Relativistic Klein-Gordon Equation & H-atom

refs. Davydov ¶ 54 & 58; Sakurai Sec. 3.1.★

1) We have by now calculated the H-atom energies to terms of $\mathcal{O}(\alpha^2)$ [Bohr energies] and $\mathcal{O}(\alpha^4)$ [$\vec{S}\cdot\vec{L}$ coupling + relativistic K.E. correction]. It would be "nice" to have a wave equation, beyond Schrodinger's $i\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$, whose solutions gave the H-atom energies correct to all orders in α.

The first attempt to produce a relativistically correct wave equation was made by E. Schrödinger, and proceeded from the relativistic energy-momentum relation...

$$\rightarrow E^2 = (\vec{p}c)^2 + (mc^2)^2, \text{ for a particle of rest-mass } m. \tag{1}$$

Here $E = \gamma mc^2$ is the total particle energy, $\vec{p} = \gamma m\vec{v}$ is its relativistic three-momentum, and $\gamma = 1/\sqrt{1-(v/c)^2}$ is the usual dilation factor. If we define a momentum four-vector by...

$$P = \left(\vec{p}, \tfrac{i}{c}E\right) = (P_\mu) \text{ w/ } \mu = 1,2,3,4 \begin{cases} P_k = p_k,\ k = 1,2,3 \text{ [ordinary 3-mom}^{\underline{m}}\text{]}, \\ P_4 = i(E/c) \text{ [4th comp}^{\underline{t}} = i \times \text{energy]}; \end{cases} \tag{2}$$

$$\text{so } P^2 = P_\mu P_\mu = P_k P_k + P_4^2 = \vec{p}^{\,2} - (E/c)^2 \leftarrow \text{summation convention}$$

... then Eq. (1) is succinctly written as:

$$\boxed{P_\mu P_\mu + (mc)^2 = 0}. \tag{3}$$

Clearly P has the Lorentz-invariant length: $P_\mu P_\mu = -(mc)^2$. Conversion of Eq. (3) to a QM wave equation proceeds by the standard operator prescription:

$$P_k = p_k \rightarrow (-)i\hbar\frac{\partial}{\partial x_k}\ ;\quad P_4 = \frac{i}{c}E \rightarrow -i\hbar\frac{\partial}{\partial x_4},\ \text{w/ } \underline{x_4 = ict}$$

...[the position 4-vector is: $R = (\mathbf{r}, ict)$, i.e. $R_k = x_k$ & $R_4 = ict$]...

$$\xrightarrow{\text{So}} P_\mu \rightarrow -i\hbar\,\partial/\partial x_\mu, \text{ for passage to QM.} \tag{4}$$

★ Sakurai's "other book", i.e. "Advanced QM" (Addison-Wesley, 1967). A real page-turner...

Derivation of KG Eq. Remarks.

By multiplying Eq. (3) on the right by a wave function $\psi(\mathbf{r},t)$, and using Eq. (4):

$$[P_\mu P_\mu + (mc)^2]\psi = 0 \longrightarrow \left[-\hbar^2 \frac{\partial^2}{\partial x_\mu^2} + (mc)^2\right]\psi = 0$$

or $\boxed{[\partial^2/\partial x_\mu^2 - k_0^2]\,\psi(\mathbf{r},t) = 0}$, sum on $\mu = 1,2,3,4$; $k_0 = mc/\hbar$ (5)

This eqtn is known as the free-particle Klein-Gordon Equation. It can be shown easily to be "Lorentz covariant" (i.e. has same form in all inertial frames) -- this is because $P_\mu P_\mu$ has an invariant length. In more familiar terms, Eq. (5) is just an inhomogeneous wave eqtn: $[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - k_0^2]\psi = 0$, whose solutions are well known from classical EM theory.

Schrödinger actually wrote Eq. (5) in ~1925, but quickly discarded it, because -- as we shall show -- it did not predict the correct H-atom energies. In fact Eq. (5) "works" only for spin-zero particles. Klein & Gordon realized this in 1926, and got some mileage out of it.

REMARKS Re free-particle KG Eqtn: $(\partial^2/\partial x_\mu^2 - k_0^2)\psi = 0$.

1. The wavefcn ψ here has only one component (it is not a spinor), so it must transform a scalar under a Lorentz transf$^{\underline{n}}$. This means that the particles m described by ψ can have no degrees of freedom other than translations in spacetime -- in particular, m cannot have a nonzero spin. So the KG Eqtn can only handle spinless particles (e.g. π or K-mesons); it can't handle electrons.

