This implies that $(\vec{\sigma}\cdot\vec{a})^2 = |\vec{a}|^2$. Thus

$$\underline{\vec{\sigma}\cdot\vec{p}} = \underbrace{\frac{1}{|\vec{r}|^2}(\vec{\sigma}\cdot\vec{r})(\vec{\sigma}\cdot\vec{r})}_{=1}(\vec{\sigma}\cdot\vec{p}) =$$

$$= \frac{1}{|\vec{r}|^2}(\vec{\sigma}\cdot\vec{r})\left[\vec{r}\cdot\vec{p} + i\,\vec{\sigma}\cdot(\vec{r}\times\vec{p})\right] =$$

$$= \underline{(\vec{e}_r\cdot\vec{\sigma})\left[\vec{e}_r\cdot\vec{p} + \frac{i}{r}\,\vec{\sigma}\cdot\vec{L}\right]}$$

with $\vec{e}_r = \frac{\vec{r}}{r}$ the radial unit vector.

Obviously

$$\underline{\vec{e}_r\cdot\vec{p}} = -i(\vec{e}_r\cdot\nabla) = \underline{-i\frac{\partial}{\partial r}}$$

$$\underline{\vec{\sigma}\cdot\vec{L}} = 2\,\vec{S}\cdot\vec{L} = (\vec{L}+\vec{S})^2 - \vec{L}^2 - \vec{S}^2 = \underline{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}$$

Thus the application of $\vec{\sigma}\cdot\vec{L}$ on $\mathcal{Y}_l^{j\mu}$ gives

$$(\vec{\sigma}\cdot\vec{L})\,\mathcal{Y}_l^{j\mu} = \Big(j(j+1) - l(l+1) - \underbrace{s(s+1)}_{=\frac{3}{4}}\Big)\,\mathcal{Y}_l^{j\mu}$$

$$=: \kappa(j,l)\,\mathcal{Y}_l^{j\mu}$$

We distinguish two cases:

(i) $\underline{l = j - \frac{1}{2}}$: $\quad \kappa = j(j+1) - (j - \frac{1}{2})(j + \frac{1}{2}) - \frac{3}{4}$

$$= j^2 + j - j^2 - \frac{1}{2} = \underline{j - \frac{1}{2}}$$

(ii) $\underline{l = j + \frac{1}{2}}$: $\quad \kappa = j^2 + j - (j + \frac{1}{2})(j + \frac{3}{2}) - \frac{3}{4}$

$$= j - 2j - \frac{3}{2} = -j - \frac{3}{2} = \underline{-(j + \frac{3}{2})}$$

To summarize, we introduce the integer variable $\lambda = j + \frac{1}{2}$ and write

$$\kappa = \begin{cases} \lambda - 1 & l = j - \frac{1}{2} \\ -(\lambda + 1) & l = j + \frac{1}{2} \end{cases}$$

It remains to consider the action of $\vec{e}_r \cdot \vec{\sigma}$. Since this is a (pseudo) scalar operator, the action should not depend on θ, ϕ and we may choose

$$\theta = 0 \quad \Rightarrow \quad \vec{e}_r \cdot \vec{\sigma} = \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

It is also known that $Y_l^m(\theta = 0, \phi) = \underline{\sqrt{\frac{2l+1}{4\pi}}\, \delta_{m,0}}$

$$\Rightarrow \underline{\sigma^3 \, \mathcal{Y}_l^{j = l \pm \frac{1}{2}, m}(\theta = 0, \phi)} =$$

$$= \frac{1}{\sqrt{4\pi}} \, \sigma^3 \begin{pmatrix} \pm\sqrt{l \pm m + \frac{1}{2}}\, \delta_{m, \frac{1}{2}} \\ \sqrt{l \mp m + \frac{1}{2}}\, \delta_{m, -\frac{1}{2}} \end{pmatrix} =$$

$$= \frac{1}{\sqrt{4\pi}} \begin{pmatrix} \pm\sqrt{j+\frac{1}{2}}\ \delta_{m,\frac{1}{2}} \\ -\sqrt{j+\frac{1}{2}}\ \delta_{m,-\frac{1}{2}} \end{pmatrix} = \underline{-\mathcal{Y}_l^{j=l\mp\frac{1}{2}, m}(0,\phi)}$$

and we conclude that for any θ, ϕ

$$\underline{(\vec{e}_r \cdot \vec{\sigma})\, \mathcal{Y}_l^{j=l\pm\frac{1}{2}, m} = -\mathcal{Y}_l^{j=l\mp\frac{1}{2}, m}}$$

