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NEW CONNECTIONS BETWEEN QUANTUM AND CLASSICAL EQUATIONS WITH APPLICATIONS TO THE MODELING OF ATOMIC, MOLECULAR AND ELECTRODYNAMICAL SYSTEMS

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In previous papers we proved the existence of exact connections between quantum and classical equations in the cases of two different quantum systems, namely the stationary atomic and molecular systems and the systems composed by electrons and very intense electromagnetic field. We proved that the geometrical elements of the wave described by the Schrödinger equation, namely the characteristic surfaces and curves, denoted, respectively, by Σ and C, are solutions of the Hamilton-Jacobi equations, written for the same system, in the case of multidimensional stationary systems. The Σ surfaces, which have the significance of wave surfaces, and the C curves, which are their normals, correspond to the same constants of motion as the eigenvalues of the Schrödinger equation. In three recent papers we presented a central field method for the calculation of the C curves, and of the corresponding energetic values. We have verified this method for a large number of atoms and diatomic molecules, and we found that its accuracy is comparable to the accuracy of the Hartree-Fock method applied to the same atoms and diatomic molecules. In another papers we proved that the Klein-Gordon equation for the system electron-very intense electromagnetic field is verified exactly by the function associated to the classical motion of the electron. An exact connection follows between the solutions of the Klein-Gordon and the relativistic Hamilton-Jacobi equations, for that system. This result explains the accuracy of numerous classical models from the literature, belonging to the new field studying the interactions between very intense laser beams and electron plasmas. We present now a short review of these results.

Key words: Quantum-classical connections, Schrödinger equation, Hamilton-Jacobi equation, Klein-Gordon equation, Relativistic Hamilton-Jacobi equation, Stationary systems, Electromagnetic field, Electrons.

1. INTRODUCTION

This paper belongs to a series of results establishing accurate connections between the classical and quantum equations for various physical systems, without using the WKB approximation. We start by recalling briefly these results.

In a series of papers [1–6] we presented a method for calculating the energetic values of atomic and molecular systems, which is based on the following property [1, 4]: the energy of the Schrödinger equation can be rigorously calculated by line integrals of analytical functions, if the Hamilton-Jacobi equation, written for the same system, is satisfied by a periodical trajectory. We proved [3] that this property is a consequence of the fact that, for stationary systems, the Schrödinger equation is equivalent to the wave equation. Starting from this equivalence, we have proposed [3, 7, 8] a wave model for stationary atomic and molecular systems. In recent papers [9–11] we have elaborated a central field method for calculation of energetic values of atomic and molecular systems, which is based on the above wave model. The central point of this method is the following property [7, 8]: the geometrical elements of the wave described by the Schrödinger equation, namely the wave surfaces and their normals (the C curves) are rigorously solutions of the Hamilton-Jacobi equation, written for the same system. The method was verified for the atoms He, Li, Be, B, C, N and O and for the molecules Li_2, Be_2, B_2, C_2, LiH, BeH, BH and CH. The accuracy of the method is comparable to the accuracy of the Hartree-Fock method, for the same system.

We emphasize that all our above approaches do not use the approximation of geometrical optics or the WKB approximation. Such methods, which avoid direct calculation of the wave function, may become important in the future. This point of view is supported by our article [12], in which it is shown that such methods provide good results for modeling nonlinear properties of compound semiconductors.

Remarkably, a similar connection between the quantum and classical equations holds for systems of an entirely different nature, namely systems composed of electrons in a very intense electromagnetic field. We establish such a connection, in both nonrelativistic [13] and relativistic cases [14, 15]. As for the systems discussed above, this result can lead to a strong simplification of the modeling of these systems. In recent papers, we presented classical models for the relativistic scattering of very intense electromagnetic waves on electrons, when the initial velocities of the electrons are small [16] or are in the relativistic domain [17]. An exact model of the relativistic Thomson scattering is presented in [15]. These models are in very good agreement with the experimental data from literature.

