On the Hamiltonian of a Multi-Electron Atom

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1 Introduction

In this paper, we will exhibit the process of achieving the Hamiltonian for an electron gas. Making the simplification that the electron gas be in a static electromagnetic field, as well as the simplification that their velocities be much smaller than the speed of light, we end up with a multi-term expression which, in the non-relativistic limit, is a very good approximation.

Along the way to this final expression, explanations will accompany intermediate steps. In addition to this, a physical description of each term will also be provided for the benefit of the reader.

2 Procedure

2.1 Electron-Field Interactions

A good place to start will be the relativistic energy of a single electron.

$$E_{e^-} = \sqrt{(m_{e^-}c^2)^2 + (pc)^2} \tag{1}$$

In order to expand this energy into multiple terms we must slightly alter its current form.

$$E_{e^-} = m_{e^-}c^2\sqrt{1 + (\frac{pc}{m_{e^-}c^2})^2} \tag{2}$$

Making use of the binomial expansion, we get:

$$E_{e^-} = m_{e^-}c^2\left[1 + \frac{1}{2}\left(\frac{pc}{m_{e^-}c^2}\right)^2 - \frac{1}{8}\left(\frac{pc}{m_{e^-}c^2}\right)^3 + ..\right] \tag{3}$$

Let's now look in more depth at the terms that came from this expansion. By multiplying the factor of $(m_{e^-}c^2)$ through the bracket, the first term which appears is the rest energy of the electron.

$$E_0 = m_{e^-}c^2 \tag{4}$$

The second term which appears is the classical kinetic energy of the electron.

$$E_1 = \frac{p^2}{2m_{e^-}} \tag{5}$$

The next term is the first order relativistic correction to the electron kinetic energy.

$$E_2 = -\frac{p^4}{8{m_{e^-}}^3c^2} \tag{6}$$

Where:

$$p^4 = (\vec{p}\cdot\vec{p})^2 \tag{7}$$

By the principle of minimal electromagnetic coupling to (5), we can express the Hamiltonian in terms of the magnetic vector potential $\vec{A}$. The principle of electromagnetic coupling says that the equation of motion of a charged particle in some external electromagnetic field will be obtained from the free equation by the following substitution: $\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}$. The energy E_1 will become:

$$E_1 = \frac{p^2}{2m_{e^-}} + \frac{e^2}{2m_{e^-}c^2}\vec{A}\cdot\vec{A} + \frac{e}{c}\frac{\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}}{2m_{e^-}} \tag{8}$$

Let us now consider multiple electrons, an electron gas. So far, we have only considered the kinetic energy of an electron with the addition of performing the gauge transformation: $\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}$. The Hamiltonian then becomes:

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} - \sum_{j=1}^{N} \frac{p_j^4}{8m^3c^2} + \sum_{j=1}^{N} \frac{e}{c} \frac{\vec{p_j} \cdot \vec{A}(r_j) + \vec{A}(r_j) \cdot \vec{p_j}}{2m} + \sum_{j=1}^{N} \frac{e^2}{2mc^2} \vec{A}(r_j) \cdot \vec{A}(r_j) \quad (9)$$

Where m is now understood to be m_{e^-} (the mass of the electron) the index j represents the j^{th} electron, and r_j represents the coordinate of the j^{th} electron.

Point particles under the influence of the Lorentz Force ($\vec{F} = -e\vec{E}_{ext}(r_j) - \frac{e}{c}[\vec{v}_j \times \vec{H}_{ext}(r_j)]$), would give us a Hamiltonian including these terms:

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{j=1}^{N} \frac{e}{mc} \vec{p}_j \cdot \vec{A}_{ext} r_j + \sum_{j=1}^{N} \frac{e^2}{2mc^2} \vec{A}_{ext}(r_j)^2 - \sum_{j=1}^{N} e\Phi_{ext}(r_j) \quad (10)$$

So with this interaction in mind, we add the last term ($-\sum e\phi_{ext}$) to our growing list of terms in the total Hamiltonian of our electron gas. We must also consider the spin of the electron interacting with the external field. The classical Hamiltonian of a single electron in an external magnetic field is: $H = -\mu \cdot \vec{B_{ext}}$. Quantum Mechanically, we can replace this hamiltonian with:

$$\hat{H} = \frac{e}{mc} \hat{S} \cdot \vec{B}_{ext}(r_j) \quad (11)$$

Again, for multiple electrons:

$$\sum_{j=1}^{N} \frac{e}{mc} \hat{S}_j \cdot \vec{B}_{ext}(r_j) \quad (12)$$

This result is of course based on the approximation that the magnetic moment of an electron is $2 \times \mu_B$, where the Bohr Magneton $\mu_B = \frac{e\hbar}{2mc}$. It's really: $\mu_B \times 2(1 + \frac{\alpha}{2\pi} + ...)$, where the fine structure constant $\alpha \approx \frac{1}{137}$. In addition to the term involving the interaction between the electrons' dipole moments and the external magnetic field, we also obtain a contribution to the precession of the spin in the external electric field:

$$\sum_{j=1}^{N} \frac{1}{2} \frac{e}{m^2c^2} \hat{S}_j \cdot (\vec{E}(r_j) \times p_j) \quad (13)$$

