Rotation of a Rigid Diatomic Dipole Molecule in a Homogeneous Electric Field I. Schrodinger Equation. Quantization Conditions according to Phase-Integral Method

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Rotation of a rigid diatomic dipole molecule in a homogeneous electric field

I. Schrödinger equation. Quantization conditions according to phase-integral method

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After a brief historical discussion of the energy quantization according to quantum mechanics of the rigid diatomic dipole molecule in a static electric field, the Schrödinger equation for that system is recalled. Previous attempts to obtain the energy levels clearly indicate that there is a need for a reliable method yielding very accurate eigenvalues for all values of the electric field strength. This is accomplished with the aid of new quantization conditions obtained by means of a phase-integral method involving a general phase-integral approximation of arbitrary order generated from an unspecified base function, which is chosen in two different ways such that, when the electric field strength is equal to zero, simple limiting forms of the quantization conditions give the exact values of the energy levels. The two choices of the base function are expected to be appropriate in the cases when the absolute value of the magnetic quantum number m is sufficiently large and sufficiently small respectively. For every value of m at least one of the two base functions should be useful.

1. Introduction

Information concerning the Stark effect for a rigid diatomic dipole molecule (also called linear rigid polar rotator or dumb-bell model of a polar molecule) is necessary for the analysis of spectroscopic data and results from molecular beam resonance experiments. In all cases where a thorough analysis of a complicated experimental situation is necessary, analytical expressions for physical quantities such as energy levels and matrix elements of electric dipole transitions have considerable advantages over numerical solutions. Furthermore, in the calculation of numerical solutions there appear sometimes serious numerical difficulties. The first quantal treatments of the problem concerning the rotation of a rigid diatomic dipole molecule in a homogeneous electric field were given very soon after the birth of quantum mechanics. It may be noted that the problem is identical with that of the spherical pendulum in quantum mechanics.

In the following review of the *quantal* treatments we do not consider papers concerning the two-dimensional rigid rotator (i.e. the simple rotator in a plane), the symmetric top model of a rigid rotator, the asymmetric rigid rotator or the non-rigid rotator, except for treatments from which valuable conclusions concerning the linear rigid polar molecule can be drawn.

The energy levels of a linear rigid polar molecule in the absence of fields, i.e. a free

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linear rigid rotator, were determined by Schrödinger (1926, pp. 520–522) according to his wave mechanics. Somewhat later Dennison (1926) and Kronig (1926*a*) applied Heisenberg's matrix mechanics to the same physical system; see also Manneback (1927, p. 76) and Mensing (1926). The Schrödinger equation of a free linear rigid rotator is the same as the differential equation of the associated Legendre functions. It was shown by Bechert (1927) that one can determine the eigenvalues of this differential equation without integrating it. Treatments of the field-free case can also be found in standard treatises on spherical harmonics and in texts on quantum mechanics; see, for instance, Sommerfeld (1929, pp. 10–14), Courant & Hilbert (1931, pp. 280–282) and Pauling & Wilson (1935, pp. 118–121, 271). It should, however, be mentioned that the treatments often side-step the task of showing that the energy levels and wavefunctions obtained are the only characteristic values and functions. Therefore, and since a full proof of the formula for the energy levels in the field-free case is seldom found in the literature, such a proof, essentially along the lines sketched in Courant & Hilbert (1931, pp. 280–282), will be given in the following paper (this Volume), designated II. This proof is valid for an arbitrary real (not necessarily integer) value of the magnetic quantum number; this fact is of importance for the validity of equations (5.33) and (5.34) in the present paper for arbitrary real values of M. The determination of the energy levels of a free linear rigid rotator can be reduced to the problem of determining the energy levels of a particle moving in a one-dimensional potential proportional to $\cot^2 \vartheta$, the wavefunction being equal to zero for $\vartheta = 0$ and $\vartheta = \pi$. This problem can be solved by means of special functions; see Flügge & Marschall (1952, pp. 64–67) and ter Haar (1964, pp. 2, 72–74). The exact values of these energy levels can also be obtained by means of the phase-integral method, if the base function is chosen conveniently (see Fröman & Fröman 1978).

For sufficiently weak fields one can use conventional perturbation theory (with the perturbation proportional to the electric field strength parameter) for calculating the energy levels. However, such calculations of Stark levels are wholly inadequate at higher field strengths. Furthermore, when high precision is required, the levels thus obtained may be significantly in error even at weak fields. The first-order perturbation theory gives no correction to the unperturbed energy levels. The second-order correction was calculated by Manneback (1926); see also Mensing & Pauli (1926) and Kronig (1926*b*). The perturbation theory calculations were extended by Brouwer (1930) up to the fourth order for $j > 0$ and up to the sixth order for $j = 0$, where j is our notation for the rotational quantum number. Hughes (1949) reported (as a personal communication from Professor J. W. Trischka of Syracuse University) a minor error in the work by Brouwer (1930) and also found that for $j = 1$ the fourth-order perturbation theory energy levels were not sufficiently accurate for his purpose. Therefore Hughes added (for $j = 1$) sixth-order terms which he obtained empirically by fitting to numerically calculated energies for $j = 1$. Of the above-mentioned perturbation theory results for the Stark energy levels of a rigid diatomic dipole molecule Kusch & Hughes (1959, p. 139) quoted the formulas for the levels with the rotational quantum number j equal to 0, 1 and 2. The general expression for the fourth-order result according to Rayleigh–Schrödinger perturbation theory, which was first given by Brouwer (1930), can also be obtained as a particular case of more general formulas given by Scharpen *et al.* (1967) in their appendix. Obviously unaware of the results in the papers by Brouwer (1930) and Scharpen *et al.* (1967), Wijnberg (1974) gave anew the fourth-order result. It is possible, at least in principle, to obtain still higher-order contributions to the perturbation series by means of standard perturbation calculations, but the complexity of the calculations increases rapidly. Propin (1978*b*) gave recurrence relations which enable in principle all coefficients to be found in the perturbation series for the energy of a rigid diatomic polar molecule in a uniform electric field. He found the dependence of the coefficients in the perturbation series on the quantum numbers up to terms of the sixth order and made computer calculations up to terms of the 42nd order. The calculation of the convergence radius of the perturbation series for weak fields was also considered by Propin (1978*b*) and in a different way by Fernández & Castro (1985). The above-mentioned results for the zero-, second-, fourth- and sixth-order coefficients of the perturbation series will be given in convenient form in II.

Tomutza & Mizushima (1972) applied their own form of perturbation theory to the Stark effect of a linear rigid polar rotator, but Propin (1978*b*) pointed out several errors in their results.

