Relativistic Effects in Atomic Physics

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Relativistic Effects in Atomic Physics

1. Review of Dirac Equation

- Dirac found relativistically invariant equations which play the same role for electrons as Maxwell's equations do for photons. They are ($\hbar = c = 1$)

$$i\frac{\partial \phi}{\partial t} = m\phi + \vec{\sigma}\cdot\vec{p}\,\chi \qquad (1)$$

$$i\frac{\partial \chi}{\partial t} = -m\chi + \vec{\sigma}\cdot\vec{p}\,\phi \qquad (2)$$

where ϕ and χ are two-component spinor functions

$p = -i\nabla$

$m =$ electron mass.

1.1 Relation to Maxwell's equations

- Make the formal substitutions

$$\begin{aligned} \phi &\to \vec{E} \\ \chi &\to i\vec{H} \\ \vec{\sigma} &\to \vec{s} \\ m &= 0. \end{aligned} \qquad (3)$$

Here, $\vec{s}$ is the photon spin operator defined by

$$s_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad s_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$$

$$s_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad s^2 = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

The result of s_i operating ~~on~~ on an arbitrary vector

$$\vec{F} = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix}$$

is $\quad (s_i \vec{F})_j = -i \epsilon_{ijk} F_k$

where ϵ_{ijk} is the unit antisymmetric tensor

$$\epsilon_{ijk} = \begin{cases} 1 & \text{for } i,j,k \text{ cyclic} \\ -1 & \text{for } i,j,k \text{ anticyclic} \\ 0 & \text{otherwise} \end{cases}$$

The above is equivalent to

$$(s_i \vec{F})_j = +i(\hat{e}_i \times \vec{F})_j$$

or $\quad s_i \vec{F} = +i\, \hat{e}_i \times \vec{F}$

Recall that the infinitesimal rotation operator for a vector field is

$$\vec{A}'(r,\theta,\phi) = (1 - i\alpha J_z)\vec{A}$$

with $\quad J_z = -i\dfrac{\partial}{\partial\phi} + i\,\hat{e}_z \times$

$$= L_z + S_z .$$

- Making the substitutions (3) in (1) and (2) yields

$$\frac{\partial \vec{E}}{\partial t} = (\vec{p}\cdot\vec{s})\vec{H} = +\sum_i \nabla_i \hat{e}_i \times \vec{H} = \nabla \times \vec{H}$$

$$-\frac{\partial \vec{H}}{\partial t} = (\vec{p}\cdot\vec{s})\vec{E} = \sum_i \nabla_i \hat{e}_i \times \vec{E} = \nabla \times \vec{E}$$

which are two of Maxwell's equations.

The other two equations

$\nabla \cdot \vec{E} = 0$
$\nabla \cdot \vec{H} = 0$

express the absence of electric and magnetic sources in a vacuum. It is the first two equations which determine the dynamics of the field.

1.2 The Four-Component Dirac Equation

- Define the four-component bispinor

$$\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} \varphi^{1/2} \\ \varphi^{-1/2} \\ \chi^{1/2} \\ \chi^{-1/2} \end{pmatrix} = \begin{pmatrix} \psi^1 \\ \psi^2 \\ \psi^3 \\ \psi^4 \end{pmatrix}$$

and the matrices $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$, $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

Then equations (1) and (2) can be combined into the single equation

$$i \frac{\partial \psi}{\partial t} = (\vec{\alpha} \cdot \vec{p} + \beta m) \psi \qquad (4)$$
$$= H \psi$$

ie. $H = \vec{\alpha} \cdot \vec{p} + \beta m$ is the relativistic Hamiltonian.

The $\vec{\alpha}$ and β matrices satisfy

$$\alpha_i \alpha_j + \alpha_j \alpha_i = 2 \delta_{ij}, \quad \alpha \beta + \beta \alpha = 0.$$

Also, define $\vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}$. This has the same properties as $\vec{\sigma}$ and so is the 4-component spin operator.

1.3 Symmetric Form of the Dirac Equation

- Define the matrices γ_μ ($\mu = 1, 2, 3, 4$) as follows

$$\gamma_j = -i\beta\alpha_j \qquad (j = 1, 2, 3)$$

$$\gamma_4 = \beta$$

They satisfy $\gamma_\mu \gamma_\nu + \gamma_\nu \gamma_\mu = 2\delta_{\mu\nu}$

$$\gamma_\mu^{\dagger} = \gamma_\mu .$$

Multiply (4) through by $i\beta$ to obtain

$$(\gamma_4 p_4 + \vec{\gamma}\cdot\vec{p} - im)\psi = 0 \tag{5}$$

where $p_4 = -i\dfrac{\partial}{\partial x_4} = -\dfrac{\partial}{\partial t}$.

