221B Lecture Notes
Relativistic Quantum Mechanics

1 Need for Relativistic Quantum Mechanics

We discussed the interaction of matter and radiation field based on the Hamiltonian

$$H = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} - \frac{Ze^2}{r} + \int d\vec{x} \frac{1}{8\pi}(\vec{E}^2 + \vec{B}^2). \tag{1}$$

(Coulomb potential is there only if there is another static charged particle.) The Hamiltonian of the radiation field is Lorentz-covariant. In fact, the Lorentz covariance of the Maxwell equations is what led Einstein to propose his special theory of relativity. The problem here is that the matter Hamiltonian which describes the time evolution of the matter wave function is not covariant. A natural question is: can we find a new matter Hamiltonian consistent with relativity?

The answer turned out to be yes and no. In the end, a fully consistent formulation was not obtained by modifying the single-particle Schrödinger wave equation, but obtained only by going to quantum field theory. We briefly review the failed attempts to promote Schrödinger equation to a relativistically covariant one.

2 Klein–Gordon Equation

The Schrödinger equation is based on the non-relativisitc expression of the kinetic energy

$$E = \frac{\vec{p}^2}{2m}. \tag{2}$$

By the standard replacement

$$E \to i\hbar \frac{\partial}{\partial t}, \qquad \vec{p} \to -i\hbar \vec{\nabla}, \tag{3}$$

we obtain the Schrödinger equation for a free particle

$$i\hbar \frac{\partial}{\partial t}\psi = -\frac{\hbar^2 \Delta}{2m}\psi. \tag{4}$$

A natural attempt is to use the relativistic version of Eq. (2), namely

$$\left(\frac{E}{c}\right)^2 = \vec{p}^2 + m^2c^2. \tag{5}$$

Then using the same replacements Eq. (3), we obtain a wave equation

$$\left(\frac{\hbar}{c}\frac{\partial}{\partial t}\right)^2 \phi = (\hbar^2\Delta - m^2c^2)\phi. \tag{6}$$

It is often written as

$$\left(\Box + \frac{m^2c^2}{\hbar^2}\right)\phi = 0, \tag{7}$$

where $\Box = (\frac{1}{c}\partial_t)^2 - \Delta$ is called D'Alambertian and is Lorentz-invariant. This equation is called Klein–Gordon equation.

You can find plane-wave solutions to the Klein–Gordon equation easily. Taking $\phi = e^{i(\vec{p}\cdot\vec{x}-Et)/\hbar}$, Eq. (6) reduces to Eq. (5). Therefore, as long as energy and momentum follows the Einstein's relation Eq. (5), the plane wave is a solution to the Klein–Gordon equation. So far so good!

The problem arises when you try to rely on the standard probability interpretation of Schrödinger wave function. If a wave function ψ satisfies Schrödinger equation Eq. (4), the total probability is normalized to unity

$$\int d\vec{x}\psi^*(\vec{x},t)\psi(\vec{x},t) = 1. \tag{8}$$

Because the probability has to be conserved (unless you are interested in seeing 5 times more particles scattered than what you have put in), this normalization must be independent of time. In other words,

$$\frac{d}{dt}\int d\vec{x}\psi^*(\vec{x},t)\psi(\vec{x},t) = 0. \tag{9}$$

It is easy to see that Schrödinger equation Eq. (4) makes this requirement satisfied automatically thanks to Hermiticity of the Hamiltonian.

On ther other hand, the probability defined the same way is not conserved for Klein–Gordon equation. The point is that the Klein–Gordon equation is second order in time derivative, similarly to the Newton's equation of motion in mechanics. The initial condtions to solve the Newton's equation of motion are the initial positions and initial velocities. Similarly, you have to give both

initial configuration $\phi(\vec{x})$ and its time derivative $\dot{\phi}(\vec{x})$ as the initial conditions at time t. The time derivative of the "total probability" is

$$\frac{d}{dt}\int d\vec{x}\phi^*(\vec{x},t)\phi(\vec{x},t) = \int d\vec{x}(\dot{\phi}^*(\vec{x},t)\phi(\vec{x},t) + \phi^*(\vec{x},t)\dot{\phi}(\vec{x},t)), \tag{10}$$

and ϕ and $\dot{\phi}$ are independent initial conditions, it in general does not vanish, and hence the "total probability" is not conserved. In other words, this is an unacceptable definition for the probability, and the standard probability interpretation does not work with Klein–Gordon equation.

One may then ask, if there is a conserved quantity we can possibly call "probability." It is easy to see that the following quantity is conserved:

$$\int d\vec{x}(i\phi^*\dot{\phi} - i\dot{\phi}^*\phi) \tag{11}$$

using the Klein–Gordon equation. However, this quantity cannot be called probability either because it is not positive definite.

Overall, the Klein–Gordon equation appears to be a good relativistic replacement for the non-relativistic Schrödinger equation at the first sight, but it completely fails to give the conventional probability interpretation of a single-particle wave function. In other words, the Klein–Gordon equation, if useful at all, does not describe the probability wave, which the Schrödinger equation does, but describes something else. Because of this reason, the Klein–Gordon equation was abandoned for a while. We will come back to the question what it actually describes later on.

3 Dirac Equation

3.1 Heuristic Derivation

Dirac was the first to realize the problem with the probability interpretation for equations with second-order time derivatives. He insisted on finding an equation with only first-order time derivatives. Because the relativity requires to treat time and space on equal footing, it means that the equation has to be only first-order in spatial derivatives, too. Given the replacements Eq. (3), the Hamiltonian must be linear in the momentum. Then the only equation you can write down is of this form:

$$i\hbar\frac{\partial}{\partial t}\psi = H\psi = [c\vec{\alpha}\cdot\vec{p} + mc^2\beta]\psi. \tag{12}$$

At this point, we don't know what $\vec{\alpha}$ and β are. The Dirac further required that this equation gives Einstein's dispersion relation $E^2 = \vec{p}^2c^2 + m^2c^4$ like the Klein–Gordon equation. Because the energy E is the eigenvalue of the Hamitonian, we act H again on the Dirac wave function and find

$$H^2\psi = [c^2\alpha^i\alpha^j p^i p^j + mc^3(\alpha^i\beta + \beta\alpha^i)p^i + m^2c^4\beta^2]\psi. \tag{13}$$

In order for the r.h.s. to give just $\vec{p}^2c^2 + m^2c^4$, we need

$$\alpha^i\alpha^j + \alpha^j\alpha^i = 2\delta^{ij}, \qquad \beta^2 = 1, \qquad \alpha^i\beta + \beta\alpha^i = 0. \tag{14}$$

These equations can be satisfied if α^i, β are *matrices*! Setting the issue aside why the hell we have to have matrices in the wave equation, let us find solutions to the above equations. There are of course infinite number of solutions related by unitary rotations, but the canonical choice Dirac made was

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{15}$$

They are four-by-four matrices, and σ^i are the conventional Pauli matrices. You can easily check the relations Eq. (14) using the matrices in Eq. (15). Correspondingly, the wave function ψ must be a four-component column vector. We will come back to the meaning of the multi-component-ness later. But the first point to check is that this equation does allow a conserved probability

$$i\hbar\frac{d}{dt}\int d\vec{x}\psi^\dagger\psi = \int d\vec{x}[\psi^\dagger(H\psi) - (H\psi)^\dagger\psi] = 0, \tag{16}$$

simply because of the hermiticity of the Hamiltonian (note that $\vec{\alpha}$, β matrices are hermitean). This way, Dirac found a wave equation which satisfies the relativistic dispersion relation $E^2 = \vec{p}^2c^2 + m^2c^4$ while admitting the probability interpretation of the wave function.

