Quantal Aspects in Chemistry & Physics

A tribute in memory of Ruy Couceiro da Costa

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The interpretation of Quantum Mechanics revisited

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When teaching quantum mechanics we enjoy to call student’s attention to the interpretation and some lopsided aspects of the theory.

Here, we shall revisit the matter, also referring to a recent non-linear approach to quantum physics.

It is our tribute in memory of Professor Couceiro da Costa.

Achievements of Quantum Theories

- Properties of molecules, atoms, nuclei and elementary particles
- Chemical and nuclear reactivity
- Applications from cosmology to biology
- Breakdown of complete causality, determinism and locality
- Challenge to objective reality
- Philosophy, ontology and epistemology
- Unification of classical and quantum physics?

The roots of Quantum Theories

- ***Experiments and first models*** (photons and material particles):

  $E = h\upsilon$ (Planck, Einstein, Bohr, Millikan, Compton...)

  $p = h/\lambda$ (de Broglie, Davisson, Germer, G.Thomson...)

  Clearly show wave-particle duality

- Classical wave theory and classical mechanics are unable to rationalize those experimental facts.
- Any new theory should reproduce experimental results and predict new ones; approach classical theories where they prove right; support the design of new instruments.

Theories

- Matrix mechanics, MM (Heisenberg, Born, Jordan, 1925)
- Wave mechanics, WM (Schrödinger, 1926)
- Equivalence of MM and WM (Schrödinger, 1926)
- Transformation theory (Dirac, Jordan ~1926)
- Relativistic QM (Dirac, Pauli ~1928)
- Space-time QM (path-integral), equivalent to MM and WM (Feynman, 1948)
- Quantum electrodynamics (Bethe,Tomonaga, Schwinger, Feynman, Dyson 1940's - …)
- Gauge theories (Yang, Mills, Glashow, Salam, Weinberg, 1950-1970's - …)
- Renormalization group (Kadanoff, Fisher, Wilson, Gell-Mann, 1970's - …)
- Strings theory (…;Green, Schwarz, 1984; Witten, 1995 - ….)
- Hidden variables (Bohm, Bell, Leggett, 1950-2000's)
- Relative states or "Many worlds" (Everet III…, 1957-…)
- Decoherence (Zeh, Zurek,…1970-…)
- Nonlinear QM (…,Weinberg, 1989; Croca, 2003)

Bohr's interpretation of the wave-particle duality
(complementary, indeterminacy and Fourier analysis)

- To a free particle with sharp momentum (p) is associated an harmonic monochromatic wave (λ), extending in all space and time, $p=h/\lambda$.
- Wave and particle concepts are mutually exclusive, though *complementary* to rationalize experimental observations.
- The state of a free particle with well-defined position (a):

$$|\Psi\rangle = \delta\left(x-a\right) = \hbar^{-1/2}\int_{-\infty}^{+\infty} e^{-ip_x a/\hbar}\, e^{ixp_x/\hbar} dp_x \;\; ; \; \Delta x = 0$$

($\exp(ix\, p_x / \hbar)$ are the eigenfunctions of the momentum operator)

p_x is totally undefined; there exists, however, a set of simultaneous possibilities *only made real* by mesurements; *what is known is what is measured.*

Bohr's interpretation of the wave-particle duality (complementary, indeterminacy and Fourier analysis)

- By means of very many measurements of the momentum, providing that before each one the particle is in the same state $\delta(x-a)$, a distribution of results is obtained: Δp_x is proportional to its width. As the position function encodes all possible momentum values (in this case a continuous spectrum) with equal weights (probabilities) $\Delta p_x = \Delta E = \infty$.
- Conversely, if $\Delta p_x = \Delta E = 0$, then $\Delta x = \infty$, the position is totally undefined.
- In general: $\Delta x \, \Delta p_x \geq h$; $\Delta t \, \Delta E \geq h$ (Heisenberg-Bohr's indeterminacy principle).
- *The principle tell us not what is measurable but what is knowable*. Position and momentum, for example, can not be known simultaneously with arbitrary certainty. Before a measurement on a single particle, the position or the momentum, or both, are unknown.

Bohr's interpretation of wave-particle duality
(complementary, indeterminacy and Fourier analysis)

- Although Δx and/or Δp_x can only be estimated from very many *repeated* measurements, the indeterminacy principle must not be interpreted (as Heisenberg initially did and Einstein believed) supposing that position and momentum of a single particle exist simultaneously before a measurement, and that the principle expresses nothing more than unpredictable and uncontrollable statistical errors of the observations.
- Such errors are generally present, but one can, at least conceptually, eliminate them. Even so, an errorless measurement of the position on a single particle in the state $|\Psi>$ generates, non-deterministically, an eigenstate $\delta(x-a)$ which is Fourier composed by an infinite number of momentum eigenstates. If this is followed by an errorless measurement of the momentum it generates, non-deterministically, an eigenstate $\delta(p_x-b)$ which is Fourier composed by an infinite number of position eigenstates, and so forth. For other properties, the same scenario results.
- In the context of non-local Fourier analysis, the indeterminacy is intrinsic, not at all, a matter of statistical errors in the measurements.The reality *of physical properties* generally depends on the measurement.
- There is, however, an *empirical reality* which not being independent of the measurement it is the *same for all observers*.

Wave Packets

Phase velocity of a pure harmonic material wave:

$$v_{ph} = c^2/v_{par}$$

The wave preceeds the particle!

$$\Psi(x,t) = \int_{-\infty}^{+\infty} f(k)\exp\left[i(kx - \omega t)\right]dk$$

$$k_0 - \Delta k \le k \le k_0 + \Delta k$$

$$v_g = \left(\partial\omega(k)/\partial k\right)_{k_0} \cong v_{par}$$

$$p = mv_{par} \cong \hbar k_0 \,;\, E \cong \hbar\omega_0$$

- Bohr rederived Heisenberg’s relations from gaussian wavepackets.
- Wave packets recover the image of “localized” classical particles moving in space-time.
- Material wave packets disperse rapidly.
- Trajectories in space-time are nonsense.
- Trajectories *apparently* observed in cloud chambers.
- Contraditions? Against common sense?

