THE CLASSICAL ORIGIN OF THE SCHRÖDINGER EQUATIONS AND THE DARWIN CORRECTION TERMS

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The Thesis[2]

The evolution of Wave Mechanics is a tale full of wonder. It was based in part on knowledge, progressed through guesswork, and succeeded with luck. It resulted in a great deal of understanding, was the crowning achievement of, and most bitter disappointment to, its architects.

In 1905, Einstein proposed that light consisted of quantized bundles of energy, called photons [1], possessing particle-like, as well as wave-like properties. The momentum to be associated with a photon of wave length λ is

$$p = h/\lambda = h\nu/c.$$

In order to explain quantization in the microscopic domain, de Broglie turned this relation around, and assumed that matter in general might possess wave-like as well as particle-like properties[2]. He found that the only relativistically invariant way to associate a wavelength λ with a particle of momentum $\bar{p}$ was through the relationship

$$\lambda = h / |\bar{p}| .$$

This equation set the stage for Schrödinger, who was thoroughly familiar with physics. He was aware, as was Hamilton almost 100 years earlier[4b], of a very close relationship between classical mechanics and geometrical optics (classical optics). The eikonal[3] equation, which describes the phase of a disturbance in classical optics, is formally identical to the Hamiltonian-Jacobi equation[4a] of classical mechanics.

Schrödinger knew that classical optics was the short wavelength limit of wave optics. He also knew that photons with both wave- and particle-like properties were at the bottom of optics. He felt, with de Broglie, that massive particles with both particle- and wave-like properties were at the bottom of mechanics. Could classical mechanics be just the short wavelength limit of something more general, which should be proper analogy be called wave mechanics? (Fig. 1) He set out to find the answer.

The Analysis

Maxwell's equations in a material medium are

$$\begin{aligned} \bar{\nabla} \times \bar{H} - \frac{1}{c}\frac{\partial \bar{D}}{\partial t} &= \frac{4\pi}{c}\bar{j} \\ \bar{\nabla} \times \bar{E} + \frac{1}{c}\frac{\partial \bar{B}}{\partial t} &= 0 \\ \bar{\nabla} \cdot \bar{D} &= 4\pi\rho \\ \bar{\nabla} \cdot \bar{B} &= 0 \end{aligned} \qquad (1)$$

The two constitutive equations relating $\bar{D}$ and $\bar{B}$ to $\bar{E}$ and $\bar{H}$ are

$$\begin{aligned} \bar{D}(\bar{x}, t) &= \varepsilon(\bar{x})\, \bar{E}(\bar{x}, t) \\ \bar{B}(\bar{x}, t) &= \mu(\bar{x})\, \bar{H}(\bar{x}, t) \end{aligned} \qquad (2)$$

We have assumed that $\varepsilon(\bar{x})$ and $\mu(\bar{x})$ are scalar functions of position only. In the absence of sources, these four equations (1) can be reduced to a pair, one involving only the components of the $\bar{E}$ field, the other involving $\bar{H}$ field components only:

$$\left(\nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2}\right)\bar{E} + \frac{\bar{\nabla}\mu}{\mu} \times (\bar{\nabla} \times \bar{E}) + \bar{\nabla}\left(\frac{\bar{\nabla}\varepsilon}{\varepsilon} \cdot \bar{E}\right) = 0 \qquad (3E)$$

$$\left(\nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2}\right)\bar{H} + \frac{\bar{\nabla}\varepsilon}{\varepsilon} \times (\bar{\nabla} \times \bar{H}) + \bar{\nabla}\left(\frac{\bar{\nabla}\varepsilon}{\mu} \cdot \bar{H}\right) = 0 \qquad (3H)$$

The classical optics approximation is this: the disturbance propagates locally (over a few wavelengths) as if it were in free space or a uniform medium. This is equivalent to saying that the fractional changes in $\varepsilon(\bar{x})$ and $\mu(\bar{x})$ are small over the distance of a wavelength.

