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Semiclassical quantisation of the hydrogen atom in crossed electric and magnetic fields

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Abstract. This method, based on the adiabatic invariance of semiclassical quantisation conditions (Solov'ev 1978), is used to calculate the energy levels of a three-dimensional, non-integrable system: a hydrogen atom in crossed electric and magnetic fields. The results are presented for a ground state and two excited states, for various ratios of field strengths and angles between the fields. The limitations of the method are discussed.

1. Introduction

Semiclassical quantisation of non-integrable systems is important both for fundamental and practical reasons. It contributes to the clarification of the not completely understood relations between the classical and quantum mechanics, and also appears to be competitive with the corresponding quantal calculations for large quantum numbers. In the last case the quantal treatments become very complicated and expensive, due to the large number of basis states involved in calculations.

In classical mechanics, non-integrable systems are described by non-linear equations (Hamilton–Jacobi equation or equations of motion), which are qualitatively more complicated than the corresponding linear equations of quantum mechanics, and so far, the problem of quantisation has not been rigorously formulated for them. Most practical semiclassical calculations of energy spectra of non-integrable systems performed up to now, used the Einstein–Brillouin–Keller (EBK) quantisation procedure (see, for example, Percival (1977) and references therein). The main points of this procedure are briefly summarised below.

An integrable classical system of s degrees of freedom can be characterised by a set of fundamental frequencies $\{\omega_j, j = 1, 2, \ldots, s\}$, and a set of canonically conjugate, angle (linear in time) and action variables:

$$\theta_j = \omega_j t + \delta_j$$
$$I_j = \frac{1}{2\pi} \oint_{C_j} \sum_{k=1}^{s} p_k \, \mathrm{d}q_k \qquad j = 1, 2, \ldots, s \tag{1}$$

where δ_j are initial phases, (p_k, q_k) are canonically conjugate momenta and coordinates and C_j are closed paths in phase space, defined by: $0 \leqslant \theta_j < 2\pi$, $\theta_i = \text{constant}$ for $i \neq j$. Action variables I_j are single-valued integrals of motion. By fixing them one defines an s-dimensional hypersurface in phase space, called the invariant toroid. Any path

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C_j from equation (1) can be deformed on the invariant toroid, leaving unchanged the action integral I_j. According to EBK, the stationary quantal states correspond to those toroids whose action integrals, taken along the topologically independent paths, are quantised:

$$I_j = \left(n_j + \frac{\alpha_j}{4}\right)\hbar \qquad j = 1, 2, \ldots, s \tag{2}$$

where n_j are integers (for vibrations $n_j = 0, 1, 2, \ldots$, whilst for rotations $n_j = 0, \pm 1, \pm 2, \ldots$) and α_j are the Maslov indices, which depend on certain topological characteristics of the paths C_j; $\alpha_j = 0$ for the paths describing rotations and $\alpha_j = 2$ for the paths describing vibrations. The quantised energies are found by expressing the classical Hamiltonian function of the system in terms of action variables i.e. quantum numbers.

If two or more fundamental frequencies are commensurable, the classical system is said to be degenerate. In this case, the number of single-valued integrals of motion is larger than the number of degrees of freedom, and the set of quantisation conditions (2) cannot be chosen in a unique way. In fact, the dimensionality of invariant toroids (the number of topologically independent paths C_j in phase space), and hence the number of EBK quantisation conditions, is reduced. The energy of a degenerate system depends only on a linear combination (with integer coefficients) of action variables I_j.

When applying the EBK quantisation conditions (2) to non-integrable systems (see, e.g. Percival 1977), the essential hypothesis is the existence of the invariant toroids. This has been proved rigorously only for the systems sufficiently close to integrable systems (the Kolmogorov–Arnol'd–Moser theorem). The hypothesis of the existence of invariant toroids is an alternative to the ergodic hypothesis. This last hypothesis states that the trajectory in phase space, independently of initial conditions, fills up in time the whole isoenergetic hypersurface; i.e. the state is unambiguously defined by the energy and the problem of quantisation cannot be formulated.