Bohr’s philosophy and mathematics

- Harald Høffding: “in our endeavour to get knowledge there exists an irreducible irrational residue impossible to overpass whichever our efforts are”
- Niels Bohr: “such a residue, in quantum mechanics, is mathematically expressed in a lucid form”
- Ultimately, the underlying mathematics is non-local Fourier analysis (just one of the possible mathematical techniques to represent functions) which is endowed with full physical meaning, that is, as the ontology of the axiomatics.
- In the orthodox Copenhagen’s view quantum mechanics is a complete theory, the end-road of our possible knowledge. *Indeed, there is always a logical limit in any closed system of axioms…*

Schrödinger's time-dependent equation
Born's interpretation

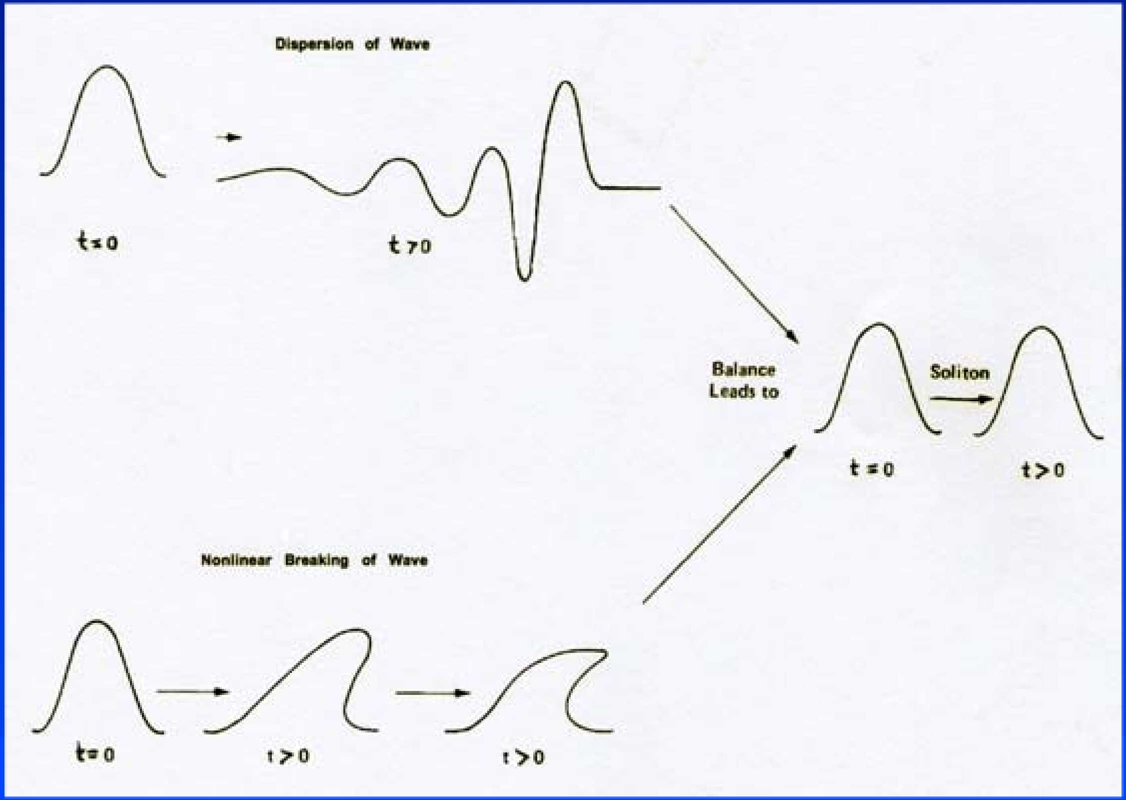
$$\hat{\mathbf{H}} \mid \Psi \rangle = i\hbar \frac{\partial \mid \Psi \rangle}{\partial t}$$

Erwin with his "psi" can do
Calculations quite a few.
But one thing has not been seen:
Just what does "psi" really mean?
(a 1926 ditty)

- Established from the concept of wave packets for free-particles.
- Duality wave-particle interpreted in pure undulatory terms (contrasting with Heisenberg´s view of particles and discontinuities).
- Wave functions exist in reality as amplitudes of a "material field scalar".
- The equation gives a deterministic time evolution of the wave function for ***unperturbed*** systems.
- *Problems*: disperson of the wave packet and implicit non-locality, multidimensional and complex functions, $|\Psi>$ exp(iø) also a valid solution, experimental detection of wave functions...
- *Max Born*: the wave function is an *abstract* non-local entity, just giving the probability density: $|\Psi|^2$. Incidentally, how can abstract entities interfere?

Dispersion + nonlinear effects = wave without dispersion

(J.S. Russel, 1800's; soliton phenomena)



Solitons obey to a nonlinear equation. In this context, it is possible to derive a *kind* of *nonlinear* Schrödinger equation.

Some postulates of the orthodox theory (Hilbert´s space and von Neumann's formulation)

- To each physical observable A, corresponds in Hilbert's space a linear Hermitian operator $\hat{\mathbf{A}}$, which has a complete, orthonormal set of eigenvectors $|\alpha_i>$, and corresponding eigenvalues A_i, such that: $\hat{\mathbf{A}}\,|\alpha_i> = A_i\,|\alpha_i>$, being the A_i's the only *possible* values obtainable from any measurement of A.
- If A is measured on a general state $|\Psi>$, the strongest predictive statement that can be made is that the probability of obtaining the value A_k is: $|<\alpha_k|\Psi>|^2$.
- The measurement generally changes *non-deterministically* the state vector. Regardless of the state before the measurement, immediately after it the new state will coincide with the eigenvector corresponding to the obtained eigenvalue (*reduction or collapse of the state vector*).
- A general state vector $|\Psi>$ can be expanded in the vectors of any basis:

$$|\Psi\rangle = \sum_{\mathrm{i}} |\alpha_{\mathrm{i}}\rangle\langle\alpha_{\mathrm{i}}|\Psi\rangle$$

The direct link between cause and effect appear to be severed. This is the big clash with classical mechanics. Measurements on *exactly the same* state generally give different results. The *key role* of the measurement process is not described by the theory: *how* does the state vectors reduce?

