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Connection between the periodic solutions of the Hamilton–Jacobi equation and the wave properties of the conservative bound systems

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Abstract
It is well known that the Schrödinger equation is equivalent to the wave equation for conservative bound quantum systems. Consequently, the motion of such a system is represented—from a mathematical point of view—by the motion of the characteristic surface of the wave equation. In this paper we present a demonstration of the periodic motion of the characteristic surface. It results that the normal curves of the characteristic surface are periodic solutions of the Hamilton–Jacobi equation written for the same system. This leads to a direct connection between the periodic solutions of the Hamilton–Jacobi equation and the wave properties of the system. The constants of motion corresponding to the above periodic solutions of the Hamilton–Jacobi equation are identical to the eigenvalues of the Schrödinger equation. These properties are proved without any approximation and they are valid for all the values of the principal quantum number.

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1. Introduction

It is well known that the classical and quantum treatments of discrete conservative systems lead, mathematically, to waves, which are associated with the motion of these systems. The waves associated with the classical motion are studied, for example, in [1, 2]. On the other hand, in the quantum approach, the Schrödinger equation itself is equivalent to the wave equation in the case of conservative systems. A natural question appears: what is the connection between the two waves? In this paper we show that this connection results from a parallel analysis of the same system, using the quantum Schrödinger and the classical Hamilton–Jacobi equations respectively.

We present the wave properties of the characteristic surfaces and curves of the system. This paper is intended as a contribution to 'mathematical' physics rather than to 'naturalistic'

physics, as these words are interpreted by Synge in [1]. That is, the curves and surfaces that are considered in this paper are viewed only as mathematical objects, and are void of any physical interpretation. However, these mathematical objects prove to be useful tools for calculating the energetic eigenvalues of the systems studied [3–9].

The equations are written in the international system.

2. Initial hypotheses

We shall analyse 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 $q_1 = x_1, q_2 = y_1, q_3 = z_1, \ldots, q_{3N} = z_N$), j taking values between 1 and $3N$. We consider the following initial hypotheses:

(h1) The system is closed and conservative (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 potential and total energies have real negative values (i.e. the system is in a bound state). We remark that this is a natural assumption, which is satisfied by systems formed of atoms and molecules in conservative bound states. Indeed, for such systems the negative potential energy due to the interaction between electrons and nuclei is dominant in the expression for the potential energy of the system (see, for example, [10, 11]).

(h3) The behaviour of the system is completely described by the Schrödinger equation

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

where Ψ, m, t and i are, respectively, the wavefunction, the electron mass, the time and the imaginary constant, while $\hbar$ is the normalized Planck constant ($\hbar = h/2\pi$).

According to the hypothesis (h3), the wavefunction of a conservative system is of the form $\Psi = \Psi(q, t, E, c)$ (see [12], p 330), where the total energy E and $c = (c_1, c_2, \ldots, c_{3N-1})$ are the eigenvalues of the constants of motion. These eigenvalues have discrete values which depend on the quantum numbers of the system, according to the relation

$$c_j = c_j(n_j) \tag{2}$$

where n_j is the quantum number which corresponds to the constant of motion with eigenvalue c_j. The number of quantum numbers is equal to the number of constants of motion, and to the number of coordinates of the system. We briefly recall the theory leading to these facts.

In the case of a hydrogenoid system (for $N = 1$), there are three constants of motion: the energy, orbital momentum and its projection on the z axis. The corresponding quantum numbers are, respectively, the principal, azimuthal and magnetic orbital. In the expression of the wavefunction, the quantum numbers enter explicitly, while the constants of motion enter implicitly, because they are functions of the three quantum numbers.

For a general atomic system with N electrons, the wavefunction Ψ is a function of N hydrogenoid wavefunctions, using the approximation of the atomic orbitals (see [10, 13, 14]). Since each hydrogenoid wavefunction depends (explicitly) on three quantum numbers, and (implicitly) on three constants of motion, it follows that Ψ depends on $3N$ quantum numbers, corresponding to $3N$ constants of motion.