The paper is structured as follows. In Section 2 we demonstrate the connection between the Schrödinger and Hamilton-Jacobi equations in the case of the multidimensional stationary systems. Starting from the equivalency between the Schrödinger and wave equations, we write the characteristic equation of the wave equation, from where we obtain the equations of the wave surfaces and of their normals, which are the C curves. We prove that these last equations results from the solution of the Hamilton-Jacobi equation. We present briefly the application of the properties of the C curves for the calculation of the energetic values of atomic and molecular systems. In Section 3 we prove that the Klein-Gordon equation for the system electron-very intense electromagnetic field is verified exactly by the function associated to the classical motion of the electron. An exact connection follows between the solutions of the Klein-Gordon and the relativistic Hamilton-Jacobi equations. We consider the most general case, when the electromagnetic field is elliptically polarized and when the WKB, eikonal and dipole approximations are not taken into account. We present also the basic applications of this property.

The analysis is made in the International System.

2. CONNECTION BETWEEN THE SCHRÖDINGER AND HAMILTON-JACOBI EQUATIONS

We shall analyze a discrete system composed of N mobile points (electrons) and N' fixed points (nuclei). The Cartesian coordinates of the electrons are x_a, y_a, z_a, where a takes values between 1 and N. Our analysis is made in the space R^{3N} of the electron coordinates, which are denoted by q_j (where $q_1 = x_1$, $q_2 = y_1, \ldots\ldots q_{3N} = z_N$) j taking values between 1 and $3N$. We denote by $q = (q_1, q_2, ..., q_{3N})$ the coordinates of a point in the space R^{3N}.

We consider the following initial hypotheses:

(h1-2) The system is closed and stationary (i.e. the total energy, denoted by E, is constant and the potential energy, denoted by U, does not depend explicitly on time).

(h2-2) The total energy has real negative values (i.e. the system is in a bound state).

(h3-2) The behavior of the system is completely described by the Schrödinger equation:

$$-i\bar{h}\frac{\partial \Psi}{\partial t} - \frac{\bar{h}^2}{2m}\sum_j \frac{\partial^2 \Psi}{\partial q_j^2} + U\Psi = 0, \tag{1}$$

where Ψ, m, t and i are, respectively, the wave function, the electron mass, the time and the imaginary constant, while $\hbar$ is the normalized Planck constant ($\hbar = h/2\pi$). The wave function of a stationary system is of the form $\Psi = \Psi(q, t, E, c)$ [18, p. 330], where E is the total energy and $c = c_1, c_2, ..., c_{3N-1}$ are the eigenvalues of the constants of motion. The number of quantum numbers is equal to the number of constants of motion, and to the number of coordinates of the system. We have presented in detail this property in Ref. [7].

(h4-2) The relativistic and magnetic effects are neglected.

(h5-2) The nuclei are fixed on average positions and their motion is neglected.

Since the system is stationary, the Schrödinger equation can be solved using the separation of variables [18]:

$$\Psi = \Psi_0 \exp\left(-iEt/\bar{h}\right), \tag{2}$$

where $\Psi_0 = \Psi_0\left(q, E, c\right)$ is the time independent wave function, which is a complex valued function satisfying:

$$-\frac{\bar{h}^2}{2m}\sum_j \frac{\partial^2 \Psi_0}{\partial q_j^2} + \left(U - E\right)\Psi_0 = 0. \tag{3}$$

Eq. (3) is equivalent to the system that comprises Eq. (2) and the wave equation

$$\sum_j \frac{\partial^2 \Psi}{\partial q_j^2} - \frac{1}{v_w^2}\frac{\partial^2 \Psi}{\partial t^2} = 0, \tag{4}$$

where

$$v_w = \pm\left|E\right|\Big/\sqrt{2m\left(E - U\right)}. \tag{5}$$

Mathematically, the motion of the wave described by Eq. (4) is completely determined by the motion of its *characteristic surface* [19–21], the latter having the significance of a wave surface [19]. In Refs. [7, 8] we have analyzed the motion of this surface in the classically allowed (CA) domain, corresponding to real values of v_w given by Eq. (5). The characteristic surface of Eq. (4), denoted by Σ, is given by the following equation [19–21]:

$$\chi\left(q, t\right) = 0 \qquad (\Sigma \text{ surface}), \tag{6}$$

where χ is a single valued function, called *characteristic function*, which satisfies the *characteristic equation*:

$$\sum_j \left(\frac{\partial \chi}{\partial t}\right)^2 - \frac{1}{v_w^2}\left(\frac{\partial \chi}{\partial t}\right)^2 = 0. \tag{7}$$