Another method of semiclassical quantisation of non-integrable systems, proposed by one of the authors (Solov'ev 1978), relies on the adiabatic principle. This states that the action variables I_j, from equation (1), are adiabatic invariants, i.e. they remain unchanged when one or a few parameters in the classical Hamiltonian function are slowly varying (see, for example, Landau and Lifshitz 1976). The rigorous proof of the adiabatic principle exists only for one-dimensional systems (see e.g. Arnol'd 1962, 1963, 1979) although some plausible arguments can be found for integrable systems (see e.g. Landau and Lifshitz 1976). The method under consideration assumes that the principle also holds for non-integrable systems. As a supporting argument, one can use the fact that if the opposite were true, the correspondence principle, applied to the adiabatic theorem of quantum mechanics, would not be fulfilled. As a consequence of the adiabatic principle EBK quantisation conditions (2) remain unchanged, when an interaction in the system is slowly varying in time. This fact is used for semiclassical quantisation of a system described by the Hamiltonian function H in the following way. One starts by choosing the Hamiltonian function H_0 (an integrable one), for which the classical trajectories, obeying the EBK quantisation conditions, are known. After that, the interaction $V = H - H_0$ is being adiabatically switched, and, by solving the classical equations numerically, the evolution of quantised trajectories in time is investigated. At the moment when the switching of the interaction is complete, the quantised trajectories and energies, corresponding to the Hamiltonian function

H, are obtained. The smaller the switching rate used in calculations, the more exactly the quantisation conditions are fulfilled. The method has been used successfully for semiclassical quantisation of two-dimensional non-integrable systems (Solov'ev 1978).

The aim of the present paper is to apply the above described method to the semiclassical quantisation of a three-dimensional non-integrable system, i.e. to the non-relativistic motion of an electron in the Coulomb field of a proton (with infinite mass) and in crossed electric and magnetic fields. Atomic units ($m_e = e = \hbar = 1$) are used throughout the work.

2. The choice of the 'proper' initial trajectories

We choose as H_0 the unperturbed Hamiltonian function of the hydrogen atom. Due to the high dynamic symmetry of the Coulomb interaction, we deal here with the degenerate system. The classical, three-dimensional bound motion of the electron is characterised by one fundamental frequency:

$$\omega_0 = (-2\mathscr{E}_0)^{3/2} \tag{3}$$

where $\mathscr{E}_0$ is the electron energy. All trajectories in configuration space and all invariant toroids in phase space are closed lines (ellipses). We can write down just one EBK quantisation condition (2), fixing the allowed electron energies:

$$\mathscr{E}_0 = -\frac{1}{2n^2} \qquad n = 1, 2, \ldots . \tag{4}$$

When an external perturbation is introduced, the degeneracy is removed and the trajectories fill up a certain domain in the configuration space. In the phase space the invariant toroids arise and additional EBK quantisation conditions can be formulated, depending on the type (symmetry properties, etc) of the perturbation. For example, in the case of a spherically symmetric perturbation, as well as the energy, the electron orbital angular momentum is also quantised. So, if the spherically symmetric perturbation is to be adiabatically switched on, the 'proper' initial trajectories would be those, with quantised orbital angular momentum, because only they would evolve into the quantised trajectories of the perturbed system (see also Solov'ev 1978).

To formulate the additional quantisation conditions for the system under consideration, we recall the semiclassical perturbation theory of a hydrogen atom in crossed electric and magnetic fields (see, for example, Born 1960). The unperturbed elliptical trajectory of the electron is defined by the principal quantum number n (or energy $\mathscr{E}_0$, equation (4)), the orbital angular momentum $\boldsymbol{L}$ and the Runge–Lenz vector

$$\boldsymbol{a} = n(\boldsymbol{v} \times \boldsymbol{L} - \boldsymbol{r}/r) \tag{5}$$

where $\boldsymbol{r}$ is the position and $\boldsymbol{v}$ the velocity of the electron. In the presence of small electric $\boldsymbol{E}$ and magnetic $\boldsymbol{B}$ fields, the slow change of the unperturbed trajectory can be described as independent precessions of the vectors

$$\boldsymbol{I}_{1,2} = \tfrac{1}{2}(\boldsymbol{L} \pm \boldsymbol{a}) \tag{6}$$