The case of a molecule with N' nuclei and N electrons is similar. Indeed, the linear combination of atomic orbitals (LCAO) approximation [11] shows that the wavefunction of the molecule is a function of N atomic wavefunctions, each of them corresponding to three constants of motion, and the same conclusion follows.

(h4) The relativistic and magnetic effects are neglected.

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

We recall that the nucleus of an atom has a periodic motion with respect to a fixed point (the centre of mass), while each of the nuclei of a molecule has a vibratory motion with respect to a well-defined fixed point (see [10, 11]). These fixed points are called average positions.

Since the system is conservative, the Schrödinger equation can be solved using separation of variables [12]:

$$\Psi = \Psi_0 \exp(-\mathrm{i}Et/\hbar) \tag{3}$$

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

$$-\frac{\hbar^2}{2m}\sum_j \frac{\partial^2 \Psi_0}{\partial q_j^2} + (U - E)\Psi_0 = 0. \tag{4}$$

It is well known that for conservative systems, equation (1) is equivalent to the system which comprises equation (3) and the wave equation

$$\sum_j \frac{\partial^2 \Psi}{\partial q_j^2} - \frac{1}{v_w^2}\frac{\partial^2 \Psi}{\partial t^2} = 0 \tag{5}$$

where

$$v_w = \pm|E|/\sqrt{2m(E - U)}. \tag{6}$$

Consequently, the behaviour of the system is described by the wave equation. Mathematically, the motion of the wave described by equation (5) is completely determined by the motion of its *characteristic surface* [15–17], the latter having the significance of a wave surface [15]. We analyse the motion of this wave in the classically allowed (CA) domain (where $E > U$), corresponding to the real values of v_w, given by equation (6).

The characteristic surface of equation (5) is given by the following equation [15–18]:

$$\chi(q, t) = 0 \tag{7}$$

where χ is called the *characteristic function*. It is a single-valued function which satisfies the *characteristic equation*:

$$\sum_j \left(\frac{\partial \chi}{\partial q_j}\right)^2 - \frac{1}{v_w^2}\left(\frac{\partial \chi}{\partial t}\right)^2 = 0. \tag{8}$$

The characteristic surface is denoted by Σ and is defined in the space R^{3N} of coordinates, corresponding to a fixed value of time in (7).

In the space R^{3N+1} of coordinates and time, the surface given by equation (7) is a conoid [15–17, 19], usually called the *characteristic conoid*.

In virtue of the theory [15], an equation of the form $F\left(\frac{\partial u}{\partial q_1}, \ldots, \frac{\partial u}{\partial q_s}, \frac{\partial u}{\partial t}\right) = 0$ for which $\frac{\partial u}{\partial t}$ can be written explicitly in terms of the other partial derivatives, has a solution of the form $u = u(q, t, c') + c'_0$, where $c' = (c'_1, c'_2, \ldots, c'_s)$ are the constants of the system, which belong to a continuous real domain, and c'_0 is an integration constant, which will be chosen to be zero.

Consequently, the characteristic function is of the form

$$\chi = \chi(q, t, c') \tag{9}$$

where $c' = (c'_1, c'_2, \ldots, c'_{3N})$. Since the characteristic surface is an intrinsic mathematical element of the system described by the wave equation, the constants which enter in the

characteristic function are constants of motion of the system, and we assume that the following relations are valid:

$$c'_j = c_j \qquad \text{for} \quad 1 \leqslant j \leqslant 3N-1 \quad \text{and} \quad c'_{3N} = E \tag{10}$$

$$\chi = \chi(q, t, E, c). \tag{11}$$

The assumption (10) can be made because χ is a solution of an equation of first grade and the constants c' in (9) belong to a continuous real domain which includes the eigenvalues c and E of the Schrödinger equation.

3. Properties of the characteristic curves and surfaces

Equation (8) has the following solution:

$$\chi(q, t, E, c) = \sin k[f(q, E, c) \mp |E|t] \tag{12}$$

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

$$\sum_j \left(\frac{\partial f}{\partial q_j}\right)^2 + 2m(U - E) = 0. \tag{13}$$

We limit our analysis to the case corresponding to the plus sign in equation (6) and the minus sign in equation (12). The case of a minus sign in equation (6) and a plus sign in equation (12) corresponds to a set of characteristic surfaces moving in the opposite direction, as we will show later. The two choices are symmetric, and there is no loss of generality in our choice.