We can now evaluate the stationary Schrödinger equation for $\psi_A(\vec{r})$:

$$0 = (E-m-V(r))\, u_A\, \mathcal{Y}_{j-\frac{1}{2}}^{jm} + \underbrace{(\vec{\sigma}\cdot\vec{p})}\, i v_A\, \mathcal{Y}_{j+\frac{1}{2}}^{jm}$$

$$= \left(-i\partial_r - \frac{i}{r}(\lambda+1)\right) i v_A\, \underbrace{(\vec{e}_r\cdot\vec{\sigma})\, \mathcal{Y}_{j+\frac{1}{2}}^{jm}}_{= -\mathcal{Y}_{j-\frac{1}{2}}^{jm}}$$

$$= \Big\{ \underbrace{(E-m-V(r))\, u_A - \left(\partial_r + \frac{\lambda+1}{r}\right) v_A}_{\overset{!}{=}\,0} \Big\}\, \mathcal{Y}_{j-\frac{1}{2}}^{jm}$$

$$\Rightarrow \underline{(E-m-V(r))\, u_A - \left(\frac{\partial}{\partial r} + \frac{\lambda+1}{r}\right) v_A = 0} \qquad \text{R1}$$

Similarly the evaluation of the second equation yields

R2 $$\left(E + m - V(r)\right) v_A + \left(\frac{\partial}{\partial r} - \frac{\lambda - 1}{r}\right) u_A = 0$$

The equation for ψ_B turn out to be equivalent and don't need to be considered further.

Thus we are left with two coupled, linear, first order differential equations.

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c) Solution for the Coulomb potential

We set $V = -\frac{Ze^2}{r}$ and use scaled variables

$$\varepsilon := E/m, \quad x = mr$$

which yields $(u = u_A, \, v = v_A)$

R $$\left(\varepsilon - 1 + \frac{Z\alpha}{x}\right) u - \left(\frac{d}{dx} + \frac{\lambda+1}{x}\right) v = 0$$

$$\left(\varepsilon + 1 + \frac{Z\alpha}{x}\right) v + \left(\frac{d}{dx} - \frac{\lambda - 1}{x}\right) u = 0$$

where $\alpha = e^2 = e^2/\hbar c$ is the fine structure constant, $\alpha \simeq 1/137$ for the electron. Note that $Z\alpha = v_c/c$, where v_c is the classical velocity of an electron in the non-relativistic ground state.

- Large x: $\frac{dv}{dx} \simeq -(1-\varepsilon)u$, $\frac{du}{dx} \simeq -(1+\varepsilon)v$

$$\Rightarrow \quad \frac{d^2v}{dx^2} \simeq (1-\varepsilon^2)v.$$

In the original units

$$\varepsilon = \frac{E}{mc^2} < 1 \quad \text{for bound states}$$

$\Rightarrow$ u, v decay exponentially as $e^{-\sqrt{1-\varepsilon^2}\,x}$.

- Small x: We make an ansatz

$$u(x) = a_0 x^\nu e^{-\mu x}, \quad v(x) = b_0 x^\nu e^{-\mu x}$$

with $\mu = \sqrt{1-\varepsilon^2}$. Inserting into (R) yields

$$\left(\varepsilon - 1 + \frac{Z\alpha}{x}\right)u - \left(-\mu + \frac{\nu+\lambda+1}{x}\right)v = 0$$

$$\left(\varepsilon + 1 + \frac{Z\alpha}{x}\right)v + \left(-\mu + \frac{\nu-\lambda+1}{x}\right)u = 0$$