with the angular frequencies

$$\boldsymbol{\omega}_{1,2} = \tfrac{1}{2}(\boldsymbol{B}/c \mp 3n\boldsymbol{E}) \tag{7}$$

respectively (c is the velocity of light), with the projections of $\boldsymbol{I}_i$ onto the $\hat{\boldsymbol{\omega}}_i = \boldsymbol{\omega}_i/\omega_i$ being quantised according to

$$\boldsymbol{I}_i \cdot \hat{\boldsymbol{\omega}}_i = k_i \qquad i = 1, 2$$
$$k_i = -(n-1)/2, -(n-1)/2+1, \ldots, (n-1)/2. \tag{8}$$

The corresponding energy levels are given by

$$\mathscr{E}_{nk_1k_2} = -\frac{1}{2n^2} + k_1\omega_1 + k_2\omega_2 \tag{9}$$

so that the degeneracy is completely removed. We note that result (9) and operator analogues of (8) were rederived quantum mechanically (Demkov *et al* 1970), using the O(4) symmetry group of the hydrogen atom.

In our calculations we shall adiabatically switch-on the fields according to the law:

$$\boldsymbol{E} = \lambda t \boldsymbol{E}_0 \qquad \boldsymbol{B} = \lambda t \boldsymbol{B}_0 \tag{10}$$

where λ is the switching rate, and $\boldsymbol{E}_0$ and $\boldsymbol{B}_0$ are given vectors. In this way, the angle between the fields ($\theta = \measuredangle(\boldsymbol{E}, \boldsymbol{B}) = \measuredangle(\boldsymbol{E}_0, \boldsymbol{B}_0)$), the ratio of their magnitudes ($E/B = E_0/B_0$), and consequently the unit vectors $\hat{\boldsymbol{\omega}}_{1,2}$, are time independent. Now, we can define the 'proper' initial trajectories as those, obeying (apart from the energy quantisation condition (4)) additional conditions (8).

3. Numerical solution of the classical equations

In Descartes coordinate system, centred on the proton, we define in the yz plane the vectors

$$\boldsymbol{E}_0 = E_0\{0, 0, 1\} \qquad \boldsymbol{B}_0 = B_0\{0, \sin\theta, \cos\theta\} \tag{11}$$

and introduce the vector potential ($\boldsymbol{B} = \operatorname{rot} \boldsymbol{A}$)

$$\boldsymbol{A} = -\lambda t B_0\{y\cos\theta, 0, x\sin\theta\}. \tag{12}$$

The classical equations for the electron are

$$\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} + \frac{\boldsymbol{r}}{r^3} = -\boldsymbol{E} - \frac{1}{c}(\boldsymbol{v}\times\boldsymbol{B}) + \frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t} \tag{13}$$

with $\boldsymbol{E}$ and $\boldsymbol{B}$ given by (10) and (11)). The last term on the RHS of equation (13) is the additional force arising as a consequence of the time dependence of the magnetic field. Although this force, being proportional to λ, disappears in the adiabatic limit ($\lambda \to 0$), it cannot be neglected. For example, it ensures the adiabatic invariance in the case of a pure magnetic field ($\boldsymbol{E} = 0$). Obviously, if it were neglected in the last case, the electron energy would be conserved exactly, independently of the time variation of the magnetic field.

The initial conditions associated with (13) were chosen in accordance with the preceeding section. Without losing generality, we can assume that the vectors $\boldsymbol{I}_{1,2}$ (and consequently $\boldsymbol{L}$ and $\boldsymbol{a}$) are located in the yz plane at $t = 0$. With the help of relations $\boldsymbol{a} \cdot \boldsymbol{L} = 0$ and $a^2 + L^2 = n^2$, equations (8) can be solved for $\boldsymbol{a}$ and $\boldsymbol{L}$, defining the proper initial trajectory. The initial position and velocity of the electron can be arbitrarily taken on that trajectory (see appendix).