For sufficiently strong fields one can, by a simple transformation (which can be chosen in somewhat different ways) of the Schrödinger equation, reformulate the problem into a perturbation problem, for which the unperturbed problem is that of a two-dimensional isotropic harmonic oscillator, and the perturbation is a series in inverse powers of the square root of the field strength parameter. The energy levels for strong fields can then be expressed as a series in which the ratio of an arbitrary term to the preceding term is inversely proportional to the square root of the electric field strength parameter. The Stark effect of a linear rigid electric dipole molecule in so strong fields has been considered by Brouwer (1930), Peter & Strandberg (1957), Gaponov *et al.* (1965), von Meyenn (1970, p. 156), Propin (1978*a*), Cohen & Feldmann (1982) and Cohen *et al.* (1984). The strong-field case is considered in some detail in II.

In the region of intermediate field strengths conventional perturbation theory calculations of the Stark effect are more or less inadequate. However, intermediate fields can occur in experiments, and the treatment of this case is therefore important. Lennard–Jones (1930) treated the energy eigenvalue problem for a rotating linear rigid polar molecule in a homogeneous electric field of arbitrary strength by expressing the solution of the perturbed differential equation as a series of unperturbed eigenfunctions and requiring that the coefficients in this series are not all equal to zero. In this way one obtains a secular equation of infinite order which is to be solved with respect to the energy. For a small perturbation this is accomplished if one retains only certain elements in the determinant of the secular equation and solves the resulting equation approximately. For a linear rigid polar molecule in a weak uniform electric field Lennard-Jones (1930) thus obtained the second-order correction of perturbation theory to the unperturbed energy from a three-by-three-determinant. When the perturbation is not necessarily small, one obtained from the secular equation of infinite order for the energy eigenvalues an implicit equation containing a continued fraction, as Lennard-Jones (1930) demonstrated for the ground state of a linear rigid polar molecule in a uniform electric field. Considering the exact solution of the Schrödinger equation for a linear rigid polar molecule rotating in a uniform electric field of arbitrary strength, one can also determine the energy levels from a three-term recursion formula, which yields the same continued fraction method for the determination of the energy eigenvalues. The result of this treatment, which was worked out by W. E. Lamb (unpublished work) for an arbitrary state of the rotating dipole, is quoted by Hughes (1947, p. 620) and by Kusch & Hughes (1959, pp. 440–441) who, obviously unaware of the paper by Lennard-Jones (1930), attributed the continued fraction method to Lamb. Hughes (1947) used this method for obtaining a short table of energy level values and a corresponding figure for j equal to 0, 1 and 2. Kusch & Hughes (1959, p. 141) published a large table (although with fewer digits), including also values of j equal to 3 and 4 and higher field strengths. Shirley (1963) used the method of continued fractions for calculating the energy levels of rigid symmetric-top molecules, but the paper contains also numerical results concerning the rigid diatomic dipole molecule. Thomson & Dalby (1968) solved the continued fraction equation numerically by a computer and fitted to the results polynomials containing even powers (up to the tenth power) of the field strength parameter by a least-mean-square procedure. Thus they obtained explicit formulas useful for a certain range of the field strength parameter. The case of an electric field of arbitrary strength was also treated by von Meyenn (1970), who calculated the energy levels by solving numerically the secular equation. Cohen *et al.* (1984) used rational fraction representations of the weak-field series, of the strong-field series, and of both series simultaneously; these representations are very accurate over limited ranges of the field strength. Cohen *et al.* (1984) also presented a scaled variational perturbation theory which yields high accuracy over the entire range.

In connection with the treatment of the strong-field case, Gaponov *et al.* (1965) also gave a semi-classical quantization condition, but for the rest, to our knowledge, such treatments seem to be lacking for a rigid diatomic dipole molecule rotating in an electric field.

In this paper (called I) we recall in §2 the Schrödinger equation of a rotating rigid diatomic dipole molecule in a homogeneous static electric field. For any value of the field strength, this problem can be treated by means of the phase-integral approximation of arbitrary order devised in successively generalized form by Fröman (1966, 1970) and by Fröman & Fröman (1974*a*, *b*, 1991), and summarized here in §3. The main purpose of this series of papers, I–IV (this Volume), is to use quantization conditions based on this phase-integral approximation for treating anew the problem of a rigid electric dipole in a homogeneous static electric field. In §4 we use new phase-integral formulas, which have been derived by Fröman *et al.* (1994) on the basis of comparison equation technique with the regular Coulomb wavefunction as comparison equation solution, to derive new quantization conditions for the electric dipole in a homogeneous electric field. The derivation of these quantization conditions is the main purpose of this paper. In §5 we derive an alternative quantization condition based on the use of comparison equation technique with the Schrödinger equation for the free linear rigid rotator as comparison equation. The relation of this quantization condition to those obtained in §4 is also discussed.

In paper II the energy levels for the case of field-free space are first established, since the resulting formula is often quoted in the literature without full proof. For very weak fields the available results of conventional sixth-order perturbation theory are then presented in convenient form. For very strong fields the problem can, as already mentioned above, be reduced to another perturbation problem; a detailed treatment of the energy levels in this case is also given in II. The accuracy of the results collected in II for the limits of very weak and very strong fields is also discussed in that paper. In papers III and IV (this Volume) the quantization conditions given in §4 of this paper are expressed in terms of complete elliptic integrals in the first, third and fifth order of the phase-integral approximation, and the accuracy of the energy levels obtained from the resulting analytical expressions for the quantization conditions is discussed in some detail for arbitrary field strengths. In this discussion the perturbation theory results for very weak and very strong fields collected in II are also used.

2. The Schrödinger equation for a rigid diatomic dipole molecule in an electric field

The moment of inertia of a rigid diatomic dipole molecule with respect to an axis through the centre of mass and perpendicular to the internuclear axis is denoted by I, and the polar angles of the internuclear axis are called ϑ and φ. Because of the external field the dipole has a potential energy, which is assumed to be independent of φ, and which will be denoted by $V(\cos\vartheta)$. The Schrödinger equation for the stationary rotation of the dipole with the energy E in the external electric field is

$$\left\{-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\vartheta\varphi^2}\right]+V(\cos\vartheta)\right\}\Psi=E\Psi. \tag{2.1}$$

We put

$$\Psi=\psi(\vartheta)\,\mathrm{e}^{\mathrm{i}m\varphi}, \tag{2.2}$$

where m must be an integer (positive, negative or zero) so that the wavefunction be single-valued. Inserting (2.2) into (2.1), and defining the dimensionless energy parameter W by the formula

$$W=(2I/\hbar^2)E \tag{2.3}$$

and the dimensionless potential energy function $U(\cos\vartheta)$ by the formula

$$U(\cos\vartheta)=(2I/\hbar^2)\,V(\cos\vartheta), \tag{2.4}$$

we get the differential equation

$$\left[\frac{1}{\sin\vartheta}\frac{\mathrm{d}}{\mathrm{d}\vartheta}\left(\sin\vartheta\frac{\mathrm{d}}{\mathrm{d}\vartheta}\right)-\frac{m^2}{\sin^2\vartheta}+W-U(\cos\vartheta)\right]\psi=0, \tag{2.5}$$

which for $U(\cos\vartheta)=0$ and $W=l(l+1)$ goes over into the differential equation for the associated Legendre function $P_l^m(\cos\vartheta)$.

