Analysis of Itoh's Many Electron Hamiltonian Paper

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I. INTRODUCTION

This paper presents the derivation of the effective quantum mechanical Hamiltonian for a multielectron atom found in Takashi Itoh's work, "Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics."[1] The Hamiltonian of each electron in Itoh's multielectron system involve four space-time fields. The first two fields are of the four-vector potential, $\boldsymbol{A}(x,t)$, and the scalar potential, $\phi(x,t)$. The third and fourth fields are the electromagnetic fields, $\boldsymbol{B}(x,t)$ and $\boldsymbol{E}(x,t)$ which are derived from the scalar and vector potential in the following way:

$$\boldsymbol{E} = -\nabla\phi(\boldsymbol{r}) \tag{1}$$

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

Each of these fields may be separated into an intrinsic and extrinsic part. That is, for some generic field G,

$$G(x,t) \rightarrow G_{ext}(x,t) + G_{int}(x,t).$$

We will use both the intrinsic and extrinsic parts of the aforementioned fields and construct the total Hamiltonian accordingly.

II. ELECTRON-FIELD INTERACTIONS

We will begin our derivation with the relativistic energy of an electron of mass m and momentum p,

$$E = \sqrt{(mc^2)^2 + (pc)^2} \tag{3}$$

which we can rewrite as

$$E = (mc^2)\sqrt{1 + \left(\frac{pc}{mc^2}\right)^2}. \tag{4}$$

After a series expansion of Equation (4) we may write the Hamiltonian of one electron as

$$\hat{H} = (mc^2) + \frac{\boldsymbol{p}^2}{2m} - \frac{\boldsymbol{p}^4}{8m^3c^2} + \cdots . \tag{5}$$

Here, (mc^2) is the rest energy of the electron, $\frac{\boldsymbol{p}^2}{2m}$ is the kinetic energy of the electron, and $\frac{\boldsymbol{p}^4}{8m^3c^2}$ is the first relativistic correction term. Where $\boldsymbol{p}^2$ denotes $\boldsymbol{p}\cdot\boldsymbol{p}$ and $\boldsymbol{p}^4$ denotes $(\boldsymbol{p}\cdot\boldsymbol{p})^2$.

If we look at a multielectron system, we may sum the individual electron energies together to get the total Hamiltonian of the system. We will first apply the "Principle of Minimal

Electromagnetic Coupling," a gauge transformation, which states

$$\boldsymbol{p} \rightarrow \boldsymbol{p} + \frac{e}{c}\boldsymbol{A},$$

to the kinetic energy term of the Hamiltonian. In this substitution, e is the charge of an electron, c is the speed of light, $\boldsymbol{p}$ is the electron's momentum, and $\boldsymbol{A}$ is the vector potential. Dotting p into itself using the transformation gives us

$$\boldsymbol{p}^2 = \boldsymbol{p} \cdot \boldsymbol{p} = p_j^2 + \frac{e}{c}\frac{\boldsymbol{p_j} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p_j}}{2mc} + \frac{e^2}{c^2}A^2 \tag{6}$$

Applying the gauge transformation to our total Hamiltonian yields

$$\begin{aligned}\hat{H} = &\sum_j \frac{\boldsymbol{p_j^2}}{2m} - \sum_j \frac{\boldsymbol{p_j^4}}{8m^3c^2} \\ &+ \sum_j \frac{e}{c}\frac{\boldsymbol{p_j} \cdot \boldsymbol{A}(\boldsymbol{r_j}) + \boldsymbol{A}(\boldsymbol{r_j}) \cdot \boldsymbol{p_j}}{2m} + \sum_j \frac{e^2}{2mc^2}\boldsymbol{A}(\boldsymbol{r_j})^2.\end{aligned} \tag{7}$$

We must now also consider the effects of the Lorentz force; therefore, we must add another term to the Hamiltonian:

$$-\sum_j e\phi(\boldsymbol{r_j}).$$

With this new addition to our Hamiltonian, we have

$$\begin{aligned}\hat{H} \;=\; &\sum_j \frac{\boldsymbol{p_j^2}}{2m} - \sum_j \frac{\boldsymbol{p_j^4}}{8m^3c^2} + \sum_j \frac{e}{mc}\boldsymbol{p_j} \cdot \boldsymbol{A}(\boldsymbol{r_j}) \\ &+ \sum_j \frac{e^2}{2mc^2}\boldsymbol{A}(\boldsymbol{r_j})^2 - \sum_j e\phi(\boldsymbol{r_j}).\end{aligned} \tag{8}$$