From (7) and (12) it follows that the equation of the characteristic surface is

$$f(q, E, c) = |E|t - p\pi/k \tag{14}$$

where p is an integer. The family of surfaces associated with the classical motion by the Hamilton–Jacobi equation, written for the same system, has the following similar equation [2]:

$$f(q, E, c) = \kappa \tag{15}$$

where κ is a variable parameter. This yields the following properties:

Property 1. *The family of characteristic surfaces of the wave equation is the same as the family of surfaces associated with the classical motion by the Hamilton–Jacobi equation, and corresponding to the constants c and E.*

Property 2. *The normal curves to the Σ surfaces are the C trajectories resulting from the Hamilton–Jacobi equation and corresponding to the constants c and E.*

Property 3. *The characteristic surfaces and the C trajectories of the system are situated inside the CA domain.*

These properties are derived from the corresponding properties of the Hamilton–Jacobi equation [2, 20].

In virtue of the theory [2, 20], the C trajectories depend on $6N$ constants: $c = (c_1, c_2, \ldots, c_{3N-1})$, E and $d = (d_1, d_2, \ldots, d_{3N})$, where $d_j = \partial f(q, c, E)/\partial c_j$ for $j = 1, 2, \ldots, 3N-1$ and $d_{3N} = -t_0$, t_0 being the initial time.

The characteristic Σ surface has the following properties:

Property 4. *Two surfaces, Σ_1 and Σ_2, that correspond to the same values of the constants c and E, and have, respectively, the equations $f(q, E, c) = \kappa_1$ and $f(q, E, c) = \kappa_2$ are either non-intersecting (when $\kappa_1 \neq \kappa_2$) or identical (when $\kappa_1 = \kappa_2$). In other words, at most one characteristic surface passes through a point of the CA domain.*

Proof. If Σ_1 and Σ_2 have a common point q, then $f(q, E, c) = \kappa_1 = \kappa_2$ and the property follows. □

Property 5. *If the moving Σ surface passes at the moment t_0 through a given surface Σ_0 and at a later time t_1 it intersects again the surface Σ_0, then at time t_1 it passes exactly through the surface Σ_0, moving in the same sense.*

Proof. In virtue of property 4, the Σ surface passes again exactly through its initial position Σ_0. On the other hand, by (14) we have $\mathrm{d}f = |E|\mathrm{d}t$, resulting that the Σ surface moves only in the sense which the function f increases, along a given C curve. As these values are fixed on the CA domain, it follows that the sense of motion of the Σ surface is the same, anytime when it passes through the fixed surface Σ_0, and the property follows. □

Property 6. *The velocity of an arbitrary point of the surface Σ which moves on a C trajectory is equal to v_w, given by equation (6).*

Proof. The coordinates of a point $P \in \Sigma \cap C$ are functions $q = q(s)$ of the parameter s, the distance along the C trajectory. The s values are assigned to each point of the curve C, and by convention, the sense of increasing of s is the same as the sense of increasing of f. The following relations are valid:

$$\frac{\mathrm{d}f}{\mathrm{d}s} = |E|\frac{\mathrm{d}t}{\mathrm{d}s} \tag{16}$$

$$\frac{\mathrm{d}f}{\mathrm{d}s} = \sqrt{\sum_j \left(\frac{\partial f}{\partial q_j}\right)^2} = \sqrt{2m(E-U)}. \tag{17}$$

The velocity of the point P follows from (6), (16) and (17) (recalling that we consider the case corresponding to the plus sign in (6)):

$$\frac{\mathrm{d}s}{\mathrm{d}t} = v_w \tag{18}$$

and the property is demonstrated. □

Since the constants of motion E and c are fixed, we will omit them from the notation and write $f(q) = f(q, E, c)$. Since f is determined up to an arbitrary constant, we choose the following initial condition:

$$f(q) = 0 \qquad \text{for} \quad t = 0. \tag{19}$$

We will see in the proof of property 8 that the function f is bounded.