The compatibility theorem

- Given two observables A and B with corresponding operators **A** and **B**, then any one of the following conditions implies the other two:

  (i) A and B are compatible observables

  (ii) **A** and **B** have a common eigenbasis

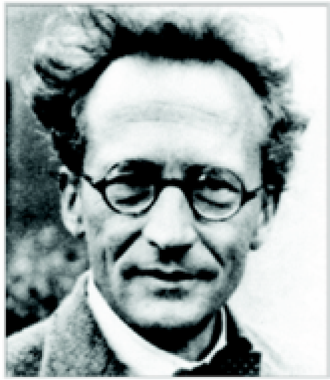
  (iii) **A** and **B** commute

- The theorem *does not assert* the *impossibility* of two non-commuting operators having *some* eigenvectors in common, but *just the impossibility of all* the eigenvectors of a basis being common. For example, the x and z operators of the angular momentum.

- Bohr and Einstein discussed this matter. "…quantum mechanics, properly understood, does not prohibit or restrict simultaneous measurement of non-commuting observables, but rather it does not deal with such measurements at all" (L.E. Ballentine, Am. J. Phys., 40 (1972) 1763)

The Three Pictures of Quantum Mechanics

- Quantum systems are regarded as wave functions which solve the Schrödinger equation.
- Observables are represented by Hermitian operators which act on the wave function.
- In the Schrödinger picture, the operators stay fixed while the Schrödinger equation changes the basis with time.



Schrödinger

$$|\,\Psi\,\rangle = |\,\Psi(t)\,\rangle$$

$$\hat{O} \neq \hat{O}\,(t)$$

The Three Pictures of Quantum Mechanics

- In the Heisenberg picture, it is the operators which change in time while the basis of the space remains fixed.
- Heisenberg's matrix mechanics actually came before Schrödinger's wave mechanics but were too mathematically different to catch on.
- A fixed basis is, in some ways, more mathematically pleasing. This formulation also generalizes more easily to relativity - it is the nearest analog to classical physics.

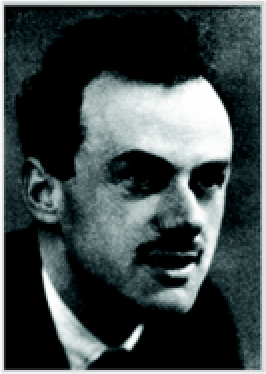
Heisenberg

$$|\,\Psi\,\rangle \neq |\,\Psi(t)\,\rangle$$

$$\hat{O} = \hat{O}(t)$$

The Three Pictures of Quantum Mechanics

- In the Dirac (or, interaction) picture, both the basis and the operators carry time-dependence.
- The interaction picture allows for operators to act on the state vector at different times and forms the basis for quantum field theory and many other newer methods.



Dirac

$$|\,\Psi\,\rangle = |\,\Psi(t)\,\rangle$$

$$\hat{O} = \hat{O}(t)$$

Beautiful! It seems Spinoza's God in action!

Matrix Elements

- **Schrödinger Picture**

$$\langle\, \mathcal{O}\,\rangle_S = \langle\, \Psi(t)\,|\,\hat{O}_S\,|\,\Psi(t)\,\rangle$$

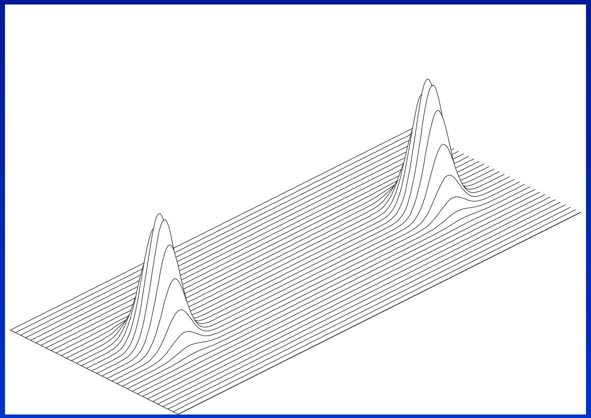
- **Heisenberg Picture**

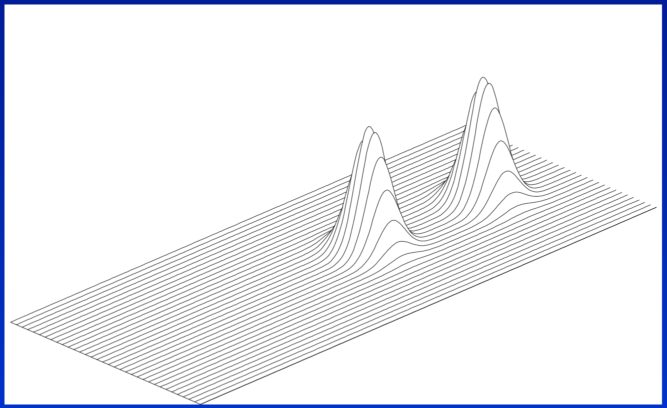
$$\begin{aligned}\langle\, \mathcal{O}\,\rangle_H &= \langle\, \Psi_H\,|\,\hat{O}_H(t)\,|\,\Psi_H\,\rangle \\ &= \langle\, \Psi_S(0)\,|\,e^{i\hat{H}_S t/\hbar}\hat{O}_S e^{-i\hat{H}_S t/\hbar}\,|\,\Psi_S(0)\,\rangle \\ &= \langle\, \Psi_S(t)\,|\,\hat{O}_S\,|\,\Psi_S(t)\,\rangle = \langle\, \mathcal{O}\,\rangle_S\end{aligned}$$

- **Dirac Picture**

$$\begin{aligned}\langle\, \mathcal{O}\,\rangle_I &= \langle\, \Psi_I\,(t)\,|\,\hat{O}_I\,|\,\Psi_I\,(t)\,\rangle \\ &= \langle\, \Psi_S\,(t)\,|\,e^{-i\hat{H}_{0,S} t/\hbar}\hat{O}_I e^{i\hat{H}_{0,S} t/\hbar}\,|\,\Psi_S\,(t)\,\rangle \\ &= \langle\, \Psi_S\,(t)\,|\cdot 1\cdot \hat{O}_S\cdot 1\cdot|\,\Psi_S\,(t)\,\rangle = \langle\, \mathcal{O}\,\rangle_S\end{aligned}$$

Two interacting particles





Orthodox interpretation:

- The wave functions are *non-local*, that is, two global instances of the same entity. The particles behave as they were just one, *at all distances*. *Entangled for ever!*
- Both are Fourier composed by the same basic elements: monochromatic harmonic waves extending through all space and time.
- Position and momentum of each can not be known simultaneously.
- Yet, $x_A - x_B$ and $p_A + p_B$ can be known simultaneously since the respective operators commute.