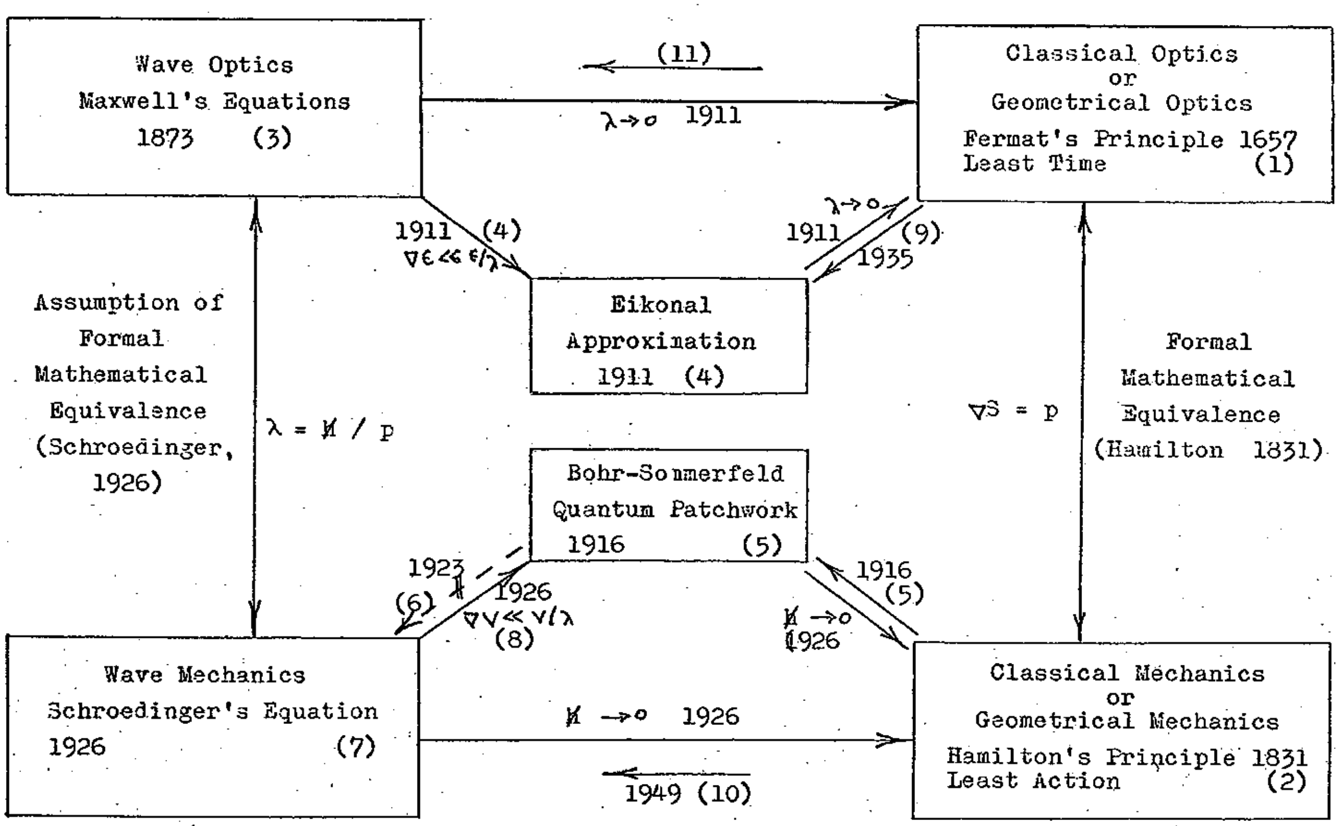

Figure 1: Schroedinger's attempt to understand atomic structure within the framework of Newtonian particle-field concepts

$$\nabla\varepsilon \ll \varepsilon/\lambda$$
$$\nabla\mu \ll \varepsilon/\lambda \qquad (4)$$

In this limit, the equations for $\bar{E}$ and $\bar{H}$ become simply

$$(\nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2})\ \bar{E} = 0 \qquad (3')$$

$$(\nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2})\ \bar{H} = 0 \qquad (4')$$

Each component of the $\bar{E}$ and $\bar{H}$ field separately obeys an equation of the form

$$(\nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2})\ \phi(\bar{x}, t) = 0 \qquad (5)$$

For a disturbance of fixed frequency ω, the substitution of a solution $\phi(\bar{x}, t) = \phi(\bar{x})\ e^{i\omega t}$ gives the equation

$$(\nabla^2 + \frac{\mu(\bar{x})\ \varepsilon(\bar{x})\ \omega^2}{c^2})\ \phi(\bar{x}) = 0 \qquad (5')$$