When an arbitrary point $P \in \Sigma$, moves on the corresponding C trajectory in the sense of the increasing of f and s (in the sense of motion of a classical point), we say that the Σ surface moves in *forward direction*.

Property 7. *The Σ surface always moves in the forward direction.*

Proof. In virtue of equation (14) the surface moves in the sense of increasing of f. On the other hand, by convention, $\mathrm{d}f/\mathrm{d}s > 0$ and the property results. □

The analysis of the case corresponding to the minus sign in (6) and plus in (12) shows that there is another characteristic surface that moves in the opposite direction.

4. The periodicity of the system described by the wave equation

The next periodicity result is to be expected, since the behaviour of the system is described by the wave equation and a wave is always periodical.

Property 8. *The motion of the surface Σ is periodical, and the C trajectories are closed curves.*

Proof. Let P_0 be a fixed point on the C trajectory, corresponding to $f = 0$ and $t = 0$, and let P be a point moving along C together with the surface Σ. Taking into account (14) and integrating (17) between P_0 and P, we find that at any time t before the surface crosses the initial position, the point P is situated on the surface Σ having the equation

$$f(q) = |E|t = \int_{P_0}^{P} \sqrt{2m(E-U)}\,\mathrm{d}s. \tag{20}$$

If the surface Σ having equation (20) intersects again its initial position (having the equation $f(q) = 0$), then property 5 implies that the surface Σ passes exactly through the initial position, moving in the same sense. Letting τ_w be the minimal time after which the Σ surface intersects itself, it follows that the motion of the surface Σ is periodical of period τ_w, and that the C trajectories are closed. We will show that this is the case, proving thus the claim of the proposition.

Indeed, assume by contradiction that the moving surface Σ never intersects its initial position. In virtue of equation (20), the surface Σ passes through distinct positions in the CA domain, corresponding to different values of the time t. Since it moves with positive velocity (property 6), it follows that in a time T the surface Σ scans a volume of the CA domain, whose measure is given by $V(T) = \int_0^T S_\Sigma(t) v_w(t)\,\mathrm{d}t$, where $S_\Sigma(t)$ is the area of the Σ surface at time t. We will show briefly that the product $S_\Sigma v_w$ is bounded below along the trajectory C. It follows that the volume V is unbounded in time, contradicting the fact that the CA domain has finite volume for the system in discussion (because the total energy of the system is negative and the CA domain is bounded by the surface having the equation $E = U$). This contradiction would prove the claim.

To finish the proof, it remains to show that the product $S_\Sigma v_w$ is bounded below along the C trajectory. We limit our analysis to the case of atomic systems, the case of molecular systems being similar. Since a qualitative analysis suffices, we can use the approximation of atomic orbitals [10, 13, 14], which leads to an exact value of the total angular moment, and to a total energy within 2% of the experimental values. In virtue of this approximation we have $\Psi_0(q, E, c) = \psi_{01}(x_1, y_1, z_1, n_1, l_1, m_1)\,\psi_{02}(x_2, y_2, z_2, n_2, l_2, m_2)\ldots \psi_{0N}(x_N, y_N, z_N, n_N, l_N, m_N)$ where $\psi_{0a}(x_a, y_a, z_a, n_a, l_a, m_a)$ is the wavefunction of the atomic orbital of the electron a. This wavefunction depends only on the coordinates of the electron a, and of the quantum numbers corresponding to the state of the electron a (the principal quantum number n_a, the azimuthal quantum number l_a and the magnetic orbital quantum number m_a).