Einstein, Podolsky and Rosen (EPR) thought experiment

- Suppose the particles A and B have moved years-light apart. Once the position of A has been measured it is known exactly and (from $q_A - q_B$) so is the position of B without any perturbation on it. The position of B is an *element of physical reality*.
- Next, measure the momentum of A. From $p_A + p_B$, the momentum of B is known exactly without perturbing it. The momentum of B is also an element of physical reality.
- The position and momentum of B must be, simultaneously, elements of physical reality. They exist independently of the observer. Otherwise, all would depend upon the measurement choice on A and *locality* would be violated. "No reasonable definition of reality could be expected to permit this".
- "While we have thus shown that the wave function does not provide a *complete* description of the physical reality, we left open the question of whether or not such a description exists. We believe, however, that such a theory is possible."

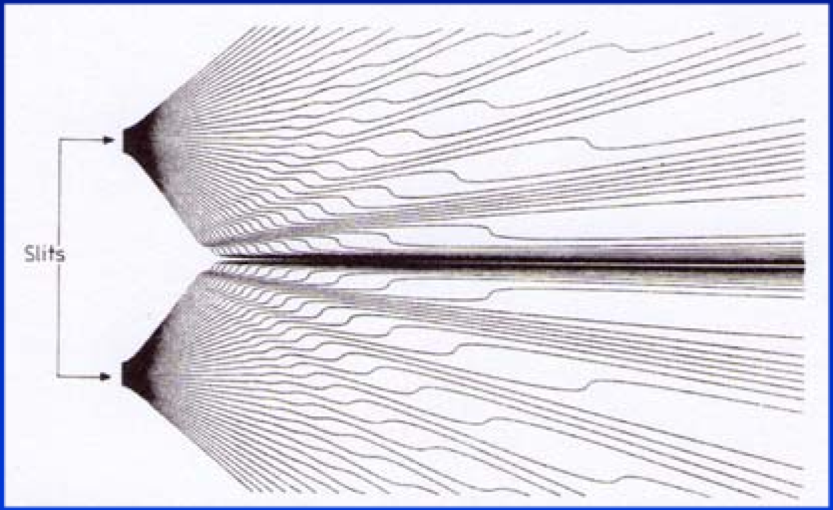
[Phys. Rev. 47 (1935) 777]

Hidden variables theories (1950-2000's)

- David Bohm: "lawlessness of individual behaviour in the context of a given statistical law is, in general, consistent with the notion of more detailed individual laws applying in a broader context".
- Existence of a deeper quantum-mechanical level expressed by "hidden variables" describing individual laws which explain the statistical realm of the orthodox theory (analogies with the Brownian motion theory and statistical mechanics).
- Von Neumann's impossibility proof versus John Bell's possibility proof.
- Bell's inequality; Clauser and Aspect's experiments. Locality versus non-locality. The "bells tolled" for locality, though preserving objective reality.
- Leggett's new inequality; Aspelmeyer and Zeilinger's experiments. Orthodox theory versus non-local hidden variables theories. *Apparently*, the "bells tolled" for non-local h.v. theories.
- Einstein did not like hidden variables theories at all. To him, *no amendments* to the orthodox theory should be made. Instead, a new deeper unified field theory from which the orthodox one should come out naturally.
- Einstein believed that the orthodox theory is an excellent statistical theory, but the wave function *only* expresses the behaviour of an *ensemble* of systems, *not* an individual system.

Two-slit experiment from Bohm hidden variables theory

(Philipidis et al., Il Nuovo Cimento, 52B, 15, 1979)



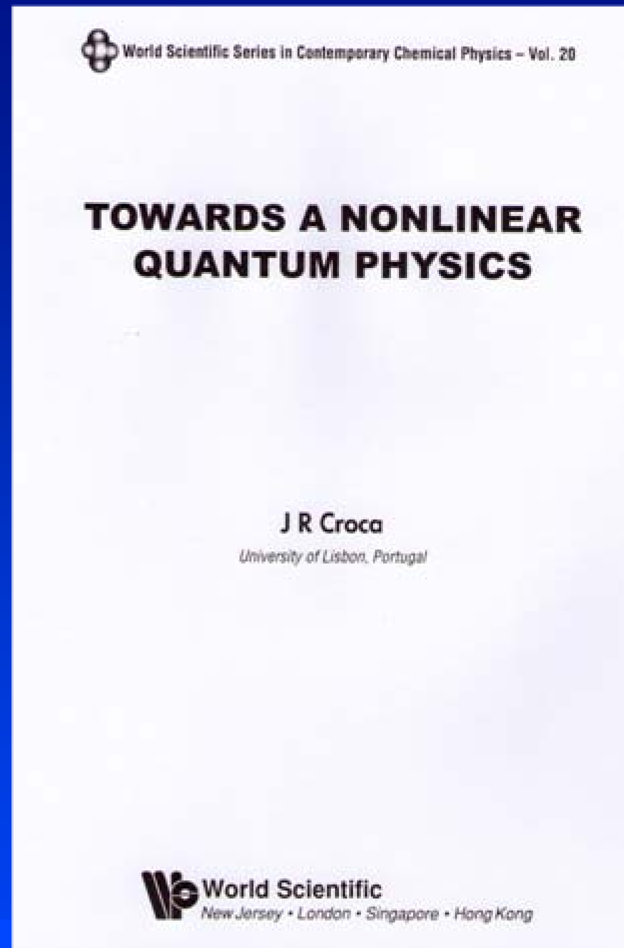
- The wave function guides the motion of the particles (de Broglie's "pilot" wave).