The eikonal approximation is the statement that the amplitude of the disturbance is a much more slowly varying function of position than the phase. The trial solution

$$\phi(\bar{x}) = \phi_o(\bar{x})\ e^{ik_o S(\bar{x})}$$

($k_o = 1/\lambda\!\!\!^{-}_o = \omega/c$) leads to two equations:

$$(\nabla S)^2 = \mu(x)\ \varepsilon(x) + \frac{(\lambda\!\!\!^{-}_o \bar{\nabla})^2\ \phi_o(x)}{\phi_o(x)} \qquad (6\mathrm{Re})$$

$$\nabla S \cdot \frac{2\nabla\phi_o}{\phi_o} + \nabla^2 S = 0 \qquad (6\mathrm{Im})$$

The equation 6Re gives, in the limit $\lambda\!\!\!^{-}_o \to 0$

$$(\nabla S)^2 = \mu(x)\ \varepsilon(x) = n^2(x) \geq 1 \qquad (7\ \mathrm{Cl.0})$$

The Hamilton-Jacobi equation for a particle of fixed energy (corresponding to an optical disturbance of fixed frequency) is

$$H(q, \bar{\nabla}S(q)) = E \qquad (8)$$

For a negatively charged particle ($Q = -e$) in a potential Φ, this is

$$\sqrt{(c\,\bar{\nabla} S)^2 + (mc^2)^2} - e\Phi = E \qquad (7\ \text{Cl. M})$$

This may be rewritten in such a way as to emphasize its relation to equation 7:

$$(\bar{\nabla} S)^2 = \frac{1}{c^2}(E + e\Phi)^2 - (mc)^2 \qquad (7'\text{Cl. M})$$

The non-relativistic limit may be taken by shifting the energy zero point, $E = W + mc^2$, and neglecting small terms:

$$(\bar{\nabla} S)^2 = 2m(W + e\Phi) \quad . \qquad (7''\text{Cl. M})$$

The Synthesis

If each fixed frequency component of the electric and magnetic field obeys an equation of the form

$$\left(\nabla^2 + \frac{1}{\lambda^2(\bar{x})}\right)\psi(x) = 0 \qquad (5')$$

why shouldn't a matter wave field also obey this same equation, reasoned[5] Schrödinger ? It was not difficult to make the substitution $2\pi/\lambda = p/\hbar$

$$\left(\nabla^2 + \frac{1}{\hbar^2}p^2\right)\psi(\bar{x}) = 0 \qquad (9)^*$$

Nor was it difficult to write the momentum in terms of the energy in a relativistically invariant way

$$(E + e\Phi)^2 - (cp)^2 = (mc^2)^2 \qquad (10\ \text{Rel})$$

The equation which Schrödinger derived by these analogies and this reasoning was

$$\left\{(E + e\Phi)^2 - \left(c\frac{\hbar}{i}\bar{\nabla}\right)^2\right\}\psi(x) = (mc^2)^2\psi(x) \qquad (11\ \text{Rel})$$

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* If we demand this to be an identity for all matter fields, then a trivial consequence is $\bar{p} = (\hbar/i)\, R\bar{\nabla}$, where R is an orthonormal transformation. If we choose $R = I$, then

$$\bar{p} = \frac{\hbar}{i}\bar{\nabla}$$

He assumed that this relativistically invariant equation governed the structure of matter on the atomic scale.

Disappointment.

When he solved this equation for the energy level structure of the hydrogen atom, he found that his results disagreed with experimental findings. He tucked this equation away in his drawer. Several months later, he tried the same kind of derivation, using the non relativistic relation

$$\frac{p^2}{2m} - e\Phi = W \qquad \text{(10 NR)}$$

This time, the equation which he found gave more reasonable results

$$\left\{\frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 - e\Phi\right\}\psi(\bar{x}) = W\psi(\bar{x}) \qquad \text{(11 NR)}$$

Schrödinger solved this equation for the hydrogen atom, compared his calculations with spectrographs, published the results, and thereby founded Wave Mechanics.

