Derivation of Electron-Electron Interaction Terms in the Multi-Electron Hamiltonian

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1 Introduction

The Hamiltonian for a multi-electron atom with n electrons is derived by Itoh (1965) by accounting for both the terms that involve only a single electron, which we will reference as the jth electron, and the terms that involve electron-electron interactions. The terms in the Hamiltonian come from four space-time fields: the scalar potential $\Phi(x,t)$, the vector potential $\mathbf{A}(x,t)$, the electric field $\mathbf{E}(x,t)$, and the magnetic field $\mathbf{B}(x,t)$. Each of these fields has two parts: extrinsic and intrinsic. The extrinsic parts of each field is taken exclusively from the jth electron and does not take into account the other electrons. The intrinsic parts, however, come from the interaction of the other n - 1 electrons. We also do not take the electrons to be stationary; thus they experience an "effective" electric and magnetic fields due to motion. The effective electric field is

$$\mathbf{E}_{\text{eff}} = \gamma(\mathbf{E} + \frac{\mathbf{v}}{c} \times \mathbf{B})$$

and the effective magnetic field is

$$\mathbf{B}_{\text{eff}} = \gamma(\mathbf{B} - \frac{\mathbf{v}}{c} \times \mathbf{E})\ .$$

However, since we know that the ratio of the speed of the electron to the speed of light is small, we can take $\gamma \simeq 1$. For the extrinsic parts of the fields we will leave the equations as stated; however, for the intrinsic parts of the fields we must remember that the velocities used are actually the velocity differences between the kth and jth electrons.

2 Single Electron Terms

We begin with the single electron terms of the Hamiltonian:

$$
\begin{aligned}
H_{\text{single}} &= \sum_j \frac{1}{2m}\,\mathbf{p}_j^2 && (1)\\
&- \sum_j \frac{1}{8m^3c^2}\,\mathbf{p}_j^4 && (2)\\
&+ \sum_j \frac{e}{mc}\mathbf{p}_j \cdot \mathbf{A}_{\text{ex}}(\mathbf{r}_j) && (3)\\
&+ \sum_j \frac{e}{2mc^2}\mathbf{A}_{\text{ex}}(\mathbf{r}_j)^2 && (4)\\
&- \sum_j e\phi_{ex}(\mathbf{r}_j) && (5)\\
&+ \sum_j \frac{e}{mc}\mathbf{s}_j \cdot \mathbf{B}_{\text{ex}}(\mathbf{r}_j) && (6)\\
&+ \sum_j \frac{e}{2m^2c^2}\mathbf{s}_j \cdot [\mathbf{E}_{\text{ex}}(\mathbf{r}_j)\times\mathbf{p}_j] && (7)\\
&+ \sum_j \frac{\pi e\hbar^2}{2m^2c^2}\rho_{\text{ex}}(\mathbf{r}_j) && (8)
\end{aligned}
$$

The terms (1) and (2) are derived from the usual relativistic equation for energy

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

Taking a binomial expansion of the square root gives

$$E = mc^2 + \frac{p^2}{2m} - \frac{p^2}{8m^2c^2}\ ,$$

neglecting higher order terms. Here we see that (1) is the second term of the previous equation, summed over all electrons, and (2) is the third term. The terms (3) and (4) come from the principle of minimum electromagnetic coupling, which causes us to redefine momentum as follows:

$$\mathbf{p} \to \mathbf{p} - \frac{q}{c}\mathbf{A}\ .$$

Plugging this into (1) gives back (1) as well as (3) and (4). We get (5) from the relationship between potential and potential energy, which are related by a factor of charge. We can see that the terms (1), (3), (4), and (5) make up the usual Hamiltonian for a single electron under the Lorentz force [1]

$$-e\mathbf{E}_{\text{ex}}(\mathbf{r}_j) - \frac{e}{c}[\mathbf{v}_j \times \mathbf{B}_{\text{ex}}(\mathbf{r}_j)] \ .$$