- The system is defined by the wave function, and positions and velocities of all particles.

- From the wave function a "quantum force" is derived, and added to the "classical" forces.

- The particles paths are calculated by Newton's law.

Main conclusions: (i) overall agreement with the orthodox theory, but *no new unexpected results*; (ii) exact paths ; (iii) the "quantum force" operates over arbitrarily large distances to guaranty "interference"; and (iv) ***locality is violated***.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TOWARDS A NONLINEAR QUANTUM PHYSICS
J R Croca
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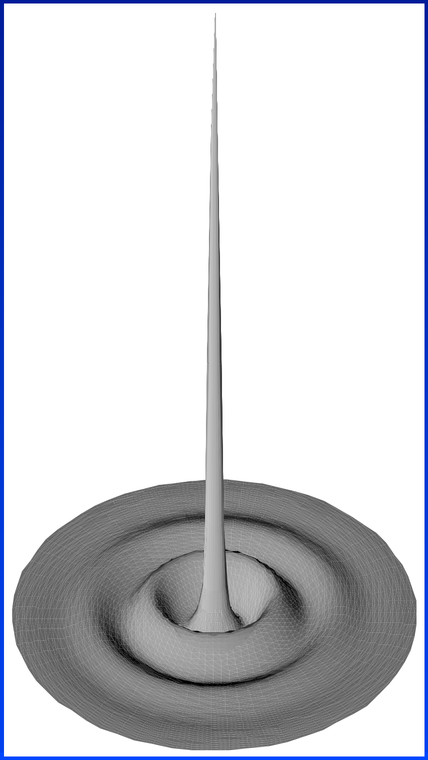
The non-linear formulation assumes:

- An objective reality, causal and local. Position and momentum, for example, exist independently of the observer.
- Inclusion of corpuscular (local) **and** undulatory (extended) properties.
- Local wavelet analysis instead of non-local Fourier analysis.
- The *indeterminacies* express the ever-present unpredictable and uncontrollable *uncertainties* in every measurement process.
- A basic natural chaotic sub-quantum medium where all physical processes occur.
- Particles are complex entities, stable organizations of the sub-quantum medium, composed by a guiding wave (θ) enclosing a very narrow localized structure (*acron*, ξ). The acron carries most of the energy.
- A non-linear master equation that, in special cases, is identical to the linear Schrödinger's equation. The master equation incorporates the corpuscular **and** continuity sides of classical physics.

The quantum particle
(revival of de Broglie's idea)

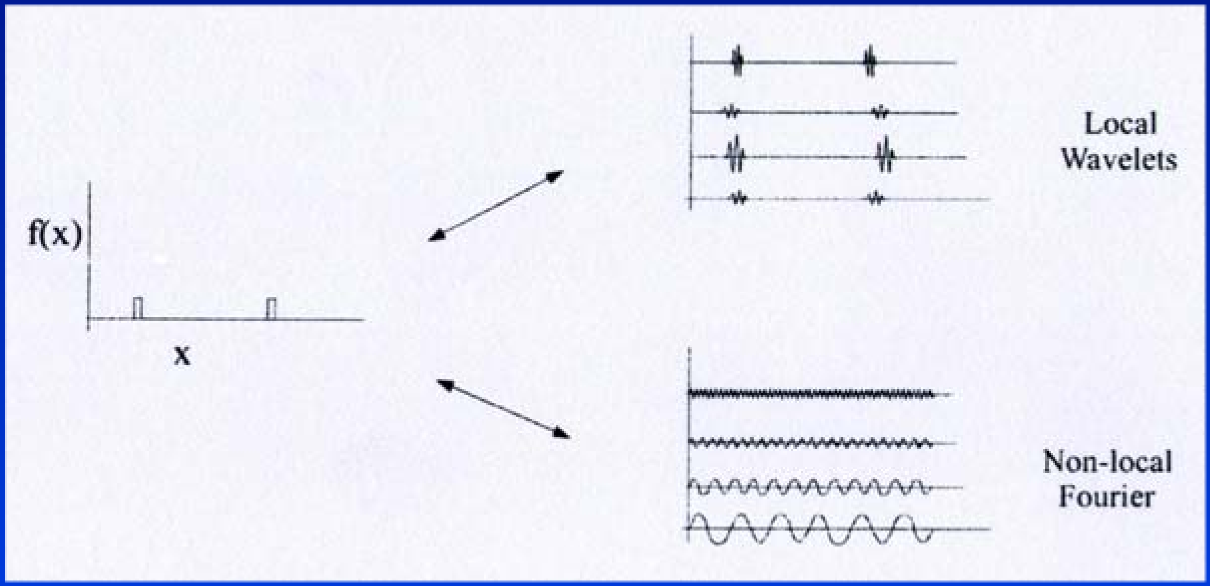


(From J.R. Croca, 2003)

$$\Psi = \theta + \xi$$

"pilot" wave (θ) + "acron" (ξ) which carries most of the energy

Local wavelets versus non-local Fourier analysis



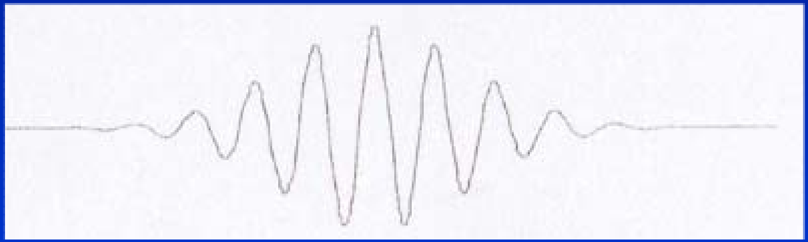
(From J.R. Croca, 2003)

Wavelets are *localized* entities with well-defined frequencies; harmonic monochromatic waves have well-defined frequencies but *extend through all space and time*.