Define $\hat{p} = \sum_\nu p_\nu \gamma_\nu = \vec{\gamma}\cdot\vec{p} + \gamma_4 p_4$. Then (5) becomes

$$(i\hat{p} + m)\psi = 0 \tag{6}$$

- Although (6) is obtained from (4), its physical meaning is less apparent because the operator $i\hat{p}$ is not Hermitian. The advantages of (6) are that it is more compact, and the relativistic invariance is more immediately apparent. Equation (4) is recovered by multiplying (6) through by β.

- Since $i\hat{p}$ is not Hermitian, the equation satisfied by ψ^* is not the same. For convenience, define

$$\bar{\psi} = \psi^* \beta$$

Then $\bar{\Psi}$ satisfies

$$\bar{\Psi}(-i\hat{p} + m) = 0 \quad \text{(Here, } \hat{p} \text{ operates to the left.)} \qquad (7)$$

1.4 Equation of Continuity

- Multiply (6) on the left by $\bar{\Psi}$ and (7) on the right by Ψ and subtract to obtain

$$\bar{\Psi}\,\gamma_\mu\, p_\mu \Psi + (p_\mu \bar{\Psi})\,\gamma_\mu \Psi = 0 \qquad \text{(Summation over } \mu \text{ is implied.)}$$

ie $p_\mu(\bar{\Psi}\gamma_\mu\Psi) = 0$

or $$\frac{\partial s_\mu}{\partial x_\mu} = 0 \qquad (8)$$

where $s_\mu = i\bar{\Psi}\gamma_\mu\Psi$.

This is the equation of continuity. In 3-dimensional form, it reads

$$\frac{\partial s_0}{\partial t} + \nabla \cdot \vec{s} = 0$$

where $s_0 = \bar{\Psi}\gamma_4\Psi = \Psi^*\Psi$ (probability density)

$\vec{s} = i\bar{\Psi}\vec{\gamma}\Psi = \Psi^*\vec{\alpha}\Psi$ (flux density)

- The latter equation leads to the interpretation of $\vec{\alpha}$ (ie. $c\vec{\alpha}$) as the <u>velocity</u> operator. Note that $\vec{p}$ and $\vec{v}$ are represented by quite different operators.

1.5 Positive and Negative Frequency Solutions

- The general solution to the Dirac equation can be written in the form of a Fourier integral

$$\psi(\vec{r}) = \int \psi_{\vec{k}}\, e^{i\vec{k}\cdot\vec{r}}\, d\vec{k}$$

$\psi_{\vec{k}}$ is the electron wave function in momentum space. It satisfies the Fourier transform of eq (4)

$$i\frac{\partial \psi_{\vec{k}}}{\partial t} = (\vec{\alpha}\cdot\vec{k} + \beta m)\psi_{\vec{k}}.$$

i.e.
$$i\frac{\partial \phi_{\vec{k}}}{\partial t} = m\phi_{k} + \vec{\sigma}\cdot\vec{k}\,\chi_{\vec{k}}$$
$$i\frac{\partial \chi_{\vec{k}}}{\partial t} = -m\chi_{\vec{k}} + \vec{\sigma}\cdot\vec{k}\,\phi_{\vec{k}}.$$
prove (9)

.. Look for stationary state solutions of the form
$$\psi_{\vec{k}} = \psi_0(\vec{k})\, e^{-i\omega t}$$

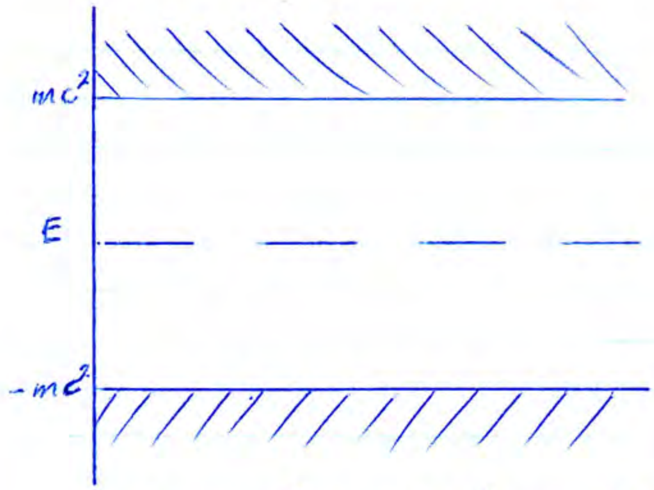
Substituting in (9) yields

$$(\omega - m)\phi_{\vec{k}} - \vec{\sigma}\cdot\vec{k}\,\chi_{\vec{k}} = 0$$
$$-\vec{\sigma}\cdot\vec{k}\,\phi_{\vec{k}} + (\omega + m)\chi_{\vec{k}} = 0 \qquad (10)$$