3.2 Solutions to the Dirac Equation

Let us solve the Dirac equation Eq. (12) together with the matrices Eq. (15). For a plane-wave solution $\psi = u(p)e^{i(\vec{p}\cdot\vec{x}-Et)/\hbar}$, the equation becomes

$$\begin{pmatrix} mc^2 & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -mc^2 \end{pmatrix} u(p) = Eu(p). \tag{17}$$

This matrix equation is fairly easy to solve. The first point to note is that the matrix $\vec{\sigma}\cdot\vec{p}$ has eigenvalues $\pm|\vec{p}|$ because $(\vec{\sigma}\cdot\vec{p})^2 = \sigma^i\sigma^j p^i p^j = \frac{1}{2}\{\sigma^i,\sigma^j\}p^i p^j = \delta^{ij}p^i p^j = \vec{p}^2$. Using polar coordinates $\vec{p} = |\vec{p}|(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, we find

$$\vec{\sigma}\cdot\vec{p} = \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix} = |\vec{p}| \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}, \tag{18}$$

and their eigenvectors

$$\vec{\sigma}\cdot\vec{p}\chi_+(\vec{p}) = \vec{\sigma}\cdot\vec{p}\begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2}e^{i\phi} \end{pmatrix} = +|\vec{p}|\chi_+(\vec{p}), \tag{19}$$

$$\vec{\sigma}\cdot\vec{p}\chi_-(\vec{p}) = \vec{\sigma}\cdot\vec{p}\begin{pmatrix} -\sin\frac{\theta}{2}e^{-i\phi} \\ \cos\frac{\theta}{2} \end{pmatrix} = -|\vec{p}|\chi_-(\vec{p}). \tag{20}$$

Once $\vec{\sigma}\cdot\vec{p}$ is replaced by eigenvalues $\pm|\vec{p}|$, the rest of the job is to diagonalize the matrix

$$\begin{pmatrix} mc^2 & \pm|\vec{p}|c \\ \pm|\vec{p}|c & -mc^2 \end{pmatrix}. \tag{21}$$

This is easily done using the fact that $E = \sqrt{|\vec{p}|^2c^2 + m^2c^4}$. In the end we find two eingenvectors

$$u_+(p) = \begin{pmatrix} \sqrt{\frac{E+mc^2}{2mc^2}}\chi_+(\vec{p}) \\ \sqrt{\frac{E-mc^2}{2mc^2}}\chi_+(\vec{p}) \end{pmatrix}, \qquad u_-(p) = \begin{pmatrix} \sqrt{\frac{E+mc^2}{2mc^2}}\chi_-(\vec{p}) \\ -\sqrt{\frac{E-mc^2}{2mc^2}}\chi_-(\vec{p}) \end{pmatrix}. \tag{22}$$

In the non-relativistic limit $E \to mc^2$, the upper two components remain $O(1)$ while the lower two components vanish. Because of this reason, the upper two components are called "large components" while the lower two "small components." This point will play an important role when we systematically expand from the non-relativistic limit.

An amazing thing is that there are two solutions with the same momentum and energy, and they seem to correspond to two spin states. Then the wave equation describes a particle of spin 1/2! In order to make this point clearer, we look at the conservation of angular momentum. The commutator

$$[H, L^i] = [c\vec{\alpha}\cdot\vec{p} + mc^2\beta, \epsilon_{ijk}x^j p^k] = -i\hbar c\epsilon_{ijk}\alpha^j p^k \neq 0 \tag{23}$$

does not vanish, and hence the orbital angular momentum is not conserved. On the other hand, the matrix

$$\vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}, \tag{24}$$

has the commutator

$$[H, \Sigma^i] = [c\vec{\alpha} \cdot \vec{p} + mc^2\beta, \Sigma^i] = cp^j[\alpha^j, \Sigma^i] = -2i\epsilon_{ijk}cp^j\alpha^k. \tag{25}$$

Therefore, the sum

$$\vec{J} = \vec{L} + \frac{\hbar}{2}\vec{\Sigma} \tag{26}$$

commutes with the Hamiltonian and hence is conserved. Clearly, the matrix $\frac{\hbar}{2}\vec{\Sigma}$ has eigenvalues $\pm\frac{\hbar}{2}$ and hence corresponds to spin 1/2 particle. The eigenvectors $u_\pm(p)$ we obtained above are also eigenvectors of $\vec{\Sigma} \cdot \vec{p} = \pm|\vec{p}|$ by construction, and hence $\vec{J} \cdot \vec{p} = \frac{\hbar}{2}\vec{\Sigma} \cdot \vec{p} = \pm\frac{\hbar}{2}|\vec{p}|$. In other words, they are *helicity* eigenstates $(\vec{J} \cdot \vec{p})/|\vec{p}| = \pm\frac{\hbar}{2}$. Helicity is the angular momentum projected along the direction of the momentum, where the orbital angular momentum trivially drops out because of the projection. And hence the helicity is purely spin. This analysis demonstrates that the Dirac equation indeed describes a particle of spin 1/2 as guessed above.

This line of reasoning is fascinating. It is as if the consevation of probability requires spin 1/2. Maybe that is why all matter particles (quarks, leptons) we see in Nature have spin 1/2!

But the equation starts showing a problem here. The Dirac wave function ψ has four components, while we have obtained so far only two solutions. There must be two more independent vectors orthogonal to the ones obtained above. What are they? It turns out, they correspond to *negative energy* solutions. Writing $\psi = v(p)e^{-i(\vec{p}\cdot\vec{x}-Et)/\hbar}$, the vectors $v(p)$ must satisfy the following matrix equation similar to Eq. (17) but with the opposite sign for the mass term

$$\begin{pmatrix} -mc^2 & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & mc^2 \end{pmatrix} v(p) = Ev(p). \tag{27}$$

Therefore the solutions are obtained in the same manner but the upper two and lower two components interchanged

$$v_+(p) = \begin{pmatrix} \sqrt{\frac{E-mc^2}{2mc^2}}\chi_+(\vec{p}) \\ \sqrt{\frac{E+mc^2}{2mc^2}}\chi_+(\vec{p}) \end{pmatrix}, \qquad v_-(p) = \begin{pmatrix} -\sqrt{\frac{E-mc^2}{2mc^2}}\chi_-(\vec{p}) \\ \sqrt{\frac{E+mc^2}{2mc^2}}\chi_-(\vec{p}) \end{pmatrix}. \tag{28}$$

Note that the definition $\psi = v(p)e^{-i(\vec{p}\cdot\vec{x}-Et)/\hbar}$ has the energy and momentum in the plane wave with the opposite sign from the normal one, and hence positive $E = \sqrt{|\vec{p}|^2c^2 + m^2c^4}$ means *negative* energy solution. There is no

reason to prefer positive energy solutions over negative energy ones as far as the Dirac equation itself is concerned.

What is wrong with having negative energy solutions? For example, suppose you have a hydrogen atom in the $1s$ ground state. Normally, it is *the* ground state and it is absolutely stable because there is no lower energy state it can decay into. But with the Dirac equation, the story is different. There are *infinite* number of negative energy solutions. Then the $1s$ state can emit a photon and drop into one of the negative energy states, and it happens *very* fast (it is of the same order of magnitude as the $2p$ to $1s$ transition and hence happens within 10^{-8} sec for a *single* negative energy state. If you sum over all final negative-energy states, the decay rate is infinite and hence the lifetime is zero)! Such a situation is clearly unacceptable.

Dirac is ingenious not just to invent this equation, but also to solve the problem with the negative energy states. He proposed that all the negative energy states are already filled in the "vacuum." In his reasoning, the $1s$ state cannot decay into any of the negetive energy states because they are already occupied. It indeed makes the $1s$ state again absolutely stable. Now the equation is saved again. The "vacuum" with all the negative energy states (an infinite number of them) occupied is called the "Dirac sea."

