_{ext} + \frac{\vec{v}}{c}\times\vec{E}_{ext}) \quad (17)$$

Because we are assuming that the electrons are moving at speeds much lower than the speed of light, the Lorenz factor $\gamma \simeq 1$. Substituting the effective magnetic field into equation (16) and replacing the electron's velocity vector $\vec{v}$ with $\frac{\vec{p}}{m}$ gives the complete spin-magnetic field interaction:

$$\hat{H} = \sum_j^n \frac{e}{m_e c}\vec{S}_j\cdot\vec{B}_{ext}(\vec{r}_j) + \sum_j^n \frac{e}{2m_e^2c^2}\vec{S}_j\cdot[\vec{E}_{ext}\times\vec{p}_j] \quad (18)$$

where the second factor was multiplied by the Thomas precession factor ($\simeq \frac{1}{2}$).

The final electron-field interaction term is an expansion on the electrons' interaction with the external electric field. Previously, this term was found by treating the electron as a point particle. In reality, electron's are extended particles; therefore, the charge of the electron is spread out with a charge density $\rho(\vec{r})$ with its center at the electron's location, $\vec{r}_0$. The charge density has spherical symmetry and must satisfy the condition $\int\rho(\vec{r})dV = 1$. By expanding the scalar potential $\Phi(\vec{r})$ around the $\vec{r}_0$, the electric field interaction can be written as:

$$E_E = -\int e\rho(\vec{r})\Phi(\vec{r}) \quad (19)$$

$$E_E = -e\int\rho(\vec{r})[\Phi(\vec{r}_0) + \Delta\vec{r}_i\Phi_i(\vec{r}_0) + \frac{1}{2}\Delta\vec{r}_i\Delta\vec{r}_j\Phi_{ij}(\vec{r}_0) + ...]dV \quad (20)$$

where $\Delta\vec{r}$ is a small displacement from $\vec{r}_0$. After integrating and simplifying, the first term in the expansion is the electric field interaction previously calculated, $-e\Phi(\vec{r}_0)$; the second term disappears due to symmetry; and the third term in the expansion becomes:

$$E_{E,3} = \frac{e}{2}\frac{\Delta r^2}{3}\Phi_{ij}\delta_{ij} \quad (21)$$

where $\Phi_{ij}\delta_{ij} = \Phi_{ii} = \nabla^2\Phi$. The scalar potential, Φ_{ext}, is produced by a distribution of charges, $\rho_{ext}(\vec{r})$, excluding the electrons. The scalar potential is related to the external charge distribution by Poisson's equation $\nabla^2\Phi_{ext} = -4\pi\rho_{ext}$. Assuming Δr is on the order of the Compton wavelength of an electron, $\lambda_{Compton} = \frac{\hbar}{m_e c}$, then $\Delta r^2 = \frac{3}{4}(\frac{\hbar}{m_e c})^2$. Using this information, $E_{E,3}$ can be expressed as:

$$E_{E,3} = (\frac{\pi e n\hbar^2}{2m_e^2c^2})\rho_{ext}(\vec{r}_j). \quad (22)$$

With this last term in place, the Hamiltonian for only the electron-field interactions in this system is:

$$\begin{aligned}\hat{H} &= \sum_j^n \frac{p_j^2}{2m_e} - \sum_j^n \frac{p_j^4}{8m_e^3c^3} + \sum_j^n \frac{e}{m_e c}\vec{p_j}\cdot\vec{A}_{ext}(\vec{r_j}) \\ &+ \sum_j^n \frac{e^2}{2m_e c^2}\vec{A}_{ext}(\vec{r_j})^2 - \sum_j^n e\Phi_{ext}(\vec{r_j}) \\ &+ \sum_j^n \frac{e}{m_e c}\vec{S}_j\cdot\vec{B}_{ext}(\vec{r}_j) + \sum_j^n \frac{e}{2m_e^2c^2}\vec{S}_j\cdot[\vec{E}_{ext}\times\vec{p}_j] \\ &+ \sum_j^n(\frac{\pi e n\hbar^2}{2m_e^2c^2})\rho_{ext}(\vec{r}_j) \quad (23)\end{aligned}$$

B. Electron-Electron Interactions

The Hamiltonian obtained in the previous section fully described the interactions of the n electrons with the external electromagnetic field. To completely describe the system, the Hamiltonian must also account for the interactions of each electron with the other n-1 electrons in the system.