We now know why the second equation (11 NR) which Schrodinger found is a better representation for physical realtiy than the first (11 Rel). The electron is a spin 1/2 particle and as such must be described by a relativistically invariant equation for a spin 1/2 particle (the Dirac equation). Equation (11 Rel) is a relativistic equation for a spin 0 particle, which the electron is not. However, within a few spin-dependent terms, the Klein-Gordon equation (11 Rel) and the Dirac equation have practically the same non-relativistic limit. Therefore, except for the relativistic S-like states, the Schrödinger equation should present a better picture of the hydrogen atom's energy level structure than the Klein-Gordon equation. And it does.

The Antithesis

The immediate successes of the Wave Mechanics had a profound effect. It was assumed that the Schrödinger equation was an exact description of Nature in the non-relativistic regime. The procedure for computing energy levels of a system was reduced to an algorithm: set up the classical Hamiltonian for the system, replace $\bar{p}$ everywhere by $\bar{p} = (\hbar/i)\bar{\nabla}$, and solve the resulting eigenvalue equation

$$H(\bar{q}, (\hbar/i)\bar{\nabla})\,\psi(\bar{q}) = E\,\psi(\bar{q})$$

In the light of success after success, the assumptions and analogies underlying the Schrödinger equation were generally overlooked and forgotten. These assumptions and analogies are not always reasonable.

One such assumption is that the fractional changes in the indices of refraction are small over the distance of an optical wavelength. This corresponds to the assumption of an electrostatic potential varying slowly over an electron wavelength. However, in near a nuceus, the electrostatic potential does change appreciably over such a small distance. On the strength of these qualitative arguments, the Schrodinger equation should not be expected to provide an accurate description for S-like (L = 0) states[6].

Can we make more quantitative statements?

The Synthesis Again

When the fractional change per wavelength for either $\mu(\bar{x})$ or $\varepsilon(\bar{x})$ is no longer negligible, equations (3E) and (3H) tell us that it is no longer possible to write down a simple scalar equation which the components of the E and B fields separately satisfy.

However, in the spirit of Schrödinger's approach, we are still able to proceed. We know that the electromagnetic field components do not in general satisfy equation 5'. It is possible to add a correction term to this equation in such a way that the field components satisfy this augmented equation to a better approximation, than they satisfy 5'. Then, proceeding as before, it is possible to derive a wave equation which can be assumed to be a correspondingly better approximation to physical reality than is the Schrodinger equation.

Such a procedure is open to even more criticism than the derivation of the Schrodinger equation; nevertheless, it gives us the Darwin[6] correction term which is usually described in textbooks on Quantum Mechanics as having no classical analogue. We will, by this ad hoc procedure, see exactly what the classical analogue is.

The E field obeys the equation (with $\nabla\mu = 0$)

$$\begin{pmatrix} \Box^2(\bar{x}) + \frac{\partial}{\partial x_1}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_1} & \frac{\partial}{\partial x_1}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_2} & \frac{\partial}{\partial x_1}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_3} \\ \frac{\partial}{\partial x_2}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_1} & \Box^2(\bar{x}) + \frac{\partial}{\partial x_2}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_2} & \frac{\partial}{\partial x_2}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_3} \\ \frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_1} & \frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial x_2} & \Box^2(\bar{x}) + \frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\varepsilon x_3} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} = 0$$

with $\Box^2(\bar{x}) = \nabla^2 - \frac{\mu(x)\,\varepsilon(x)}{c^2}\frac{\partial^2}{\partial t^2}$. There is no convient way to diagonalize these equations. Instead, we can form approximate diagonal equations by neglecting the offdiagonal terms

$$\left\{ \nabla^2 - \frac{\mu(\bar{x})\ \varepsilon(\bar{x})}{c^2}\frac{\partial^2}{\partial t^2}\right\} E_i + \frac{\partial}{\partial x_i}\ \frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial x_i}\ E_i = 0 \qquad \text{(3E'')} \quad \text{no sum on } i$$

In the same crude approximation, the magnetic field components obey the equation

$$\left\{ \nabla^2 - \frac{\mu(\bar{x})\ \varepsilon(\bar{x})}{c^2}\frac{\partial^2}{\partial t^2}\right\} H_i = 0 \qquad \text{(3H'')}$$

We are looking for a single scalar equation which each field component separately approximately satisfies. To find such an approximate equation, we take the mean of the six equations represented by 3E'' and 3H'', using

$$\sum_{i=1}^{3} \frac{\partial}{\partial x_i}\left(\frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial x_i}\ E_i\right) \cong \frac{1}{2}\sum_{i=1}^{3} \frac{\partial}{\partial x_i}\ \frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial x_i}\ (E_1+E_2+E_3)$$

The single scalar equation approximately obeyed by each field component is then

$$\left\{ \nabla^2 - \frac{\mu\varepsilon}{c^2}\frac{\partial^2}{\partial t^2}\right\}\psi + \frac{1}{4}\ \nabla \cdot \left(\frac{\nabla\varepsilon}{\varepsilon}\ \psi\right) = 0 \qquad (12)$$

The first bracket has already been analyzed.