By this approximation, one can assume that the motion of the electron a takes place in the averaged field of the other electrons, and that the state of the electron a is represented by the wavefunction $\psi_{0a}(x_a, y_a, z_a, n_a, l_a, m_a)$, which obeys the equation

$$-\frac{\hbar^2}{2m}\Delta_a\psi_{0a} + [U_a(x_a, y_a, z_a) - E_a]\psi_{0a} = 0 \tag{21}$$

where E_a is the energy of the electron a and Δ_a is the Laplace operator in which the differentiation is made with respect to the coordinates of the electron a. The potential energy

$U_a(x_a, y_a, z_a)$ is the sum of a term due to the interaction between the electron a and the nucleus, and a term averaging the interaction of the electron a with the other electrons. The time-dependent wavefunction of the electron a satisfies the following equation:

$$-\mathrm{i}\hbar\frac{\partial\psi_a}{\partial t} - \frac{\hbar^2}{2m}\Delta_a\psi_a + U_a\psi_a = 0. \tag{22}$$

In virtue of the theory from section 2, this equation is equivalent to

$$\Delta_a\psi_a - \frac{1}{v_{wa}^2}\frac{\partial^2\psi_a}{\partial t^2} = 0 \tag{23}$$

where

$$v_{wa} = \pm|E_a|/\sqrt{2m(E_a - U_a)}. \tag{24}$$

The characteristic surface and its normal curve, corresponding to equation (23), are denoted, respectively by Σ_a and C_a.

By the approximation of the atomic orbitals, the states of the electrons and the motion along the C_a trajectories associated with these states, are separated. It follows that with good approximation, the projections of the Σ surface and of the C trajectory on the space of coordinates of the electron a, are, respectively, the Σ_a surface and the C_a trajectory. But the properties of the Σ_a surface and of the C_a trajectory can be exactly determined, since they are the same as those for hydrogenoid systems [1]. In particular, the size of the surface Σ_a is comparable to the size of the CA domain for the reduced system containing the electron a, and the velocity v_{wa} is bounded below (the C_a trajectory is elliptical for the reduced system).

It follows that the area of the Σ surface and the value v_w are bounded below by some constant depending on the size of the CA domain. This finishes the proof. □

From the proof of property 8, it follows that the function f is bounded. Indeed, we have shown that the surface Σ moves periodically, with a period τ_w, and from equation (20) it follows that $0 \leqslant f(q) < f_M$, where

$$f_M = |E| \cdot \tau_w. \tag{25}$$

The equation of the characteristic surface can now be written explicitly as

$$f(q) = |E|t - p|E|\tau_w \qquad \text{for} \quad p\tau_w \leqslant t < (p+1)\tau_w \tag{26}$$

which is seen to agree with equation (14).

We emphasize that the motion of the wave represented by the Schrödinger equation, as well as the motion of a classical point on the C trajectory, has only mathematical significance. The connection between the two motions can be described as follows.

A point P on the C trajectory moving together with the characteristic surface of the wave equation has velocity v_w. On the other hand, the velocity of a classical point moving on the same trajectory is given by the equation $E = U + mv^2/2$, whence

$$v = \pm\sqrt{2(E-U)/m}. \tag{27}$$

From equations (6) and (27) it follows that

$$vv_w = |E|/m. \tag{28}$$

It is worth noting that our approach is fundamentally different from the approaches based on the semiclassical approximation. While the semiclassical approaches are based on the correspondence between the quantum and classical solutions, for very high values of the principal quantum number (when the well-known semiclassical approximation holds), our approach does not use any approximation, and it is valid for all values of the principal quantum number.

5. An example

To illustrate the practical applications of our wave model, we apply the theory developed so far to the fundamental state of helium-like systems (He, Li^+, Be^{2+}, B^{3+} and so on). These systems are composed of a nucleus and two electrons, and $3N = 6$. The six constants of motion of the electrons a, in the approximation of the atomic orbitals, are the energy, orbital momentum and its projection on the z axis, and are denoted, respectively, by E_a, $p_{\theta a}$ and $p_{\theta z a}$, where $a = 1, 2$. The corresponding quantum numbers are, respectively, the principal, azimuthal and magnetic orbitals, denoted by n_a, l_a and m_a. For the fundamental state, the values l_a and m_a are zero.

To calculate the energetic eigenvalues for such systems, we proceed by finding the normal curves C_a corresponding to the constants of motion given above.