The condition for simultaneous solutions to exist is

$$\begin{vmatrix} \omega - m & -\vec{\sigma}\cdot\vec{k} \\ -\vec{\sigma}\cdot\vec{k} & \omega + m \end{vmatrix} = 0$$

$$\therefore \omega = \pm\left[(\vec{\sigma}\cdot\vec{k})^2 + m^2\right]^{1/2}$$
$$= \pm\left[k^2 + m^2\right]^{1/2} = \pm\mathcal{E}, \quad \mathcal{E} > 0$$



Eigenvalue Spectrum for Free Particles

- An arbitrary solution can be written

$$\psi = \psi^{(+)} + \psi^{(-)}$$

$$\psi^{(+)}(\vec{r},t) = \int \psi_0^{(+)}(\vec{k})\, e^{i(\vec{k}\cdot\vec{r} - Et)}\, d\vec{k}$$

$$\psi^{(-)}(\vec{r},t) = \int \psi_0^{(-)}(-\vec{k})\, e^{-i(\vec{k}\cdot\vec{r} - Et)}\, d\vec{k}$$

This decomposition is relativistically invariant since no Lorentz transformation can connect the positive and negative frequency domains due to the finite energy gap.

- Note that one of $\varphi_{\vec{k}}$ and $\chi_{\vec{k}}$ can be an arbitrary function of $\vec{k}$. The other is determined by (10).

$$\text{e.g.} \quad \chi_{\vec{k}}^{(+)} = \frac{\vec{\sigma}\cdot\vec{k}}{E+m}\, \varphi_{\vec{k}}^{(+)} . \qquad (11)$$

1.6 States of Definite Angular Momentum and Parity

- The total angular momentum operator is

$$\vec{J} = \vec{L} + \frac{1}{2}\vec{\Sigma} \qquad (17)$$

where $\vec{L} = \vec{r} \times \vec{p}$

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

As in non-relativistic quantum mechanics, the eigenvectors of $\vec{J}$ can be constructed by vector coupling.

- Using the commutation relations

$$[\beta, \vec{\Sigma}] = 0, \qquad [\alpha_i, \Sigma_j] = 2i\epsilon_{ijk}\alpha_k$$

it can be shown that

$$[\vec{J}, H] = 0 \qquad \text{(prove this)}$$

so that J^2 and J_z can be taken as constants of the motion.

The eigenvectors of σ^2, σ_z are $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

The corresponding eigenvectors of Σ^2, Σ_z are

$$\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}$$

The more general forms

$$\begin{pmatrix}\alpha\\0\\\beta\\0\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}0\\\gamma\\0\\\delta\end{pmatrix}$$

are also eigenvectors.

- Define $\chi_{1/2} = \begin{pmatrix}1\\0\end{pmatrix}$ and $\chi_{-1/2} = \begin{pmatrix}0\\1\end{pmatrix}$ and consider first the top spinor Φ_{jLM}, $j = L \pm 1/2$.

The simultaneous eigenvectors of J^2, J_z are

$$\Phi_{jLM} = g(r) \sum_{\mu, m} \langle l m \tfrac{1}{2} \mu | j M \rangle Y_l^m(\hat{r}) \chi_\mu . \qquad (13)$$

where $g(r)$ is a radial function.

Then $J^2 \Phi_{jLM} = j(j+1) \Phi_{jLM}$

$$J_z \Phi_{jLM} = M \Phi_{jLM}.$$

- The above suggests that it is useful to define a spherical spinor $\Omega_{jLM}(\hat{r})$ with components

$$\Omega_{jLM}(\hat{r}) = \begin{pmatrix} \langle L\, M-\tfrac{1}{2}, \tfrac{1}{2}\, \tfrac{1}{2} | j M \rangle Y_L^{M-1/2}(\hat{r}) \\ \langle L\, M+\tfrac{1}{2}, \tfrac{1}{2} -\tfrac{1}{2} | j M \rangle Y_L^{M+1/2}(\hat{r}) \end{pmatrix} \qquad (14)$$

Then $\Phi_{jLM} = g(r) \Omega_{jLM}(\hat{r})$

(These spherical harmonics are the same as in Akhiezer and Berestetskii, and Brink and Satchler. They differ by a factor of $(-1)^m$ from those in Bethe and Salpeter.)