2. Another "problem" with the KG Eqtn... it is 2nd order in $\partial/\partial t$ (compare with Schrödinger Eqtn, 1st order in $\partial/\partial t$), and so to solve it we must specify initial conditions on both ψ and $\partial\psi/\partial t$. We no longer have the convenient Schrodinger-type time evolution: $\psi(0) \to \psi(t) = \exp(-\frac{i}{\hbar}\mathcal{H}t)\psi(0)$; we also need to know $\partial\psi/\partial t$, in addition to the initial state.

3. There is also a problem with the sign of the energy: $E = \pm\sqrt{(\vec{p}c)^2 + (mc^2)^2}$ are both valid solutions to Eq. (1). This shows up in a more subtle way when we try to write a QM continuity eqtn for KG. Do the usual maneuver for a free particle, viz.

$$\psi^* \left(\frac{\partial^2}{\partial x_\mu^2} - k_0^2\right)\psi = 0 \text{ , and : } \psi\left(\frac{\partial^2}{\partial x_\mu^2} - k_0^2\right)\psi^* = 0 \leftarrow \text{subtract these...}$$

$$\xrightarrow{\text{so}} \partial S_\mu / \partial x_\mu = 0 \text{ , w/ } S_\mu = \frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x_\mu} - \psi \frac{\partial \psi^*}{\partial x_\mu}\right). \quad (6)$$

(S_μ) is the QM probability 4-current. In more familiar terms...

$$(S_\mu) = (\vec{S}, ic\rho) \text{ , w/ } \frac{\partial S_\mu}{\partial x_\mu} = 0 \Rightarrow \boxed{\vec{\nabla}\cdot\vec{S} + \frac{\partial \rho}{\partial t} = 0}, \quad (7)$$

where: $\vec{S} = \frac{\hbar}{2im}(\psi^* \vec{\nabla}\psi - \psi \vec{\nabla}\psi^*) \leftarrow$ probability 3-current; (8a)

and: $\rho = \frac{i\hbar}{2mc^2}\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t}\right) = -\frac{\hbar}{mc^2}\mathrm{Im}\left(\psi^* \frac{\partial \psi}{\partial t}\right)$ } probability density for KG eqtn. (8b)

The current $\vec{S}$ is exactly the same as for the Schrödinger eqtn [ref. Sakurai, Eq. (2.4.16); Davydov, Eq. (15.8)], but the probability density is profoundly different than the old familiar $\rho = \psi^*\psi$ from Schrödinger theory. In fact the ρ(KG) of Eq. (8b) is not even positive-definite... it can be (+)ve, (−)ve, or zero, depending on how ψ & $\partial\psi/\partial t$ are assigned as initial values.

By virtue of Eq. (7), we still have a conserved quantity however. Integrate the eqtn over all space and convert $\int_\infty \vec{\nabla}\cdot\vec{S}\, d^3x = \oint_\infty \vec{S}\cdot d\vec{A} = 0$. Then...

$$\rightarrow \partial S_\mu/\partial x_\mu = 0 \Rightarrow \frac{\partial}{\partial t}\int_\infty \rho\, d^3x = 0 \text{ , i.e. } \boxed{\int_\infty \rho\, d^3x = \text{time-indpt cnst.}} \quad (9)$$

So the total "probability" $\int_\infty \rho\, d^3x$ is conserved, but the "time-indpt cnst" in Eq. (9) can still be (+)ve, (−)ve, or zero. In fact ρ(KG) cannot be interpreted as a probability density; it can be interpreted as the particle's charge density [ρ(KG) → +, −, 0 corresponds to charge +e, −e, zero]. See Davydov, ¶55.

KG Eqtn in External EM Fields

2) It is clear that the KG Eqtn needs new interpretation, and that it cannot possibly give the correct energies for the H-atom (because it applies to <u>spinless</u> ψ-fields). But we shall solve the KG Eqtn for a Coulomb interaction anyway, for two reasons: <u>(1)</u> we can find out how "pionium" works (atom $= p\pi^-$), <u>(2)</u> it will give us practice for a later big game: solution of the <u>Dirac Eqtn</u> for the H-atom. The Dirac Eqtn is in fact the correct relativistic eqtn for spin-$\frac{1}{2}$ ψ-fields.