Introducing instead of ψ a new variable u by the definition

$$u=\psi\sin^{\frac{1}{2}}\vartheta, \tag{2.6}$$

we can write the differential equation (2.5) as

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\vartheta^2}+(W+\tfrac{1}{2}-m^2)-(m^2-\tfrac{1}{4})\cot^2\vartheta-U(\cos\vartheta)\right)u=0. \tag{2.7}$$

One obtains the eigenvalues of W by solving this differential equation with the boundary conditions that u be equal to zero for $\vartheta=0$ and for $\vartheta=\pi$. In the particular case when the dipole is rigid and has a pure electric dipole moment of the magnitude p, directed along the internuclear axis, and is situated in an external homogeneous static electric field of the strength F with the direction corresponding to $\vartheta=0$ we have

$$V(\cos\vartheta)=-pF\cos\vartheta \tag{2.8}$$

and hence, according to (2.4),

$$U(\cos\vartheta) = -\omega\cos\vartheta, \tag{2.9}$$

where ω is a dimensionless, non-negative field strength parameter defined by

$$\omega = (2I/\hbar^2)\,pF\,(\geqslant 0). \tag{2.10}$$

With the expression (2.9) for $U(\cos\vartheta)$ the differential equation (2.7) can be written as follows

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\vartheta^2} + (W+\tfrac{1}{2}-m^2) - (m^2-\tfrac{1}{4})\cot^2\vartheta + \omega\cos\vartheta\right)u = 0. \tag{2.11}$$

Introducing instead of ϑ the new variable z by the definition

$$z = \cos\vartheta, \tag{2.12}$$

we can write the differential equation (2.5) as follows

$$\left(\frac{\mathrm{d}}{\mathrm{d}z}(1-z^2)\frac{\mathrm{d}}{\mathrm{d}z} - \frac{m^2}{1-z^2} + W - U(z)\right)\psi = 0. \tag{2.13}$$

Introducing instead of ψ the new variable v by the definition (cf. (2.12) and (2.6))

$$v = (1-z^2)^{\frac{1}{2}}\psi = \psi\sin\vartheta = u\sin^{\frac{1}{2}}\vartheta = (1-z^2)^{\frac{1}{4}}u, \tag{2.14}$$

we can write the differential equation (2.13) in the form

$$\frac{\mathrm{d}^2 v}{\mathrm{d}z^2} + R(z)\,v = 0 \tag{2.15}$$

where

$$R(z) = \frac{W-U(z)}{1-z^2} + \frac{1-m^2}{(1-z^2)^2}. \tag{2.16}$$

For a dipole in a homogeneous electric field we have according to (2.9), (2.12) and (2.16)

$$R(z) = \frac{W+\omega z}{1-z^2} + \frac{1-m^2}{(1-z^2)^2}. \tag{2.17}$$

One obtains the eigenvalues of W by solving the differential equation (2.15) with the boundary conditions that v be equal to zero for $z = \pm 1$.

In the discussion of an electric dipole in a very strong electric field, which will be given in II, it is convenient to use the differential equation (2.11), while in the phase-integral treatment of the problem concerning the energy levels for arbitrary field strength, which is the main purpose of our series of papers, it is very convenient to use the differential equation (2.15).

3. Arbitrary-order phase-integral approximation generated from an unspecified base function

The differential equation (2.15), i.e.

$$\frac{\mathrm{d}^2 v}{\mathrm{d}z^2} + R(z)\,v = 0, \tag{3.1}$$

has, according to Fröman & Fröman (1974*a*, *b*, 1991), as approximate solutions the two linearly independent phase-integral functions

$$v = q^{-\frac{1}{2}}(z)\exp\left(\pm\mathrm{i}\int^{z} q(z)\,\mathrm{d}z\right), \tag{3.2}$$

where, for the phase-integral approximation of the order $2N+1$,

$$q(z) = \sum_{s=0}^{N} Y_{2s}\,Q(z) \tag{3.3}$$

with the base function $Q(z)$ unspecified and the first few quantities Y_{2s} given by

$$Y_0 = 1, \tag{3.4a}$$

$$Y_2 = \tfrac{1}{2}\epsilon_0, \tag{3.4b}$$

$$Y_4 = -\tfrac{1}{8}\epsilon_0^2 - \frac{1}{8}\frac{1}{Q(z)}\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{1}{Q(z)}\frac{\mathrm{d}\epsilon_0}{\mathrm{d}z}\right), \tag{3.4c}$$

ϵ_0 being defined by

$$\epsilon_0 = \frac{R(z)-Q^2(z)}{Q^2(z)} + Q^{-\frac{3}{2}}(z)\frac{\mathrm{d}^2}{\mathrm{d}z^2}Q^{-\frac{1}{2}}(z). \tag{3.5}$$

The appearance of the unspecified base function $Q(z)$ in the above phase-integral approximation is very important from several points of view (see Fröman & Fröman 1991). It can be chosen in a way which is appropriate for the problem under consideration.

We remark that the notations used above differ from the notations in the original papers by Fröman (1966, 1970) and by Fröman & Fröman (1974*a*, *b*) concerning the phase-integral approximation in question in the respect that $Q^2(z)$ and $Q^2_{\mathrm{mod}}(z)$ in those papers correspond to $R(z)$ and $Q^2(z)$, respectively, in this paper.

It is important to note that those terms in the expressions for $Y_{2s}Q(z)$, which are derivatives with respect to z of single-valued functions of z, do not contribute to the closed contour integrals that occur in the quantization conditions to be obtained. In these contour integrals $q(z)$ is integrated along contours enclosing two zeros of $Q^2(z)$ and/or two first-order poles of $Q^2(z)$ or a zero and a first-order pole of $Q^2(z)$. In such a closed contour integral the terms in the integrand which do not contribute to the value of the integral can be split off and the functions Y_{2s} can be replaced by corresponding functions Z_{2s}, the first few of which are given by

$$Z_0 = 1, \tag{3.6a}$$

$$Z_2 = \tfrac{1}{2}\epsilon_0, \tag{3.6b}$$

$$Z_4 = -\tfrac{1}{8}\epsilon_0^2. \tag{3.6c}$$

The Schrödinger equation for a rigid electric dipole rotating in a homogeneous electric field can be written in the form (2.15), i.e. (3.1), with $R(z)$ given by (2.17), i.e.

$$R(z) = \frac{W+\omega z}{1-z^2} + \frac{1-m^2}{(1-z^2)^2}. \tag{3.7}$$

The square of the base function $Q(z)$ is chosen to be

$$Q^2(z) = \frac{C+\omega z}{1-z^2} - \frac{4\xi_0^2}{(1-z^2)^2}, \tag{3.8}$$

where C and ξ_0 are so far unspecified constants.