The first interaction to consider is the Coloumb repulsion between each pair of electrons. For the interaction between the jth and kth electron, the energy is given by:

$$E_{Coloumb} = \frac{e^2}{\vec{r}_{jk}} \tag{24}$$

where $\vec{r}_{jk} = |\vec{r}_j - \vec{r}_k|$ is the distance between the two electrons. In order to account for every pair without double counting, the Hamiltonian is the sum of Coloumb repulsion for each each pair with j < k:

$$\hat{H} = \sum_{j<k} \frac{e^2}{\vec{r}_{jk}} \tag{25}$$

The other electron-electron interactions are similar in form to the terms derived for the electron-field interactions in the previous section. The electron-field interactions were derived from the interactions of each electron with the external electromagnetic field. For electron-electron interactions, the electrons interact with the fields created by the other electrons in the system. For the kth electron, the effective vector potential taking into account the electron's translational motion but neglecting spin, $\vec{A}_k(\vec{r})$, is:

$$\vec{A}_k = -\frac{e}{2m_e c}[\frac{(\vec{r}-\vec{r}_k)(\vec{r}-\vec{r}_k) + \vec{p}_k(\vec{r}-\vec{r}_k)^2}{|\vec{r}-\vec{r}_k|^3}] \tag{26}$$

At the position of the jth electron this potential can be written as:

$$\vec{A}_k = -\frac{e}{2m_e c}[\frac{(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{\vec{r}_{jk}^3} + \frac{1}{\vec{r}_{jk}}] \cdot \vec{p}_k \tag{27}$$

The jth electron will interact with this field in the same way it interacted with the external field. Using the potential given above and summing over each individual pair of electrons gives:

$$\hat{H} = -\sum_{j<k} \frac{e^2}{2m_e^2 c^2} \vec{p}_j \cdot [\frac{(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{\vec{r}_{jk}^3} + \frac{1}{\vec{r}_{jk}}] \cdot \vec{p}_k \tag{28}$$

The next electron-electron interaction contribution comes from the interaction between the spin of the jth electron, $\vec{S}_j$, and the magnetic field created by the orbital motion of the kth electron. Using the Biot-Savart Law, the magnetic field, $\vec{B}_k$, produced at the position of the jth electron is:

$$\vec{B}_k(\vec{r}_j) = \frac{e}{m_e c} \frac{(\vec{r}_j - \vec{r}_k) \times \vec{p}_k}{|\vec{r}_j - \vec{r}_k|^3} \tag{29}$$

The jth electron is in motion when it is interacting with this field, so it will in fact interact with effective magnetic field, $\vec{B}_{eff}(\vec{r}_j)$ given by:

$$\vec{B}_{eff}(\vec{r}_j) = \gamma(\vec{B}_k(\vec{r}_j) - \vec{v}_j \times \vec{E}_k(\vec{r}_j)) \tag{30}$$

where $\gamma \simeq 1$ as before. The electric field of the kth electron at the position of the jth electron is given by:

$$\vec{E}_k(\vec{r}_j) = -\frac{e(\vec{r}_j - \vec{r}_k)}{|\vec{r}_j - \vec{r}_k|^3} \tag{31}$$

Replacing the jth electron's velocity vector $\vec{v}_j$ with $\frac{\vec{p}_j}{m_e}$ gives the effective magnetic field produced by the kth electron as seen by the jth electron.