But there is a catch with the "Dirac sea." We wanted to find a single-particle wave function which is consistent with both relativity and probability interpretation. The Dirac equation indees seems to be consistent both with relativity and probability interpretation. But the correct implementation calls for a multi-body state (actually, an infinite-body state)! We can't just talk about a single particle wave function $\psi(\vec{x})$ for a single electron, but only a multi-particle one $\psi(\vec{x}; \vec{y}_1, \vec{y}_2, \cdots)$ with an inifinite number of negative energy electrons at positions $\vec{y}_k$. What it means is that we can't talk about single-particle wave mechanics in the end.

The hope for a good-old single-particle Schrödinger-like wave mechanics is gone. We couldn't do it with the Klein–Gordon equation because it didn't allow probability interpretation. We couldn't do it with the Dirac equation either because it ended up as a multi-particle problem. In the end, the only way to go is the quantum field theory.

3.3 Dirac Field

Filling all negative energy states required a multi-body treatment of the electron, but this can be dealt with very easily within quantum field theory. It

is the same techinique when we dealt with Fermi-degenerate gas by interchanging the creation and annihilation operators. In other words, we will talk about the "holes."

Instead of talking about the Dirac equation as the probability wave, we now talk about the Dirac field starting from the action

$$\int d\vec{x}dt[\psi^\dagger i\hbar\dot{\psi} - \psi^\dagger \hat{H}\psi], \tag{29}$$

where $\hat{H}$ is not longer the Hamiltonian acting on states, but rather a differential operator acting on the field ψ

$$\hat{H} = -i\hbar c\vec{\alpha}\cdot\vec{\nabla} + mc^2\beta. \tag{30}$$

By varying the action with respect to $\psi^\dagger$, we recover the Dirac equation

$$\left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)\psi = \left(i\hbar\frac{\partial}{\partial t} + i\hbar c\vec{\alpha}\cdot\vec{\nabla} - mc^2\beta\right)\psi = 0. \tag{31}$$

But the interpretation of the equation is now completely different, because ψ is now an operator acting on the Hilbert space. The canonical anti-commutation relation (remember the Dirac equation describes a spin 1/2 particle and we need Fermi statistics) is

$$\{\psi^*_\alpha(\vec{x}), \psi_\beta(\vec{y})\} = \delta(\vec{x} - \vec{y}), \tag{32}$$

where α, β indices refer to components (out of four) of the Dirac field. Using the solutions to the Dirac equation we had obtained earlier, we expand the Dirac field operator as

$$\psi(\vec{x}, t) = \frac{1}{L^{3/2}}\sum_{\vec{p}}\left(\sum_{\pm} u_\pm(p)e^{i(\vec{p}\cdot\vec{x}-Et)/\hbar}a^u_\pm(p) + \sum_{\pm} v_\pm(p)e^{-i(\vec{p}\cdot\vec{x}-Et)/\hbar}a^v_\pm(p)\right). \tag{33}$$

The creation and annihilation operators satisfy the usual anti-commutation relations

$$\{a^u_\lambda(p), a^{u\dagger}_{\lambda'}(p')\} = \delta_{\vec{p},\vec{p}'}\delta_{\lambda,\lambda'}, \qquad \{a^v_\lambda(p), a^{v\dagger}_{\lambda'}(p')\} = \delta_{\vec{p},\vec{p}'}\delta_{\lambda,\lambda'}. \tag{34}$$

All other anti-commutators vanish.

The trick we used in multi-body systems is that we can fill all states up to the Fermi energy (which is the same as the chemical potential at zero temperature) μ by defining new creation and annihilation operators

$$b^v_\pm(p) = a^{v\dagger}_\pm(p), \qquad b^{v\dagger}_\pm(p) = a^v_\pm(p). \tag{35}$$

In our case, the Fermi energy is zero to fill all negative energy states while keeping all positive energy states unoccupied in the grounnd state. Then the new creation/annihilation operators also satisfy the standard anti-commutation relation

$$\{b^v_\lambda(p), b^{v\dagger}_{\lambda'}(p')\} = \delta_{\vec{p},\vec{p}'}\delta_{\lambda,\lambda'}. \tag{36}$$

From this point on, I drop the superscript u, v with the understanding that the a, $a^\dagger$ operators refer to the positive energy solutions u, while the b, $b^\dagger$ to the negative energy ones v.

Then the expansion of the Dirac field is then

$$\psi(\vec{x},t) = \frac{1}{L^{3/2}}\sum_{\vec{p}}\left(\sum_\pm u_\pm(p)e^{i(\vec{p}\cdot\vec{x}-Et)/\hbar}a_\pm(p) + \sum_\pm v_\pm(p)e^{-i(\vec{p}\cdot\vec{x}-Et)/\hbar}b^\dagger_\pm(p)\right). \tag{37}$$

The ground state ("vacuum") is defined by

$$a_\pm(p)|0\rangle = b_\pm(p)|0\rangle = 0. \tag{38}$$

The last requirement is the rephrasement of the fact that you can't fill in any more negative-energy electrons $a^{v\dagger}_\pm(p)|0\rangle = 0$ in the original notation.

The particles created by the operators $a^\dagger$ are the normal electrons. What are the states created by the operators $b^\dagger$, then? As in the case of degenerate Fermi gas, if you create a hole, by removing a particle that already fills a state below the Fermi energy, the excitation behaves as a postively charged particle. It has the momentum $\vec{p}$, because you have removed the momentum $-\vec{p}$ of the solution $v(p)e^{-i\vec{p}\cdot\vec{x}/\hbar}$, and also has a positive energy $E = \sqrt{\vec{p}^2c^2 + m^2c^4}$ because you have removed the energy $-E$ of the solution $v(p)e^{+iEt/\hbar}$. Therefore, the relation between the energy and the momentum is precisely that of Einstein's, and the "hole" behaves as a normal particle, except that its charge is the opposite, and the same mass as the electron. It is the *anti-particle* of the electron, namely the positron. Dirac theory hence predicts the existence of an anti-particle for any spin 1/2 particles.[1] The

[1]Dirac himself, being afraid of predicting a non-existing particle, initially claimed that this positively charged hole must be the proton. But other people pointed out that the hole must have the same mass as the electron.

Fock space is constructed by acting electron creation operators $a^\dagger_\pm(p)$ and positron creation operators $b^\dagger_\pm(p)$ on the vacuum.

Indeed the positron was discovered in cosmic rays by Anderson in 1932. This was the first anti-particle.

One remark is that Fermi statistic is essential for the Dirac sea idea to work. If we had tried to quantize the Dirac field as a boson (using commutator instead of anti-commutator), we can never fill the negative energy states enough, and system keep falling into lower and lower energy states by creating more and more negative-energy electrons. This point shows an amazing connection between spin and statistics: spin 1/2 particle must obey Fermi statistics to obtain a consistent quantum fiedl theory.

3.4 Coupling to the Radiation Field

The gauge invariance discussed in 221A uniquely fixes the form of the interaction between the Dirac field and the Radiation Field. It follows the same rule in the Schrödinger theory $\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}$, or equivalently, $-i\hbar\vec{\nabla} \to -i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}$. Its Lorentz-covariant generalization also determines the time-derivative: $i\hbar\frac{\partial}{\partial t} \to i\hbar\frac{1}{c}\frac{\partial}{\partial t} - \frac{e}{c}\phi$. (The relative sign difference is due to the fact that $A_\mu = (\phi, -\vec{A})$ transforms the same way as the derivative $\partial_\mu = (\frac{1}{c}\frac{\partial}{\partial t}, \vec{\nabla})$.) Therefore, the Dirac action is now

$$\int d\vec{x}dt\psi^\dagger \left(i\hbar\frac{\partial}{\partial t} - e\phi - c\vec{\alpha}\cdot(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}) - mc^2\beta \right)\psi. \tag{39}$$

The Dirac equation is again obtained by varying it with respect to $\psi^\dagger$,

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi - c\vec{\alpha}\cdot(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}) - mc^2\beta \right)\psi. \tag{40}$$

When there is classical background field, such as an external Coulomb potential in the hydrogen atom, we quantize the Dirac field by expanding it in terms of the solutions to the Dirac equation in the presence of the background field. Even though we do not regard Dirac equation any more as the probability wave equation as in conventional quantum mechanics, but rather a field equation, it is therefore necessary to solve the Dirac equation in the presence of external fields. And for stationary solutions $\psi \propto e^{-iEt/\hbar}$, the proces is the same as solving the Dirac equation as if we are solving the single-particle quantum mechanics problem.