In order to derive (6) and (7), we must take into account the interaction between the spin magnetic moment of the electron with the magnetic field [1]. The energy of this interaction for the jth electron is given by

$$-\mu_{\mathbf{s}} \cdot \mathbf{B}_{\text{eff}}$$

where μ_{s} is the spin magnetic moment. This is related to the spin by

$$\mu_{\text{s}} = -g_{\text{s}}\mu_{\text{B}}\frac{\mathbf{s}_j}{\hbar} \ .$$

where $g_{\text{S}} = 2$ is the g-factor for the electron, and μ_{B} is the Bohr magneton. The Bohr magneton is given by

$$\mu_{\text{B}} = \frac{e\hbar}{2mc} \ .$$

Plugging this and g_{S} into the equation for the spin magnetic moment we get

$$\mu_{\text{s}} = -2\frac{e\hbar}{2mc}\frac{\mathbf{s}_j}{\hbar} = -\frac{e}{mc}\mathbf{s}_j$$

and plugging this back into our original equation for the energy due to the spin magnetic moment in a magnetic field, we get

$$\frac{e}{mc}\mathbf{s}_j \cdot \mathbf{B}_{\text{eff}} \ .$$

Finally, plugging in for our $\mathbf{B}_{\text{eff}}$, we get two terms:

$$\frac{e}{mc}\mathbf{s}_j \cdot \mathbf{B}_{\text{ex}} - \frac{e}{mc}\mathbf{s}_j \cdot \left(\frac{\mathbf{v}}{c} \times \mathbf{E}_{\text{ex}}\right) \ .$$

The first term, summed up over all j electrons, gives us (6), which is the interaction of the spin magnetic moment of the electron with the external magnetic field [1]. We would like to put the second term in terms of momentum instead of velocity, which gives us

$$-\frac{e}{m^2c^2}\mathbf{s}_j \cdot (\mathbf{p} \times \mathbf{E}_{\text{ex}}) \ .$$

Multiplying by the Thomas precession factor of $\frac{1}{2}$ which comes from making two Lorentz transformations and summing over all j gives us (7), which is the term that causes the precession of the spin in the external electric field [1].

To derive (8), we will take the electron to be an extended particle with probability density $\rho(\mathbf{r})$ centered at x_0 with spherical symmetry around this point. The energy for this electron would be

$$E = \int_{-\infty}^{\infty} -e\rho(\mathbf{x})\Phi(\mathbf{x})\, dx \ .$$

We then want to expand Φ about x_0 and neglect terms higher than second order in x, which gives us

$$E = -e\int_{-\infty}^{\infty} \rho(\mathbf{x})[\Phi(x_0) + \Delta x_i \Phi_i(x_0) + \frac{1}{2}\Delta x_i \Delta x_j \Phi_{ij}(x_0)\cdots]\, dx \ .$$

The integral in the first term of this equation integrates to 1 and the second term is zero by symmetry. The third term becomes:

$$-e\Phi_{ij}(x_0)\delta_{ij}\left(\frac{1}{2}\right)\left(\frac{1}{3}\Delta r^2\right)$$

where $\langle \Delta r^2 \rangle = \langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle + \langle \Delta z^2 \rangle$. The energy then becomes

$$\begin{aligned} E &= -e\Phi_{\text{ex}} - e\left(\frac{1}{2}\right)\left(\frac{\Delta r^2}{3}\right)(\Phi_{ij}\delta_{ij}) \\ &= -e\Phi_{\text{ex}} - e\left(\frac{\Delta r^2}{6}\right)(\Phi_{ii}) \end{aligned}$$

The first term is just (5). Since $\Phi_{ii} = \nabla^2\Phi_{\text{ex}} = -4\pi\rho_{\text{ex}}$ where ρ_{ex} is the charge density, we can take the second term to be

$$e\left(\frac{\Delta r^2}{6}\right)(4\pi\rho_{\text{ex}})$$

We can now plug in for the mean square radius, which is $\langle r^2 \rangle = \frac{3}{4}\left(\frac{\hbar}{mc}\right)^2$, which gives us

$$\left(\frac{\pi e \hbar^2}{2m^2c^2}\right)\rho_{\text{ex}}(\mathbf{r}_j)$$

which, summed over all j, gives us (8).