Comparing the coefficients of the leading order terms for $x \to 0$ it follows that

$$\left.\begin{aligned} Z\alpha\, a_0 - (\nu+\lambda+1)\, b_0 &= 0 \\ Z\alpha\, b_0 + (\nu-\lambda+1)\, a_0 &= 0 \end{aligned}\right\} \quad (R_0)$$

which has a nontrivial solution a_0, b_0 if

$$(Z\alpha)^2 + (\nu+1+\lambda)(\nu+1-\lambda) =$$
$$= (Z\alpha)^2 + (\nu+1)^2 - \lambda^2 = 0$$
$$\Rightarrow \quad \nu = -1 \pm \sqrt{\lambda^2 - (Z\alpha)^2}$$

Two remarks:

(i) The negative solution has $\nu < -1$ which spoils the integrability for $x \to 0$
$\Rightarrow$ choose $\nu = -1 + \sqrt{\lambda^2 - (Z\alpha)^2}$

(ii) ν becomes complex for sufficiently large $Z\alpha$, which is a first hint to the breakdown of the single particle theory

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To find the full set of solution to R we make a ansatz as power series

$$u(x) = x^\nu e^{-\mu x} \sum_{i=0}^{\infty} a_i x^i$$
$$v(x) = x^\nu e^{-\mu x} \sum_{i=0}^{\infty} b_i x^i$$

which leads to the recursion relations

$$\text{I} \quad (1-\varepsilon)\, a_{i-1} - Z\alpha\, a_i - \mu\, b_{i-1} + (\nu + 1 + i + \lambda)\, b_i = 0$$

$$\text{II} \quad (1+\varepsilon)\, b_{i-1} + Z\alpha\, b_i - \mu\, a_{i-1} + (\nu + 1 + i - \lambda)\, a_i = 0$$

which can be solved recursively starting from a solution (a_0, b_0) of R_0.

Combining I and II the a_{i-1}, b_{i-1} - terms can be eliminated and it follows that

$$\text{III} \quad \frac{b_i}{a_i} = \frac{\sqrt{1+\varepsilon}\,(Z\alpha) - \sqrt{1-\varepsilon}\,(\nu + 1 + i - \lambda)}{\sqrt{1-\varepsilon}\,(Z\alpha) + \sqrt{1+\varepsilon}\,(\nu + 1 + i + \lambda)}$$

Assuming that the series a_i, b_i do not terminate, we can evaluate III for large i:

$$\frac{b_i}{a_i} \xrightarrow{i \to \infty} -\sqrt{\frac{1-\varepsilon}{1+\varepsilon}}$$

Using this in I and II it follows that

$$a_i \simeq \frac{2\mu}{i}\, a_{i-1}, \quad b_i \simeq \frac{2\mu}{i}\, b_{i-1}$$

for $i \to \infty$, and therefore

$$a_i, b_i \simeq \frac{(2\mu)^i}{i!}$$

$$\Rightarrow \sum_{i=0}^{\infty} a_i x^i \simeq \sum_{i=0}^{\infty} \frac{(2\mu x)^i}{i!} \sim e^{2\mu x}$$

$$\sum_{i=0}^{\infty} b_i x^i \sim e^{2\mu x}$$

which implies that $u(x)$, $v(x)$ diverge exponentially.

It follows that the series have to terminate, which yields a quantization condition for ε.

Suppose that $a_i, b_i = 0$ for $i > n'$. Then

$$(1-\varepsilon) a_{n'} - \mu b_{n'} = (1+\varepsilon) b_{n'} - \mu a_{n'} = 0$$

$$\Rightarrow \frac{b_{n'}}{a_{n'}} = \frac{1-\varepsilon}{\mu} = \sqrt{\frac{1-\varepsilon}{1+\varepsilon}}$$

Combining this with III it follows that

$$Z\alpha\varepsilon = \sqrt{1-\varepsilon^2}\,(1+\nu+n')$$

$$\Rightarrow \varepsilon = \frac{(1+\nu+n')}{\left[(Z\alpha)^2 + (1+\nu+n')^2\right]^{1/2}} =$$

$$= \frac{1}{\left[1 + \frac{(Z\alpha)^2}{(1+\nu+n')^2}\right]^{1/2}}, \quad n' \geq 0$$

Remarks

(i) The ground state energy is obtained setting $n' = 0$ and

$$1+\nu = \sqrt{\left(j+\tfrac{1}{2}\right)^2 - (Z\alpha)^2} = \sqrt{1-(Z\alpha)^2}$$

for $j = 1/2$, the smallest possible value. This gives

$$\varepsilon_0 = \sqrt{1-(Z\alpha)^2} \Rightarrow E_0 = mc^2\sqrt{1-(Z\alpha)^2}$$

which makes sense as long as $Z\alpha < 1$.

