Dirac Equation and Hydrogen Atom

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Outline

Schrödinger Equation and Lorentz Transformation

$$i\hbar \frac{\partial}{\partial t}\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi$$

- The Schrödinger equation is based on a non-relativistic ansatz.
- The Schrödinger equation is linear in time, but not in space.
- The Schrödinger equation is invariant under Galilei transformation, but not under Lorentz transformation.

Formalism (1)

Coordinates

A point in space and time is represented by a 4-vector $x^\mu \equiv (x^0, x^k) \equiv (x^0, x^1, x^2, x^3)$ where $x^0 = ct$ and $x^k = \mathbf{r}$

Covariant and contravariant vectors

We have to distinguish between covariant and contravariant vectors. They are connected by

$$a_\mu = \sum_\nu g_{\mu\nu} a^\nu = g_{\mu\nu} a^\nu$$

where $g_{\mu\nu}$ is a metric tensor with $g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$

Formalism (2)

Lorentz Transformation

The Lorentz transformation along the x-axis is given by

$$x' = \gamma(x - vt)$$

$$t' = \gamma(t - \frac{v}{c^2}x)$$

where $\gamma = 1/\sqrt{1 - \frac{v^2}{c^2}}$. By introducing the matrix Λ^{μ}_{ν} the transformation becomes

$$x'^{\mu} = \Lambda^{\mu}_{\nu} x^{\nu}.$$

Formalism (3)

Scalar product of vectors

The scalar product of two vectors a^μ and b^μ is defined as follows:

$$a_\mu b^\mu = a^\mu b_\mu = a^0 b^0 - \mathbf{a}.\mathbf{b}$$

Gradient

We keep the differential operator ∇ and define a covariant and contravariant vector

$$\partial_\mu \equiv (\partial / \partial ct, \nabla)$$

$$\partial^\mu \equiv g^{\mu\nu} \partial_\nu \equiv (\partial / \partial ct, -\nabla)$$

Formalism (4)

Electromagnetic fields

The electrical potential $\varphi(\mathbf{r}, t)$ and the vector potential $\mathbf{A}(\mathbf{r}, t)$ are combined to a 4-vector

$$A^\mu \equiv (\varphi, \mathbf{A})$$

Units

Without getting any problems we can set $\hbar = c = 1$.

$$\begin{aligned} x^\mu &= (ct, \mathbf{r}) \rightarrow (t, \mathbf{r}) \\ p^\mu &= (E/c, \mathbf{p}) \rightarrow (E, \mathbf{p}) \end{aligned}$$

Relativistic Wave Equation

In order to obtain a relativistic wave equation we start with the relativistic relation between the energy, the momentum and the mass of a particle:

$$E^2 = \mathbf{p}^2 + m^2$$

From analytical mechanics we get the Hamiltonian for the motion of a charged particle in an electromagnetic field:

$$H = \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2 + e\varphi$$

Comparing this to the Hamiltonian for a free particle ($H_0 = \frac{\mathbf{p}^2}{2m}$) we obtain a substitution for H and $\mathbf{p}$:

$$H \rightarrow H - e\varphi \quad \text{and} \quad \mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}$$

Klein-Gordon equation

Making the substitutions for E and $\mathbf{p}$ leads us to

$$(E - e\varphi)^2 = (\mathbf{p} - e\mathbf{A})^2 + m^2.$$

Now we can perform the substitutions given by Schrödinger ($E \rightarrow i\frac{\partial}{\partial t}$, $\mathbf{p} \rightarrow -i\nabla$) to get a quantum mechanical equation, the **Klein-Gordon equation:**

$$\boxed{\left[(i\frac{\partial}{\partial t} - e\varphi)^2 - (\frac{1}{i}\nabla - e\mathbf{A})^2\right]\psi = m^2\psi}$$

Klein-Gordon equation (2)

Now we can rewrite the Klein-Gordon equation to obtain a more compact form.