$$\vec{B}_{eff}(\vec{r}_j) = \frac{e}{m_e c}\frac{(\vec{r}_j - \vec{r}_k) \times \vec{p}_k}{|\vec{r}_j - \vec{r}_k|^3} - \frac{e}{m_e c}(\frac{\vec{p}_j \times (\vec{r}_j - \vec{r}_k)}{|\vec{r}_j - \vec{r}_k|^3}) \tag{32}$$

The spin of the jth electron will interact with this field the same way it ineracted with the effective external magnetic field. Therefore, the contribution of all n electrons is given by:

$$\hat{H} = \sum_{j \neq k} \frac{e}{m_e c} \vec{S}_j \cdot \vec{B}_{eff}(\vec{r}_j) \tag{33}$$

$$\begin{aligned} \hat{H} \ = \ & -\sum_{j\neq k} \frac{e^2}{m_e^2 c^2} \frac{1}{\vec{r}_{jk}^3} \vec{S}_j \cdot [(\vec{r}_k - \vec{r}_j) \times \vec{p}_k] \\ & - \sum_{j \neq k} \frac{e^2}{2m_e^2 c^2} \frac{1}{\vec{r}_{jk}^3} \vec{S}_j \cdot [(\vec{r}_j - \vec{r}_k) \times \vec{p}_j] \end{aligned} \tag{34}$$

where the extra factor of $\frac{1}{2}$ in the second term comes from the Thomas precession factor.

Additional contributions to the Hamiltonian come from the interactions amongst the electrons' spin magnetic moments. By calculating the magnetic fields produced by the electrons' spin magnetic moments, the spin-spin interaction can be treated as a spin-field interaction. The vector potential, $\vec{A}_k$, produced by the spin of the kth electron at the general position, $\vec{r}$, is:

$$\vec{A}_k(\vec{r}_j) = \frac{e}{m_e c} \frac{\vec{S}_k \times \vec{r}}{\vec{r}^3} \tag{35}$$

The magnetic field given by $\vec{B}_k = \nabla \times \vec{A}_k$ is then:

$$\vec{B}_k = -\frac{e}{m_e c}[\frac{3(\vec{S}_k \cdot \vec{r})\vec{r} - \vec{S}_k(\vec{r} \cdot \vec{r})}{\vec{r}^5}] \tag{36}$$

Thus, the spin-spin interaction of the jth and kth electrons' spin magnetic moments is equivalent to the interaction of the jth electron's spin magnetic moment with the magnetic field created by the kth electron's spin magnetic moment at the position of the jth electron, $\vec{B}_k(\vec{r}_j)$.

$$\hat{H} = \frac{e}{m_e c} \vec{S}_j \cdot \vec{B}_k(\vec{r}_j) \tag{37}$$

Then substituting the expression for the magnetic field and summing over all interacting pairs give:

$$\hat{H} = -\sum_{j<k} \frac{e^2}{m_e^2 c^2} \vec{S}_j \cdot [\frac{3(\vec{r}_j - \vec{r}_k)(\vec{r}_j - \vec{r}_k)}{\vec{r}_{jk}^5} - \frac{1}{\vec{r}_{jk}^3}] \cdot \vec{S}_k \quad (38)$$

This term accounts for the spin-spin interactions of all the electrons in the system. However, there is a small correction term needed to take into account that electrons cannot penetrate other electrons and therefore $\vec{r}_j \neq \vec{r}_k$. To correct for all of the points where $\vec{r}_j = \vec{r}_k$, the interaction of the spins at these points is subtracted:

$$\hat{H} = -\sum_{j<k} \frac{8\pi e^2}{3m_e^2 c^2} \delta(\vec{r}_j - \vec{r}_k) \vec{S}_j \cdot \vec{S}_k \quad (39)$$