(ii) In the nonrelativistic limit $Z\alpha \ll 1$,

$$1+\nu = \sqrt{\lambda^2-(Z\alpha)^2} \simeq \lambda = j+\tfrac{1}{2}$$

$$\Rightarrow \varepsilon \simeq \sqrt{1-\frac{(Z\alpha)^2}{(1+\nu+n')^2}} \simeq 1-\frac{(Z\alpha)^2}{2\underbrace{\left(j+\tfrac{1}{2}+n'\right)}_{=:n}{}^2}$$

$$\Rightarrow E_n = mc^2\left(1-\frac{Z^2e^4}{2\hbar^2c^2n^2}\right) =$$

$$= mc^2 \underbrace{-\frac{Z^2e^4m}{2\hbar^2n^2}}_{\text{Balmer series}}$$

(iii) The next order correction

$$\Delta E_{n,j} = -\frac{mc^2 (Z\alpha)^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)$$

determines the fine structure of the hydrogen atom. In non-relativistic quantum mechanics it is obtained perturbatively and attributed to three different physical mechanisms:

- Relativistic kinetic energy:

$$E = \sqrt{c^2 |\vec{p}|^2 + m^2 c^4} \simeq mc^2 + \frac{\vec{p}^{\,2}}{2m} - \underbrace{\frac{(\vec{p}^{\,2})^2}{8m^3c^2}}_{=:\,H_1}$$

Perturbation theory applied to this operator gives

$$\Delta E^{(1)} = -\frac{mc^2(Z\alpha)^4}{2n^4}\left(\frac{n}{l+1/2} - \frac{3}{4}\right)$$

- Spin-orbit coupling: An electron moving in the electric field of the nucleus feels an effective magnetic field that couples to the spin

$$\Rightarrow \quad H_2 = \frac{1}{2m^2c^2}\,\vec{S}\cdot\vec{L}\,\frac{Ze^2}{r^3}$$

The perturbative result for $H_1 + H_2$ is

$$\Delta E^{(1)} + \Delta E^{(2)} = -\frac{mc^2(Z\alpha)^4}{2n^4}\left\{\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right\}, \quad l>0$$

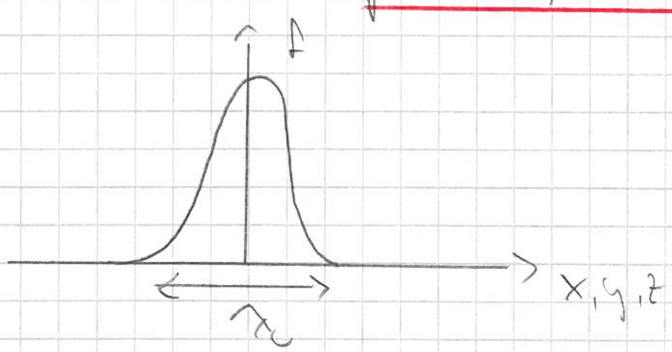
which is almost the full correction. However the spin-orbit contribution vanishes for $l=0$.

- Darwin term: This contributes only for $l=0$ and is physically attributed to the fact that the relativistic electron becomes "fuzzy" on the scale of the Compton wave length λ_c.

