A secondary solution of the Schrödinger and Klein-Gordon equations in modeling atomic, molecular and electrodynamic systems

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Abstract. We study atomic and molecular (AM) stationary systems and electrodynamic (ED) systems, composed of an electron interacting with an electromagnetic field. We show that the Schrödinger and Klein-Gordon equations written for these systems have a secondary solution, which is the wave function associated to a classical system. For AM systems, the wave surfaces (Σ surfaces) and their normals (C curves) are solutions of the Hamilton-Jacobi equation, written for the same system. The Σ surfaces have a periodical motion and the C curves are closed. The integral relation of the Schrödinger equation on the C curve has a solution identical to the wave function associated to the classical motion. This solution leads to the generalized Bohr quantization relation and to the generalized de Broglie relations, which are valid in the space of the electron coordinates. An identical wave function verifies the Klein-Gordon equation, in the case of the EM systems. The above properties lead to a central field method for calculation of the energetic values and symmetry properties for AM systems, whose accuracy is comparable to the accuracy of the Hartree-Fock method. They also lead to an accurate method for modeling EM systems, which is verified by experimental data from the literature. The above properties are deduced without using any approximation.

1. Introduction
Despite the fact that AM and ED systems are very different, our analysis shows that they share common features. In both cases a solution associated to the classical motion results, without any approximation, from the mathematical properties of both, the Schrödinger and Klein-Gordon equations. Another important common feature of AM and ED systems is that in both cases the solutions exhibit periodicity properties. These properties have a practical importance, because they lead to accurate models for the calculation of properties of AM and ED systems. We prove these properties with the aid of our previous results, published in the papers [1]-[6]. The calculation models were verified on numerous experimental data from literature. In Refs. [7]-[9] we presented models for the calculation of the energetic relations and of the symmetry properties of numerous atoms and atomic molecules, whose accuracy is comparable to the accuracy of the Hartree-Fock method. In Refs. [6] and [10]-[14] we presented accurate calculations of the spectral and geometric distributions of the radiations generated at the interaction between very intense laser beams and electron plasmas or atomic gases.
2. Secondary solution of the Schrödinger equation

We shall analyze a discrete system composed of $N$ mobile points (electrons) and $N'$ fixed points (nuclei). Our analysis is made in the space $R^{3N}$ of the electron coordinates, which are denoted by $q_j$, where $j$ takes values between 1 and $3N$. We denote by $q = (q_1, q_2, ..., q_N)$ the coordinates of a point in the space $R^{3N}$. The equations are written in the International System.

We consider the following initial hypotheses. (h1) 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) The total energy has real negative values (i.e. the system is in a bound state). (h3) The behavior of the system is completely described by the Schrödinger equation. (h4) The relativistic and magnetic effects are neglected. (h5) The nuclei are fixed on average positions and their motion is neglected.

We prove that the mathematical properties of this system lead exactly to a secondary solution for the wave function of the system, as follows [1]-[5].

The Schrödinger equation $-i\hbar \partial \Psi / \partial t - (\hbar^2/2m) \sum_j \left( \partial^2 \Psi / \partial q_j^2 \right) + U \Psi = 0$ is equivalent to the system composed by the wave equation $\sum_j \left( \partial^2 \Psi / \partial q_j^2 \right) - (1/v_w^2) \partial^2 \Psi / \partial t^2 = 0$ and the equation

$$\Psi = \Psi_0 \exp(-iT)/h \tag{1}$$

which reflects the stationarity property of the system. In the above equations, $\Psi$, $m$, $t$ and $i$ are, respectively, the wave function, the electron mass, the time and the imaginary constant, while $h$ is the normalized Planck constant ($h = h/2\pi$). The function $\Psi_0$ is the time independent wave function, which is the solution of the equation $- \left( \hbar^2/2m \right) \sum_j \left( \partial^2 \Psi_0 / \partial q_j^2 \right) + (U - E) \Psi = 0$, and the quantity $v_w$ is given by the relation

$$v_w = \pm |E|/\sqrt{2m(E-U)} \tag{2}$$

The functions $\Psi$ and $\Psi_0$ are of the form $\Psi = \Psi(q,t,E,c)$ and $\Psi_0 = \Psi_0(q,E,c)$ [see [15], page 330], where $E$ and $c = (c_1, c_2, ..., c_{3N-1})$ are the eigenvalues of the constants of motion.

The wave surfaces of the system are the same as the characteristic surfaces of the wave equation [16], [17]. The characteristic surface of the wave equation, denoted by $\Sigma$, is given by the following equation: [17]-[18]:

$$\chi(q,t,E,c) = 0 \tag{3}$$

where $\chi$ is a single valued function, called characteristic function, which satisfies the characteristic equation $\sum_j \left( \partial \chi / \partial q_j \right)^2 - (1/v_w^2) \left( \partial \chi / \partial t \right)^2 = 0$.

The equation (3) leads to the following equation of the $\Sigma$ surfaces, $f(q,E,c) = |E|t - p\pi/k$, where $k$ is a real constant, $p$ is an integer and $f(q,E,c)$ is a single valued function (the complete integral), which verifies the time independent Hamilton-Jacobi equation $\sum_j \left( \partial f / \partial q_j \right)^2 + 2m(U - E) = 0$. Since the velocity of a point of the $C$ curve, which results from the time independent Hamilton-Jacobi equation, is $\nabla f(q,E,c)$ [19], it follows that the $C$ curve is normal to the $\Sigma$ surface.