$$\left[-(i\frac{\partial}{\partial t} - e\varphi)^2 + (-i\nabla - e\mathbf{A})^2 + m^2\right]\psi = 0$$

$$\left[(\frac{\partial}{\partial t} + ie\varphi)^2 + (\nabla - ie\mathbf{A})(-\nabla + ie\mathbf{A}) + m^2\right]\psi = 0$$

By introducing the 4-vector operators
$D_\mu \equiv \partial_\mu + ie\mathbf{A}_\mu \equiv (\frac{\partial}{\partial t} + ie\varphi, \nabla - ie\mathbf{A})$ and
$D^\mu \equiv \partial^\mu + ie\mathbf{A}^\mu \equiv (\frac{\partial}{\partial t} + ie\varphi, -\nabla + ie\mathbf{A})$ we finally get

$$\left[D_\mu D^\mu + m^2\right]\psi = 0.$$

Problems of the Klein-Gordon Equation

- Energies can be negative
- Probability density is negative for negative energies
- The time dependence is not linear
- The equation describes particles with spin 0

Solution

We have to linearize the equation, i.e. to find an equation that is linear in p^μ and leads to the Dirac equation.

Dirac equation

Ansatz

In order to find a wave equation that describes a free electron Dirac made the ansatz

$$H_D = \boldsymbol{\alpha}.\mathbf{p} + \beta m.$$

$\boldsymbol{\alpha} \equiv (\alpha_x, \alpha_y, \alpha_z)$ and β are hermitian operators only working on the spin variables of the system.

The wave equation becomes

$$E\psi = H_D\psi = [\boldsymbol{\alpha}.\mathbf{p} + \beta m]\,\psi$$

or

$$[E - \boldsymbol{\alpha}.\mathbf{p} - \beta m]\,\psi = 0.$$

Properties of $\boldsymbol{\alpha}$ and β

Furthermore we claim that solutions to $[E - \boldsymbol{\alpha}.\mathbf{p} - \beta m]\,\psi = 0$ also solve the Klein-Gordon equation. To obtain an equation with second order in time we multiply with $[E + \boldsymbol{\alpha}.\mathbf{p} + \beta m]$ from the left side and compare the result to the Klein-Gordon equation $\left[E^2 - \mathbf{p}^2 - m^2\right]\psi = 0$.
This leads to the following constaints for $\boldsymbol{\alpha}$ and β:

$$\begin{aligned} (\alpha_k)^2 &= 1 \\ (\beta)^2 &= 1 \\ \alpha_k\alpha_l + \alpha_l\alpha_k &= 0 \quad (k \neq l) \\ \alpha_k\beta + \beta\alpha_k &= 0 \end{aligned}$$

Dirac equation with electromagnetic fields

Starting from the Dirac equation for a free electron

$$[E - \boldsymbol{\alpha}.\mathbf{p} - \beta m]\,\psi = 0$$

we perform the substitutions $E \rightarrow E - e\varphi$ and $\mathbf{p} \rightarrow \mathbf{p} - e\mathbf{A}$ and get

$$[(E - e\varphi) - \boldsymbol{\alpha}.(\mathbf{p} - e\mathbf{A}) - \beta m]\,\psi = 0$$

or

$$\left[(i\frac{\partial}{\partial t} - e\varphi) - \boldsymbol{\alpha}.(-i\nabla - e\mathbf{A}) - \beta m\right]\psi = 0.$$

The Hamiltonian becomes

$$H_D = e\varphi + \boldsymbol{\alpha}.(\mathbf{p} - e\mathbf{A}) + \beta m.$$

Covariant Dirac equation

To get a covariant form of the Dirac equation we multiply

$$\left[(i\frac{\partial}{\partial t} - e\varphi) - \boldsymbol{\alpha}.(-i\nabla - e\mathbf{A}) - \beta m\right]\psi = 0$$

from the left side with β and get

$$\left[\beta(i\frac{\partial}{\partial t} - e\varphi) - \beta\boldsymbol{\alpha}.(-i\nabla - e\mathbf{A}) - \beta\beta m\right]\psi = 0.$$