3 Electron-Electron Terms

We now turn our attention to the terms in the Hamiltonian that come from electron-electron interactions, which are as follows:

$$\begin{aligned}
H_{\text{multiple}} &= \sum_{j<k} \frac{e^2}{r_{jk}} && (9)\\
&- \sum_{j<k} \frac{e^2}{2m^2c^2}\,\mathbf{p}_j \cdot \left[\frac{(\mathbf{r}_j-\mathbf{r}_k)(\mathbf{r}_j-\mathbf{r}_k)}{r_{jk}^3} + \frac{1}{r_{jk}}\right]\cdot \mathbf{p}_k && (10)\\
&- \sum_{j\neq k} \frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\,\mathbf{s}_j \cdot [(\mathbf{r}_k-\mathbf{r}_j)\times \mathbf{p}_k] && (11)\\
&- \sum_{j\neq k} \frac{e^2}{2m^2c^2}\frac{1}{r_{jk}^3}\,\mathbf{s}_j \cdot [(\mathbf{r}_j-\mathbf{r}_k)\times \mathbf{p}_j] && (12)\\
&- \sum_{j<k} \frac{e^2}{m^2c^2}\,\mathbf{s}_j \cdot \left[\frac{3(\mathbf{r}_j-\mathbf{r}_k)(\mathbf{r}_j-\mathbf{r}_k)}{r_{jk}^5} - \frac{1}{r_{jk}^3}\right]\cdot \mathbf{s}_k && (13)\\
&- \sum_{j<k} \frac{8\pi e^2}{3m^2c^2}\,\delta(\mathbf{r}_j-\mathbf{r}_k)\,\mathbf{s}_j\cdot\mathbf{s}_k && (14)\\
&- \sum_{j<k} \frac{\pi e^2\hbar^2}{m^2c^2}\,\delta(\mathbf{r}_j-\mathbf{r}_k) && (15)
\end{aligned}$$

In order to derive any of these terms, we must first construct equations for the intrinsic portions of the scalar potential, vector potential, electric field, and magnetic field. The scalar potential produced by the kth electron on the jth electron is

$$\Phi_k(\mathbf{r}) = -\frac{e}{|\mathbf{r}_j-\mathbf{r}_k|} \quad (16)$$

where $j \neq k$. This is simply the Coulomb potential.

The vector potential produced by the kth electron on the jth electron is [1]

$$\mathbf{A}_k(\mathbf{r}) = -\frac{e}{2m}\left[\frac{(\mathbf{r}_j - \mathbf{r}_k)(\mathbf{r}_j - \mathbf{r}_k) + (\mathbf{r}_j - \mathbf{r}_k)^2}{|\mathbf{r}_j - \mathbf{r}_k|^3}\right] \cdot \mathbf{p}_k \tag{17}$$

but this is not the only component of the vector potential. There is also a portion of the overall potential that is produced by the spin of the kth electron, which is

$$\mathbf{A}_{k,\text{spin}}(\mathbf{r}) = \frac{\mu \times (\mathbf{r}_j - \mathbf{r}_k)}{|\mathbf{r}_j - \mathbf{r}_k|^3} \tag{18}$$

The electric field due to the kth electron on the jth electron is given by

$$\mathbf{E}_k(\mathbf{r}) = -\frac{e(\mathbf{r}_j - \mathbf{r}_k)}{|\mathbf{r}_j - \mathbf{r}_k|^3} \ . \tag{19}$$