The second term presents somewhat of a problem. Specifically, how can we get something sensible from $\nabla\varepsilon/\varepsilon$? Within classical optics, ε has the following properties:

1. $\varepsilon \geq 1$
2. ε is a slowly varying function of position except in regions of extreme inhomogeneity, that is, near singularities.

For photons, $\varepsilon/\varepsilon_o = (\lambda_o/\lambda)^2 = (p/p_o)^2 = \dfrac{p^2 + (m_o c)^2}{p_o^2 + (m_o c)^2}$

where the subscript $_o$ refers to free space behavior, and m_o is the zero 'rest-mass' of the photon. For an electron, the choice $\varepsilon/\varepsilon_o = p^2$ does not endow ε with the desirable properties 1. and 2., which we would like to maintain in wave mechanics as well as wave optics. However, the choice

$$\varepsilon/\varepsilon_o = (pc)^2 + (m_o c^2)^2 / (m_o c^2)^2$$

does have these properties. Although this choice for ε is inconsistent with 5', it gives reasonable results, and is thus in the spirit of the game.

To proceed, we compute

$$\frac{\nabla\varepsilon}{\varepsilon} = \frac{\nabla (E + e\Phi)^2}{(E + e\Phi)^2} = \frac{2\nabla e\Phi}{(E + e\Phi)}$$

$$\left\{(\not{h} c \nabla)^2 + (E + e\Phi)^2 - (mc^2)^2 \psi + \frac{(\not{h} c)^2}{2} \bar{\nabla} \cdot \frac{\bar{\nabla} e\Phi}{E + e\Phi} \psi\right\} = 0 \quad (13)$$

Although this does not look familiar in its present form, it is familiar in its non-relativistic limit. We take this limit by putting $E = mc^2 + W$ and expanding:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - e\Phi - \frac{(W + e\Phi)^2}{2mc^2} - \frac{\not{h}^2}{4m} \left\{ \frac{\nabla^2 e\Phi}{mc^2 + W + e\Phi} + \frac{\bar{\nabla} e\Phi \cdot \bar{\nabla}}{mc^2 + W + e\Phi} - \frac{(\nabla e\Phi)^2}{(mc^2 + W + e\Phi)^2} \right\} \right] \psi = W\psi \quad (14)$$

Finally, keeping only first order corrections, this equation becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - e\Phi - \frac{\hbar^4}{8m^3c^2} (\nabla^2)^2 - \frac{\not{h}^2}{4m^2c^2} \left\{ \nabla^2 e\Phi + \bar{\nabla} e\Phi + e\Phi \cdot \bar{\nabla} \right\} \right] \psi = W\psi \quad (15)$$

The first two terms on the left are the standard terms of the Schrodinger equation approximation. The third term is the relativistic mass-velocity correction. It comes directly from the non relativistic limit of any relativistic equation, and is obtained by putting $(W + e\Phi) = -\frac{\not{h}^2}{2m} \nabla^2 = \frac{p^2}{2m}$. It holds for the Dirac as well as the Klein-Gordon equation. The last two terms are the leading terms in corrections which take into account the fact that Maxwell's equations in a material medium are not exactly of the form 3E', 3H', but are actually of the form 3E, 3H. These are called the Darwin correction terms (the numerical factor should be 1/8 rather than 1/4). They were first discovered by Darwin[6] in taking the non-relativistic limit of the Dirac equation.

These two correction terms are not of relativistic origin. Contrary to belief, they do have a classical analogue. It is this: The change induced in the E field by a rapidly varying dielectric constant cannot be taken into account solely by equations of the form

$$\left\{ \nabla^2 + k^2(\bar{x}) \right\} \psi(\bar{x}) = 0$$

The more accurate optical equations must have some additional correction terms; it is these terms which are the classical analogues of the Darwin terms.