Now we define some new operators:

$$\gamma^\mu \equiv (\gamma^0, \gamma^1, \gamma^2, \gamma^3) \equiv (\gamma^0, \boldsymbol{\gamma})$$

$$\gamma^0 \equiv \beta \qquad \boldsymbol{\gamma} \equiv \beta\boldsymbol{\alpha}$$

Covariant Dirac equation (2)

Finally we put it all together and get $(\beta^2 = 1, D_\mu = \partial_\mu + ieA_\mu)$:

$$\left[\gamma^0 (i\frac{\partial}{\partial t} - e\varphi) - \boldsymbol{\gamma}.(-i\nabla - e\mathbf{A}) - m\right]\psi = 0.$$

$$[i\gamma^\mu(\partial_\mu + ieA_\mu) - m]\,\psi = 0$$

$$\boxed{[i\gamma^\mu D_\mu - m]\,\psi = 0}$$

Representation of $\boldsymbol{\alpha}$ and β

We found earlier:

$$\begin{aligned} (\alpha_k)^2 &= 1 \\ (\beta)^2 &= 1 \\ \alpha_k\alpha_l + \alpha_l\alpha_k &= 0 \quad (k \neq l) \\ \alpha_k\beta + \beta\alpha_k &= 0 \end{aligned}$$

- The relations above can not be satisfied with real or complex numbers $\rightarrow$ $\boldsymbol{\alpha}$ and β could be matrices.
- The Hamiltonian $H_D = e\varphi + \boldsymbol{\alpha}.(\mathbf{p} - e\mathbf{A}) + \beta m$ is hermitian, so must be $\boldsymbol{\alpha}$ and β.
- $(\alpha_k)^2 = I$ and $(\beta)^2 = I$ $\rightarrow$ The Eigenvalues are ± 1.

Representation of $\boldsymbol{\alpha}$ and β (2)

- The trace of $\boldsymbol{\alpha}$ and β is zero:

$$Tr(\alpha_k) = Tr(\beta\beta\alpha_k) = Tr(\beta\alpha_k\beta) = -Tr(\alpha_k\beta\beta) = -Tr(\alpha_k)$$

$\rightarrow$ The dimension N of $\boldsymbol{\alpha}$ and β is even.

- For $N = 2$ there are only three linear independant hermitian matrices with a trace of zero (Pauli matrices):

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- The smallest possible dimension is $N = 4$ and one representation is

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}.$$

Representation of γ^μ

And finally we can write down $\gamma^\mu \equiv (\beta, \beta\boldsymbol{\alpha})$:

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

$$\gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \quad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

Solutions with negative Energies

For an electron in rest the Dirac equation becomes

$$i\frac{\partial}{\partial t}\binom{\phi}{\chi} = m\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\binom{\phi}{\chi}.$$

The solutions are $\phi = e^{-i\omega_0 t}$ and $\chi = e^{+i\omega_0 t}$. The energies become $E_\phi = +\hbar\omega_0 = +mc^2$ and $E_\chi = -\hbar\omega_0 = -mc^2$.

Interpretation

- Dirac $\rightarrow$ All energy levels below zero are occupied (Dirac sea).
- Stückelberg $\rightarrow$ The solutions with negative energies are propagating backwards in time. So these solutions describe antiparticles propagating forward in time with a positive ernergy.

g factor of the electron

$$i\frac{\partial}{\partial t}\begin{pmatrix}\phi\\ \chi\end{pmatrix} = \left[\begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0\end{pmatrix}(\mathbf{p}-e\mathbf{A}) + \begin{pmatrix} 1 & 0 \\ 0 & -1\end{pmatrix} m + e\varphi\right]\begin{pmatrix}\phi\\ \chi\end{pmatrix}$$