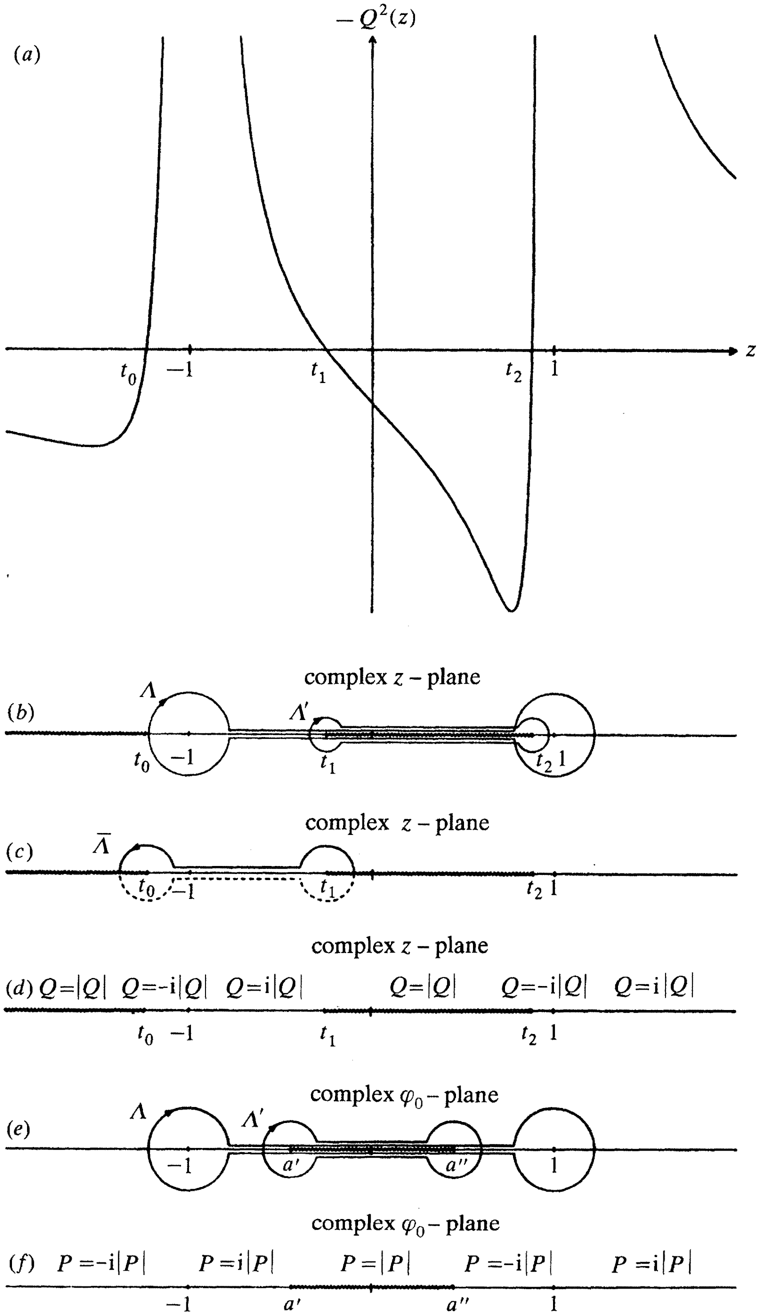

Figure 1. This figure, which refers to the case when $\xi_0 > 0$ (and $\omega > 0$), applies when $W+\frac{1}{4} > -\omega$ and (3.9*b*) with $C = W+\frac{1}{4}$ is fulfilled (see (3.8), (3.9*a*, *b*) and (3.22)). (*a*) Gives, for real values of z, a graphical representation of the function $-Q^2(z)$, defined according to (3.8), (3.20) and (3.22). When $\omega > 0$ and $m \neq 0$ there are three zeros ($t_0 < -1 < t_1 < t_2 < +1$) of $Q^2(z)$, and the distance of the turning point t_2 from the pole $+1$ is smaller than the distance of the turning point t_1 from the pole -1. When ω tends to zero while $m \neq 0$, t_0 tends to $-\infty$, and in the limit $\omega = 0$ only the two zeros t_1 and t_2 ($-1 < t_1 = -t_2 < 0 < t_2 < +1$) of $Q^2(z)$ remain. (*b*) Shows the contours of integration Λ' and Λ. The contour Λ' encloses the zeros t_1 and t_2 but not the poles -1 and $+1$, while the contour Λ encloses both the zeros t_1 and t_2 and the poles -1 and $+1$ but not the zero t_0. (*c*) Shows the

Because of the nature of the physical problem under consideration we assume ξ_0 ($\geqslant 0$) and C to be chosen such that $Q^2(z)$ is positive at least in part of the interval $-1 \leqslant z \leqslant +1$ for every value of $\omega \geqslant 0$. This condition is fulfilled if

$$C > -\omega \tag{3.9a}$$

and

$$0 \leqslant \xi_0^2 < \frac{\omega}{54}\left\{\left[\left(\frac{C}{\omega}\right)^2+3\right]^{\frac{3}{2}} - \left(\frac{C}{\omega}\right)^3 + 9\frac{C}{\omega}\right\}, \tag{3.9b}$$

the right-hand side of (3.9b) increasing monotonically from 0 to $+\infty$ when C increases from $-\omega$ to $+\infty$.

To define the base function $Q(z)$ completely, we introduce a cut along the classically allowed region (in the generalized sense), which is the part of the region $-1 \leqslant z \leqslant +1$ where $Q^2(z)$ is positive, and define $Q(z)$ to be positive on the upper lip of this cut (see figures 1, 2 and 3).