Where the $\frac{1}{2}$ is the Thomas Precession Factor, a kinematic correction included due to the fact that the electron is not in its rest-frame, it is accelerating. This term takes care of the electrons' orbital angular momenta. A moving electron sees:

$$\vec{B}_{eff} = \gamma(\vec{B}_{ext} - \frac{\vec{p}}{mc} \times \vec{E}_{ext}) \quad (14)$$

and

$$\vec{E}_{eff} = \gamma(\vec{E}_{ext} + \frac{\vec{p}}{mc} \times \vec{B}_{ext}) \quad (15)$$

Plugging the effective magnetic field in for $\vec{B}$ in equation (12), we get:

$$\sum_{j=1}^{N} \frac{e\gamma}{mc} \hat{S}(\vec{B} - \frac{\vec{p}}{mc} \times \vec{E}) \quad (16)$$

After some multiplication, and in the limit of $|\vec{v}| << c \to \gamma \approx 1$:

$$\sum_{j=1}^{N} \frac{e}{mc} \hat{S}_j \cdot \vec{B}_{ext}(r_j) - \sum_{j=1}^{N} \frac{e}{2m^2c^2} \hat{S}_j \cdot [\vec{E}_{ext}(r_j) \times \vec{p}_j] \quad (17)$$

Now suppose the electron is an extended particle - i.e. that is has some probability density $\rho(r)$ centered around r_0, with the condition that: $\int \rho(r) dV = 1$. After all, it must be found somewhere! If we express the last summation in equation (10) as:

$$-\int e\rho(r)\phi(r) dV \quad (18)$$

And, expanding $\Phi(r)$ about r_0 we get:

$$-e \int \rho(r)[\Phi(r_0) + \Delta r_i \Phi_i(r_0) + \frac{1}{2} \Delta r_i \Delta r_j \Phi_{ij}(r_0) + ...] \quad (19)$$

By multiplication and later integration of equation (19), we achieve:

$$-e\Phi_{ext}(r_0) - e\frac{1}{2}\frac{\Delta r^2}{3}\nabla^2\Phi \tag{20}$$

Keep in mind some important steps:

$$1 : \int \rho(r)dV = 1$$

By symmetry:

$$2 : \int \Delta r_i \rho(r)dV = 0$$

$$3 : \int \Delta r_i \Delta r_j \rho(r)dV = \delta_{ij}\frac{1}{3}\langle\Delta r^2\rangle$$

The source of the external potential is all of the charge external to each individual electron. The relationship is:

$$\nabla^2\Phi_{ext} = -4\pi\rho_{ext} \tag{21}$$

Generalizing for all of the electrons:

$$-\sum_{j=1}^{N} e\Phi_{ext}(r_j) + \sum_{j=1}^{N}\frac{\pi e\hbar^2}{2m^2c^2}\rho_{ext}(r_j) \tag{22}$$

At this point we are done with all single electron-field interaction terms which contribute to our total Hamiltonian. Here is all of the work we have done so far in constructing the Hamiltonian of a gas of electrons:

$$H = \sum_{j=1}^{N}\frac{p_j^2}{2m} - \sum_{j=1}^{N}\frac{p_j^4}{8m^3c^2} + \sum_{j=1}^{N}\frac{e}{mc}\vec{p}_j\cdot\vec{A}_{ext}(r_j)$$

$$+\sum_{j=1}^{N}\frac{e^2}{2mc^2}\vec{A}_{ext}(r_j)^2 - \sum_{j=1}^{N}e\Phi(r_j) + \sum_{j=1}^{N}\frac{e}{mc}\hat{S}\cdot\vec{B}_{ext}(r_j)$$

$$+\sum_{j=1}^{N}\frac{e}{2m^2c^2}\hat{S}\cdot[\vec{E}_{ext}(r_j)\times\vec{p}_j] + \sum_{j=1}^{N}\frac{\pi e\hbar^2}{2m^2c^2}\rho_{ext}(r_j) \tag{23}$$