Prior to numerical integration, the classical equations (13) were regularised following the Kustanheimo–Steifel regularisation procedure, borrowed from the celestial mechanics (for details and further references see Stiefel and Schiefele 1971). Besides the overall improvement of the numerical accuracy, this procedure eliminates the Coulombic singularity from the equations of motion. This is advantageous for our application, since the domain in the configuration space spanned by the electron trajectory could, eventually, contain the centre of Coulomb force.

In the course of numerical integration, at each step, the classical energy of the electron is calculated:

$$\mathscr{E} = \frac{v^2}{2} - \frac{1}{r} - \boldsymbol{E} \cdot \boldsymbol{r}. \tag{14}$$

According to the basic (adiabatic) hypothesis adopted in our method, the quantity (14) represents the quantised energy of the system at corresponding, instantaneous values of electric and magnetic fields.

Figure 1 shows the ground-state (small-field quantum numbers: $n = 1$, $k_1 = 0$, $k_2 = 0$) energy shift as a function of the field strengths (with constant parameters $B/cE = 1$, $\cos\theta = 0.5$), for two different values of switching rate. The energy exhibits the complicated oscillations, caused by the change of the interaction in one part of the classically accessible region, while the electron is moving in another one. Roughly speaking, the amplitude of these oscillations is proportional to the switching rate λ, the frequency is of the order of magnitude of the characteristic frequencies of the electron motion and the phase depends on the initial conditions. These oscillations have no relation to the adiabatic principle, since the latter contains the statements

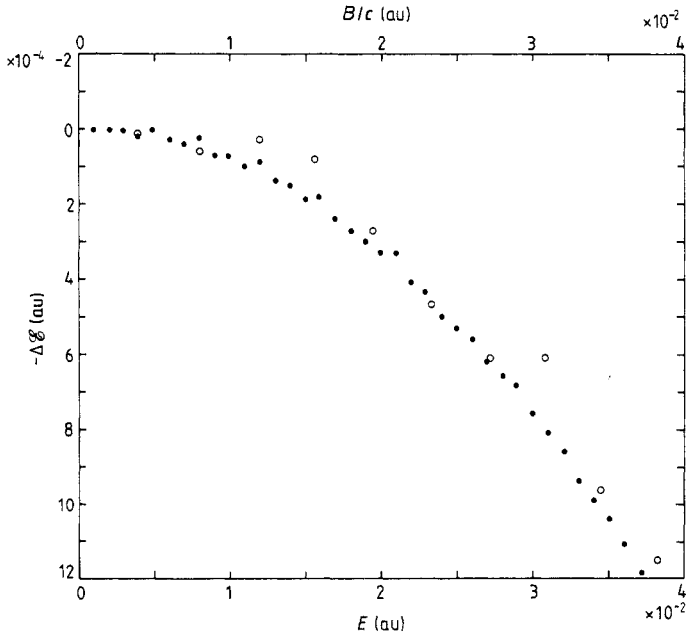

Figure 1. Ground-state energy level shift as a function of field strength with constant parameters $B/cE = 1$, $\cos\theta = 0.5$ and for two values of switching rate: $\lambda = 1 \times 10^{-4}$ au (open circles), $\lambda = 2.5 \times 10^{-5}$ au (dots). $\{n, k_1, k_2\} = \{1, 0, 0\}$.

concerning the quantities averaged over the characteristic periods of electron motion. By decreasing λ the amplitude of the oscillations is also decreased, enabling us to achieve the desired numerical accuracy.

4. Results

In order to explore the limitations of the method, the calculations have been carried out, up to the unrealistically strong fields where the ionisation occurs (note that: $B(\mathrm{T}) = 2.35 \times 10^5 B/c(\mathrm{au})$ and $E(\mathrm{V\,m^{-1}}) = 5.142 \times 10^{11} E(\mathrm{au})$). If a highly excited state were treated this might not be the case, since the characteristic electric field scales with the principal quantum number as n^{-4} and magnetic field as n^{-3}. Also, a graphical presentation of results is preferred, since the large number of parameters are involved in calculations: quantum numbers, magnitudes of both magnetic and electric fields, as well as the angle between them.