We note that

$$\lim_{z \to \pm 1} (z \mp 1)^2 R(z) = \tfrac{1}{4}(1-m^2) \tag{3.10}$$

and

$$\lim_{z \to \pm 1} (z \mp 1)^2 Q^2(z) = -\xi_0^2. \tag{3.11}$$

With due regard to the phase of $Q(z)$, shown in figures 1d, 2c and 3c, we also note that

$$\operatorname*{Res}_{z=\pm 1} Y_0\, Q(z) = \operatorname*{Res}_{z=\pm 1} Z_0\, Q(z) = \mathrm{i}\xi_0, \tag{3.12a}$$

$$\operatorname*{Res}_{z=\pm 1} Y_2\, Q(z) = \operatorname*{Res}_{z=\pm 1} Z_2\, Q(z) = \tfrac{1}{2}\mathrm{i}\xi_0 \frac{m^2-4\xi_0^2}{4\xi_0^2}, \tag{3.12b}$$

$$\operatorname*{Res}_{z=\pm 1} Y_4\, Q(z) = \operatorname*{Res}_{z=\pm 1} Z_4\, Q(z) = -\tfrac{1}{8}\mathrm{i}\xi_0 \left(\frac{m^2-4\xi_0^2}{4\xi_0^2}\right)^2. \tag{3.12c}$$

For later use we now discuss one of the contour integrals, which appears in our derivation of the quantization condition in §4 when $\xi_0 \neq 0$ (see figure 1a). In that case there are two generalized classical turning points, t_1 and t_2. We first consider

$$L = \frac{1}{2}\int_{\Lambda'} q(z)\,\mathrm{d}z, \tag{3.13}$$

Λ' being a contour of integration which encircles in the negative sense the turning points t_1 and t_2, but leaves the poles at $z = \pm 1$ outside Λ' (see figure 1b). With the aid of (3.3) the definition (3.13) can be written as

$$L = \sum_{s=0}^{N} L^{(2s+1)}, \tag{3.14}$$

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contour $\bar{\Lambda}$ enclosing the zeros t_0 and t_1 and the pole -1 but no other transition point. (d) Shows the phase chosen for the base function $Q(z)$. (e) Shows the contours of integration in the complex φ_0-plane which correspond to the contours Λ' and Λ in the complex z-plane. The former contours are also denoted by Λ' and Λ, respectively, since this should not cause any confusion. (f) Shows the phase chosen for the function $P(\varphi_0)$, the square of which is given by (5.11).

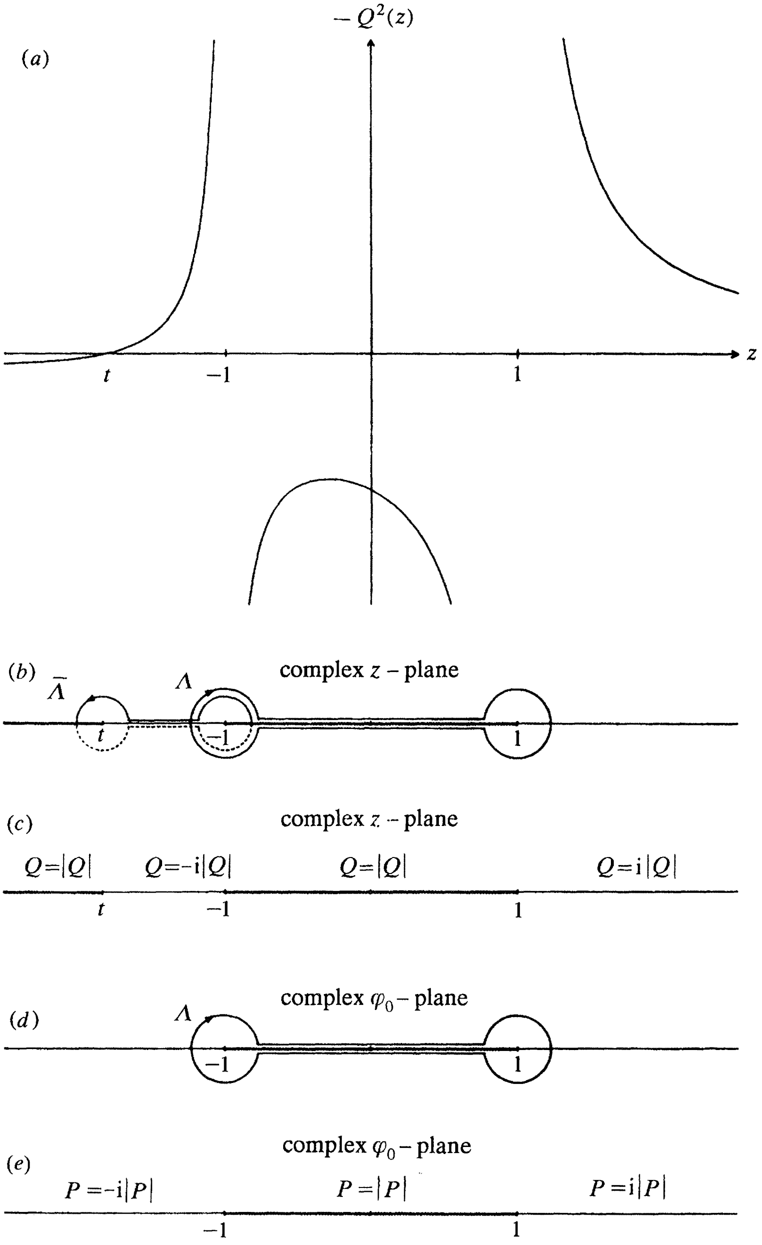

Figure 2. Figures 2 and 3 refer to the two different situations that can occur when $\xi_0 = 0$ and $\omega > 0$. Figure 2 applies when $W+\frac{1}{4} > \omega$; see (3.8) and (3.22). In this case $t < -1$ and $\eta_0 < 0$. It occurs when ω is sufficiently small (in which situation the turning point t tends to $-\infty$ as $\omega \to 0$). Figure 3 applies when $-\omega < W+\frac{1}{4} < \omega$; see (3.8) and (3.22). In this case $\eta_0 > 0$ and $-1 < t < +1$, t being positive when $W+\frac{1}{4} < 0$ and negative when $W+\frac{1}{4} > 0$. It occurs when ω is sufficiently large (in which situation the turning point t tends to $+1$ as $\omega \to \infty$). For the case in figure 3 the comparison equation technique in §5 involving the function $P(\varphi_0)$ cannot be used, and there is therefore no figure 3*d*, *e* involving φ_0. (*a*) Gives, for real values of z, a graphical representation of the function $-Q^2(z)$, defined according to (3.8), (3.21) and (3.22). (*b*) Shows the contours of integration Λ and $\bar{\Lambda}$. (*c*) Shows the phase chosen for the base function $Q(z)$. (*d*) Shows the contour of integration in the complex φ_0-plane which corresponds to the contour Λ in the complex z-plane. The former contour is also denoted by Λ, since this should not cause any confusion. (*e*) Shows the phase chosen for the function $P(\varphi_0)$, the square of which is given by (5.11).