This equation has the following solution:

$$\chi\left(q, t, E, c\right) = \sin k\left[f\left(q, E, c\right) \mp \left|E\right| t\right], \tag{8}$$

where k is a real constant and $f\left(q, E, c\right)$ is a single valued function (the complete integral), which verifies the time independent Hamilton-Jacobi equation.

$$\sum_j \left(\frac{\partial f}{\partial q_j}\right)^2 + 2m\left(U - E\right) = 0. \tag{9}$$

Thus we have obtained an accurate connection between the wave equation and the Hamilton-Jacobi equation, because Eq. (8) is deduced without using any approximation, such as the approximation of the geometrical optics, or the WKB approximation. Similar connections, which have been derived through entirely different methods, are presented in Refs. [22, 23], where it is shown that the discontinuities of the partial second derivatives of the wave function propagate following the trajectories determined by the Hamilton-Jacobi equation, written for the same system.

From Eqs. (6) and (8) it results that the equation of the Σ surface is $f\left(q, E, c\right) = \left|E\right| t - p\pi/k$, where p is an integer. In virtue of the theory of the Hamilton-Jacobi equation [24] it follows that the normal curves to the Σ surfaces, denoted by C, are the trajectories resulting from the Hamilton-Jacobi equation and corresponding to the constants c and E.

In a previous mathematical paper [7], we have proven that the motion of the Σ surface is periodic, the C curves are closed and the motion of the system has the properties of a wave because:

1) A point of the wave $P \in \Sigma$ moves on a closed *C* curve with velocity $|v_w|$, in only one direction, and the amplitude of the wave function Ψ in that point varies periodically.

2) The point *P* moves synchronously with the Σ surface, which is perpendicular on the *C* curve. This surface has the significance of a wave surface.

The periodic motion of the Σ surface is illustrated by the following equation [7]

$$f(q,E,c) = |E|t - p|E|\tau_w \text{ for } p\tau_w \le t < (p+1)\tau_w,\ p = 0, 1, 2 \ldots, \tag{10}$$

where τ_w is the period of the wave motion and *p* is a positive integer (*p=0* for the first period, *p*=1 for the second period, and so on). The function *f* is bounded, namely

$$0 \le f(q,E,c) < f_M \text{ where } f_M = |E| \cdot \tau_w. \tag{11}$$

It follows that the point *P* passes successively through all the values of the function *f* when it runs on the curve *C*.

We have also shown in Ref. [7] that there is another characteristic surface which moves in the opposite sense.

The reduced action function along the *C* trajectory, denoted by S_0, is given by the equation

$$S_0(q,E,c) = f(q,E,c) + pf_M. \tag{12}$$

Note that S_0 increases continuously along the curve *C*. The variation of the function S_0 along the closed curve *C*, denoted by $\Delta_C S_0$, is given by:

$$\Delta_C S_0 = f_M. \tag{13}$$

A point of the wave moves on the curve *C* with the velocity v_w, while the velocity of the electron in the same point of the curve is *v*. We have proven [8] the following relations:

$$v_w v = |E|/m \text{ and } \tau_w = 2\tau, \tag{14}$$

where τ is the period of the motion of the electron on the curve C.

We analyze next the motion of an arbitrary point, denoted by *P*, that belongs to the surface Σ, and moves along the corresponding closed *C* curve in a period. We denote by t_i, t_f, Ψ_i, Ψ_f, q_i, q_f, respectively, the initial and final moments, wave functions and corresponding coordinates.