In Refs. [3] and [4] we have deduced following properties of the $\Sigma$ surfaces. The motion of the $\Sigma$ surface is periodic and the $C$ curves are closed. An arbitrary point $P \in \Sigma$ moves on a closed $C$ curve with velocity $|v_w|$, in only one direction, and the amplitude of the wave function $\Psi$ in that point varies periodically. The point $P$ moves synchronously with the $\Sigma$ surface. The periodic motion of the $\Sigma$ surface is illustrated by the following equation: $f(q,E,c) = |E|t - p|E|\tau_w$ for $p\tau_w \leq t < (p + 1)\tau_w$, where $\tau_w$ 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 $0 \leq f(q,E,c) < f_M$, and the maximum value of $f$ is

$$f_M = |E| \cdot \tau_w \tag{4}$$
It follows that the point $P$ passes successively through all the values of the function $f$ when it runs on the curve $C$.

The reduced action function along the $C$ curve, denoted by $S_0$, is given by the equation $S_0(q, E, c) = f(q, E, c) + pf_M$. Note that $S_0$ increases continuously along the curve $C$. The variation of the function $S_0$ along the closed curve $C$, denoted by $\Delta S_0$, is given by:

$$\Delta_C S_0 = f_M$$

(5)

Two motions are associated with the $C$ curve, the motion of a point of the quantum wave and the motion of a classical point, which results from the Hamilton-Jacobi equation. The corresponding velocities are, respectively, $v_w$ and $v$. We have proven [3], [5] the following relation, which reflect the connection between the two motions:

$$vv_w = |E|/m$$

(6)

The relation between the periods of the two motions is $\tau_w = 2\tau$.

In Refs. [3] and [5] we have proven a general equation which connects the quantum and classical solutions. With the substitution

$$\Psi_0 = \exp(i\sigma/\hbar)$$

(7)

where $\sigma$ is a complex valued function of the electron coordinates, we have proven the following integral relation of the Schrödinger equation on the $C$ curve [see Eq. (37) from [5]]:

$$\int_C \sum_j \left( \frac{\partial \sigma}{\partial q_j} \right)^2 dt - i\hbar \int_C \left( \sum_j \frac{\partial^2 \sigma}{\partial q_j^2} \right) dt = \int_C \sum_j \left( \frac{\partial S_0}{\partial q_j} \right)^2 dt$$

(8)

An integral relation admits a specific supplementary solution (in addition to the solution coming from the initial equation that has been integrated, which in our case is $\Psi_0$), called generalized solution [18]. We proved [5] that the generalized solution of Eq. (8) is $\sigma_g = S_0$. By virtue of this equation, the time independent wave function corresponding to the generalized solution is:

$$\Psi_{0g} = A \exp(iS_0/\hbar)$$

(9)

The corresponding time dependent wave function results from Eqs. (1) and (9), as follows:

$$\Psi_g = A \exp(iS/\hbar) \quad \text{where} \quad S = S_0 - Et$$

(10)

Since $S$ and $S_0$ are, respectively, the action and reduced action corresponding to the $C$ curve, it follows that $\Psi_g$ is the wave function associated to the classical motion on the $C$ curve. Since $\Psi_{0g}$ is single valued, it must have the same value when we go along the curve $C$ and arrive again in the initial point. This property leads to the generalized Bohr quantization relation:

$$\Delta_C S_0 = nh$$

(11)

where $n$ is a positive integer. By virtue of Eqs. (4), (5) and (11), we have:

$$|E|\tau_w = nh$$

(12)

Since the wavelength and angular frequency of the Broglie wave are, respectively, $\lambda_w = \tau_w \cdot v_w$ and $\omega_w = 2\pi/\tau_w$, from Eqs. (6) and (12) we obtain the de Broglie relations:

$$p = nh\bar{k}_w \quad \text{and} \quad |E| = nh\omega_w$$

(13)
where $\vec{p} = m\vec{v}$ and $\vec{k}_w$ is the wave vector of the de Broglie wave, which is given by relation $\vec{k}_w = (2\pi/\lambda_w)(v_w/v_w)$.

Is follows that there is a de Broglie wave associated to the motion on the $C$ curve, which results from the Hamilton-Jacobi equation. This wave is characterized by the wave vector $\vec{k}_w$ and the angular frequency $\omega_w$. We note that the motion on the $C$ curve is associated also with the wave function $\Psi_g$, which results from the integral relation of the Schrödinger equation on the $C$ curve [see Eq. (10)].

3. Secondary solution of the Klein-Gordon equation

We consider a system composed of an electron interacting with an elliptic polarized electromagnetic field in the general case, when the electron velocity and the phase of the field are arbitrary. In Ref. [6] we proved that the Klein-Gordon equation, written for this system, which is

$$c^2 \left( -i\hbar \nabla + eA \right)^2 - \left( i\hbar \partial/\partial t \right)^2 + (mc^2)^2 \right) \Psi = 0,$$

is verified exactly by the wave function associated with the classical motion of the electron in electromagnetic field, which is

$$\Psi = A \exp(iS/\hbar)$$

The existence of this solution, which is a classical type wave function associated to the classical trajectory of the electron in the electromagnetic field, justifies the accuracy of the classical models presented in Refs. [6] and [10]-[14].

4. Conclusions

A solution of the type $A \exp(iS/\hbar)$ which is associated to the classical motion results, without any approximation, from the mathematical properties of both, the Schrödinger and Klein-Gordon equations. The solution $A \exp(iS/\hbar)$ in the case of AM systems is associated with the geometric elements of the wave described by the Schrödinger equation, which result from the Hamilton-Jacobi equation, written for the same system. The same solution in the case of ED systems is associated to the classical electron trajectory which results from the relativistic Hamilton-Jacobi equation. There is a similitude between our result and the double solution theory of de Broglie, despite the fact that the two treatments are completely different. In the double solution theory [20], it is shown that Schrödinger’s equation admits a second wave solution, which is a classical-type wave function, as in our analysis.

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