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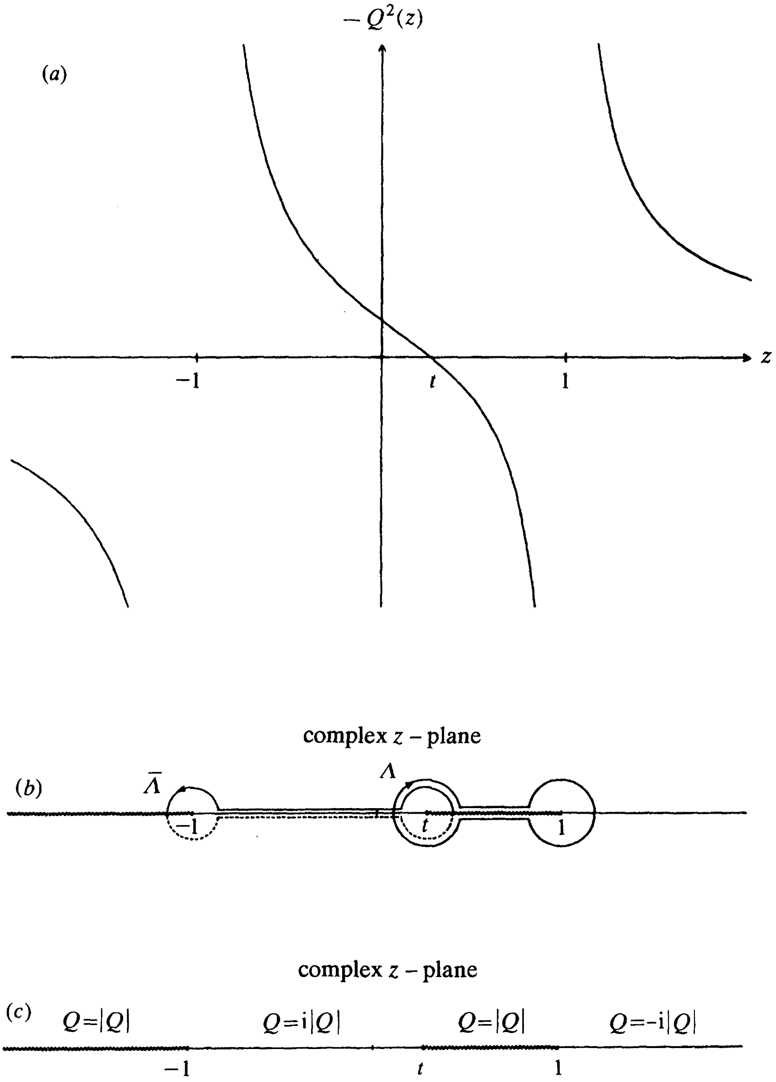

Figure 3. For details see figure 2 caption.

where, according to the remark immediately above (3.6*a*–*c*),

$$L^{(2s+1)} = \frac{1}{2}\int_{\Lambda'} Y_{2s}\, Q(z)\,\mathrm{d}z = \frac{1}{2}\int_{\Lambda'} Z_{2s}\, Q(z)\,\mathrm{d}z. \tag{3.15}$$

Taking the poles of $q(z)$ at $z = \pm 1$ into account, we can express the contour integral (3.13) in terms of the contour integral

$$\mathscr{L} = \frac{1}{2}\int_{\Lambda} q(z)\,\mathrm{d}z, \tag{3.16}$$

where Λ is a contour encircling in the negative sense the poles ± 1 as well as the turning points t_1 and t_2 but not the transition point t_0 (see figure 1*b*). In passing we remark that with the aid of (3.3) the definition (3.16) can also be written as

$$\mathscr{L} = \sum_{s=0}^{N} \mathscr{L}^{(2s+1)} \tag{3.17}$$

where, according to the remark immediately above (3.6*a*–*c*),

$$\mathscr{L}^{(2s+1)} = \frac{1}{2}\int_{\Lambda} Y_{2s}\, Q(z)\, \mathrm{d}z = \frac{1}{2}\int_{\Lambda} Z_{2s}\, Q(z)\, \mathrm{d}z. \tag{3.18}$$

It is obvious from (3.15), (3.18) and (3.12*b*, *c*) that when $\xi_0 \neq 0$ and $s > 0$ the difference $\mathscr{L}^{(2s+1)} - L^{(2s+1)}$ is equal to zero if and only if $\xi_0 = \frac{1}{2}|m|$. By means of residue calculus one thus finds that when $\xi_0 > 0$ the difference $\mathscr{L} - L$ depends on the order of the phase-integral approximation unless $\xi_0 = \frac{1}{2}|m|$. It is advantageous that the difference between $\mathscr{L}$ and L be simple and order-independent, and therefore a very useful choice of ξ_0 is $\xi_0 = \frac{1}{2}|m|$ if $m \neq 0$. This choice has also the advantage that the arbitrary-order phase-integral approximation remains valid at the points $z = \pm 1$ if $m \neq 0$. With $\xi_0 = \frac{1}{2}|m| \neq 0$ we obtain, with the aid of residue calculus,

$$\mathscr{L} = L + |m|\,\pi. \tag{3.19}$$

There are two natural ways of choosing ξ_0. One is, as we have just seen,

$$\xi_0 = \tfrac{1}{2}|m|, \tag{3.20}$$

which is most appropriate when $|m|$ is not too small, and the other, which is most appropriate when $|m|$ is sufficiently small, is

$$\xi_0 = 0. \tag{3.21}$$

In both these cases, i.e. $\xi_0 = \frac{1}{2}|m| \neq 0$ and $\xi_0 = 0$, it is very convenient to choose (see the end of §4)

$$C = W + \tfrac{1}{4}, \tag{3.22}$$

since the simple, limiting forms of the phase-integral quantization conditions, which will be given in §4, then give the exact values of the energy levels when the electric field disappears, i.e. when $\omega = 0$. This is very important, since the inherent accuracy of the phase-integral approximation decreases with decreasing values of ω. By choosing the base function such that the above-mentioned simple limiting forms of the quantization conditions reproduce the exact values of the energy levels for $\omega = 0$ we thus improve the results considerably for small values of ω. If we had not chosen the base function in that way, the phase-integral eigenvalues would not be particularly good for small values of ω.

In the case $\xi_0 > 0$, illustrated in figure 1, the classically allowed region is confined between two zeros t_1 and t_2 of $Q^2(z)$, and there exists a third zero $t_0 < -1$ on the real axis.

In the case $\xi_0 = 0$ there exists only one zero, t, of $Q^2(z)$ located at $z = -C/\omega$, as is seen from (3.8). Depending on the value of the dimensionless energy parameter W and of the dimensionless field strength parameter ω, the turning point t may lie on the real axis, either to the left of $z = -1$, or in the interval between -1 and $+1$, as is shown in figures 2*a* and 3*a* respectively (cf. (3.9*a*)). For the case in figure 2, which occurs when $C/\omega > 1$, the physically relevant region of the real axis is a classically allowed region, confined between the two first-order poles of $Q(z)$ at $z = \pm 1$. For the case in figure 3, which occurs when $-1 < C/\omega < 1$, the classically allowed region is confined between the turning point t (>-1) and the first-order pole of $Q^2(z)$ at $z = +1$. The turning point t in figure 3*a* lies to the left of the origin when $C > 0$ but to the right of the origin when $C < 0$.