4.1. Ground state

The small-field quantum numbers which define the ground state are $\{n, k_1 k_2\} = \{1, 0, 0\}$. As seen from (9), the first-order perturbation theory shift is zero, and we expect the effects of quadratic and higher-order terms to appear in this case. Figure 2 shows the energy levels (full curves) of the ground state as a function of field strengths, for different combinations of constant parameters $\alpha = B/cE$ and $\cos\theta$. As a limit, quantum-mechanical results (chain curves) for the ground-state energies of a hydrogen atom in a magnetic field only ($E = 0$) and in an electric field only ($B = 0$) are shown. The curve labelled by $E = 0$ is the result of Cabib *et al* (1972), obtained by diagonalising the energy matrix in an extensive basis of hydrogenic wavefunctions. The curve labelled by $B = 0$ is a quantal fourth-order perturbation theory result (see, for example, Silverstone 1978). Note that, in figure 2, the lower (electric field) scale is common to all curves (except to $E = 0$) whereas the upper (magnetic field) scale corresponds only to curves labelled by $E = 0$ and $\alpha = 9$. The arrows in figure 2 indicate the points where the classical overbarrier ionisation occurs (the electron escapes to infinity accelerated by the electric field).

In a pure electric field case ($B = 0$) the level is shifted downwards and the critical field for ionisation is related to electron binding energy through the relation $2E_{\mathrm{cr}} = \mathscr{E}^2$ (see, for example, Bethe and Saltpeter 1957). The effect of an applied magnetic field ($\alpha = 1$) is to shift the level upwards and to move the ionisation threshold through the larger electric fields. In the case labelled by $\alpha = 3$, the influences of electric and magnetic fields are almost compensated and the level is slightly shifted upwards. When relatively stronger magnetic fields are applied (the curves labelled by $\alpha = 9$) the level is shifted upwards strongly and the situation is more similar to the pure magnetic field case ($E = 0$).

The structures, shown by broken curves (especially in the cases labelled by $\alpha = 9$, $\cos\theta = 0.1$ and $\cos\theta = 0.5$), indicate the violation of the adiabatic evolution of the system. Most probably, this is caused by the approach of the quantised energy level to the top of certain complicated three-dimensional barriers. This hypothesis is supported by the fact that such a non-adiabatic behaviour was not found in the case $\alpha = 9$, $\cos\theta = 0.9$. By decreasing the switching rate λ this structure could not be eliminated. Also, in all cases, similar behaviour (but less pronounced) has been found near the

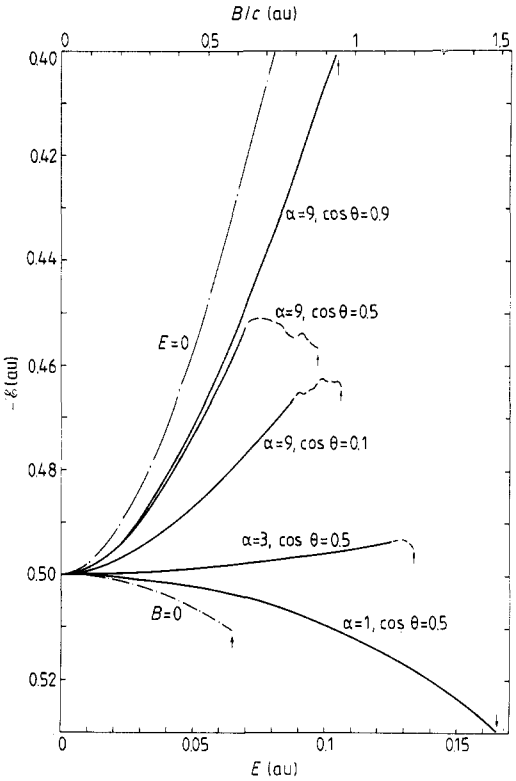

Figure 2. Ground-state energy levels (full curves) as functions of field strength for various combinations of parameters $\alpha = B/cE$ and $\cos\theta$. In all cases, the switching rate used in calculations was $\lambda = 2.5 \times 10^{-5}$ au. Chain curves are the quantal results for the cases of pure electric (Silverstone 1978) and magnetic (Cabib *et al* 1972) fields. Broken curves demonstrate the non-adiabatic evolutions of the system, and the arrows indicate ionisation. The electric field scale is common to all curves (except to $E = 0$), while the magnetic field scale corresponds to curves labelled by $E = 0$ and $\alpha = 9$. $\{n, k_1, k_2\} = \{1, 0, 0\}$.

ionisation thresholds. At the end, we note that the overall energy level dependance on the mutual orientation of the fields is less pronounced in the cases of smaller ratios ($\alpha = 1$ and $\alpha = 3$, not shown in figure 2) than in the $\alpha = 9$ case.