The effective potential felt by the electron is therefore

$$V_{eff}(\vec{r}) = \int d^3r' \, f(\vec{r}') \underbrace{V(\vec{r}+\vec{r}')}_{\text{Coulomb potential at } \vec{r}+\vec{r}'}$$

where $f(\vec{r})$ is a probability distribution of width λ_c



$$\int d^3r \, f(\vec{r}) = 1$$

Using $V(\vec{r}+\vec{r}') = V(\vec{r}) + \vec{r}' \cdot \nabla V +$

$$+ \frac{1}{2}(\vec{r}' \cdot \nabla)^2 V + \text{higher order terms}$$

it follows that

$$V_{eff}(\vec{r}) = V(\vec{r}) + \underbrace{\left(\int d^3r' f(\vec{r}')\vec{r}'\right)}_{=0 \text{ by symmetry}} \cdot \nabla V$$

$$+ \frac{1}{2}\int d^3r' f(\vec{r}') \underbrace{(\vec{r}' \cdot \nabla)^2}\, V(\vec{r})$$

$$= (x'\partial_x + y'\partial_y + z'\partial_z)^2 = x'^2\partial_x^2 + y'^2\partial_y^2 + z'^2\partial_z^2 \quad \text{+ mixed terms}$$

$$= V(\vec{r}) + \left(\frac{1}{6}\underbrace{\int d^3r' |\vec{r}'|^2 f(\vec{r})}_{\simeq \lambda_c^2}\right)\nabla^2 V(\vec{r})$$

which leads to a perturbation of the form

$$\lambda_c^2 \nabla^2 V(\vec{r}) = 4\pi \underbrace{\lambda_c^2 Ze^2}_{\frac{\hbar^2 Ze^2}{m^2c^2}} \delta(\vec{r})$$

The exact calculation yields

$$H_3 = \frac{\pi \hbar^2 Ze^2}{2m^2c^2}\delta(\vec{r})$$

Because this acts only at the origin, it contributes only to the $l=0$ state. As a consequence the expression obtained for $\Delta E^{(1)} + \Delta E^{(2)}$ holds for all j.

7° Quantization of the Klein-Gordon equation

We summarize the state of affairs regarding the negative energy solutions, which has not really been resolved.

- Negative energy solutions appear both in the Dirac and Klein-Gordon equation and thus are an unavoidable feature of single particle relativistic quantum mechanics.

- The Dirac interpretation resolves this problem partially, but at the expense of introducing a sea of unobservable filled negative energy states. Moreover this picture only works for fermions.

- What the Dirac interpretation is really telling us is that we need a theory that allows for the creation and annihilation of particles. Such a theory is provided by the formalism of second quantization, which we have constructed along two different routes:

(i) Construction of Fock space as a direct sum of N-particle Hilbert spaces (Chapter II). Here annihilation and creation operators appear as calculational devices.

(ii) Quantization of the classical electromagnetic field (Chapter IV), leading to the concept of the photon as a massless relativistic particle.

Here we follow the second route and apply it to the Klein-Gordon equation, which is now interpreted as a classical field equation.

Reminder of Chapter IV:

- Starting point is the electromagnetic wave equation

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\vec{A}(\vec{r},t) = 0$$

with general solution

$$\vec{A}(\vec{r},t) = \sum_{\vec{k}}\left(\vec{A}_{\vec{k}}\, e^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)} + \vec{A}^*_{\vec{k}}\, e^{-i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}\right)$$

with $\omega_{\vec{k}} = c|\vec{k}|$.

- Next the Fourier coefficients $\vec{A}_{\vec{k}}, \vec{A}^*_{\vec{k}}$ are replaced by operators according to

$$\vec{A}_k = \sqrt{\frac{2\pi \hbar c}{Vk}}\, \vec{e}_{\vec{k}}\, a_{\vec{k}} \qquad \text{annihilation}$$

$$\vec{A}^*_k = \sqrt{\frac{2\pi \hbar c}{Vk}}\, \vec{e}_{\vec{k}}\, a^\dagger_{\vec{k}} \qquad \text{creation}$$

of a photon

We now apply the same procedure to the Klein-Gordon equation:

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \left(\frac{mc}{\hbar}\right)^2 \right) \psi(\vec{r},t) = 0$$

$\Rightarrow$ general solution:

$$\psi(\vec{r},t) = \sum_{\vec{k}} B_{\vec{k}}\, e^{i(\vec{k}\cdot\vec{r} - \omega_{\vec{k}} t)} + C^*_{\vec{k}}\, e^{-i(\vec{k}\cdot\vec{r} - \omega_{\vec{k}} t)}$$

with $\omega_{\vec{k}} = \sqrt{c^2|\vec{k}|^2 + \frac{m^2c^4}{\hbar^2}}$. Because ψ is complex, the coefficients $B_{\vec{k}}$ and $C_{\vec{k}}$ are now independent. Formally, the $B_{\vec{k}}$ and $C_{\vec{k}}$ are the amplitudes of the positive and negative energy states, respectively.