Therefore, we are interested in solving the equation

$$\left[c\vec{\alpha}\cdot\left(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}\right)+mc^2\beta+e\vec{A}^0\right]\psi=E\psi. \tag{41}$$

The way we will discuss it is by a sytematic expansion in $\vec{v}=\vec{p}/m$. It is basically a non-relativisic approximation keeping only a few first orders in the expansion. Let us write Eq. (41) explicitly in the matrix form, and further write $E=mc^2+E'$ so that E' is the energy of the electron on top of the rest energy. We obtain

$$\left(\begin{array}{cc} e\phi & c\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}) \\ c\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}) & -2mc^2+e\phi \end{array}\right)\psi=E'\psi. \tag{42}$$

The solution lives mostly in the large components, *i.e.*. the upper two components in ψ. The equation is diagonal in the absence of $\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A})$, and we can regard it as a perturbation and expand systematically in powers of it. To simplify notation, we will write $\vec{p}=-i\hbar\vec{\nabla}$, even though it must be understood that we are not talking about the "momentum operator" $\vec{p}$ acting on the Hilbert space, but rather a differential operator acting on the field ψ. Let us write four components in terms of two two-component vectors,

$$\psi=\left(\begin{array}{c}\chi\\ \eta\end{array}\right), \tag{43}$$

where the large component χ is a two-component vector describing a spin two particle (spin up and down states). η is the small component which vanishes in the non-relativistic limit. Writing out Eq. (42) in terms of χ and η, we obtain

$$e\phi\chi+c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\eta=E'\chi \tag{44}$$

$$c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi+(-2mc^2+e\phi)\eta=E'\eta. \tag{45}$$

Using Eq. (45) we find

$$\eta=\frac{1}{E'+2mc^2-e\phi}c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi. \tag{46}$$

Substituting it into Eq. (45), we obtain

$$e\phi\chi+c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\frac{1}{E'+2mc^2-e\phi}c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi=E'\chi. \tag{47}$$

In the non-relativistic limit, $E', e\phi \ll mc^2$, and hence we drop them in the denominator. Within this approximation (called Pauli approximation), we find

$$e\phi\chi + \frac{[\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})]^2}{2m}\chi = E'\chi. \tag{48}$$

The last step is to rewrite the numerator in a simpler form. Noting $\sigma^i\sigma^j = \delta^{ij} + i\epsilon_{ijk}\sigma^k$,

$$\begin{aligned}
[\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})]^2 &= (\delta^{ij}+i\epsilon_{ijk}\sigma^k)(p^i-\frac{e}{c}A^i)(p^j-\frac{e}{c}A^j) \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 + \frac{i}{2}\epsilon_{ijk}\sigma^k[p^i-\frac{e}{c}A^i, p^j-\frac{e}{c}A^j] \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 + \frac{ie}{2c}\epsilon_{ijk}\sigma^k i\hbar(\nabla_i A^j - \nabla_j A^i) \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 - \frac{e\hbar}{c}\vec{\sigma}\cdot\vec{B}.
\end{aligned} \tag{49}$$

Then Eq. (48) becomes

$$\frac{(\vec{p}-\frac{e}{c}\vec{A})^2}{2m}\chi - 2\frac{e\hbar}{2mc}\vec{s}\cdot\vec{B} + e\phi\chi = E'\chi. \tag{50}$$

In other words, it is the standard non-relativistic Schrödinger equation except that the g-factor is fixed. The Dirac theory predicts $g = 2$! This is a great success of this theory.

3.5 Tani–Foldy–Wouthuysen Transformation

One can extend the systematic expansion further to higher orders. It is done usually with the method so-called Tani-Foldy–Wouthuysen transformation. The basic idea is keep performing unitary basis transformation on ψ to eliminate small components at a given order in the expansion. The note here is based on Bjorken–Drell, "Relativisc Quantum Mechanics," McGraw-Hill, 1964.

Let us start with the free case, $H = c\vec{\alpha}\cdot\vec{p} + mc^2\beta$. The problem is to remove the mixing beween large and small components caused by the matrices $\vec{\alpha}$. Can we eliminate α completely from the Hamiltonian by a unitarity rotation? The answer is yes. You choose the unitarity rotation as

$$\psi' = e^{iS}\psi, \tag{51}$$

where $S = \beta\vec{\alpha}\cdot\vec{p}\theta(\vec{p})$ (it has nothing to do with the classical action). The Hamitonian is also correspondingly unitarity transformed to

$$\begin{aligned} H' &= e^{iS}He^{-iS} \\ &= \left(\cos|\vec{p}|\theta + \frac{\beta\vec{\alpha}\cdot\vec{p}}{|\vec{p}|}\sin|\vec{p}|\theta\right)(c\vec{\alpha}\cdot\vec{p} + mc^2\beta)\left(\cos|\vec{p}|\theta - \frac{\beta\vec{\alpha}\cdot\vec{p}}{|\vec{p}|}\sin|\vec{p}|\theta\right) \\ &= c\vec{\alpha}\cdot\vec{p}\left(\cos 2|\vec{p}|\theta - \frac{mc^2}{|\vec{p}|c}\sin 2|\vec{p}|\theta\right) + \beta(mc^2\cos 2|\vec{p}|\theta + c|\vec{p}|\sin 2|\vec{p}|\theta) \end{aligned} \quad (52)$$

To eliminate the mixing between the large and small components, we choose the parameter θ so that the first term vanishes:

$$\tan 2|\vec{p}|\theta = \frac{|\vec{p}|}{mc}. \quad (53)$$

Then we find $\cos 2|\vec{p}|\theta = mc^2/\sqrt{c^2\vec{p}^2 + m^2c^4}$, $\sin 2|\vec{p}|\theta = c|\vec{p}|/\sqrt{c^2\vec{p}^2 + m^2c^4}$, and finally

$$H' = \beta\sqrt{c^2\vec{p}^2 + m^2c^4}. \quad (54)$$

This form correctly shows both positive and negative energy solutions.

Now we try to generalize this method in the presence of external radiation field, starting again from the Hamiltonian

$$H = c\vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A}) + mc^2\beta + e\phi. \quad (55)$$

In this case, we must also allow ourselves to consider a time-dependent unitarity transformation. The Dirac equation

$$i\hbar\dot{\psi} = H\psi \quad (56)$$

rewritten for the unitarity transformed field $\psi' = e^{iS}\psi$ is

$$i\hbar\dot{\psi'} = \left[e^{iS}He^{-iS} - i\hbar e^{iS}\frac{\partial}{\partial t}e^{-iS}\right]\psi' = H'\psi' \quad (57)$$

which defines the transformed Hamiltonian ψ'. (Notice the similarity to the canonical transformations in the classical mechanics.)