4.2. Excited states

The same method has been applied in calculating excited-state energy levels. Figure 3 shows the results (full curves) for the states defined by the small-field quantum numbers $\{n_1, k_1, k_2\} = \{3, -1, -1\}$ (the levels shifted downwards) and $\{n, k_1, k_2\} = \{3, 1, 1\}$ (the levels shifted upwards). The angle between the fields has been kept constant ($\cos\theta = 0.5$) and the results are presented for two different ratios of field strengths: $\alpha = 9$ and $\alpha = 27$. Again, the electric field scale is common to all curves and the magnetic field scale refers only to the curves labelled by $\alpha = 27$.

Unlike the ground-state case, here the linear shift, given by (9) (broken lines), dominates in the limit of small fields. The state $\{3, -1, -1\}$ is bound stronger and the ionisation limit was not reached in the range of fields shown in figure 3. For the $\{3, 1, 1\}$ state the non-adiabatic behaviour was found only very close to the ionisation

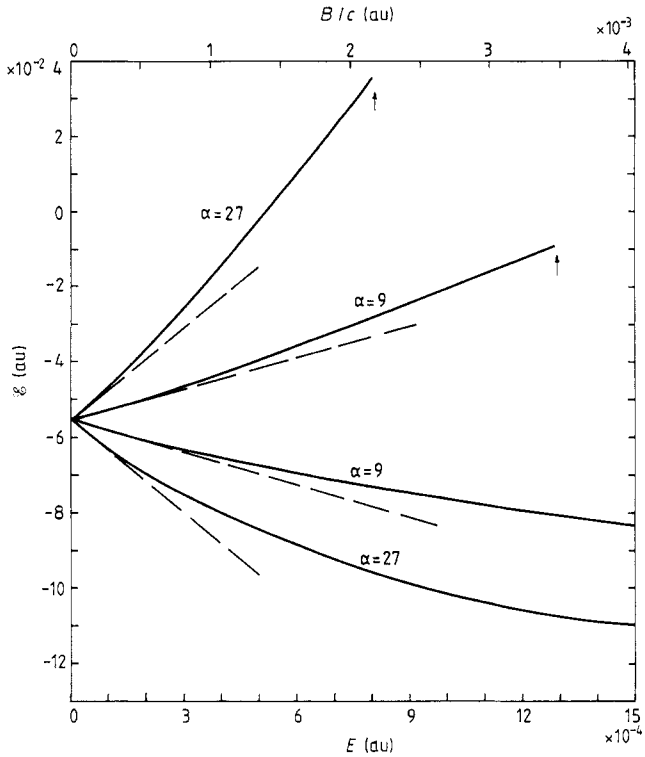

Figure 3. Energy levels (full curves) of excited states, $\{n, k_1, k_2\} = \{3, -1, -1\}$ (the levels shifted downwards) and $\{n, k_1, k_2\} = \{3, 1, 1\}$ (the levels shifted upwards), as functions of field strength with constant parameters $\alpha = B/cE = 9$, 27 and $\cos\theta = 0.5$. The switching rate of the fields was $\lambda = 5 \times 10^{-5}$ au. Broken lines are the first-order perturbation theory results (9), and the arrows indicate ionisation. Electric field scale is common to all curves, while the magnetic field scale corresponds to curves labelled by $\alpha = 27$.

limits. Again, the overall dependance on the mutual orientations of the fields (not shown in figure) was found to be more pronounced in the cases with larger values of α.