We must take the electron's spin into account as well. The classical Hamiltonian of an electron in a magnetic field is

$$\hat{H} = -\mu \cdot \boldsymbol{B_{ext}},$$

where

$$\mu = \begin{cases} -\frac{g_e e}{2m_e c}\boldsymbol{S} & \text{for electrons} \\ -\frac{g_n e}{2m_n c}\boldsymbol{J} & \text{for neutrons} \end{cases} \tag{9}$$

is the magnetic moment, giving us an additional term to our Hamiltonian:

$$\sum_j \frac{2e}{mc}\boldsymbol{S} \cdot \boldsymbol{B}(\boldsymbol{r_j}). \tag{10}$$

This term originates from the interaction between the spin magnetic moment of the electron and the extrinsic magnetic field. We do need to make a small correction to this term though. The electron is accelerating, so we need to account for a correction known as the Thomas Precession; this is, in effect, a series of Lorentz transformations from one inertial frame to the other.[2] The Thomas precession throws in a factor of a half, giving us:

$$\sum_j \frac{e}{mc}\boldsymbol{S}\cdot\boldsymbol{B}(\boldsymbol{r_j}). \tag{11}$$

In the frame of the electron,

$$\boldsymbol{E}_{eff} = \gamma\left(\boldsymbol{E} + \frac{\boldsymbol{v}}{c}\times\boldsymbol{B}\right)$$

and

$$\boldsymbol{B}_{eff} = \gamma\left(\boldsymbol{B} - \frac{\boldsymbol{v}}{c}\times\boldsymbol{E}\right).$$

Where $\boldsymbol{v}$ is the difference between between the velocities of the j^{th} and k^{th} electrons. Since $\frac{\boldsymbol{v}}{c} \ll 1$, we may infer that $\gamma \simeq 1$. We may now plug the effective magnetic field into Equation (11) to get:

$$\sum_j \frac{e}{mc}\boldsymbol{S}_j\cdot\boldsymbol{B}(\boldsymbol{r}_j) \tag{12}$$

plus another term:

$$\sum_j \frac{e}{2m^2c^2}\boldsymbol{S}_j\cdot\left[\boldsymbol{E}(\boldsymbol{r}_j)\times\boldsymbol{p}_j\right]. \tag{13}$$

Next we assume the electron is an extended particle with a probability density, $\rho(\boldsymbol{r})$, centered at some point x_0 and has spherical symmetry around that point. We require that $\int \rho(r)dV = 1$. If we rewrite the last term of Equation (8) in continuous form, we will get that the change in energy is:

$$\Delta E = -e\int \rho(x)\phi(x_0)dV \tag{14}$$

If we expand this to second order about the point x_o, we get

$$\Delta E = -e\int \rho(x)\left[\phi(x_0) + \Delta x_i\phi_i(x_0) + \frac{1}{2}\Delta x_i\Delta x_j\phi_{ij}(x_0)\right]. \tag{15}$$

We know that$\int \rho(x)dV = 1$; this tells us that $-e\int \rho(x)\phi(x_0)dV = -e\phi(x_0)$. Also, we know $-e\int \rho(x)\Delta x_i\phi_i(x_0)dV = 0$ by symmetry; this leaves us with $-e\int \rho(x)\frac{1}{2}\Delta x_i\Delta x_j\phi_{ij}(x_0)dV$. This last term here reduces to

$$-e\frac{1}{2}\frac{1}{3}\phi_{ij}(x_0)\delta_{ij}\langle\Delta r^2\rangle.$$

Putting these three pieces together, we get

$$\Delta E = -e\phi(x_0) - e\frac{\Delta \boldsymbol{r}^2}{6}\phi_{ij}\delta_{ij} \tag{16}$$

where $\phi_{ij}\delta_{ij} = \phi_{ii} = \nabla^2\phi$ Again, $\rho(x)$ is the charge density that gives rise to the potential, so $\nabla^2\phi = -4\pi\rho(r)$. Now, if we take each of the electrons into account, we get a new term to add to our growing Hamiltonian:

$$-\sum_j e\phi_{ext}(r_j) + \sum_j \frac{\pi e\hbar^2}{2m^2c^2}\rho(r_j). \tag{17}$$