Morlet's wavelet and its real part representation

$$\Psi(x,t) = e^{-\frac{(x-vt)^2}{2\sigma^2} + i(kx - \omega t)}$$

σ is the width and v the velocity



- Wavelets are now the "bricks" for composing functions, instead of monochromatic harmonic waves.
- When the width aproaches ∞, the wavelet approaches a monochromatic harmonic wave.

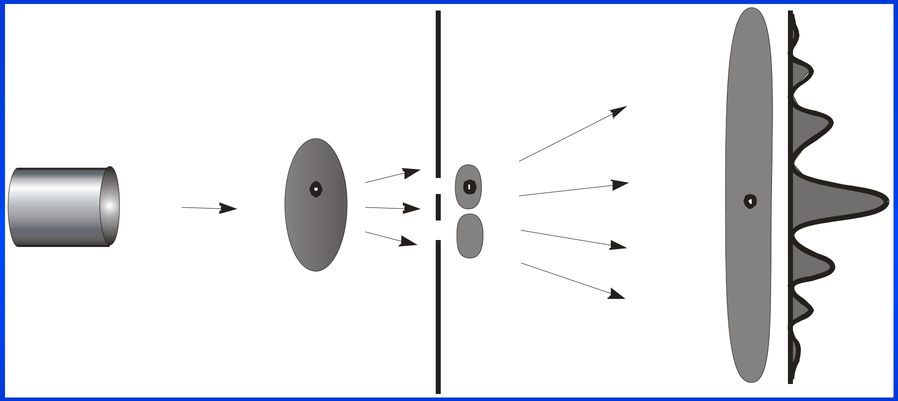
Two-slit experiment

Orthodox (dependent of the observer; collapse):

- the particle passes through one slit **or** the other
- the "particle" passes through one slit **and** the other

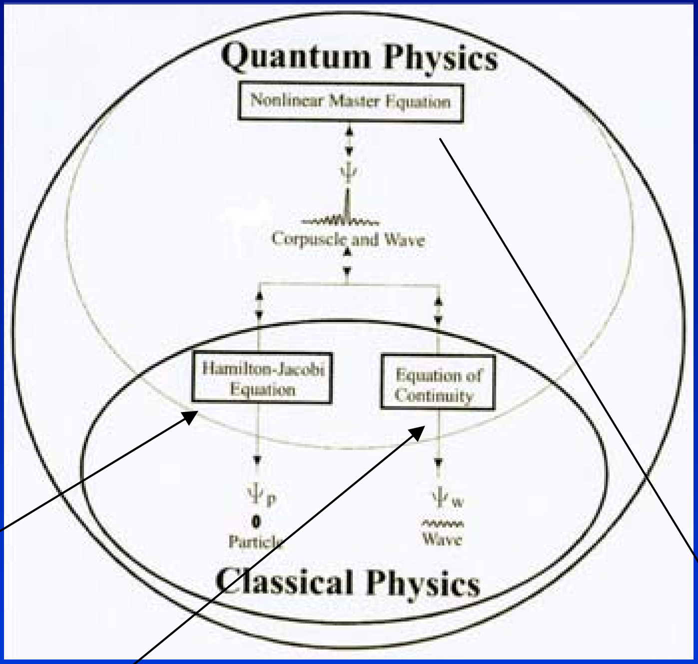
Causal (independent of the observer; no collapse):

- the indivisible "acron" passes through one slit **or** the other
- the "pilot wave" passes through one slit **and** the other



(From J.R. Croca, 2003)

Non-linear master equation



(From J.R. Croca, 2003)

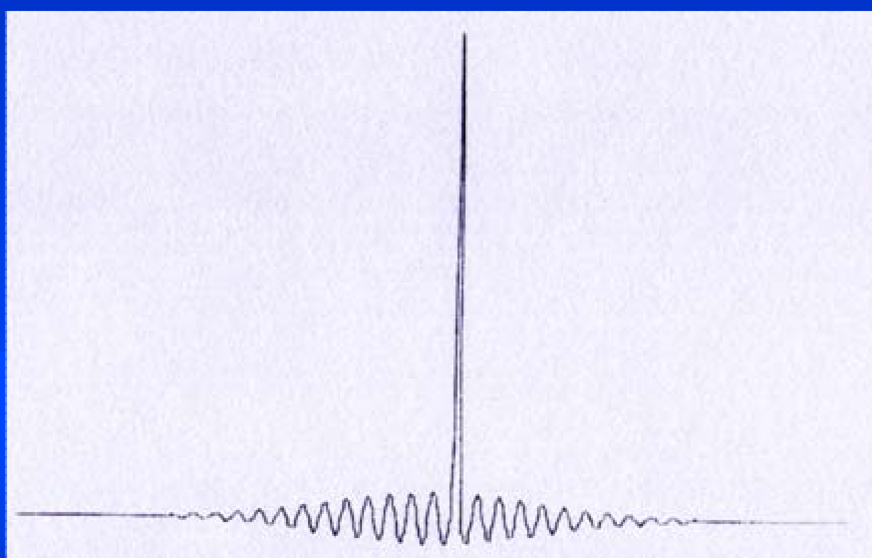
$$\psi(\vec{r},t) = a(\vec{r},t)\, e^{-\frac{i}{\hbar}\varphi(\vec{r},t)}$$

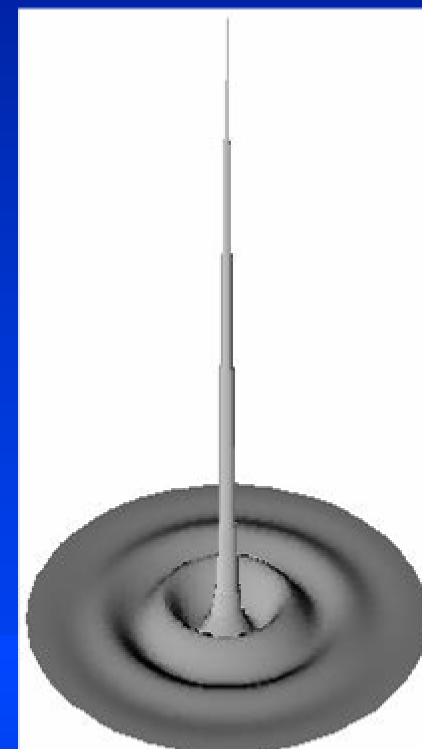
$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{\hbar^2}{2m}\frac{\nabla^2(\psi\psi^*)^{\frac{1}{2}}}{(\psi\psi^*)^{\frac{1}{2}}}\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