The necessary vector coupling coefficients can be obtained from

	j	
μ	$l+\frac{1}{2}$	$l-\frac{1}{2}$
$\frac{1}{2}$	$\sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}$	$-\sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}$
$-\frac{1}{2}$	$\sqrt{\frac{l-M+\frac{1}{2}}{2l+1}}$	$\sqrt{\frac{l+M+\frac{1}{2}}{2l+1}}$

(15)

Note that $\int \Omega_{jLM}^{*} \, \Omega_{j'L'M'} \sin\theta \, d\theta \, d\varphi = \delta_{jj'} \delta_{LL'} \delta_{MM'}$.

- The angular dependence of the lower spinor χ_{jLM} is obtained from φ_{jLM} from the Dirac equation (2) for stationary states; ie.

$$\chi_{jLM} = \frac{\vec{\sigma}\cdot\vec{p}}{(\mathcal{E}+m)} \, \varphi_{jLM}$$

Using $\vec{\sigma}\cdot\vec{p} = \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix}$

together with the relations

$$\frac{\partial}{\partial z}\left[g(r)\, Y_l^m(\theta,\varphi) \right] = \left[\frac{(l+m+1)(l-m+1)}{(2l+3)(2l+1)} \right]^{1/2} Y_{l+1}^m \times \left(\frac{d}{dr} - \frac{l}{r} \right) g$$

$$+ \left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1}^m \times \left(\frac{d}{dr} + \frac{l+1}{r} \right) g$$

$$\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y} \right)\left[g(r)\, Y_l^m(\theta,\varphi) \right] = \mp \left[\frac{(l\pm m+2)(l\pm m+1)}{(2l+3)(2l+1)} \right]^{1/2} Y_{l+1}^{m\pm1} \left(\frac{d}{dr} - \frac{l}{r} \right) g$$

$$\pm \left[\frac{(l\mp m)(l\mp m-1)}{(2l+1)(2l-1)} \right]^{1/2} Y_{l-1}^{m\pm1} \left(\frac{d}{dr} + \frac{l+1}{r} \right) g$$

and the coefficients (15), it can be shown that

$$(\vec{\sigma}\cdot\vec{p})\, g(r)\, \Omega_{jLM} = i\left(\frac{dg}{dr} + \frac{\kappa+1}{r} g\right) \Omega_{jL'M} \qquad (16)$$

$$\text{where } \begin{cases} L' = L+1, & \kappa = -(L+1) \quad \text{if } j = L + 1/2 \\ L' = L-1, & \kappa = L \quad \text{if } j = L - 1/2 \end{cases}$$

Thus χ_{jLM} must be proportional to $\Omega_{jL'M}$.

This result could have been anticipated because χ_{jLM} must be a spherical spinor, and L' is the only other angular momentum that can couple with $s = 1/2$ to form the same j as in φ_{jLM}.

- Write the complete solutions in the form

$$\varphi_{jLM} = i\, g(r)\, \Omega_{jLM}(\hat{r})$$

$$\chi_{jLM} = -f(r)\, \Omega_{jL'M}(\hat{r})$$

and substitute into

$$(\mathcal{E}-m)\,\varphi = \vec{\sigma}\cdot\vec{p}\,\chi \qquad (17)$$

$$(\mathcal{E}+m)\,\chi = \vec{\sigma}\cdot\vec{p}\,\varphi \qquad (18)$$

Using (16), together with its analogue

$$(\vec{\sigma}\cdot\vec{p})\, f(r)\, \Omega_{jL'M} = i\left(\frac{d}{dr} - \frac{(\kappa-1)}{r}\right) f\, \Omega_{jLM}$$

(17) and (18) become

$$(\varepsilon - m)\, i\, g(r)\, \Omega_{jLM} = -i\left(\frac{d}{dr} - \frac{(\kappa-1)}{r}\right) f(r)\, \Omega_{jLM}$$

and

$$-(\varepsilon + m)\, f(r)\, \Omega_{jL'M} = -\left(\frac{d}{dr} + \frac{\kappa+1}{r}\right) g(r)\, \Omega_{jL'M}$$

i.e.

$$\left.\begin{aligned} \frac{df}{dr} + (1-\kappa)\frac{f}{r} + (\varepsilon - m) g &= 0 \\ \frac{dg}{dr} + (1+\kappa)\frac{g}{r} - (\varepsilon + m) f &= 0 \end{aligned}\right\} \qquad (19)$$

These are the radial equations for a free particle. As in non-relativistic quantum mechanics, the solutions are proportional to spherical Bessel functions. (see Akhiezer and Berestetskii, pp. 107-112)

- The complete wave-function $\Psi_{jLM} = \begin{pmatrix} \varphi_{jLM} \\ \chi_{jLM} \end{pmatrix}$

as constructed above is also a state of definite parity. If $\underset{\sim}{I}$ is the inversion operator, then

$$\beta \underset{\sim}{I}\, \Psi_{jLM} = (-1)^L \Psi_{jLM}$$

where $(-1)^L$ is the parity.