The equations of motion of the electrons, which are equivalent to the Hamilton–Jacobi equation [2, 20], in a Cartesian system of coordinates with the origin at the nucleus, are

$$-\frac{C_1 Z \bar{r}_a}{r_a^3} + \frac{C_1(\bar{r}_a - \bar{r}_b)}{|\bar{r}_a - \bar{r}_b|^3} = m\frac{\mathrm{d}^2\bar{r}_a}{\mathrm{d}t^2} \qquad \text{with} \quad a, b = 1, 2 \quad \text{and} \quad a \neq b \tag{29}$$

where Z is the order number of the nucleus, m is the electron mass, $\bar{r}_a$ is the position vector of the electron a and C_1 is a constant given by the relation

$$C_1 = \frac{e^2}{4\pi\varepsilon_0}. \tag{30}$$

Here e and ε_0 are the electron charge and the vacuum permittivity, respectively.

The system has the following solution [3]:

$$\bar{r}_1 = -\bar{r}_2 \tag{31}$$

$$\bar{r}_1 \cdot \bar{k} = \bar{r}_2 \cdot \bar{k} = 0 \tag{32}$$

$$\bar{v}_1 = -\bar{v}_2 \tag{33}$$

where $\bar{i}, \bar{j}, \bar{k}$ are the versors of the Cartesian system of coordinates, while $\bar{v}_1$ and $\bar{v}_2$ are the electron velocities. According to equation (32), the motion takes place in the xy plane.

The system (29) is solved using polar coordinates with centre at the nucleus. Let r_a, θ_a, for $a = 1, 2$, denote the polar coordinates of the two electrons. Elementary calculations lead to two symmetrical elliptic periodic trajectories (for $a = 1, 2$), which have the following parametric equations:

$$\frac{\mathrm{d}r_a}{\mathrm{d}t} = \pm\frac{1}{m r_a}\sqrt{-2E_a m {r_a}^2 + 2\left(Z - \frac{1}{4}\right) m C_1 r_a - {p_{\theta a}}^2} \tag{34}$$

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} = \frac{p_{\theta a}}{m {r_a}^2} \tag{35}$$

where the total energy and angular momentum of the electron a are given by

$$-E_a = -\frac{C_1\left(Z - \frac{1}{4}\right)}{r_a} + \frac{m {v_a}^2}{2} \tag{36}$$

$$p_{\theta a} = m {r_a}^2 \frac{\mathrm{d}\theta_a}{\mathrm{d}t} = \text{const.} \tag{37}$$

In these relations all the symbols denoting energies represent positive quantities and the signs are written explicitly.

Table 1. Theoretical and experimental normalized values of the total energy of some atoms and ions with the same structure [3].

Z	2	3	4	5	6	7	8
System	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
E/E_H	5.833	14.667	27.500	44.333	65.167	90.000	118.833
$E_{\exp}/E_H$	5.798	14.556	27.306	44.058	64.815	89.579	118.353

In recent papers [3, 6], we have shown that if the trajectory C_a corresponds to an energy equal to that resulting from the Schrödinger equation, then this trajectory satisfies the Bohr quantization relation. Applied to the present case, this leads to the relation

$$\oint_{C_a} m\bar{v}_a \, \mathrm{d}\bar{s}_a = n_a h \qquad \text{with} \quad n_a = 1, 2 \tag{38}$$

where h is the Planck constant, $\mathrm{d}\bar{s}_a$ is the infinitesimal length along the closed curve C_a.

Equation (38) leads to the following expression for the absolute value of the total energy:

$$E = 2E_a = \frac{2E_H}{n_a^2} Z^{*2} \tag{39}$$

where

$$Z^* = Z - \frac{1}{4} \tag{40}$$

and

$$E_H = \frac{mC_1^2}{2\hbar^2}. \tag{41}$$

The fundamental state corresponds to $n_1 = n_2 = 1$. The curves C_a which correspond to these states are characterized by negligible values of the angular momentum, and have eccentricity very close to unity. After correcting the expression for the energy to take into account the spin interaction energy calculated by Gryzinski [21], we obtain [3]

$$E = \frac{2E_H}{k_1 n_a^2} Z^{*2} \tag{42}$$

where k_1 is a correction coefficient which depends on Z^* and it is given by the relation

$$k_1 = \left(1 - \frac{1}{12Z^*}\right)^{-1}. \tag{43}$$

The experimental values of the energy, denoted by $E_{\exp}$, are obtained by summing the two ionization energies for helium, and by summing the last two ionization energies for the other systems.

