Derivation of the Dirac Hartree Fock equations

Joshua Goings

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The Dirac-Hartree-Fock (DHF) operator for a single determinant wave function in terms of atomic spinors is identical to that in terms of atomic orbitals. The derivation is the same: you find the energetic stationary point with respect to spinor (orbital) rotations. Thus we start with the DHF operator:

$$f_{pq} = h_{pq} + \sum_{i}^{N} (pq||ii) \tag{1}$$

The first term, h_{pq}, is the one-electron part. The second term is the two-electron part. We will look at the one-electron part first. For h_{pq}, we (obviously) cannot use the Schrödinger equation equivalent. Instead, we use the Dirac equation, which is the relativistic equation for a single electron. In two-spinor form, where

$$\psi = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} \tag{2}$$

(Which is to say ψ^L is the large component and ψ^S is the small component.) We have the expression

$$\begin{bmatrix} V - E & c(\boldsymbol{\sigma} \cdot \boldsymbol{p}) \\ c(\boldsymbol{\sigma} \cdot \boldsymbol{p}) & V - E - 2mc^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = 0 \tag{3}$$

In this case c is the speed of light and m is the electron rest mass. V is the potential, which in the non-relativistic case is the point charge nucleus, though in general relativistic quantum chemistry assumes a finite nucleus. The bold operators are vectors, for example momentum $\boldsymbol{p} = (p_x, p_y, p_z)$. Same with the Pauli operators. Now we will expand ψ^L and ψ^S in a basis. Again, the bold type means a vector.

$$\psi^L = |\chi^L\rangle \boldsymbol{c}^L; \qquad \psi^S = |\chi^S\rangle \boldsymbol{c}^S \tag{4}$$

The $\boldsymbol{c}$ is a column vector containing the basis coefficients, just like in non-relativistic Hartree-Fock theory. Similarly, the $|\chi\rangle$ ket is our basis. Inserting these expressions and multiplying on the left by $\begin{bmatrix} \langle\chi^L| & \langle\chi^S| \end{bmatrix}$ (compare with Szabo and Ostlund p. 137) we transform the integro-differential equations into

a matrix equation.

$$\begin{bmatrix} \langle\chi^L|V|\chi^L\rangle - E\langle\chi^L|\chi^L\rangle & c\langle\chi^L| - i\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}|\chi^S\rangle \\ c\langle\chi^S| - i\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}|\chi^L\rangle & \langle\chi^S|V|\chi^S\rangle - (2mc^2+E)\langle\chi^S|\chi^S\rangle \end{bmatrix} \begin{bmatrix} \boldsymbol{c}^L \\ \boldsymbol{c}^S \end{bmatrix} = 0 \tag{5}$$

Which, we will simplify to

$$\begin{bmatrix} \boldsymbol{V}^{LL} - E\boldsymbol{S}^{LL} & c\boldsymbol{\Pi}^{LS} \\ c\boldsymbol{\Pi}^{SL} & \boldsymbol{V}^{SS} - (2mc^2+E)\boldsymbol{S}^{SS} \end{bmatrix} \begin{bmatrix} \boldsymbol{c}^L \\ \boldsymbol{c}^S \end{bmatrix} = 0 \tag{6}$$

Hopefully, it is obvious we made the notational replacements

$$\boldsymbol{V}^{LL} = \langle\chi^L|V|\chi^L\rangle; \quad \boldsymbol{S}^{LL} = \langle\chi^L|\chi^L\rangle; \quad \boldsymbol{\Pi}^{LS} = \langle\chi^L| - i\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}|\chi^S\rangle; \text{ etc.} \tag{7}$$

For the DHF equations, we will slide the parts containing energy E over to the right hand side to recover the eigenvalue equation. We must now consider the analog to the Coulomb and exchange integrals in the non-relativistic HF equations to the relativistic Dirac equations. There are a few extra things to consider. The first is made clearest if we recall the definition of the two electron integrals (in Mulliken notation) for the non relativistic case. In general, we have

$$(pq|rs) = \int\int \psi_p^*(\boldsymbol{r}_1)\psi_q(\boldsymbol{r}_1)\frac{1}{r_{12}}\psi_r^*(\boldsymbol{r}_2)\psi_s(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{8}$$

In the relativistic case, we swap the orbitals ψ with their four-component spinors. We will have the same equation as above, except instead of the complex conjugate, we have the adjoint.

$$(pq|rs) = \int\int \psi_p^\dagger(\boldsymbol{r}_1)\psi_q(\boldsymbol{r}_1)\frac{1}{r_{12}}\psi_r^\dagger(\boldsymbol{r}_2)\psi_s(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{9}$$

This slight change is just because we aren't dealing with scalar functions anymore. For the most part things stay the same (at least in appearance), and we deal with charge distributions between two four spinors (in two spinor form) like so:

$$\psi_p^\dagger\psi_q = \begin{pmatrix}\psi_p^{L\dagger}\psi_p^{S\dagger}\end{pmatrix}\begin{pmatrix}\psi_q^L \\ \psi_q^S\end{pmatrix} = \psi_p^{L\dagger}\psi_q^L + \psi_p^{S\dagger}\psi_q^S \tag{10}$$