For V constant and stationary solutions, the Master Equation ≡ Schrödinger’s Equation

A particular solution of the master equation (free particles)

$$\phi = \sqrt{\frac{\hbar\omega}{\sqrt{\pi}\sigma_0}}\left[e^{-\frac{(kx-2\omega t-\varepsilon_0)^2}{2\sigma_0^2}} + \alpha\, e^{-\frac{(kx-2\omega t-\varepsilon)^2}{2\sigma^2}}\right]e^{i(kx-\omega t)}$$



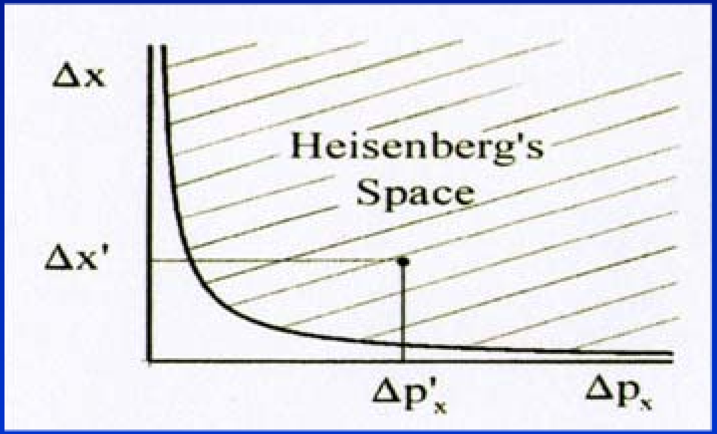


(From J.R. Croca, 2003)

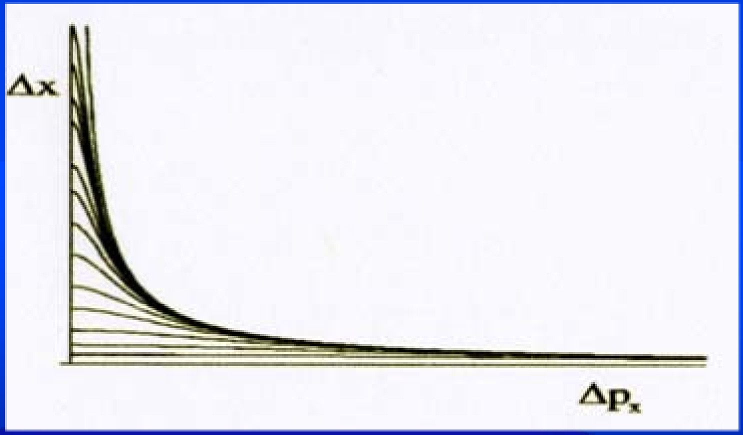
Beyond Heisenberg´s uncertainty relations

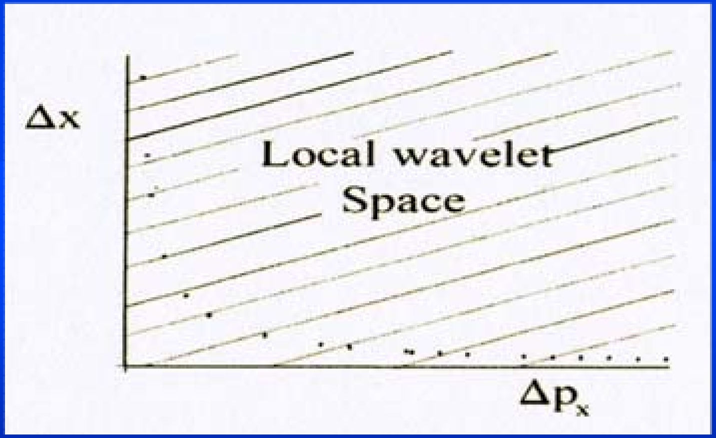
(From J.R. Croca, 2003)

$$\Delta x^2 = \frac{h^2}{\Delta p_x^2 + \frac{h^2}{\sigma_0^{\,2}}}$$



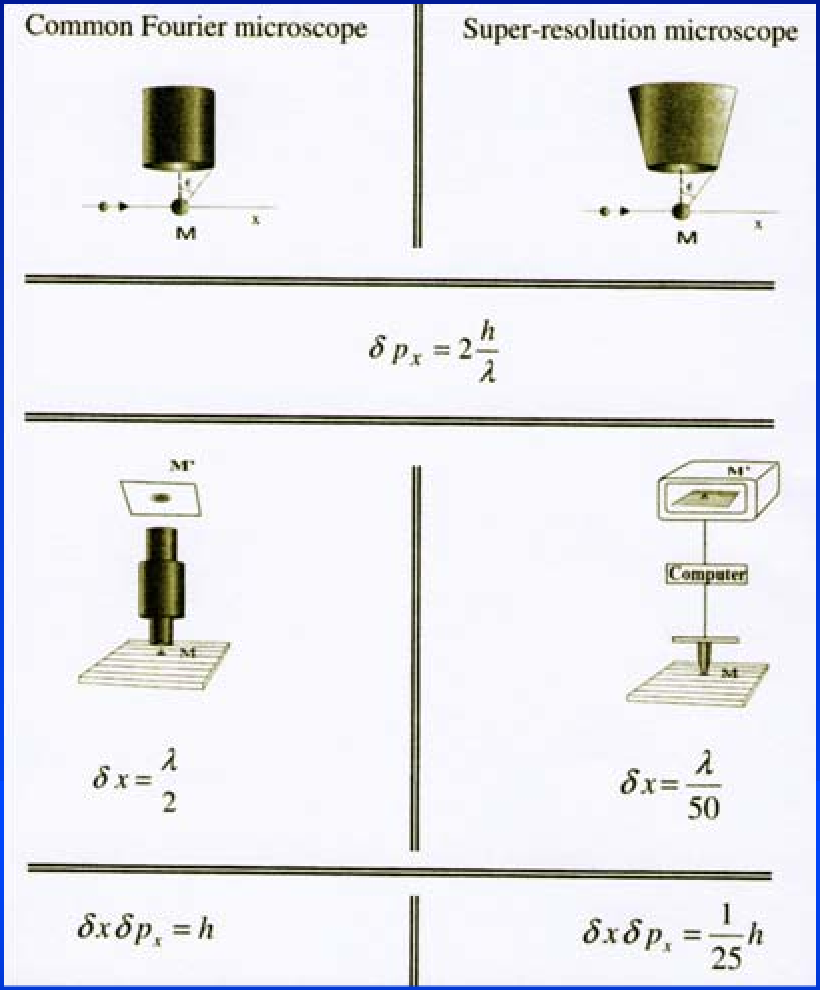
σ_0 (wavelet width) $\rightarrow \infty$: $\Delta x \, \Delta p_x = h$