The comparison between the theoretical and experimental energetic values for helium and for the ions with the same structure is presented in table 1. The experimental ionization energies are taken from [22].

The same calculation model is applied in previous papers [3–5, 9] to analyse many other systems, which differ in geometry and complexity. For example, we treat the atoms Li, Be, B, C, N, O, the ions with the same structure, and the molecules H_2, Li_2, Be_2, B_2, C_2, N_2, LiH, BeH, BH, CH. The agreement between the theoretical and experimental data (which are taken from well-known books) is of the same order of magnitude as in the present example.

We intend to apply this model to yet more complex systems in future papers.

6. Conclusions

We have presented an *ab initio* study of the wave properties of conservative bound systems, resulting from the equivalence between the Schrödinger and wave equations. We have proved that the characteristic surface of the wave equation has a periodic motion and its normal curves are closed. Moreover, these normal curves are identical to the periodic trajectories resulting from the Hamilton–Jacobi equation written for the same system. We conclude that to every conservative bounded physical system we can attach a periodical solution of the Hamilton–Jacobi equation that corresponds to the same constants of motion as those resulting from the Schrödinger equation. The theory presented in this paper can be used as a mathematical basis for a wave model for conservative bound systems, a simple example of which we gave in the previous section.

References

[1] Synge J L 1954 *Geometrical Mechanics and de Broglie Waves* (Cambridge: Cambridge University Press)
[2] Synge J L and Griffith B A 1959 *Principles of Mechanics* (New York: McGraw-Hill)
[3] Popa A 1998 *J. Phys. Soc. Japan* **67** 2645
[4] Popa A 1999 *J. Phys. Soc. Japan* **68** 763
[5] Popa A 1999 *J. Phys. Soc. Japan* **68** 2923
[6] Popa A 1996 *Rev. Roum. Math. Pures Appl.* **41** 109
[7] Popa A 1998 *Rev. Roum. Math. Pures Appl.* **43** 415
[8] Popa A 1999 *Rev. Roum. Math. Pures Appl.* **44** 119
[9] Popa A 2000 *Multiphoton and Light Driven Multielectron Processes in Organics: Materials Phenomena, Applications* ed F Kajzar (Dordrecht: Kluwer) p 526
[10] Slater J C 1960 *Quantum Theory of Atomic Structure* vol 1, 2 (New York: McGraw-Hill)
[11] Slater J C 1963 *Quantum Theory of Molecules and Solids* vol 1 (New York: McGraw-Hill)
[12] Messiah A 1965 *Quantum Mechanics* vol 1 (Amsterdam: North-Holland)
[13] Hartree D R 1957 *The Calculation of Atomic Structures* (New York: Wiley)
[14] Coulson C A 1961 *Valence* (London: Oxford University Press)
[15] Smirnov V I 1964 *A Course of Higher Mathematics* vol IV (New York: Pergamon)
[16] Courant R and Hilbert D 1962 *Methods of Mathematical Physics* vol II (New York: Wiley–Interscience)
[17] Hadamard J 1952 *Lectures on Cauchy's Problem in Linear Partial Differential Equations* (New York: Dover)
[18] Zauderer E 1983 *Partial Differential Equations of Applied Mathematics* (New York: Wiley)
[19] Vladimirov V S 1971 *Equations of Mathematical Physics* (New York: Dekker)
[20] Landau L and Lifschitz M 1980 *Mecanique* (Moscow: Mir)
[21] Gryzinski M 1973 *Phys. Lett.* A **44** 131
[22] *Handbook of Chemistry and Physics* 1972–1973 53rd edn (Cleveland, OH: CRC Press)