So far, our Hamiltonian looks like this:

$$\begin{aligned} \hat{H} \;=\; & \sum_j \frac{\boldsymbol{p_j}^2}{2m} - \sum_j \frac{\boldsymbol{p_j}^4}{8m^3c^2} \\ & + \sum_j \frac{e}{mc}\boldsymbol{p_j}\cdot\boldsymbol{A}(\boldsymbol{r_j}) + \sum_j \frac{e^2}{2mc^2}\boldsymbol{A}(\boldsymbol{r_j})^2 \\ & - \sum_j e\phi(\boldsymbol{r_j}) + \sum_j \frac{e}{mc}\boldsymbol{S}\cdot\boldsymbol{B}(\boldsymbol{r_j}) \\ & + \sum_j \frac{e}{2m^2c^2}\boldsymbol{S}_j\cdot[\boldsymbol{E}(\boldsymbol{r}_j)\times\boldsymbol{p}_j] \\ & - \sum_j \left(\frac{\pi e\hbar^2}{2m^2c^2}\right)\rho_{ext}(\boldsymbol{r_j}). \end{aligned} \tag{18}$$

III. ELECTRON-ELECTRON INTERACTIONS

Now that we've seen the effects on an electron in an electromagnetic field, we will look at the effects on the j^{th} electron moving in the field produced by the k^{th} electron's dipole moment. The strongest interaction between two electrons will be due to the Coulomb potential:

$$\sum_{j<k}\frac{e^2}{r_{jk}}$$

We require that $j < k$ in the summation to ensure that we do not overcount. Previously, in our Hamiltonian, the terms only involving the j^{th} electron (i.e. the terms independent of the other $n-1$ electrons) show the j^{th} electron interacting with the extrinsic parts of the four fields. Since we are now accounting for the electron-electron interactions, we must include the intrinsic parts of the four fields in our Hamiltonian. Decomposing each field into its intrinsic and extrinsic parts gives the following:

$$\phi = \phi_{ext} + \phi_{int}$$

$$\boldsymbol{B} = \boldsymbol{B_{ext}} + \boldsymbol{B_{int}}$$

$$\boldsymbol{E} = \boldsymbol{E_{ext}} + \boldsymbol{E_{int}}$$

$$\boldsymbol{A} = \boldsymbol{A_{ext}} + \boldsymbol{A_{int}}.$$

We will begin the process of including both the extrinsic and intrinsic parts of the fields with the vector potential, $\boldsymbol{A}(\boldsymbol{r})$. We will use this substitution in the third and fourth pieces of Equation (8). We have chosen $\boldsymbol{A}(\boldsymbol{r})$ so that the divergence of the field is zero. We define

$$\boldsymbol{A}_{int}(\boldsymbol{r}) = -\frac{e}{2c}\left[\frac{(\boldsymbol{r}-\boldsymbol{r_k})(\boldsymbol{r}-\boldsymbol{r_k})}{|\boldsymbol{r}-\boldsymbol{r_k}|^3} + \frac{\boldsymbol{1}}{|\boldsymbol{r}-\boldsymbol{r_k}|}\right]\cdot \boldsymbol{v_k}. \tag{19}$$

Plugging this vector potential into the third piece of Equation (8) gives us back

$$\sum_j \frac{e}{mc}\boldsymbol{p_j}\cdot \boldsymbol{A_{ext}}(\boldsymbol{r_j})$$

plus an extra term:

$$\sum_{j<k} \frac{e^2}{2m^2c^2}\boldsymbol{p}_j\left[\frac{(\boldsymbol{r}_j-\boldsymbol{r}_k)(\boldsymbol{r}_j-\boldsymbol{r}_k)}{r_{jk}^3} + \frac{\boldsymbol{1}}{r_{jk}}\right]\cdot \boldsymbol{p}_k.$$

We must account for the effect of the orbital motion of the k^{th} electron on the j^{th} electron. Itoh tells us that the Biot-Savart Law, the magnetic field produced by the k^{th} electron is

$$\boldsymbol{B}_{int}(\boldsymbol{r}) = \frac{e}{c}\frac{(\boldsymbol{r}-\boldsymbol{r}_k)\times \boldsymbol{v_k}}{|\boldsymbol{r}-\boldsymbol{r}_k|}.$$