The magnetic field from the kth electron on the jth electron has two components. One is produced by the orbital motion of the kth electron. According to the Biot-Savart law, this is given by [1]

$$\mathbf{B}_k(\mathbf{r}) = \left(\frac{e}{mc}\right)(\mathbf{r} - \mathbf{r}_k) \times \frac{\mathbf{p}_k}{|\mathbf{r} - \mathbf{r}_k|^3} \ . \tag{20}$$

The other component is produced by the spin of the kth electron. This field is given by

$$\begin{aligned}
\mathbf{B}_{k,\text{spin}}(\mathbf{r}) &= \nabla \times \mathbf{A}_{k,\text{spin}} = \nabla \times \frac{\mu \times (\mathbf{r}_j - \mathbf{r}_k)}{|\mathbf{r}_j - \mathbf{r}_k|^3} \\
&= \frac{3[\mu \cdot (\mathbf{r}_j - \mathbf{r}_k)](\mathbf{r}_j - \mathbf{r}_k) - \mu[(\mathbf{r}_j - \mathbf{r}_k) \cdot (\mathbf{r}_j - \mathbf{r}_k)]}{|\mathbf{r}_j - \mathbf{r}_k|^5} \qquad (21)
\end{aligned}$$

We now move on to deriving the electron-electron terms using these fields. If we consider each field in the single electron terms not to be just the extrinsic field, but the total field which includes both the extrinsic and intrinsic terms, the single electron terms will be returned and we will also get the electron-electron terms. Since the total field will also return the previously derived equations in most cases, we will just replace the extrinsic terms with the intrinsic terms. The derivation of (10) is an exception to this case.

By inspection, we see that (9) is simply the energy given by the Coulomb potential; however, to derive this we can plug (16) into (5), which will yield (9).

If we take the $\mathbf{A}_{\text{ex}}(\mathbf{r})$ terms in (3) and (4) and replace them with $(\mathbf{A}_{\text{ex}}(\mathbf{r})+\mathbf{A}_k(\mathbf{r}))$, we get for (3)

$$\frac{e}{mc}\mathbf{p}_j \cdot \mathbf{A}_{\text{ex}}(\mathbf{r}) - \frac{e^2}{2m^2c^2}\mathbf{p}_j \cdot \left[\frac{(\mathbf{r}_j-\mathbf{r}_k)(\mathbf{r}_j-\mathbf{r}_k)}{r_{jk}^3} + \frac{1}{r_{jk}}\right] \cdot \mathbf{p}_k$$

and for (4) we get

$$\frac{e^2}{2mc^2}(\mathbf{A}^2_{\text{ex}(\mathbf{r})} + \mathbf{A}_{\text{ex}}(\mathbf{r})\mathbf{A}_k(\mathbf{r}) + \mathbf{A}_k(\mathbf{r})^2) \ .$$

However, we want to neglect terms that are quadratic in $\mathbf{A}_k(\mathbf{r})$ as well as the cross term between $\mathbf{A}_{\text{ex}}(\mathbf{r})$ and $\mathbf{A}_k(\mathbf{r})$ [1]. Without these terms, we see that the replacement in (4) returns the same equation. From the replacement made in (3) we see that the same equation is returned as well as an extra term. This term, summed over $j < k$, gives us (10).

Using (20) in place of $\mathbf{B}_{\text{ex}}(\mathbf{r})$ in (6) gives us

$$\frac{e}{mc}\mathbf{s}_j \cdot \left[\frac{e}{mc}\frac{1}{r_{jk}^3}(\mathbf{r}_j - \mathbf{r}_k) \times \mathbf{p}_k\right]$$

$$\to -\frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\mathbf{s}_j \cdot [(\mathbf{r}_k - \mathbf{r}_j) \times \mathbf{p}_k]$$

which, summed over $j \neq k$ is (11), which is the interaction of the spin of the jth electron with the magentic field producted by the orbital motion of the other k electrons [1].