To "derive" the KG Eqtn for an external EM field specified by the 4-potential:

$$\rightarrow A = (\vec{A}, i\phi) \begin{cases} \text{vector potl. } \vec{A} : \ \vec{B} = \vec{\nabla}\times\vec{A}; \\ \text{scalar potl. } \phi : \ \vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\partial\vec{A}/\partial t; \end{cases} \tag{10}$$

we transform to the "canonical" 4-momentum.* For a particle of charge q...

$$\rightarrow P_\mu \rightarrow P'_\mu = P_\mu - (q/c)A_\mu \begin{cases} \text{i.e. } (P'_k) = \vec{p} - (q/c)\vec{A}, \\ \text{and } P'_4 = \frac{i}{c}(E - q\phi). \end{cases} \tag{11}$$

Then the free-particle eqtn (5) above goes to $[P'_\mu P'_\mu + (mc)^2]\psi = 0$, or...

$$\left[\left(P_\mu - \frac{q}{c}A_\mu\right)^2 + (mc)^2\right]\psi = 0 \ \leftarrow \text{set } P_\mu = -i\hbar\,\partial/\partial x_\mu$$

$$\boxed{\left[\left(\frac{\partial}{\partial x_\mu} - \frac{iq}{\hbar c}A_\mu\right)^2 - k_0^2\right]\psi = 0} \quad \text{w/ } \underline{\underline{k_0 = mc/\hbar}}; \begin{cases} (x_\mu) = (\mathbf{r}, ict), \\ (A_\mu) = (\mathbf{A}, i\phi). \end{cases} \tag{12}$$

For our application, the EM field is <u>static</u>, so $\vec{A} = 0$ and Eq. (12) becomes...

$$\rightarrow \left[\frac{\partial^2}{\partial x_k^2} - \frac{1}{c^2}\left(\frac{\partial}{\partial t} + \frac{iq}{\hbar}\phi\right)^2 - k_0^2\right]\psi = 0. \tag{13}$$

Further, we will be looking for a <u>stationary</u> state of energy E, which can be

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* The EM Hamiltonian for q in $(\vec{A}, i\phi)$ is: $H_{EM} = \left[(\vec{P} - \frac{q}{c}\vec{A})^2 c^2 + (mc^2)^2\right]^{1/2} + q\phi$ [Jkⁿ Eq. (12.14)] relativistically, and $H_{EM} \rightarrow \frac{1}{2m}(\vec{P} - \frac{q}{c}\vec{A})^2 + q\phi + mc^2$, as $c \rightarrow \infty$ [Sakurai (2.6.20)]. The "canonical momentum" $\vec{P}$ is written in this way in order to make Hamilton's eqtns-of-motion turn out right. In particular, with this $\vec{P}$, Hamilton's $-\partial H_{EM}/\partial\vec{r} = d\vec{P}/dt$ implies the Lorentz force law: $\frac{d}{dt}(\gamma m\vec{v}) = q(\vec{E} + \frac{1}{c}\vec{v}\times\vec{B})$.

defined by: $(i\hbar\,\partial/\partial t)\psi = E\psi \Rightarrow \psi(t) \propto e^{-\frac{i}{\hbar}Et}$, so that Eq. (13) becomes...

$$\left[\nabla^2 + \left(\frac{E-q\phi}{\hbar c}\right)^2 - \left(\frac{mc}{\hbar}\right)^2\right]\psi = 0,$$ KG Eq. for (q,m) in potl ϕ. (14)

This is the equation we shall solve for ϕ = Coulomb potential.

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3) Compare KG Eq. (14) with (nonrelativistic) Schrödinger Eqtn. Write...

$V = q\phi$, external potential; $E\left(\substack{\text{total}\\ \text{energy}}\right) = mc^2 + \mathcal{E}\left(\substack{\text{ordinary}\\ \text{eigenenergy}}\right)$;

Soll KG Eq. (14) is: $\left\{\nabla^2 + \frac{2m}{\hbar^2}(\mathcal{E}-V)\left[1+\left(\frac{\mathcal{E}-V}{2mc^2}\right)\right]\right\}\psi = 0,$ (15)

Schrödinger Eq is: $\left\{\nabla^2 + \frac{2m}{\hbar^2}(\mathcal{E}-V)\left[1+(\text{zero})\right]\right\}\psi = 0.$

The two eqtns are close, differing only by a term of relative order $\left(\frac{\mathcal{E}-V}{mc^2}\right)$, which vanishes in the nonrelativistic limit $c\to\infty$. In fact it is clear that the Schrödinger Eq. is just the nonrelativistic limit of the KG Eq.