In §4 we derive quantization conditions with the aid of arbitrary-order phase-integral formulas. For tracing the solution that is zero at $z = -1$ into the classically allowed region we use new such formulas (Fröman *et al.* 1994) which remain valid even when the turning point t_0, in the case $\xi_0 > 0$, and t, in the two cases possible when $\xi_0 = 0$, approach the pole at $z = -1$. For tracing the solution which is zero at $z = +1$ into the classically allowed region, we use the 'old' arbitrary-order connection formulas which exist since several years (Fröman & Fröman 1965; N. Fröman 1970) and which are obtained as limiting cases of the new phase-integral formulas derived by Fröman *et al.* (1994).

In §5 we derive an alternative quantization condition by means of comparison equation technique with the Schrödinger equation for the free linear rigid rotator as comparison equation.

4. Quantization conditions obtained with the use of new phase-integral formulas

The comparison equation technique, appropriate for obtaining supplementary quantities in the phase-integral method, is described in Fröman & Fröman (1994). This general theory is applied to the special situation that the comparison equation is the differential equation for the Coulomb wavefunctions in Fröman *et al.* (1994), where phase-integral formulas are derived for obtaining, in the classically allowed region at some distance from a pole of $Q^2(z)$, an expression for a solution which tends to zero at the pole, in both of the cases $\xi_0 > 0$ and $\xi_0 = 0$. We shall use those new phase-integral formulas for deriving quantization conditions which contain those obtainable with the aid of the 'old' connection formulas, mentioned above, as limiting cases.

For the choice $\xi_0 = \frac{1}{2}|m| > 0$, the transition zeros t_1, t_0 and the second-order pole of $Q^2(z)$ at $z = -1$ in our figure 1 have their counterparts in the transition zeros t_1, t_2 and the second-order pole of $Q^2(z)$ at $z = 0$ in figure 1 in Fröman *et al.* (1994). For the choice $\xi_0 = 0$, the transition point t and the first-order pole of $Q^2(z)$ at $z = -1$ in our figures 2 and 3 correspond to the transition point t_1 and the first-order pole of $Q^2(z)$ at $z = 0$ in figures 3 and 2, respectively, in Fröman *et al.* (1994). Furthermore, the quantity l in Fröman *et al.* (1994) shall in the present context be replaced by

$$l = \tfrac{1}{2}|m| - \tfrac{1}{2}, \tag{4.1}$$

which means that $2l + 1 = |m|$.

According to the new phase-integral formulas formed by equations (3.24), (3.36), (3.37*a*–*c*), (3.38), (3.33), (3.39), (3.9), (3.45) and (3.46*a*–*c*) in Fröman *et al.* (1994) the solution which is zero at $z = -1$ is in the classically allowed region, pertaining to each one of the three cases illustrated in figures 1, 2 and 3, given by

$$v(z) = \text{const.} \times q^{-\frac{1}{2}}(z) \sin\left(\frac{1}{2}\int_{\Gamma(z)} q(z)\,\mathrm{d}z + \Delta\right), \tag{4.2}$$

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where $z = x+\mathrm{i}0$ (see figures 1, 2 and 3), and $\Gamma(z)$ is a contour which starts at $x-\mathrm{i}0$ and ends at $x+\mathrm{i}0$ after having encircled t_1, -1 or t in the cases of figures 1, 2 or 3 respectively. The constant phase Δ is given by (cf. the above-mentioned equations in Fröman *et al.* (1994) and (4.1))

$$\Delta = -\tfrac{1}{4}(|m|-1)\pi + \arg\Gamma(\tfrac{1}{2}|m|+\tfrac{1}{2}+\mathrm{i}\eta) - \xi_0\left(\arctan\frac{\eta_0}{\xi_0}-\tfrac{1}{2}\pi\right) - \eta\ln(\xi_0^2+\eta_0^2)^{\frac{1}{2}} + \sum_{s=0}^{N}\Delta^{(2s+1)}, \tag{4.3}$$

where
$$\eta = \sum_{s=0}^{N}\eta_{2s} \tag{4.4}$$

with the quantities η_{2s} given by equation (3.9) in Fröman *et al.* (1994), i.e.

$$\eta_{2s} = \frac{\mathrm{i}}{2\pi}\int_{\bar{\Lambda}} Y_{2s}\,Q(z)\,\mathrm{d}z = \frac{\mathrm{i}}{2\pi}\int_{\bar{\Lambda}} Z_{2s}\,Q(z)\,\mathrm{d}z, \tag{4.5}$$

where the contour $\bar{\Lambda}$ and the appropriate direction of integration is depicted in figure 1*c* for the choice $\xi_0 = \frac{1}{2}|m| > 0$, and in figures 2*b* and 3*b* for the two situations possible for the choice $\xi_0 = 0$. The quantities $\Delta^{(2s+1)}$ in (4.3) are given in Fröman *et al.* (1994) by equations (3.37*a*–*c*) there with $\xi_2 = \xi_4 = \ldots = 0$ when $\xi_0 = l+\frac{1}{2} = \frac{1}{2}|m| > 0$ and by equations (3.46*a*–*c*) there when $\xi_0 = 0$ (see also (4.1)). The explicit expressions are thus as follows.

When $\xi_0 = \frac{1}{2}|m| > 0$:

$$\Delta^{(1)} = \eta_0, \tag{4.6a}$$

$$\Delta^{(3)} = -\frac{\eta_0}{24\,(\frac{1}{4}m^2+\eta_0^2)}, \tag{4.6b}$$

$$\Delta^{(5)} = -\frac{\eta_0\,\eta_2^2}{2\,(\frac{1}{4}m^2+\eta_0^2)} - \frac{(\frac{1}{4}m^2-\eta_0^2)\,\eta_2}{24\,(\frac{1}{4}m^2+\eta_0^2)^2} + \frac{7\eta_0\,(\frac{3}{4}m^2-\eta_0^2)}{2880(\frac{1}{4}m^2+\eta_0^2)^3}. \tag{4.6c}$$

When $\xi_0 = 0$:

$$\Delta^{(1)} = \eta_0, \tag{4.7a}$$

$$\Delta^{(3)} = \frac{3m^2-1}{24\eta_0}, \tag{4.7b}$$

$$\Delta^{(5)} = -\frac{\eta_2^2}{2\eta_0} - \frac{(3m^2-1)\,\eta_2}{24\eta_0^2} - \frac{15m^4-30m^2+7}{2880\eta_0^3}. \tag{4.7c}$$

Using the usual asymptotic formula for the Γ-function we find from (4.3), (4.6*a*–*c*) and (4.7*a*–*c*) that

$$\Delta \to \tfrac{1}{4}\pi \quad \text{as} \quad m \to \infty, \tag{4.8}$$

while η_0 is kept fixed, and that

$$\Delta \to \begin{cases} \tfrac{1}{4}\pi & \text{as} \quad \eta_0 \to +\infty, \\ (\tfrac{1}{4}-\tfrac{1}{2}|m|)\,\pi & \text{as} \quad \eta_0 \to -\infty, \end{cases} \tag{4.8$'$}$$

while m is kept fixed and $\eta-\eta_0$ remains finite.