The following relations result from the periodicity of the wave:

$$q_i \equiv q_f,\ t_f = t_i + \tau_w \text{ and } \Psi_i = \Psi_f. \tag{15}$$

In virtue of Eq. (2) we have $\Psi_i = \Psi_0(q_i)\exp(-iEt_i/\hbar)$ and $\Psi_f = \Psi_0(q_f)\exp(-iEt_f/\hbar)$ and taking into account Eqs. (15), we obtain

$$|E|\tau_w = nh. \tag{16}$$

From (11), (13) and (16) we obtain the generalized Bohr quantization condition:

$$\Delta_C S_0 = nh. \tag{17}$$

For systems for which the separation of variables is possible, the function S_0 can be written $S_0 = \sum_a S_{0a}$ where $S_{0a} = S_{0a}(x_a, y_a, z_a)$. In this case we have proven [8] that the following quantization relation is valid:

$$\Delta_{C_a} S_{0a} = n_a h \text{ where } n_a = 1, 2, \ldots, \tag{18}$$

n_a being the principal quantum number associated to the motion of the electron a. Here C_a is the curve corresponding to the electron a and $\Delta_{C_a} S_{0a}$ is the variation of the reduced action corresponding to the C_a curve. From Eqs. (17) and (18) we obtain

$$n = \sum_a n_a . \tag{19}$$

It follows that the minimum value of n is N, the total number of electrons.

The particular curve of a given electron is obtained from the projection of the C curve from the R^{3N} space of coordinates, on the three dimensional space of that electron. For example, the curve of the electron a is obtained from the projection of the C curve on the space of coordinates x_a, y_a, z_a. It is also a closed curve, denoted by C'_a, where $a = 1, 2, ..., N$. When the separation of the variables is possible, we have $C'_a \equiv C_a$.

In Refs. [9-11] we presented a central field method, for which the separation of the variables is possible and the C_a curves can be calculated. In this case, the energetic values are calculated with the aid of Eq. (18). We have applied this method for the atoms He, Li, Be, B, C, N and O and for the molecules Li_2, Be_2, B_2, C_2, LiH, BeH, BH and CH, resulting that the accuracy of the method is comparable to the accuracy of the Hartree-Fock method, for the same system.

3. CONNECTION BETWEEN THE KLEIN GORDON AND RELATIVISTIC HAMILTON-JACOBI EQUATIONS

A large number of papers in the new domain of the interactions between very intense electromagnetic fields and electrons or atoms present classical approaches [25, 26]. Theoretical studies of the connection between the quantum and classical equations in this field were made as early as 1964 [27], and a recent approach was presented in [13, 15].

In this section, we consider systems composed of electrons and very intense electromagnetic fields. Without using the WKB or eikonal approximations, we present an exact connection between the quantum Klein-Gordon, and the classical relativistic Hamilton-Jacobi equation for these systems [15, 27].

We analyze a system composed of an electron interacting with a very intense electromagnetic elliptically polarized field. We consider the following initial hypotheses:

(h1-3) The electromagnetic field is of the type produced by a very intense laser beam, and the value of the intensity of its electric field is of the order of one atomic unit, namely 5.1423×10^{11} V/m, or greater.

(h2-3) The interaction between the electron spin and the electromagnetic field is neglected and the behavior of the system is described by the Klein-Gordon equation [28]:

$$\left[c^2 \left(-i\hbar\nabla + e\bar{A} \right)^2 - \left(i\hbar \frac{\partial}{\partial t} \right)^2 + \left(mc^2 \right)^2 \right] \Psi = 0, \tag{20}$$

where $\bar{A}$ and c are, respectively, the vector potential of the field and the velocity of light in vacuum. We denote by e the absolute value of the electron charge, the sign being written explicitly.