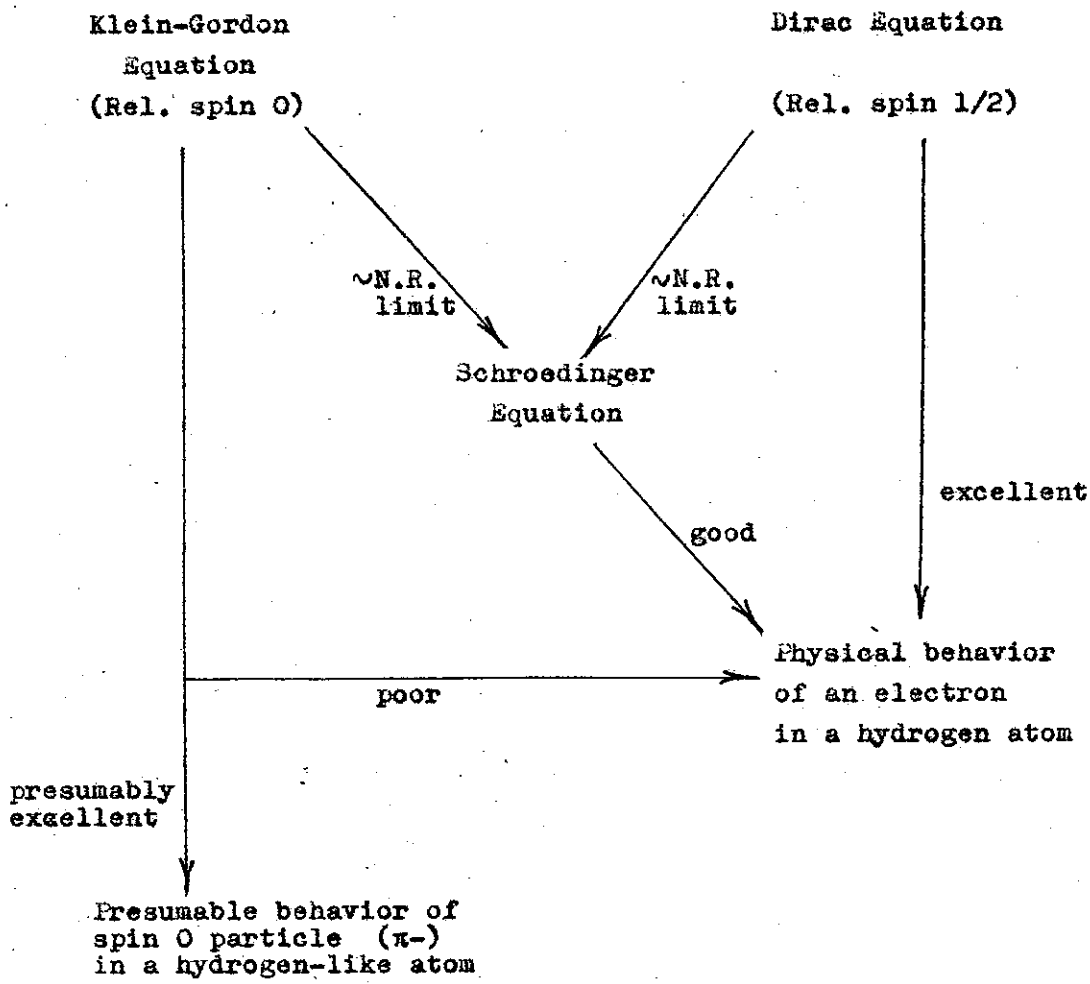

Fig. 2: Graphical representation for the adequacy of equation (XI NR) and the inadequacy of equation (XI Rel) in describing the hydrogen atom.

Conclusion

We have followed the strange path of analogy and assumption taken by Schrodinger to derive the Schrodinger equation. When some assumptions were no longer valid, we retraced our steps, and found the quantum analogues of the classical correction terms. In this way, we found all but the spin-dependent terms which result in the non-relativistic limit of the Dirac equation. Each term has a specific interpretation within the framework of classical theory.

It would be a mistake to lend too much credence either to the derivation of the equations or of the correction terms. Nevertheless, the results are generally correct. It is therefore satisfying that much better methods now exist both to derive these equations and to take their non-relativistic limits[7].

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