Next the theory is quantized by replacing

$$\begin{cases} B_{\vec{k}} \longrightarrow \dfrac{W}{\sqrt{V\omega_{\vec{k}}}}\, b_{\vec{k}} & \text{annihilation operator} \\ C^{*}_{\vec{k}} \longrightarrow \dfrac{W}{\sqrt{V\omega_{\vec{k}}}}\, c^{+}_{\vec{k}} & \text{creation operator} \end{cases}$$

where W is a normalization constant.

Because $B_{\vec{k}}$ and $C_{\vec{k}}$ are independent, the two sets of operators $b_{\vec{k}}, b^{+}_{\vec{k}}$ and $c_{\vec{k}}, c^{+}_{\vec{k}}$ create and annihilate different species of particles that we designate as particles and antiparticles.

In the electromagnetic case $b_{\vec{k}} = c_{\vec{k}}$ because $\vec{A}$ is real, and therefore the photon is its own antiparticle.

The Klein-Gordon particle is a spinless boson, and the $b_{\vec{k}}$, $c_{\vec{k}}$ satisfy the bosonic commutation relations

$$[b_{\vec{k}}, b_{\vec{k}'}] = [c_{\vec{k}}, c_{\vec{k}'}] = [b^{+}_{\vec{k}}, b^{+}_{\vec{k}'}] = [c^{+}_{\vec{k}}, c^{+}_{\vec{k}'}] = 0$$

$$[b_{\vec{k}}, b^{+}_{\vec{k}'}] = [c_{\vec{k}}, c^{+}_{\vec{k}'}] = \delta_{\vec{k}\vec{k}'}$$

Thus the solutions of the Klein-Gordon equation become field operators analogous to those considered in Chapter II:

$$\psi(\vec{r},t) = \sum_{\vec{k}} \frac{W}{\sqrt{V\omega_{\vec{k}}}} \Big(e^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}\, b_{\vec{k}} + $$

$$+ e^{-i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}\, c^+_{\vec{k}} \Big)$$

$$\psi^+(\vec{r},t) = \sum_{\vec{k}} \frac{W}{\sqrt{V\omega_{\vec{k}}}} \Big(e^{-i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}\, b^+_{\vec{k}} + $$

$$+ e^{i(\vec{k}\cdot\vec{r}-\omega_{\vec{k}}t)}\, c_{\vec{k}} \Big)$$

As an application we consider the integral of the Klein-Gordon probability density

$$\hat{\rho} = \frac{i\hbar}{2mc^2}\left[\psi^+ \frac{\partial\psi}{\partial t} - \frac{\partial\psi^+}{\partial t}\psi \right]$$

$$\Rightarrow \hat{N} = \int_V d^3r \;\hat{\rho}(\vec{r},t) =$$

$$= \frac{\hbar W}{mc^2} \underbrace{\sum_{\vec{k}} \left(b^+_{\vec{k}} b_{\vec{k}} - c^+_{\vec{k}} c_{\vec{k}} \right)}_{N_{\text{particles}} - N_{\text{antiparticles}}}$$

which shows that ρ should be interpreted as the charge density of a system of particles and antiparticles of opposite charge (see V.1°).

Finally the energy takes the form

$$H = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(b^{\dagger}_{\vec{k}} b_{\vec{k}} + c^{\dagger}_{\vec{k}} c_{\vec{k}} \right)$$

which is positive and finite for any state consisting of a finite number of particles and antiparticles. This can be derived from the Hamiltonian of the classical Klein-Gordon field, which is of the form

$$\mathcal{H}[\psi] = \int d^3r \left\{ |\partial_t \psi|^2 + c^2 |\nabla \psi|^2 + \left(\frac{mc^2}{\hbar}\right)^2 |\psi|^2 \right\}$$