5. Concluding remarks

In the present work the method, based on the adiabatic invariance of EBK quantisation conditions, has been applied to the semiclassical quantisation of a three-dimensional non-integrable system. A sufficient condition for the fulfilment of the adiabatic invariance seems to be the continuous deformation of the invariant toroids with a slow change of interaction. This demand is related to the limitations of the usual (so called 'primitive') EBK quantisation, which assumes that the motion takes place in a single, simply connected classically allowed region. Even for one-dimensional systems the adiabatic invariance is broken when the level approaches the top of a potential barrier (the fundamental frequency tends to zero). In that case the 'primitive' EBK quantisation also breaks down and one must resort to various uniformisation procedures (see, for example, Strand and Reinhardt 1979, and references therein).

Nevertheless the method employed in this work possesses certain advantages in respect to the commonly used approaches for semiclassical quantisation of non-integrable systems. It is free of such problems like searching for the initial conditions which correspond to quantised trajectories, or finding the caustics of the classical system (see, for example, Noid and Marcus 1977). In addition, by using the present method, one gets all intermediate results, i.e. the quantised energies corresponding to the classical systems with not completely switched interaction.

As far as a hydrogen atom in external fields in concerned, we make the following additional remarks. The cases in which the degeneracy is not completely removed within the first-order perturbation theory cannot be treated by using the proposed procedure of semiclassical quantisation. For example, one has $\omega_1 = \omega_2$ if and only if $\boldsymbol{E} \cdot \boldsymbol{B} = 0$, i.e. if the fields are orthogonal or one of the fields is zero ($\boldsymbol{E} = 0$ implies $\boldsymbol{\omega}_1 = \boldsymbol{\omega}_2 = \boldsymbol{B}/2c$, and $\boldsymbol{B} = 0$ implies $-\boldsymbol{\omega}_1 = \boldsymbol{\omega}_2 = 3n\boldsymbol{E}/2$). Also, if the fields are parallel (or antiparallel) and the ratio $B/cE = 3n$, one of the fundamental frequencies $\omega_{1,2}$ is zero and we deal with the degenerate system again (see also, Demkov *et al* 1970) In all these cases, to make the choice of the 'proper' initial trajectories, one needs the results of the higher-order semiclassical perturbation theory, where the degeneracy is completely removed.

Appendix

We assume that at $t = 0$ vectors $\boldsymbol{L}$ and $\boldsymbol{a}$ lie in the yz plane. With given unit vectors $\hat{\boldsymbol{\omega}}_1 = \{0, \cos\beta_i, \sin\beta_i\}$, $i = 1, 2$ from (8) and $\boldsymbol{a} \cdot \boldsymbol{L} = 0$, $a^2 + L^2 = n^2$ one readily finds

$$\begin{aligned} a_x &= 0 & L_x &= 0 \\ a_y &= \tfrac{1}{2}n\,(\cos\phi_1 - \cos\phi_2) & L_y &= \tfrac{1}{2}n\,(\cos\phi_1 + \cos\phi_2) \\ a_z &= \tfrac{1}{2}n\,(\sin\phi_1 - \sin\phi_2) & L_z &= \tfrac{1}{2}n\,(\sin\phi_1 + \sin\phi_2) \end{aligned} \tag{A.1}$$

where

$$\begin{aligned} &\sin\phi_i = [1-(2k_i/n)^2]^{1/2}\cos\beta_i + (2k_i/n)\sin\beta_i \\ &\cos\phi_i = (2k_i/n)\cos\beta_i - [1-(2k_i/n)^2]^{1/2}\sin\beta_i \\ &i = 1, 2. \end{aligned} \tag{A.2}$$

Initial position and velocity of the electron can be taken arbitrarily on the trajectory defined by (A.1). A simple choice is to take that at $t = 0$ the electron is located at the aphelion, which is at the distance

$$r_A = n^2(1 + a/n) \tag{A.3}$$

from the origin. In that case it is easy to find the initial conditions associated with equations (14)

$$\begin{aligned} x &= 0 & \dot{x} &= L/r_A \\ y &= -r_A a_y/a & \dot{y} &= 0 \\ z &= -r_A a_z/a & \dot{z} &= 0. \end{aligned} \tag{A.4}$$

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