We are interested in expanding H' up to $O(p^4)$. To this order, we find

$$\begin{aligned} H' &= H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] + \frac{1}{24}[S,[S,[S,[S,H]]]] \\ &\quad -i\hbar\dot{S} - \frac{i}{2}\hbar[S,\dot{S}] + \frac{1}{6}\hbar[S,[S,\dot{S}]]. \end{aligned} \quad (58)$$

In the free-particle case, we chose $S = -i\beta\vec{\alpha}\cdot\vec{p}\theta$ with $\theta = \frac{1}{2|\vec{p}|}\tan^{-1}\frac{|\vec{p}|}{mc} \simeq \frac{1}{2mc}$. Motivated by this, we can choose $S = -i\beta\vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A})/2mc$. By calling $\mathcal{O} = \vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A})$ and $\mathcal{E} = e\phi$, we find at this order

$$\begin{aligned} H' &= \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] \\ &\quad + \frac{\beta}{2mc}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2c} + i\hbar\beta\frac{\dot{\mathcal{O}}}{2mc}. \end{aligned} \tag{59}$$

The last three terms still mix large and small components because they are odd in $\mathcal{O}$. At this point, we perform another unitarity transformation using

$$S' = -i\beta\frac{\mathcal{O}'}{2mc} = -i\beta\frac{1}{2mc}\left(\frac{\beta}{2mc^2}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2c^2} + i\hbar\beta\frac{\dot{\mathcal{O}}}{2mc^2}\right). \tag{60}$$

Then the Hamiltonian is further transformed to

$$H'' = \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] + \mathcal{O}'', \tag{61}$$

where $\mathcal{O}''$ is still odd in α, but is suppressed by $1/m^2$. Finally, using another unitarity transformation with $S'' = -i\beta\mathcal{O}''/2mc$ eliminates the last term and we find

$$H''' = \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] \tag{62}$$

to this order. Now we write it out explicitly and find

$$\begin{aligned} H''' &= \beta\left(mc^2 + \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} - \frac{\vec{p}^4}{8m^3c^2}\right) + e\phi - \frac{e\hbar}{2mc}\beta\vec{\Sigma}\cdot\vec{B} \\ &\quad - \frac{ie\hbar^2}{8m^2c^2}\vec{\Sigma}\cdot(\vec{\nabla}\times\vec{E}) - \frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot(\vec{E}\times\vec{p}) - \frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}. \end{aligned} \tag{63}$$

The first term is nothing but the rest energy, and the second the non-relativistic kinetic term. The third term is the relativistic correction to the kinetic energy. The Coulomb potential term is there as desired, and the next term is the magnetic momentum coupling with $g = 2$ as we saw before. $\vec{\nabla}\times\vec{E} = 0$ for the Coulomb potential, while

$$-\frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot(\vec{E}\times\vec{p}) = \frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot\frac{1}{r}\frac{dV}{dr}(\vec{x}\times\vec{p}) = \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{\Sigma}\cdot\vec{L} \tag{64}$$

is the spin-orbit coupling (with the correct Thomas precession factor, where I assumed a central potential). The last term $-\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}$ is called Darwin term, in honor of the first person who solved the hydrogen atom problem exactly with the Dirac equation.[2]

The physical meaning of the relativistic correction, the spin-orbit couping, and the magnetic moment coupling are probably familiar to you. What is the Darwin term? It is attribtuted to a perculiar motion of a Dirac particle called *Zitterbewegung* (Schrödinger). One way to see it is by using Heisenberg equation of motion (well, we shouldn't use the "Hamiltonian" $\vec{\alpha}\cdot\vec{p}+m\beta$ too seriously because we abandoned the single-particle wave mechanics interpretation, but it is still instructive). The velocity operator is

$$i\hbar\frac{d}{dt}\vec{x}=[\vec{x},H]=i\hbar c\vec{\alpha}. \tag{65}$$

This is already quite strange. The velocity operator $\dot{\vec{x}}=c\vec{\alpha}$ has eigenvalues $\pm c$ and velocities in different directions do not commute (*i.e.* not simultaneously observable). Clearly, this velocity is not the motion of the particle as a whole, but something rather different. To see this, we further consider the Heisenberg equation for the velocity operator when the particle is at rest $\vec{p}=0$ ($H=mc^2\beta$). Then,

$$i\hbar\frac{d^2}{dt^2}\vec{x}=[c\vec{\alpha},H]=2mc^3\vec{\alpha}\beta, \tag{66}$$

while its further derivative is

$$-\hbar^2\frac{d^3}{dt^3}\vec{x}=[2mc^3\vec{\alpha}\beta,H]=4m^2c^5\vec{\alpha}=4m^2c^4\frac{d}{dt}\vec{x}. \tag{67}$$

Therefore,

$$\frac{d}{dt}\vec{x}(t)=c\vec{\alpha}\cos\frac{2mc^2t}{\hbar}-ic\vec{\alpha}\beta\sin\frac{2mc^2t}{\hbar}, \tag{68}$$

which oscillates very rapidly with the period $\hbar/2mc^2=6\times10^{-22}$ sec. (Note that $-i\vec{\alpha}\beta$ is hermitean, because $(-i\vec{\alpha}\beta)^\dagger=i\beta\vec{\alpha}=-i\vec{\alpha}\beta$ due to the anti-commutation relation.) The position is then obtained by integrating it:

$$\vec{x}(t)=\vec{x}(0)+\frac{\hbar}{2mc}\left(\vec{\alpha}\sin\frac{2mc^2t}{\hbar}+i\vec{\alpha}\beta\cos\frac{2mc^2t}{\hbar}\right). \tag{69}$$

This rapid motion of an "electron at rest" is the Zitterbewegung, a peculiarity in the relevatistic quantum mechanical motion of spin 1/2 particle. Because of this rapid motion of the electron, the net electric field the electron experiences is averaged over its "blur," and hence is somewhat different from the electric field at the position itself. The averaging of the electric field gives rise to the correction

$$\langle V\rangle=\frac{1}{2}\langle(\delta x^i)(\delta x^j)\rangle\frac{\partial^2V}{\partial x^i\partial x^j}, \tag{70}$$

[2]Dirac himself did not do this. An anecdote I've read is that Dirac was so proud of his equation that he was afraid of doing any tests which might falsify it. Of course we was technically capable enough to solve it exactly, but he didn't do it because of this fear.

where the isotropy tells us that $\langle(\delta x^i)(\delta x^j)\rangle = \frac{1}{3}\delta^{ij}\langle(\delta x^i)^2\rangle = \delta^{ij}(\hbar/2mc)^2$, where I used the time average of the Zitterbewegung at the last step. Then the correction to the potential energy is

$$\langle eV\rangle = e\frac{1}{2}\frac{\hbar^2}{4m^2c^2}\Delta V = -\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}, \tag{71}$$

reproducing the Darwin term.

3.6 Hydrogen-like Atoms

Now let us specialize to the case of the hydrogen atom $\vec{A} = 0$ and $e\phi = -Ze^2/r$. The energy levels of a hydrogen-like atom are perturbed by the additional terms in Eq. (63). The sum of the relativistic correction and the spin-orbit coupling gives a correction

$$(Z\alpha)^4 mc^2\left(\frac{3}{8n^4} + \frac{j(j+1) - 3l(l+1) - \frac{3}{4}}{2l(l+1)(2l+1)n^3}\right) \tag{72}$$

Due to some magical reason I don't understand, for both possible cases where $l = j \pm \frac{1}{2}$ allowed by the addition of angular momenta, it simplifies to

$$(Z\alpha)^4 mc^2\left(\frac{3}{8n^4} - \frac{1}{(2j+1)n^3}\right). \tag{73}$$

Therefore states with the same principal quantum number n and the total angular momentum j, even if they come from different l, remain degenerate.