Using the approximation $\chi \approx \frac{1}{2m}(\boldsymbol{\sigma}.\mathbf{P})\phi$ and $\mathbf{P} = \mathbf{p} - e\mathbf{A}$ we obtain a differential equation for ϕ:

$$i\frac{\partial\phi}{\partial t} = \frac{1}{2m}(\boldsymbol{\sigma}.\mathbf{P})(\boldsymbol{\sigma}.\mathbf{P})\phi + e\varphi\phi$$

Rewriting the equation by using $\mathbf{B} = \nabla \times \mathbf{A}$ and $e = -|e|$ (electron charge) leads to a Schrödinger like equation:

$$i\frac{\partial\phi}{\partial t} = \left[\frac{1}{2m}(-i\nabla + |e|\mathbf{A})^2 + \frac{|e|}{2m}\boldsymbol{\sigma}.\mathbf{B} - |e|\varphi\right]\phi$$

g factor of the electron (2)

$$i\frac{\partial \phi}{\partial t} = \left[\frac{1}{2m}(-i\nabla + |e|\mathbf{A})^2 + \frac{|e|}{2m}\boldsymbol{\sigma}.\mathbf{B} - |e|\varphi\right]\phi$$

Now we compare this equation to the Pauli equation (Schrödinger equation for a particle with spin):

$$i\frac{\partial \psi_s}{\partial t} = \left[\frac{1}{2m}(-i\nabla + |e|\mathbf{A})^2 + \boldsymbol{\mu}.\mathbf{B} - |e|\varphi\right]\psi_s$$

Comparing with $\boldsymbol{\mu} = g\frac{|e|}{2m}\mathbf{s}$, where $\mathbf{s} = \frac{1}{2}\boldsymbol{\sigma}$, leads to $g = 2$.

The Hydrogen Atom

We aim to find the energy levels of the hydrogen atom.

Therefore we have to solve the Dirac equation with a central potential $V(r) = \frac{-Ze^2}{r}$. The Hamiltonian for such a problem is

$$H_D \equiv \boldsymbol{\alpha}.\mathbf{p} + \beta m + V(r).$$

As the problem is spherical symmetric, the Hamiltonian obeys the relations

$$[H_D, \mathbf{J}] = 0 \quad \text{and} \quad [H_D, P] = 0$$

where $\mathbf{J}$ and P are the operator of the total angular momentum and the parity operator respectively.

Quantum Numbers

We assume that the wave function

$$\psi \equiv \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

is an eigenfunction of $\mathbf{J}$, J_z and P with the quantum numbers J, M and

$$\kappa = \begin{cases} +1 & \text{for states with parity } (-)^{J+\frac{1}{2}} \\ -1 & \text{for states with parity } (-)^{J-\frac{1}{2}}. \end{cases}$$

$$\mathbf{J}^2 \begin{pmatrix} \phi \\ \chi \end{pmatrix} = J(J+1) \begin{pmatrix} \phi \\ \chi \end{pmatrix} \qquad J_z \begin{pmatrix} \phi \\ \chi \end{pmatrix} = M \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

$$P^{(0)} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = (-)^{J+\frac{1}{2}\kappa} \begin{pmatrix} \phi \\ -\chi \end{pmatrix}$$

Eigenfunctions of the Angular Momentum

The function Y_{LJ}^{M} may be the eigenfunction of the state (JM). The functions parity is $(-)^{L}$. L can be obtained in two different ways:

$$L = l = J + \frac{1}{2}\kappa \qquad L = l' = J - \frac{1}{2}\kappa$$

Considering $P^{(0)}\binom{\phi}{\chi} = (-)^{J+\frac{1}{2}\kappa}\binom{\phi}{-\chi}$ we can define the wave equation

$$\psi_{\kappa J}^{M} = \frac{1}{r}\begin{pmatrix} F(r)\, Y_{lJ}^{M} \\ iG(r)\, Y_{l'J}^{M} \end{pmatrix}$$

where F and G are arbitrary functions. We separated the radial and angular components.