Another way of comparing Eqs. (15) is to say the energies $\mathcal{E}$ are "perturbed"

$$\mathcal{E},\ \text{Schrödinger Eq.} \longrightarrow \mathcal{E} + \frac{1}{2mc^2}(\mathcal{E}-V)^2,\ \text{KG Eq.} \tag{16}$$

For ~ nonrelativistic motions, $\mathcal{E} \ll mc^2$, and the additional term is just a perturbation on $\mathcal{E}$. In passing, we note that the new term is

$$\rightarrow (\mathcal{E}-V)^2/2mc^2 \rightarrow (-)\,\mathcal{V}(\text{rel.}) = p^4/8m^3c^2, \tag{17}$$

in terms of the relativistic correction we concocted on pp. fs 11-13.

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4) For spherically symmetric potentials $V = q\phi = V(r)$, Eq. (14) can be separated into radial & ∡lar eqtns. Assume: $\psi(\vec{r},t) = \frac{1}{r}R(r)Y_{lm}(\theta,\varphi)e^{-i(E/\hbar)t}$; then the KG radial eqtn is:

$$d^2R/dr^2 + \left\{\left[\frac{E-V(r)}{\hbar c}\right]^2 - \left(\frac{mc}{\hbar}\right)^2 - \frac{l(l+1)}{r^2}\right\}R = 0, \tag{18}$$

where $l = 0, 1, 2, \ldots$ is the usual ∡ mom$^{\underline{m}}$ quantum #. Put in the Coulomb potential:

$$V(r) = -Ze^2/r = -Z\alpha\hbar c/r, \quad \alpha = e^2/\hbar c \simeq \frac{1}{137} \text{ (fs cnst)};$$

Sol/

$$\left[\!\left[\frac{d^2R}{dr^2} + \left\{ \left[\frac{E^2 - (mc^2)^2}{\hbar^2 c^2}\right] + \left(\frac{2EZ\alpha}{\hbar c}\right)\frac{1}{r} - \frac{\lambda(\lambda+1)}{r^2} \right\} R = 0, \right]\!\right] \tag{19}$$

where : $\lambda(\lambda+1) = l(l+1) - (Z\alpha)^2$.

Eq. (19) has the same form as the radial Schrodinger eqtn for the H-atom [the coefficients are different, and λ replaces l (see Eq. (13) on p. H4 of notes), but the r-dependence is the same]. The standard solution yields bound state energies:

$$\rightarrow \underline{\underline{E_{nl} = mc^2 \Big/ \left[1 + \left(\frac{Z\alpha}{N+\lambda+1}\right)^2\right]^{1/2}}} \quad \int^{\text{w/}} N = 0, 1, 2, 3, \ldots \text{ radial quantum \#}; \tag{20}$$

$$\lambda = \left[(l+\tfrac{1}{2})^2 - (Z\alpha)^2\right]^{1/2} - \tfrac{1}{2} \quad (\lambda \to l \text{ for } c \to \infty).$$

The conventional eigenenergies for the problem are ...

$$\boxed{\mathcal{E}_{nl} = E_{nl} - mc^2 = mc^2\left\{\left[1 + \left(\frac{Z\alpha}{N+\lambda+1}\right)^2\right]^{-1/2} - 1\right\}}, \text{ correct to all orders in } \alpha. \tag{21}$$

Thru $O(\alpha^4)$, we get exactly the previous $\mathcal{V}$(rel) correction [Eq. (32), p. fs 13]:

$$\left[\!\left[\mathcal{E}_{nl} \simeq \mathcal{E}_n \left[1 + \underbrace{\left(\frac{Z\alpha}{n}\right)^2\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right)}_{\mathcal{V}\text{(rel.) correction}}\right] \right. \quad \int \mathcal{E}_n = -\tfrac{1}{2}(Z\alpha/n)^2 mc^2, \text{ BOHR } \mathcal{E}\text{'s}; \tag{22}$$

$$n = N + l + 1 = 1, 2, 3, \ldots, \text{ principal q\#}.$$

As we have said, this solution cannot give the correct finestructure for an H-atom, because it automatically excludes the spin-orbit interaction, which is of the same size. In fact it is not possible to include a spin-orbit term in the KG Eqtn in a Lorentz-covariant fashion, so KG must be discarded as a viable relativistic wave eqtn for particles with nonzero spin.

But KG fails here in an interesting way. It will turn out that the Dirac solution for the H-atom energies E_{nj} differs from the E_{nl} in Eq. (20) only by replacing l by $j = l + s$ (i.e. $\lambda_{\text{DIRAC}} = [(j+\frac{1}{2})^2 - (Z\alpha)^2]^{1/2} - \frac{1}{2}$). More, later.