The final contribution to the Hamiltonian comes from treating the electrons as extended particles rather than point charges. By using the same expansion of the vector potential that we used previously, and keeping only the third term as before, the energy is once again:

$$E_{E,3} = \frac{e}{2} \frac{\Delta r^2}{3} \Phi_{ij} \delta_{ij} \quad (40)$$

Again, it will be assumed that $\Delta r^2 = \frac{3}{4}(\frac{\hbar}{m_e c})^2$. The vector potential created by the kth electron at the position of the jth electron is:

$$\Phi_k(\vec{r}_j) = -\frac{e}{|\vec{r}_j - \vec{r}_k|} \quad (41)$$

Therefore:

$$\Phi_{ij}(\vec{r}_j)\delta_{ij} = \nabla^2 \frac{-e}{\vec{r}_j - \vec{r}_k} = -4\pi\delta(\vec{r}_j - \vec{r}_k) \quad (42)$$

Combining terms gives the correction as:

$$\hat{H} = -\sum_{j<k} \frac{\pi e^2 \hbar^2}{m_e^2 c^2} \delta(\vec{r}_j - \vec{r}_k) \quad (43)$$

Summing the Hamiltonians derived in this section will completely account for all electron-electron interactions in the system.

III. CONCLUSION

The nonrelativistic Hamiltonian for a system of n electrons in an external electromagnetic field originally derived by Takashi Itoh is obtained by adding up all of the electron-field and electron-electron interactions derived in the previous sections. The complete Hamiltonian is therefore:

$$\begin{aligned}
\hat{H} &= \sum_j^n \frac{p_j^2}{2m_e} \\
&- \sum_j^n \frac{p_j^4}{8m_e^3 c^3} \\
&+ \sum_j^n \frac{e}{m_e c} \vec{p}_j \cdot \vec{A}_{ext}(\vec{r}_j) \\
&+ \sum_j^n \frac{e^2}{2m_e c^2} \vec{A}_{ext}(\vec{r}_j)^2 \\
&- \sum_j^n e\Phi_{ext}(\vec{r}_j) \\
&+ \sum_j^n \frac{e}{m_e c} \vec{S}_j \cdot \vec{B}_{ext}(\vec{r}_j) \\
&+ \sum_j^n \frac{e}{2m_e^2 c^2} \vec{S}_j \cdot [\vec{E}_{ext} \times \vec{p}_j] \\
&+ \sum_j^n (\frac{\pi e n \hbar^2}{2m_e^2 c^2}) \rho_{ext}(\vec{r}_j) \\
&+ \sum_{j<k} \frac{e^2}{\vec{r}_{jk}} \qquad (44) \\
&- \sum_{j<k} \frac{e^2}{2m_e^2 c^2} \vec{p}_j \cdot [\frac{(\vec{r}_j - \vec{r}_k)(\vec{r}_j - \vec{r}_k)}{\vec{r}_{jk}^3} + \frac{1}{\vec{r}_{jk}}] \cdot \vec{p}_k \\
&- \sum_{j\neq k} \frac{e^2}{m_e^2 c^2} \frac{1}{\vec{r}_{jk}^3} \vec{S}_j \cdot [(\vec{r}_k - \vec{r}_j) \times \vec{p}_k] \\
&- \sum_{j\neq k} \frac{e^2}{2m_e^2 c^2} \frac{1}{\vec{r}_{jk}^3} \vec{S}_j \cdot [(\vec{r}_j - \vec{r}_k) \times \vec{p}_j] \\
&- \sum_{j<k} \frac{e^2}{m_e^2 c^2} \vec{S}_j \cdot [\frac{3(\vec{r}_j - \vec{r}_k)(\vec{r}_j - \vec{r}_k)}{\vec{r}_{jk}^5} - \frac{1}{\vec{r}_{jk}^3}] \cdot \vec{S}_k \\
&- \sum_{j<k} \frac{8\pi e^2}{3m_e^2 c^2} \delta(\vec{r}_j - \vec{r}_k) \vec{S}_j \cdot \vec{S}_k \\
&- \sum_{j<k} \frac{\pi e^2 \hbar^2}{m_e^2 c^2} \delta(\vec{r}_j - \vec{r}_k) \qquad (45)
\end{aligned}$$

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