Plugging $\boldsymbol{B} = \boldsymbol{B_{ext}} + \boldsymbol{B_{int}}$ into Equation (12) yields the following:[3]

$$\begin{aligned} &= \sum_j \frac{e}{mc}\boldsymbol{S}_j\cdot \boldsymbol{B}_{ext}(\boldsymbol{r}_j) \\ &- \sum_{j\neq k} \frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\boldsymbol{S}_j\cdot\left[(\boldsymbol{r}_k-\boldsymbol{r}_j)\times \boldsymbol{p}_k\right]. \end{aligned} \tag{20}$$

We know that the electric field due to the electron dipole is:

$$\boldsymbol{E}_{int} = -\frac{e(\boldsymbol{r}-\boldsymbol{r_k})(\boldsymbol{r}-\boldsymbol{r_k})}{|\boldsymbol{r}-\boldsymbol{r_k}|^3}. \tag{21}$$

Substituting

$$\boldsymbol{E} = \boldsymbol{E_{ext}} + \boldsymbol{E_{int}}$$

into Equation (13) gives us the following result:

$$\begin{aligned} &= \sum_j \frac{e}{2mc} \boldsymbol{S}_j \cdot \boldsymbol{E}_{ext}(\boldsymbol{r}_j) \\ &- \sum_{j \neq k} \frac{e^2}{2m^2c^2} \frac{1}{r_{jk}^3} \boldsymbol{S}_j \cdot [(\boldsymbol{r}_j - \boldsymbol{r}_k) \times \boldsymbol{p}_j]. \end{aligned} \tag{22}$$

We must now account for the interaction between the magnetic dipoles of two electrons. The equation for the energy of a dipole-dipole interaction is

$$\boldsymbol{H}_{dip} = -\frac{e}{m^2c^2} \frac{3(\boldsymbol{S_j} \cdot \hat{r})(\boldsymbol{S_j} \cdot \hat{r}) - \boldsymbol{S_j} \cdot \boldsymbol{S_k}}{\boldsymbol{r}_{jk}^3}. \tag{23}$$

Expanding this energy in terms of position vectors and summing over all electrons gives us:

$$\boldsymbol{H}_{dip} = -\sum_{j<k} \frac{e}{2m^2c^2} \boldsymbol{S_j} \cdot \left[\frac{3(\boldsymbol{r_j} - \boldsymbol{r_k})(\boldsymbol{r_j} - \boldsymbol{r_k})}{\boldsymbol{r_{jk}^3}} - \frac{\boldsymbol{1}}{\boldsymbol{r_{jk}}} \right] \cdot \boldsymbol{S_k}. \tag{24}$$

Equation (24) represents the mutual interaction between spin magnetic moments. When we take a closer look, we see that when $\boldsymbol{r_j} = \boldsymbol{r_k}$, mathematically, the expression blows up, but physically this is not what happens. We need to account for what happens once $\boldsymbol{r_k}$ reaches $\boldsymbol{r_j}$; at this point, the electrons are said to be mutually penetrating. The term needed to correct for this is

$$-\sum_{j<k} \frac{8\pi e^2}{3m^2c^2} \delta(\boldsymbol{r_j} - \boldsymbol{r_k}) \boldsymbol{S_j} \cdot \boldsymbol{S_k}. \tag{25}$$

Equation (25) accounts for hyperfine splitting. Looking at a single particle, let's take $\hat{H} = -\mu \cdot \boldsymbol{B_{ext}}$ in to account. When the nuclear magnetic moment associated with a nuclear spin is placed in a magnetic field, each spin state could have a different potential energy associated with it. An external magnetostatic field will produce some small amount of spin polarization. Because this hyperfine splitting is so small, the transition frequencies fall in the radiowave or microwave frequencies. Radio waves of the right frequency could flip the spin of the electron. The electron will be excited into a parallel spin state and relax back into an antiparallel spin state. During this process, energy is lost in the form of radiation. The wavelength of this radio wave is approximately 21cm. This is important in radio astronomy, because the 21-cm line is "among the most pervasive and ubiquitous forms of radiation in the universe."[2] With it we are able to detect clouds of neutral hydrogen (HI) from other galaxies, halos, etc. in our universe.

We now have one more field to replace; that is the field due to the scalar potential. We have that

$$\begin{aligned} \phi(\boldsymbol{r_j}) &= \phi_{ext} + \phi_{int} \\ &= \phi_{ext} - \sum_{j \neq k} \frac{-e}{|\boldsymbol{r_j} - \boldsymbol{r_k}|}. \end{aligned} \tag{26}$$

After substituting Equation (26) into Equation (16), we get

$$= \sum_j e\phi(\boldsymbol{r_j}) - \sum_j \left(\frac{\pi e \hbar^2}{2m^2c^2}\right) \rho_{ext}(\boldsymbol{r_j}) - \sum_{j<k} \left(\frac{\pi e^2 \hbar^2}{m^2 c^2}\right) \delta(\boldsymbol{r_j} - \boldsymbol{r_k}). \tag{27}$$

This concludes the derivation of the contributions to the total Hamiltonian due to the electron-electron interactions.