2.2 Electron-Electron Interactions

Although we have considered all possible interactions involving electrons and the electromagnetic field they are in, we haven't discussed any contributions to the Hamiltonian involving the magnetic field produced by each electron's magnetic dipole moment. In an attempt to construct terms involving electron-electron interactions we must separate out what we have already done. What we will do is to re-express the fields as the following:

$$\Phi = \Phi_{ext} + \Phi_{int}$$

$$\vec{B} = \vec{B}_{ext} + \vec{B}_{int}$$

$$\vec{E} = \vec{E}_{ext} + \vec{E}_{int}$$

$$\vec{A} = \vec{A}_{ext} + \vec{A}_{int}$$

The internal or intrinsic contributions will be the ones due to electron-electron interactions.

The most obvious electron-electron interaction term in our Hamiltonian will come from the Coulomb repulsion of the electrons.

$$\sum_{j<k}\frac{e^2}{r_{jk}} \tag{24}$$

To avoid double counting, we will sum over $j < k$ (this will be true for almost all of the terms in this section; k is the index given to the electron that the j^{th} electron will see).

The next interaction will be due to the orbital motion of the j^{th} electron in the k^{th} electron's magnetic field. By applying $\vec{A}_{ext} \to \vec{A}_{ext} + \vec{A}_{int}$ to the third term in (23), we will get:

$$\sum_{j<k}\frac{e}{mc}\vec{p}_j\cdot(\vec{A}_{ext} + \vec{A}_{int}) \tag{25}$$

Now, the intrinsic magnetic vector potential is due to the k^{th} electron. It is gotten by taking the curl of the magnetic field of the k^{th} magnetic dipole:

$$\vec{H}_k(r) = \frac{e}{c}(\vec{r} - \vec{r}_k)\times\frac{\vec{v}_k}{|\vec{r} - \vec{r}_k|^3} \tag{26}$$

The magnetic vector potential of the k^{th} electron is:

$$\vec{A}_k(r) = \frac{-e}{2c}\left[\frac{(\vec{r}-\vec{r}_k)(\vec{r}-\vec{r}_k)}{|\vec{r}-\vec{r}_k|^3} + \frac{\mathbf{1}}{|\vec{r}-\vec{r}_k|}\right]\cdot \vec{v}_k \quad (27)$$

Making the substitution of $\vec{A}_k(r)$ in for $\vec{A}_{int}$ in (25), we get the first term back along with this second term:

$$-\sum_{j<k}\frac{e^2}{2m^2c^2}\vec{p}_j\left[\frac{(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{r_{jk}^3} + \frac{\mathbf{1}}{r_{jk}}\right]\cdot \vec{p}_k \quad (28)$$

Next will be the interaction between the spin of the j^{th} electron in the magnetic field produced by the k^{th} electron's orbital angular motion. By plugging in expression (26) into the 6th term in (23) we will get:

$$-\sum_{j\neq k}\frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\hat{S}_j\cdot[(\vec{r}_k-\vec{r}_j)\times\vec{p}_k] \quad (29)$$

Next we will make the substitution that $\vec{E}_{ext} \to \vec{E}_{ext}+\vec{E}_{int}$ into the equation involving the dot product of the spin of the j^{th} electron with $(\vec{E}_{ext}\times\vec{p}_j)$:

$$\sum_{j\neq k}\frac{e}{2m^2c^2}\hat{S}_j\cdot\left[(\vec{E}_{ext}+\vec{E}_{int})\times\vec{p}_j\right] \quad (30)$$

By expanding the cross product as well as the dot product, we obtain the original result back along with another term. First I will state that at rest, the electric field of the k^{th} electron is expressed as:

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

The additional term in equation (30), after substitution of (31) is the following:

$$-\sum_{j\neq k}\frac{e^2}{2m^2c^2}\frac{1}{r_{jk}^3}\hat{S}_j\cdot[(\vec{r}_j-\vec{r}_k)\times\vec{p}_j] \quad (32)$$

This term can roughly be interpreted as the interaction of the spin of the j^{th} electron in the k^{th} electron's field (similar in nature to the 7^{th} term of (23), but caused by the k^{th} electron's field, not by the external field itself).