Similarly, using (19) in place of $\mathbf{E}_{\text{ex}}(\mathbf{r})$ in (7) gives us

$$\frac{e}{2m^2c^2}\mathbf{s}_j \cdot \left[\frac{-e(\mathbf{r}_j - \mathbf{r}_k)}{r_{jk}^3} \times \mathbf{p}_j\right]$$

$$\to -\frac{e^2}{2m^2c^2}\frac{1}{r_{jk}^3}\mathbf{s}_j \cdot [(\mathbf{r}_j - \mathbf{r}_k) \times \mathbf{p}_j]$$

which, summed over $j \neq k$ is (12), which is the term for the interaction of the spins of the jth electron with the electric field produced by the other $k$electrons [1].

Taking (21) and putting μ_s in terms of the spin s_k gives us

$$\mathbf{B}_{k,\mathrm{spin}}(\mathbf{r}) = \frac{e}{mc}\frac{3[\mathbf{s}_k \cdot (\mathbf{r}_j - \mathbf{r}_k)](\mathbf{r}_j - \mathbf{r}_k) - \mathbf{s}_k[(\mathbf{r}_j - \mathbf{r}_k)\cdot(\mathbf{r}_j - \mathbf{r}_k)]}{r_{jk}^5} .$$

Plugging this in for $\mathbf{B}_{\mathrm{ex}}(\mathbf{r})$ in (6) gives us

$$\frac{e}{mc}\mathbf{s}_j \cdot \frac{e}{mc}\frac{3[\mathbf{s}_k \cdot (\mathbf{r}_j - \mathbf{r}_k)](\mathbf{r}_j - \mathbf{r}_k) - \mathbf{s}_k[(\mathbf{r}_j - \mathbf{r}_k)\cdot(\mathbf{r}_j - \mathbf{r}_k)]}{r_{jk}^5}$$

$$\to \frac{e^2}{m^2c^2}\mathbf{s}_j \cdot \left[\frac{3(\mathbf{r}_j - \mathbf{r}_k)(\mathbf{r}_j - \mathbf{r}_k) - (\mathbf{r}_j - \mathbf{r}_k)\cdot(\mathbf{r}_j - \mathbf{r}_k)}{r_{jk}^5}\right]\cdot \mathbf{s}_k$$

$$\to \frac{e^2}{m^2c^2}\mathbf{s}_j \cdot \left[\frac{3(\mathbf{r}_j - \mathbf{r}_k)(\mathbf{r}_j - \mathbf{r}_k)}{r_{jk}^5} - \frac{1}{r_{jk}^3}\right]\cdot \mathbf{s}_k$$

which, summed over $j < k$, gives us (13). This term is the interaction between the spin magnetic moments that are not mutually penetrating [1].

The term (14) is put together by construction. This term takes mutual penetration into account, which requires that $r_j = r_k$. This is the reason for the Dirac delta function; we can see that if $r_j = r_k$ then the (13) goes to infinity, and if $r_j \neq r_k$ then there is no mutual penetration, causing the term to be zero. The dot product between the spins remain the same. However, (13) is also multipled by a correction factor of $\frac{8\pi}{3}$.

The term (15) is similar to (8) in that it is due to treating the electron as an extended particle. To derive this term we take (16) and plug this into the derivation for (8) which gives

$$-e\left(\frac{\Delta r^2}{6}\right)(\nabla^2\Phi_k)$$

$$\to -e\left(\frac{1}{6}\right)\left(\frac{3}{4}\right)\left(\frac{\hbar}{mc}\right)^2 4\pi e\,\delta(\mathbf{r}_j - \mathbf{r}_k)$$

$$\to -\frac{\pi e^2\hbar^2}{2m^2c^2}\,\delta(\mathbf{r}_j - \mathbf{r}_k)$$

Multiplying by 2 to take into account both electrons, and summing over $j < k$, gives us (15).

References

[1] Itoh, Takashi. 1965. Derivation of Nonrelativistic Hamiltonian for Electrons from Quantum Electrodynamics. *Reviews of Modern Physics* vol 37: pgs 159-166.