The case $l = 0$ is special and deserves attention. For this case, the spin-orbit interaction vanishes identically. The relativisic correction to the kinetic energy gives $(Z\alpha)^4 mc^2(\frac{3}{8n^4} - \frac{1}{n^3})$. However, for s-waves only, the Darwin term also contributes. For hydrogen-like atoms, the Darwin term is

$$-\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E} = \frac{e\hbar^2}{8m^2c^2}Ze4\pi\delta(\vec{x}) = \frac{Z\alpha\hbar^3}{8m^2c}4\pi\delta(\vec{x}). \tag{74}$$

The first-order perturbation in the Darwin term gives

$$\frac{Z\alpha\hbar^3}{8m^2c}4\pi|\psi(0)|^2 = (Z\alpha)^4 mc^2\frac{1}{2n^3}. \tag{75}$$

Therefore the sum of the relativistic correction and the Darwin term gives

$$(Z\alpha)^4 mc^2\left(\frac{3}{8n^4} - \frac{1}{2n^3}\right) = (Z\alpha)^4 mc^2\left(\frac{3}{8n^4} - \frac{1}{(2j+1)n^3}\right), \tag{76}$$

because $j = 1/2$ for $l = 0$, and hence happens to have the same form as Eq. (73) which is valid for $l \neq 0$

In the case of hydrogen-like atoms, one can also solve the Dirac equation exactly to find the energy levels. The derivation is discussed at this end of this lecture note. We find

$$E_{njlm} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2} . \quad (77)$$

The principal quantum numbers are $n = 1, 2, 3, \cdots$ as usual, and $j + 1/2 \leq n$. Expanding it up to $O(Z\alpha)^4$, we find

$$E_{njlm} = mc^2 \left[1 - \frac{(Z\alpha)^2}{2n^2} + \frac{(Z\alpha)^4}{n^3} \left(\frac{3}{8n} - \frac{1}{2j+1} \right) \right] \quad (78)$$

and agrees with the results based on Tani–Foldy–Wouthuysen transformation. One important point is the degeneracy between $2s_{1/2}$ and $2p_{1/2}$ states (similarly, $3s_{1/2}$ and $3p_{1/2}$, $3p_{3/2}$ and $3d_{3/2}$, etc) persists in the exact solution to the Dirac equation. This degeneracy is lifted by so-called Lamb shifts, due to the coupling of electron to the zero-point fluctuation of the radiation field. We will come back to this point later.

4 Klein–Gordon Field

We had abandoned the Klein–Gordon equation because it did not admit probability interpretation. We instead went to the Dirac equation because it did, but in the end the problem of negative energy solutions forced us to regard the Dirac equation as a field equation which had to be quantized to obtain the full Fock space. Then the issue with the probability interpretation was basically moot. What don't we reconsider the Klein–Gordon equation now as a field equation rather than a probability wave equation?[3]

[3] According to Tomonaga's book "The Story of Spin," which has many interesting anecdotes in the development of quantum mechanics, Pauli felt beaten by Dirac who could make Pauli's ad-hoc spin matrices to a fully relativistically covariant theory. But Pauli, together with Heisenberg, later showed that Klein–Gordon equation is as good as Dirac equation once regarded as a quantum field theory. This was Pauli's revenge.

4.1 Quantized Klein–Gordon Field

The action for the Klein–Gordon field is given by

$$S = \int d\vec{x}dt \left[\frac{1}{c^2}\dot{\phi}^*\dot{\phi} - \vec{\nabla}\phi^* \cdot \vec{\nabla}\phi - \frac{m^2c^2}{\hbar^2}\phi^*\phi \right]. \tag{79}$$

By varying the action with respect to ϕ^*, we recover the Klein–Gordon equation Eq. (6). The canonically conjugate momenta are

$$\pi(\vec{x}) = \frac{1}{c^2}\phi^*(\vec{x}), \qquad \pi^*(\vec{x}) = \frac{1}{c^2}\phi(\vec{x}). \tag{80}$$

and the canonical commutation relations are

$$[\phi(\vec{x}), \psi(\vec{y})] = i\hbar\delta(\vec{x}-\vec{y}), \qquad [\phi^*(\vec{x}), \psi^*(\vec{y})] = i\hbar\delta(\vec{x}-\vec{y}). \tag{81}$$

Following the expansion we did for the radiation field, we expand the field in momentum modes,

$$\phi(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} \frac{1}{\sqrt{\omega_p}} (a(\vec{p})e^{i\vec{p}\cdot\vec{x}/\hbar} + b^\dagger(\vec{p})e^{-i\vec{p}\cdot\vec{x}/\hbar}) \tag{82}$$

$$\dot{\phi}(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} (-i\sqrt{\omega_p}) (a(\vec{p})e^{i\vec{p}\cdot\vec{x}/\hbar} - b^\dagger(\vec{p})e^{-i\vec{p}\cdot\vec{x}/\hbar}). \tag{83}$$

Unlike the radiation field, we regard $\phi(\vec{x})$ as a complex field, and hence $a(\vec{p})$ and $b(\vec{p})$ can be different. Together with the canonical commutation relations, we find the usual commutation relations among creation and annihilation operators

$$[a(\vec{p}), a^\dagger(\vec{q})] = \delta_{\vec{p},\vec{q}}, \qquad [b(\vec{p}), b^\dagger(\vec{q})] = \delta_{\vec{p},\vec{q}}, \tag{84}$$

with all other combinations vanishing. The Fock space is constructed in the usual way, starting from the vacuum

$$a(\vec{p})|0\rangle = b(\vec{p})|0\rangle = 0, \tag{85}$$

and acting creation operators $a^\dagger(\vec{p})$ and $b^\dagger(\vec{p})$ on the vacuum.

The Hamiltonian of the Klein–Gordon field is

$$\begin{aligned} H &= \int d\vec{x} \left[\pi^*\dot{\phi}^* + \pi\dot{\phi} - \left(\frac{1}{c^2}\dot{\phi}^*\dot{\phi} - \vec{\nabla}\phi^* \cdot \vec{\nabla}\phi - \frac{m^2c^2}{\hbar^2}\phi^*\phi \right) \right] \\ &= \int d\vec{x} \left[\pi^*\pi + \vec{\nabla}\phi^* \cdot \vec{\nabla}\phi + \frac{m^2c^2}{\hbar^2}\phi^*\phi \right]. \end{aligned} \tag{86}$$

The Hamiltonian is manifestly positive and there is no concern with negative energies. Rewriting it in terms of creation and annihilation operators, we find

$$H = \sum_{\vec{p}} \sqrt{\vec{p}^2c^2 + m^2c^4}(a^\dagger(\vec{p})a(\vec{p}) + b^\dagger(\vec{p})b(\vec{p}) + 1). \tag{87}$$

The zero-point energy is present both for a and b operators and hence the term 1 in the parentheses. We see no inconsistencies in the quantized Klein–Gordon field. This is indeed the way we treat spinless bosons in the relativistic quantum field theory.

What is the difference between the a and b particles? It can be seen by coupling the Klein–Gordon field to the radiation field:

$$\begin{aligned} S &= \int d\vec{x}dt \left[\frac{1}{c^2}\left(\partial_t - \frac{ie}{\hbar}A^0\right)\phi^* \left(\partial_t + \frac{ie}{\hbar}A^0\right)\phi \right. \\ &\quad \left. - \left(\vec{\nabla} + \frac{ie}{\hbar c}\vec{A}\right)\phi^* \cdot \left(\vec{\nabla} - \frac{ie}{\hbar c}\vec{A}\right)\phi - \frac{m^2c^2}{\hbar^2}\phi^*\phi \right]. \end{aligned} \tag{88}$$

The scalar potential A^0 (here I avoided using ϕ not to be confused with the Klein–Gordon field) must couple to the electric charge, which is read off from the above action as

$$\frac{1}{4\pi}\int d\vec{x}\frac{1}{c^2}\frac{i}{\hbar}(\phi^*\dot{\phi} - \dot{\phi}^*\phi) = \sum_{\vec{p}}(a^\dagger(\vec{p})a(\vec{p}) - b^\dagger(\vec{p})b(\vec{p})). \tag{89}$$

Clearly, a and b particles have the opposite charges, while they have the same mass as seen in the Hamiltonian. They are anti-particles of each other. This is how we describe Yukawa's charged pion π^+ and its anti-particle π^- in the quantum field theory.