So it is ever so slightly more involved, but nothing too out of the ordinary. Extending this idea to the two electron integrals gives

$$(pq|rs) = (p^Lq^L|r^Ls^L) + (p^Lq^L|r^Ss^S) + (p^Sq^S|r^Ls^L) + (p^Sq^S|r^Ss^S) \tag{11}$$

Okay. Now implicit to all of this so far is that the interaction between two charge densities is just Coulombic and hasn't changed going from non relativistic to relativistic theories. This is not really the case, because the Coulombic interaction assumes an instantaneous response between electrons. QED tells us that this interaction is mediated by photons and therefore the interaction cannot occur any faster than the speed of light. In other words, there is a retardation effect

between electrons that we must account for. This correction to the Coulomb interaction is called the Breit interaction, given by

$$V^C(0, r_{ij}) = \frac{1}{r_{ij}} - \frac{\boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{(\boldsymbol{\alpha}_i \times r_{ij})(\boldsymbol{\alpha}_j \times r_{ij})}{r_{ij}^3} \tag{12}$$

We will ignore this for the rest of the derivation (thus ultimately giving the Dirac-Coulomb-Hartree-Fock equations), but to see how the interaction may be accounted for, consider that you now have new integrals that take the form

$$\psi_p^\dagger \boldsymbol{\alpha} \psi_q = \left(\psi_p^{L\dagger} \psi_p^{S\dagger}\right) \begin{pmatrix} 0_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0_2 \end{pmatrix} \begin{pmatrix} \psi_q^L \\ \psi_q^S \end{pmatrix} = \psi_p^{S\dagger} \boldsymbol{\sigma} \psi_q^L + \psi_p^{L\dagger} \boldsymbol{\sigma} \psi_q^S \tag{13}$$

Which basically adds some different coupling elements. The alpha is the dame as in the Dirac equation, and the sigma is again your Pauli matrices. Anyway, going back, we now have a form of the two-electron integrals in 2-spinor form. We can insert the same basis set expansion elements as before for the one-electron case, and we get, for example

$$(p^L q^L | r^L s^L) = \sum_{\mu\nu\kappa\lambda} c_{\mu p}^{L*} c_{\nu q}^L c_{\kappa r}^{L*} c_{\lambda s}^L (\mu^L \nu^L | \kappa^L \lambda^L) \tag{14}$$

And similar expressions hold for the other terms. This should look nearly identical to the molecular-orbital/atomic-orbital relation in Hartree Fock theory.

And that's really all there is to it! To clean up our expressions, we introduce density matrix $\boldsymbol{P}$, where, for example

$$\boldsymbol{P} = \begin{bmatrix} \boldsymbol{P}^{LL} & \boldsymbol{P}^{LS} \\ \boldsymbol{P}^{SL} & \boldsymbol{P}^{SS} \end{bmatrix} \tag{15}$$

with

$$\boldsymbol{P}^{LL} = \boldsymbol{c}^L \boldsymbol{c}^{L\dagger}, \text{ etc.} \tag{16}$$

Then our Dirac-(Coulomb-) Hartree Fock matrix looks like

$$\boldsymbol{F} = \begin{bmatrix} \boldsymbol{F}^{LL} & \boldsymbol{F}^{LS} \\ \boldsymbol{F}^{SL} & \boldsymbol{F}^{SS} \end{bmatrix} \tag{17}$$

With

$$F_{\mu\nu}^{LL} = V_{\mu\nu}^{LL} + \sum_{\kappa\lambda} P_{\kappa\lambda}^{LL} \left[(\mu^L \nu^L | \kappa^L \lambda^L) - (\mu^L \lambda^L | \kappa^L \nu^L)\right] + \sum_{\kappa\lambda} P_{\kappa\lambda}^{SS} \left[(\mu^L \nu^L | \kappa^S \lambda^S)\right] \tag{18}$$

$$F_{\mu\nu}^{LS} = c\Pi_{\mu\nu}^{LS} - \sum_{\kappa\lambda} P_{\kappa\lambda}^{SL} (\mu^L \lambda^L | \kappa^S \nu^S) \tag{19}$$

$$F_{\mu\nu}^{SS} = V_{\mu\nu}^{SS} - 2c^2 S_{\mu\nu}^{SS} + \sum_{\kappa\lambda} P_{\kappa\lambda}^{LL} (\mu^S \nu^S | \kappa^L \lambda^L) + \sum_{\kappa\lambda} P_{\kappa\lambda}^{SS} \left[(\mu^S \nu^S | \kappa^S \lambda^S) - (\mu^S \lambda^S | \kappa^S \nu^S)\right] \tag{20}$$

And of course the form of the DHF equations is the same as in the non-relativistic case (with $\boldsymbol{C}$ the matrix of all eigenvectors $\boldsymbol{c}$):

$$\boldsymbol{FC} = \boldsymbol{SC}E \tag{21}$$

The Dirac Fock matrix is Hermitian, and you can see that it depends on the density $\boldsymbol{P} = \boldsymbol{CC}^\dagger$ as well, meaning we have to solve the equations iteratively.