IV. CONCLUSION

We have now derived the non-relativistic Hamiltonian for electrons in a static electromagnetic field. Our final Hamiltonian is

$$
\begin{aligned}
\hat{H} \;=\; & \sum_j \frac{\boldsymbol{p}_{\boldsymbol{j}}^2}{2m} - \sum_j \frac{\boldsymbol{p}_{\boldsymbol{j}}^4}{8m^3c^2} \\
& + \sum_j \frac{e}{mc}\boldsymbol{p}_{\boldsymbol{j}} \cdot \boldsymbol{A}(\boldsymbol{r}_{\boldsymbol{j}}) + \sum_j \frac{e^2}{2mc^2}\boldsymbol{A}(\boldsymbol{r}_{\boldsymbol{j}})^2 \\
& - \sum_j e\phi(\boldsymbol{r}_{\boldsymbol{j}}) + \sum_j \frac{e}{mc}\boldsymbol{S} \cdot \boldsymbol{B}(\boldsymbol{r}_{\boldsymbol{j}}) \\
& + \sum_j \frac{e}{2m^2c^2}\boldsymbol{S}_j \cdot [\boldsymbol{E}(\boldsymbol{r}_j) \times \boldsymbol{p}_j] \\
& - \sum_j \left(\frac{\pi e\hbar^2}{2m^2c^2}\right)\rho_{ext}(\boldsymbol{r}_{\boldsymbol{j}}) - \sum_{j<k} \frac{e^2}{r_{jk}} \\
& - \sum_{j<k} \frac{e^2}{2m^2c^2}\boldsymbol{p}_j \left[\frac{(\boldsymbol{r}_j - \boldsymbol{r}_k)(\boldsymbol{r}_j - \boldsymbol{r}_k)}{r_{jk}^3} + \frac{\mathbf{1}}{r_{jk}}\right] \cdot \boldsymbol{p}_k \\
& - \sum_{j\neq k} \frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\boldsymbol{S}_j \cdot [(\boldsymbol{r}_k - \boldsymbol{r}_j) \times \boldsymbol{p}_k] \\
& - \sum_{j\neq k} \frac{e^2}{2m^2c^2}\frac{1}{r_{jk}^3}\boldsymbol{S}_j \cdot [(\boldsymbol{r}_j - \boldsymbol{r}_k) \times \boldsymbol{p}_j] \\
& - \sum_{j<k} \frac{e}{m^2c^2}\boldsymbol{S}_{\boldsymbol{j}} \cdot \left[\frac{3(\boldsymbol{r}_{\boldsymbol{j}} - \boldsymbol{r}_{\boldsymbol{k}})(\boldsymbol{r}_{\boldsymbol{j}} - \boldsymbol{r}_{\boldsymbol{k}})}{\boldsymbol{r}_{\boldsymbol{jk}}^{\boldsymbol{3}}} - \frac{\mathbf{1}}{\boldsymbol{r}_{\boldsymbol{jk}}}\right] \cdot \boldsymbol{S}_{\boldsymbol{k}} \\
& - \sum_{j<k} \frac{8\pi e^2}{3m^2c^2}\delta(\boldsymbol{r}_{\boldsymbol{j}} - \boldsymbol{r}_{\boldsymbol{k}})\boldsymbol{S}_{\boldsymbol{k}} \cdot \boldsymbol{S}_{\boldsymbol{k}} \\
& - \sum_{j<k} \left(\frac{\pi e^2\hbar^2}{m^2c^2}\right)\delta(\boldsymbol{r}_{\boldsymbol{j}} - \boldsymbol{r}_{\boldsymbol{k}}).
\end{aligned}
\tag{28}
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[1] Itoh, Takashi. "Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics". *Reviews of Modern Physics* 37 (1965): 159-166.

[2] David J. Griffiths, *Introduction to Quantum Mechanics* (Prentice Hall, New Jersey, 2005), 2nd ed.

[3] Robert Gilmore, (Class Lectures) September 2010