4.2 Hydrogen Atom in Klein–Gordon Equation

It has been of interest to nuclear and atomic physicists to study bound states of charged pions to nuclei, "pi-mesic atoms." The point is that the pion is more than 200 times heavier than the electron, and hence the "Bohr radius" is correspondingly shorter, down to 10^{-11} cm level. Therefore pions probe much deeper structure than electrons do. Their energy levels are obtained by solving the Klein–Gordon equation in the Coulomb potential.

We will see below that the time-independent field equation for the radial wave function $\phi = R(r)Y_l^m e^{-iEt/\hbar}$ has the same form as the non-relativistic

Schrödinger equation for the hydrogen atom,

$$\left[\frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{\lambda(\lambda+1)}{r^2}\right)-\frac{Ze^2}{r}\right]R=\epsilon R. \tag{90}$$

We write μ, λ, ϵ in terms of E, m, and l starting from the Klein–Gordon equation.

The field equation for $\phi = R(r)Y_l^m e^{-iEt/\hbar}$ is

$$\left[\frac{1}{c^2}\left(-E-\frac{Ze^2}{r}\right)^2\hbar^2\left(\frac{1}{r^2}\frac{d^2}{dr^2}r^2-\frac{l(l+1)}{r^2}\right)-m^2c^2\right]R=0. \tag{91}$$

By reorganizing terms, we find

$$\left[\frac{\hbar^2c^2}{2E}\left(-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)-Z^2\alpha^2}{r^2}\right)-\frac{Ze^2}{r}\right]R=\frac{E^2-(mc^2)^2}{2E}R. \tag{92}$$

$\alpha = e^2/\hbar c$ is the fine-structure constant. By comparing to the Schrödinger-like equation Eq. (90), we find

$$\mu = E/c^2 \tag{93}$$

$$\lambda = \sqrt{\left(l+\frac{1}{2}\right)^2-Z^2\alpha^2}-\frac{1}{2} \tag{94}$$

$$\epsilon = \frac{E^2-(mc^2)^2}{2E}. \tag{95}$$

Eq. (90) has exactly the same form as the Schrödinger equation for the hydrogen atom, except that λ is not an integer. Therefore the boundstate eigenvalues are given by

$$\epsilon = -\frac{1}{2}\frac{Z^2\alpha^2\mu c^2}{\nu^2},$$

where the "principal quantum number" ν takes values $\nu = \lambda+1, \lambda+2, \lambda+3, \cdots$. This observation allows us to solve for E.

$$\frac{E^2-(mc^2)^2}{2E} = -\frac{1}{2}\frac{Z^2\alpha^2E}{\nu^2}. \tag{96}$$

Solving for E, we find[4]

$$E = \frac{mc^2}{\sqrt{1 + Z^2\alpha^2/\nu^2}}. \tag{97}$$

We now Expand E up to $O(Z^2\alpha^2)$ and see that it agrees with the result of conventional Schrödinger equation including the rest energy. By expanding Eq. (97) up to $O(Z^2\alpha^2)$, we find

$$E = mc^2\left(1 - \frac{1}{2}\frac{Z^2\alpha^2}{\nu^2} + O(Z^4\alpha^4)\right). \tag{98}$$

Note that $\lambda = l + O(Z^2\alpha^2)$. Therefore, $\nu = \lambda + k$ (k is a non-negative integer) and hence ν is also an integer up to an $O(Z^2\alpha^2)$ correction. Neglecting $O(Z^4\alpha^4)$ terms, we find the principal quantum number $n = \nu + O(Z^2\alpha^2)$ and hence

$$E = mc^2 - \frac{1}{2}\frac{Z^2\alpha^2 mc^2}{n^2} + O(Z^4\alpha^4). \tag{99}$$

The result agrees with conventional Schrödinger equation at this order.

We next expand E in Eq. (97) up to $O(Z^4\alpha^4)$, and find

$$E = mc^2\left(1 - \frac{1}{2}\frac{Z^2\alpha^2}{\nu^2} + \frac{3}{8}\frac{Z^4\alpha^4}{\nu^4} + O(Z^6\alpha^6)\right). \tag{100}$$

The difference between ν and n at $O(Z^2\alpha^2)$ cannot be ignored in the second term because it gives rise to a term of $O(Z^4\alpha^4)$. By expanding λ up to $O(Z^2\alpha^2)$,

$$\lambda = l - \frac{Z^2\alpha^2}{2l+1} + O(Z^4\alpha^4), \tag{101}$$

we can write

$$\nu = n - \frac{Z^2\alpha^2}{2l+1} + O(Z^4\alpha^4), \tag{102}$$

and hence

$$E = mc^2\left(1 - \frac{1}{2}\frac{Z^2\alpha^2}{n^2} - \frac{Z^4\alpha^4}{(2l+1)n^3} + \frac{3}{8}\frac{Z^4\alpha^4}{n^4} + O(Z^6\alpha^6)\right). \tag{103}$$

[4]I've read somewhere that Klein–Gordon equation was the first equation considered by Schrödinger. He actually solved the hydrogen atom problem with the Klein–Gordon equation (or maybe the "original" Schrödinger equation), and found that the result does not agree with data concerning the fine structure. He then abandoned it and took the non-relativistic limit so that the equation and the data agree within the approximation. It is sometimes a good idea to ignore the failure and forge ahead!

As before, the second term is the term we obtain in non-relativistic Schrödinger equation.

The question is what are the next two terms. They are the so-called "relativistic correction," obtained by expanding the relativistic kinetic energy

$$\sqrt{\vec{p}^2c^2 + (mc^2)^2} = mc^2 + \frac{\vec{p}^2}{2m} - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2} + O(\vec{p}^6). \tag{104}$$

Because $|\vec{p}|/m = v = Z\alpha$ in hydrogen-like atoms, $O(\vec{p}^6) \sim O(Z^6\alpha^6)$ and these terms are beyond our interest. We can rewrite

$$\vec{p}^2|nlm\rangle = 2m\left(\frac{Ze^2}{r} - \frac{1}{2}\frac{Z^2\alpha^2mc^2}{n^2}\right), \tag{105}$$

and hence

$$\langle nlm| - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2}|nlm\rangle = -\frac{1}{2mc^2}\langle nlm|\left(\frac{Ze^2}{r} - \frac{1}{2}\frac{Z^2\alpha^2mc^2}{n^2}\right)^2|nlm\rangle. \tag{106}$$

Using (see below for the derivation of these expectation values)

$$\langle nlm|\frac{1}{r}|nlm\rangle = \frac{1}{n^2a}, \qquad \langle nlm|\frac{1}{r^2}|nlm\rangle = \frac{2}{(2l+1)n^3a^2}, \tag{107}$$

with $a = \hbar^2/mZe^2 = \hbar/mcZ\alpha$, we find

$$\langle nlm| - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2}|nlm\rangle = -\frac{Z^4\alpha^4}{(2l+1)n^3} + \frac{3}{8}\frac{Z^4\alpha^4}{n^4}. \tag{108}$$

This precisely reproduces the $O(Z^4\alpha^4)$ terms in Eq. (97), and hence the relativistic correction $-\frac{1}{8}\frac{\vec{p}^4}{m^3c^4}$ is their origin. Obviously, there is no spin-orbit coupling because the Klein–Gordon field does not have spin. What is more interesting is that there is no Darwin term; the Klein–Gordon particle does not do Zitterbewegung! In fact, if you take the square root of the Klein–Gordon equation and consider the Hamiltonian to be $H = \sqrt{c^2\vec{p}^2 + m^2c^4}$, the Heisenberg equation would give the velocity $\dot{\vec{x}} = [\vec{x}, H]/i\hbar = c^2\vec{p}/\sqrt{c^2\vec{p}^2 + m^2c^4}$ which is perfectly normal, showing no sign of Zitterbewegung.

The energy levels of the Klein–Gordon equation in the Coulomb potential is the starting point for the study of π-mesic atoms, *i.e*, the bound states of negative pions π^- to nuclei.