We must also take into account the mutual interaction between spin magnetic moments of the j^{th} and k^{th} electrons, which are not mutually penetrating. The contribution to the Hamiltonian will be as follows:

$$-\sum_{j<k}\frac{e^2}{m^2c^2}\hat{S}_j\cdot\vec{B}_{jk}\cdot\hat{S}_k \quad (33)$$

Where upon substituting the expression for the magnetic field $\vec{B}_{jk}$(the) into the previous expression above, it turns into:

$$-\sum_{j<k}\frac{e^2}{m^2c^2}\hat{S}_j\cdot\left[\frac{3(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{r_{jk}^5} - \frac{\mathbf{1}}{r_{jk}^3}\right]\cdot\hat{S}_k \quad (34)$$

The next term is very important in astronomy and astrophysics. Hyperfine structure is essentially the difference in energy levels of atoms and molecules due to internal fields. Hyperfine splitting occurs because the nuclear magnetic dipole moment is located in the magnetic field generated by the electrons. A neutral Hydrogen atom for instance has one electron, which upon transition of spin from $(+\frac{1}{2} \leftrightarrow -\frac{1}{2})$ will produce a change in energy, which we must take into account. It is of astrophysical importance because it is associated with interstellar regions of HI, and it is this magnetic dipole transition which produces radiation with a characteristic wavelength of about 21cm (radio). The contribution to the Hamiltonian is:

$$-\sum_{j<k}\frac{8\pi e^2}{3m^2c^2}\delta(\vec{r}_j-\vec{r}_k)\hat{S}_j\cdot\hat{S}_k \quad (35)$$

The last term in our Hamiltonian will be obtained by replacing $\Phi_{ext}\to\Phi_{ext}+\Phi_{int}$ into (20) (remember - this particular result came about by assuming the electron has a distribution in its location):

$$-e(1+\frac{\Delta r^2}{6}\nabla^2)(\Phi_{ext}+\Phi_{int}) \quad (36)$$

The intrinsic or internal potential we are speaking of is the potential produced by the k^{th} electron:

$$\Phi_{int}(r) = \sum_{j\neq k}\frac{-e}{|\vec{r}_j-\vec{r}_k|} \quad (37)$$

After substitution into (36), we obtain the previous result plus another term:

$$\sum_{j<k} -e\frac{\Delta r^2}{6}\nabla^2\frac{-e}{r_{jk}} \tag{38}$$

Which simplifies to:

$$-\sum_{j<k}\frac{\pi e^2\hbar^2}{m^2c^2}\delta(\vec{r}_j-\vec{r}_k) \tag{39}$$

Let's recapitulate. It it now time to express the full hamiltonian in all of its glory:

$$\begin{aligned}
H &= \sum_{j=1}^{N}\frac{p_j^2}{2m}-\sum_{j=1}^{N}\frac{p_j^4}{8m^3c^2}+\sum_{j=1}^{N}\frac{e}{mc}\vec{p}_j\cdot\vec{A}_{ext}(r_j)\\
&+\sum_{j=1}^{N}\frac{e^2}{2mc^2}\vec{A}_{ext}(r_j)^2-\sum_{j=1}^{N}e\Phi(r_j)+\sum_{j=1}^{N}\frac{e}{mc}\hat{S}_j\cdot\vec{B}_{ext}(r_j)\\
&+\sum_{j=1}^{N}\frac{e}{2m^2c^2}\hat{S}_j\cdot[\vec{E}_{ext}(r_j)\times\vec{p}_j]+\sum_{j=1}^{N}\frac{\pi e\hbar^2}{2m^2c^2}\rho_{ext}(r_j)\\
&+\sum_{j<k}\frac{e^2}{r_{jk}}-\sum_{j<k}\frac{e^2}{2m^2c^2}\vec{p}_j\cdot\left[\frac{(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{r_{jk}^3}+\frac{\mathbf{1}}{r_{jk}}\right]\cdot\vec{p}_k\\
&-\sum_{j\neq k}\frac{e^2}{m^2c^2}\frac{1}{r_{jk}^3}\hat{S}_j\cdot[(\vec{r}_k-\vec{r}_j)\times\vec{p}_k]\\
&-\sum_{j\neq k}\frac{e^2}{2m^2c^2}\frac{1}{r_{jk}^3}\hat{S}_j\cdot[(\vec{r}_j-\vec{r}_k)\times\vec{p}_j]\\
&-\sum_{j<k}\frac{e^2}{m^2c^2}\hat{S}_j\left[\frac{3(\vec{r}_j-\vec{r}_k)(\vec{r}_j-\vec{r}_k)}{r_{jk}^5}-\frac{\mathbf{1}}{r_{jk}^3}\right]\cdot\hat{S}_k\\
&-\sum_{j<k}\frac{8\pi e^2}{3m^2c^2}\delta(\vec{r}_j-\vec{r}_k)\hat{S}_j\cdot\hat{S}_k-\sum_{j<k}\frac{\pi e^2\hbar^2}{m^2c^2}\delta(\vec{r}_j-\vec{r}_k)
\end{aligned} \tag{40}$$

References

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