Testing Heisenberg's uncertainty relation

(From J.R. Croca, 2003)



Some issues

- If $\Psi_1, \Psi_2, \Psi_3, \ldots, \Psi_n$ are solutions of Schrödinger's equation so is:

  $$\Psi = \Psi_1 + \Psi_2 + \Psi_3 + \ldots + \Psi_n \text{ (superposition principle)}$$

- The same is not true for the master non-linear equation. Then, how to compose the solutions? $\Psi = \Psi(\Psi_1, \Psi_2, \Psi_3, \ldots, \Psi_n)$ is not known in general.
- How to incorporate symmetry aspects?
- The non-linear resolutions of the harmonic oscillator and the hydrogen atom are still under progress, showing solutions other than the usual ones. What is their meaning? Do they add new important information?
- Several experiments are proposed to detect the θ waves. At least one of them has been performed though, apparently, not conclusive.
- Apart the new picture, the appealing realistic interpretation, and the more general uncertainty relations, of the non-linear approach, will the heavy burden of solving non-linear equations, in complex chemical and physical problems, be rewarded by new and unexpected results not reachable by the orthodox linear theory?
- The approach suggests the possibility of understanding the gravitational phenomena. Is it a route to unify quantum and general relativity theories?

Steven Weinberg *in* “Dreams of a Final Theory”

“Quantum mechanics has had phenomenal successes in explaining the properties of particles and atoms and molecules, so we know that it is a very good approximation to the truth. The question then is whether there is some other logically possible theory whose predictions are very close but not quite the same as those of quantum mechanics….It is striking that it has so far not been possible to find a logically consistent theory that is close to quantum mechanics, other than quantum mechanics itself…..

In inventing an alternative to quantum mechanics I fastened on the one general feature of quantum mechanics that has always seemed somewhat more arbitrary than others, its linearity…….

This theoretical failure to find a plausible alternative to quantum mechanics, even more than the precise experimental verification of linearity, suggests to me that quantum mechanics is the way it is because ***any small change in quantum mechanics would lead to logical absurdities***. If this is true, quantum mechanics may be a permanent part of physics. Indeed, quantum mechanics may survive not merely as an approximation to a deeper truth, in the way that Newton’s theory of gravitation survives as an approximation to Einstein’s general theory of relativity, but as a precisely valid feature of the final theory”

Language and concepts

(based on "Language, Thought and Reality" by B.L. Whorf, MIT Press, Massachusetts, 1995)

- " We are thus introduced to a new principle of relativity, which holds that all observers are not led by the same physical evidence to the same picture of the universe, unless their linguistic backgrounds are similar, or can in some way be calibrated."
- The language of the American Hopi Indians contains no reference to *time* either explicitly or implicitly. Yet, it is capable of accounting for all observable phenomena of the universe. *Time* is not one of the measurement observables that the Hopi Indians employ. They use other means to speak of the universe. Their language expresses their perception, and it does not include *time*!
- Curiously, *time* is not an observable in quantum mechanics. Indeed, there is no "time operator".
- Kurt Gödel: "*Time* does not really exist in any objective sense. It's not really out there in the world at all; it's our special mode, our own particular way of perceiving the world".
- What are the representations of Schrödinger and non-linear master equations in the Hopi language?

Realism and positivism

- A. Einstein: “Physics is an attempt to capture the reality as it is thought to be, independently of being observed or not”.
- N. Bohr: “There is no quantum world. There is only an abstract physical description. It is wrong to think that the task of physics is to find out how nature is. Physics concerns what we can say about nature”.
- Vienna Circle: “The only true knowledge is scientific knowledge. To be meaningful, a scientific statement has to be a formally logical and verifiable statement”.
- D. Bohm: “The relationship between thought and reality that this thought is about is in fact far more complex than of a mere correspondence. Thus, in scientific research, a great deal of our thinking is in terms of *theories*. The word *theory* derives from the Greek *theatre*, in a word meaning *to view or to make a spectacle*. Thus, it might be said that a theory is *primarily* a form of *insight*, i.e. a way of looking at the world, and not a form of knowledge of how the world is”.

Let’s imagine!

- Einstein: “Does the Moon only exist when I look at it? I do believe in an *objective reality*, independent of the observer”.
- Bohr: “Physical properties are, essentially, “*dummy variables*” to which is not always possible to attribute a *number* without a measurement. Yet, I do believe that the Moon exists like other objects, even if I do not look at them. Otherwise, on driving my way home, I had not avoided that damn tree, *hidden out there*, crashing and killing myself”.

Misconceptions about realism and positivism?

Metaphors just for “marketing”?

Contradictions?

What’s the remedy?

Opposites are complementary
(*Contraria sunt complementa*)

Do I contradict myself ?
Very well then, I contradict myself.
I am large, I contain multitudes. (Walt Whitman, in *Song of Myself*)

Bohr's Coat-of-Arms
Knighted (Order of the Elephant) in 1947

Bohr and Einstein , 1930
by Ehrenfest

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