We can derive Eq. (107) without suffering through generating functions for Laguerre polynomials by using the Feynman-Hellman theorem which states[5]

$$\langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle = \frac{\partial E}{\partial\lambda}, \tag{109}$$

quite generally when a Hamiltonian H, its eigenstates $|\psi\rangle$, and its eigenvalues E depend on a parameter λ. (The eigenstates if degenerate must be diagonalized not to mix under infinitessimal changes in λ.) To show equation (109) start with

$$\begin{aligned} \frac{\partial}{\partial\lambda}(H|\psi\rangle) &= \frac{\partial}{\partial\lambda}(E|\psi\rangle) & (110)\\ \frac{\partial H}{\partial\lambda}|\psi\rangle + H\frac{\partial}{\partial\lambda}|\psi\rangle &= \frac{\partial E}{\partial\lambda}|\psi\rangle + E\frac{\partial}{\partial\lambda}|\psi\rangle, & (111) \end{aligned}$$

and act on the left with $\langle\psi|$. Then $\langle\psi|H = \langle\psi|E$ so that the unwanted terms drop out:

$$\begin{aligned} \langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle + E\langle\psi|\frac{\partial}{\partial\lambda}|\psi\rangle &= \langle\psi|\frac{\partial E}{\partial\lambda}|\psi\rangle + E\langle\psi|\frac{\partial}{\partial\lambda}|\psi\rangle \\ \Longrightarrow \langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle &= \frac{\partial E}{\partial\lambda}. & (112) \end{aligned}$$

Now for the non-relativistic hydrogen atom,

$$\begin{aligned} H &= \frac{\hbar^2}{2m}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right) - \frac{Ze^2}{r}, & (113)\\ E &= -\frac{Z^2\alpha^2 mc^2}{2n^2}. & (114) \end{aligned}$$

Mathematically, we can consider Z to be a continuous parameter and apply the Feynman-Hellman theorem,

$$\langle nlm|\frac{1}{r}|nlm\rangle = -\frac{1}{e^2}\langle nlm|\frac{\partial H}{\partial Z}|nlm\rangle = -\frac{1}{e^2}\frac{\partial E}{\partial Z} = \frac{1}{e^2}\frac{Z\alpha^2 mc^2}{n^2} = \frac{1}{n^2 a}, \tag{115}$$

which is the first of (107). To find the second relation we can basically repeat the above argument with l in place of Z, but there is one subtlety. For the Hamiltonian (113), the radial eigenvalue problem is well-defined even for non-integer l. But when solving for the radial wavefunction, we find a principle quantum number $n = n_r + l + 1$ where $n_r = 0, 1, 2, \ldots$ must be an integer for the hypergeometric series to terminate and give a normalizable radial wavefunction. When we differentiate with respect to l we must hold n_r, not n, fixed. In other words, $\frac{\partial n}{\partial l} = 1$. Then

$$\begin{aligned} \langle nlm|\frac{1}{r^2}|nlm\rangle &= \frac{2m}{\hbar^2(2l+1)}\langle nlm|\frac{\partial H}{\partial l}|nlm\rangle \\ &= \frac{2m}{\hbar^2(2l+1)}\frac{\partial E}{\partial l} \end{aligned}$$

[5]This derivation is by Ed Boyda.

$$= \frac{2m}{\hbar^2(2l+1)} \frac{2Z^2\alpha^2 mc^2}{2n^3} \frac{\partial n}{\partial l}$$
$$= \frac{2}{(2l+1)n^3 a^2}. \tag{116}$$

4.3 Hydrogen Atom in Dirac Equation

Now that you have seen how to obtain the energy levels for the Klein–Gordon equation, you must be wondering what we do for the Dirac equation. Here is how you do it. Starting from the Dirac equation

$$\left[E + \frac{Ze^2}{r} - c\vec{\alpha}\cdot\vec{p} - mc^2\beta\right]\psi = 0, \tag{117}$$

multiply by

$$\left[E + \frac{Ze^2}{r} + c\vec{\alpha}\cdot\vec{p} + mc^2\beta\right] \tag{118}$$

from the left. Then you find

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 - c^2\vec{p}^2 - (mc^2)^2 + c\vec{\alpha}\cdot\left(-i\hbar\vec{\nabla}\frac{Ze^2}{r}\right)\right]\psi = 0. \tag{119}$$

The anti-commutation relation $\{\alpha^i, \alpha^j\} = 2\delta^{ij}$, $\{\alpha^i, \beta\} = 0$ had been used in simplifying the expression. Writing out the derivative acting on the Coulomb potential, we find

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 - c^2\vec{p}^2 - (mc^2)^2 + i\hbar c\vec{\alpha}\cdot\hat{\vec{r}}\frac{Ze^2}{r^2}\right]\psi = 0, \tag{120}$$

using the notation $\hat{\vec{r}} = \vec{r}/r$. At this point, we also rewrite $\vec{p}^2$ using the spherical coordinates,

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2}\right) - (mc^2)^2 + i\hbar c\vec{\alpha}\cdot\hat{\vec{r}}\frac{Ze^2}{r^2}\right]\psi = 0. \tag{121}$$

We can block-diagonalize the matrix $\vec{\alpha}$ as

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & -\vec{\sigma} \end{pmatrix}. \tag{122}$$

Then depending on upper or lower two components, we have $\vec{\alpha}\cdot\hat{\vec{r}} = \pm\vec{\sigma}\cdot\hat{\vec{r}}$. Then the equation becomes

$$\left[E^2 - (mc^2)^2 + 2E\frac{Ze^2}{r} + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1) + Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}}}{r^2}\right)\right]\psi = 0. \tag{123}$$

The non-trivial point with this equation is to deal with the numerator $l(l+1)+Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}}$. The trick is to note that it commutes with $\vec{J} = \vec{L} + \vec{\sigma}/2$. Therefore, we can look at the subspace of the Hilbert space with fixed j and hence $l = j \pm 1/2$. On this space, the numerator has the form

$$l(l+1)+Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}} = \begin{pmatrix} (j+\frac{1}{2})(j+\frac{3}{2}) + Z^2\alpha^2 & \mp iZ\alpha \\ \mp iZ\alpha & (j-\frac{1}{2})(j+\frac{1}{2}) + Z^2\alpha^2 \end{pmatrix}. \tag{124}$$

The eigenvlaues of this matrix are easily obtained, but we intentionally write the eigenvalues as $\lambda(\lambda+1)$. The motiation to do so must be clear from what we did with the Klein–Gordon equation. The two solutions are

$$\lambda_+ = \left[\left(j+\frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2}, \qquad \lambda_- = \left[\left(j+\frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2} - 1. \tag{125}$$

Using λ, the Dirac equation is now

$$\left[E^2 - (mc^2)^2 + 2E\frac{Ze^2}{r} + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{\lambda(\lambda+1)}{r^2}\right)\right]\psi = 0. \tag{126}$$

It has the same form as the Klein–Gordon equation except λ. By following the same arguments, we find the energy eigenvalues

$$E = \frac{mc^2}{\sqrt{1 + Z^2\alpha^2/\nu^2}}, \tag{127}$$

with $\nu = \lambda+1, \lambda+2, \cdots$. The solutions with both λ_+ and λ_- give the same set of ν's, except that the smallest ν is obtained only from λ_- with $j = 1/2$. This corresponds to the fact that $n = 1$ state has only $l = 0$ which does not mix with an $l = 1$ state. The degeneracy of the eigenvalues for two solutions is split only by Lamb shift. The principal quantum number is ν at the lowest order in $Z\alpha$, and hence

$$\nu = n + \left[\left(j+\frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2} - \left(j+\frac{1}{2}\right). \tag{128}$$

We finally find the energy levels of the Dirac equation

$$E = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j+1/2) + [(j+1/2)^2 - Z^2\alpha^2]^{1/2}} \right)^2 \right]^{-1/2}, \qquad (129)$$

showing Eq. (77).