(h3-3) The electromagnetic field is elliptically polarized. In a Cartesian system of coordinates, the intensity of the electric field and of the magnetic induction vector, denoted respectively by $\bar{E}$ and $\bar{B}$, are polarized in the plane xoy, while the wave vector, denoted by $\bar{k}$, is parallel to the axis oz. The expressions of the electric field and of the magnetic induction vector are as follows:

$$\bar{E} = \bar{i}E_1 \cos\eta + \bar{j}E_2 \sin\eta \text{ and } \bar{B} = -\bar{i}B_2 \sin\eta + \bar{j}B_1 \cos\eta, \tag{21}$$

with

$$\eta = \omega t - kz + \varphi, \tag{22}$$

where $\bar{i}$ and $\bar{j}$ are the versors of the ox and oy axes, E_1, E_2, B_1 and B_2 are the amplitudes of the oscillations in the ox and oy directions of the electric and magnetic fields, ω is the angular frequency of the electromagnetic field and φ is an arbitrary phase.

The following relations are also valid:

$$E_1 = cB_1 \qquad \text{and} \qquad E_2 = cB_2 . \tag{23}$$

In order to obtain the connection between Klein Gordon and relativistic Hamilton-Jacobi equations, we start by rewriting the Klein-Gordon equation using the substitution

$$\Psi = C \cdot \exp\left(\frac{i\sigma}{\hbar}\right), \tag{24}$$

where σ is a complex valued function of the electron coordinates and time. The Klein-Gordon equation (20) becomes:

$$c^2\left(\nabla\sigma + e\bar{A}\right)^2 - \left(\frac{\partial\sigma}{\partial t}\right)^2 + \left(mc^2\right)^2 - i\hbar c^2\left[\nabla\left(\nabla\sigma + e\bar{A}\right) - \frac{\partial^2\sigma}{c^2\partial t^2}\right] = 0. \tag{25}$$

The relativistic Hamilton-Jacobi equation, written for the same system, is [29]:

$$c^2\left(\nabla S + e\bar{A}\right)^2 - \left(\frac{\partial S}{\partial t}\right)^2 + \left(mc^2\right)^2 = 0, \tag{26}$$

where S is the classical action.

In the paper [15] we proved that, starting from the relativistic equations of motion of the electron in the electromagnetic field, in the general case when the initial values of the components of the velocity of the electron are taken into account, the following relation is valid:

$$\nabla\left(\nabla S + e\bar{A}\right) - \frac{\partial^2 S}{c^2\partial t^2} = 0. \tag{27}$$

By (25–27) we obtain the following property: *Under hypotheses (h1-3), (h2-3) and (h3-3), the Klein-Gordon equation is verified by the wave function associated to the classical motion,* $C \cdot \exp\left(iS/\hbar\right)$*, where S is the solution of the relativistic Hamilton-Jacobi equation, written for the same system.*

This property explains the accuracy of numerous classical models from the literature, belonging to the new field studying the interactions between very intense laser beams and electron plasmas. For example, our results presented in the papers [15–17] show that the expressions of the velocity and of the acceleration of the electron, on a classical trajectory in very high electromagnetic field, lead, with the aid of the Lièнard-Wièchert equation, to the accurate modeling of the Thomson scattered spectrum.

On the other hand, a classical treatment is justified also in the case of the new field of interactions between very intense laser beams and atoms, for the ionization domain, where the interaction between the electron and the atomic core is neglected. We consider that this property justifies the accuracy of numerous semiclassical models which have been elaborated for this domain, such as, for example, the classical model of Corkum [25], which leads to the most precise – to our knowledge – expression for the cutoff of the high harmonic radiation reported in literature, or the analysis of the classical effects in ATI and HHG phenomena presented by Becker et al [26].

4. CONCLUSIONS

In this paper we presented a brief review of two accurate connections between quantum and classical equations, which have been proven in previous papers, in the case of stationary multidimensional systems and for systems comprising very intense electromagnetic fields and electron plasmas. These connections give a theoretical foundation to our papers [9-11], where we have presented accurate semiclassical models for atomic and molecular systems, and to the papers [15-17], where we have proved that models for the classical relativistic scattering of very intense electromagnetic waves on electrons are in good agreement with the experiment.

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