Separation of the Angular and Radial Components of H_D

We have to solve the problem $H_D \psi_{\kappa J}^M = E \psi_{\kappa J}^M$.

Therefore we introduce $p_r = -i \frac{1}{r} \frac{\partial}{\partial r} r$ and $\alpha_r = (\boldsymbol{\alpha}.\hat{\mathbf{r}})$. In order to obtain another expression for $\boldsymbol{\alpha}.\mathbf{p}$ we calculate

$$(\boldsymbol{\alpha}.\mathbf{r})(\boldsymbol{\alpha}.\mathbf{p}) = \mathbf{r}.\mathbf{p} + i\boldsymbol{\sigma}.\mathbf{L} = rp_r + i(1 + \boldsymbol{\sigma}.\mathbf{L}).$$

Now we multiply this equation with α_r / r from the left side and use the identity $\alpha_r^2 = 1$:

$$\boldsymbol{\alpha}.\mathbf{p} = \alpha_r \left(p_r + \frac{i}{r}(1 + \boldsymbol{\sigma}.\mathbf{L}) \right)$$

Derivation of F and G

With the expression for $\boldsymbol{\alpha}.\mathbf{p}$ we write down the problem again:

$$\left[\alpha_r\left(p_r + \frac{i}{r}(1+\boldsymbol{\sigma}.\mathbf{L})\right) + m\beta + V(r)\right]\psi_{\kappa J}^{M} = E\psi_{\kappa J}^{M}$$

From this equation we get two coupled differential equations:

$$\left[-\frac{d}{dr} + \frac{\kappa(J+\frac{1}{2})}{r}\right]G = (E-m-V)F$$

$$\left[\frac{d}{dr} + \frac{\kappa(J+\frac{1}{2})}{r}\right]F = (E+m-V)G$$

The differential equations can be solved be assuming that F and G can be represented by a power series. This leads to an expression for the energy levels of the bound states of the hydrogen atom.

Energy Levels

Finally we can write down an expression for the energy levels of the hydrogen atom:

$$E_{nJ} = m \left[1 + \frac{Z^2 e^4}{(n - \epsilon_J)^2} \right]^{-\frac{1}{2}}$$

$$\epsilon_J = J + \frac{1}{2} - \sqrt{(J + \frac{1}{2})^2 - Z^2 e^4}$$

or

$$E_{nJ} = m \left[1 - \frac{Z^2 e^4}{2n^2} - \frac{(Z^2 e^4)^2}{2n^4} \left(\frac{n}{J + \frac{1}{2}} - \frac{3}{4} \right) + \ldots \right]$$

Energy Levels for several Quantum Numbers

	n	l	J	E_{nJ}
$1S_{\frac{1}{2}}$	1	0	$\frac{1}{2}$	$m\sqrt{1-Z^2e^4}$
$2S_{\frac{1}{2}}$	2	0	$\frac{1}{2}$	$m\sqrt{\frac{1+\sqrt{1-Z^2e^4}}{2}}$
$2P_{\frac{1}{2}}$	2	1	$\frac{1}{2}$	$m\sqrt{\frac{1+\sqrt{1-Z^2e^4}}{2}}$
$2P_{\frac{3}{2}}$	2	1	$\frac{3}{2}$	$\frac{m}{2}\sqrt{4-Z^2e^4}$

- The states of the principle quantum number n are not degenerated completely any more.
- The states $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ are still degenerated. They have the same quantum numbers n and J, but a different parity.
- Experiments show that $2S_{\frac{1}{2}}$ has a higher energy than $2P_{\frac{1}{2}}$ $\longrightarrow$ Lamb shift.

Bibliography

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