When t_1 in figure 1 and t in figures 2 and 3 move away from the pole at $z = -1$, the quantity η_0 assumes large positive values for the cases in figures 1 and 3 but large negative values for the case in figure 2. From (4.2) and (4.8′) we then obtain the same results as can be obtained from the arbitrary-order generalizations of the two connection formulas (8.21) and (7.28) in Fröman & Fröman (1965); see also equations (21) and (22) in Fröman (1970). For the solution which is equal to zero (and single-valued) at the pole $z = -1$ we shall at the point $z = x + \mathrm{i}0$ in the classically allowed region use (4.2) with the expression (4.3) with (4.6*a–c*) and (4.7*a–c*) for Δ when t_1 in figure 1 and t in figures 2 and 3 lie sufficiently close to $z = -1$, but otherwise with the limiting expressions for Δ obtained from (4.8′).

For the solution which is equal to zero at the pole $z = +1$ we shall at the point $z = x + \mathrm{i}0$ always use the formulas obtained from the arbitrary-order generalizations of the connection formulas (8.21) and (7.28) in Fröman & Fröman (1965), i.e.

$$v(z) = \text{const.} \times q^{-\frac{1}{2}}(z) \cos\left(-\frac{1}{2}\int_{\Gamma_{t_2}(z)} q(z)\,\mathrm{d}z - \tfrac{1}{4}\pi\right), \quad \xi_0 = \tfrac{1}{2}|m| > 0, \qquad (4.9a)$$

and

$$v(z) = \text{const.} \times q^{-\frac{1}{2}}(z) \cos\left(-\frac{1}{2}\int_{\Gamma_{+1}(z)} q(z)\,\mathrm{d}z - (\tfrac{1}{2}|m| + \tfrac{1}{4})\,\pi\right),$$

$$\xi_0 = 0, \quad m \neq 0 \quad \text{or} \quad m = 0, \qquad (4.9b)$$

where $\Gamma_{t_2}(z)$ and $\Gamma_{+1}(z)$ are contours which start at $x - \mathrm{i}0$, encircle t_2 and $+1$, respectively, and end at $x + \mathrm{i}0$.

Joining the solution (4.2) to (4.9*a*) and (4.9*b*), respectively, we obtain new quantization conditions valid when $\xi_0 = \frac{1}{2}|m| > 0$ and $\xi_0 = 0$ respectively. In the case $\xi_0 > 0$, the resulting condition is primarily expressed in terms of the integral L in (3.13) along the contour Λ', shown in figure 1*b*, but can subsequently be expressed in terms of the integral $\mathscr{L}$ along the contour Λ, also shown in figure 1*b*, according to (3.19). In the case $\xi_0 = 0$, the joining of the solutions in question yields directly a condition expressed in terms of an integral along Λ (see figures 2*b* and 3*b*). Defining the rotational quantum number j as follows

$$j = |m| + n, \quad n = 0, 1, 2, \ldots, \qquad (4.10)$$

we thus obtain the two quantization conditions

$$\mathscr{L} = (j + \tfrac{3}{4})\,\pi - \Delta, \quad \xi_0 = \tfrac{1}{2}|m| > 0, \quad j = |m|, \quad |m| + 1, \ldots, \qquad (4.11a)$$

$$\mathscr{L} = (j + \tfrac{3}{4} - \tfrac{1}{2}|m|)\,\pi - \Delta, \quad \xi_0 = 0, \quad m \neq 0 \quad \text{or} \quad m = 0,$$

$$j = |m|, \quad |m| + 1, \ldots, \qquad (4.11b)$$

where $\mathscr{L}$ is an integral along the contour Λ, which, for the three cases under consideration, is depicted in figures 1*b*, 2*b* and 3*b*, respectively, and the quantity Δ is given by (4.3) with (4.6*a–c*) and (4.7*a–c*), when t_1 in figure 1 and t in figures 2 and 3 lie sufficiently close to $z = -1$, but otherwise by the limiting expressions of Δ obtained from (4.8′).

(*a*) *Limiting forms of the quantization conditions when t_1 and t move away from $z = -1$*

With due regard to the phase of $Q(z)$, shown in figures 1*d*, 2*c* and 3*c*, we note that, when t_1 in figure 1 and t in figures 2 and 3 lie sufficiently far from $z = -1$, we have $\eta_0 > 0$ in the situations depicted in figures 1 and 3 but $\eta_0 < 0$ in the situation depicted in figure 2. Assuming that t_1 and t are sufficiently well separated from the pole of $Q^2(z)$ at $z=-1$ so that the limiting values (4.8′) of $\varDelta$ can be used, we obtain from (4.11a,b) the simple quantization conditions

$$\mathscr{L}=(j+\tfrac{1}{2})\,\pi,\begin{cases}\xi_0=\tfrac{1}{2}|m|, & m\neq 0,\quad \text{the case in figure 1,}\\ \xi_0=0, & m\neq 0\quad\text{or}\quad m=0,\quad\text{the case in figure 2,}\end{cases}\tag{4.12a}$$

$$\mathscr{L}=(j+\tfrac{1}{2}-\tfrac{1}{2}|m|)\,\pi,\quad \xi_0=0,\quad m\neq 0\quad\text{or}\quad m=0,\quad\text{the case in figure 3,}\tag{4.12b}$$

where $j=|m|$, $|m|+1,\ldots$, and $\mathscr{L}$ is defined by (3.16) with the contour $\varLambda$, pertaining to each case, depicted in figures 1b, 2b and 3b.

When t_1 (figure 1) and t (figures 2 and 3) lie far away from -1, the simple quantization conditions (4.12a, b), i.e. the quantization conditions (4.11a, b) with the phase $\varDelta$ obtained from the limiting values (4.8′), are the natural and probably the more accurate quantization conditions. Thus, the quantization conditions (4.11a, b) with the phase $\varDelta$ given by (4.3) with (4.6a–c) and (4.7a–c) should in general be used only when t_1 (figure 1) and t (figures 2 and 3) lie sufficiently close to -1.

When ω is sufficiently small and $C\neq 0$, the case in figure 3 cannot occur, and of the simple quantization conditions (4.12a) and (4.12b) it is thus only (4.12a) that is relevant. We shall now show that the simple quantization condition (4.12a) yields the exact energy levels when $\omega=0$, if C is chosen according to (3.22), i.e. if $C=W+\frac{1}{4}$. From (3.8) with $C>-\omega=0$ (cf. (3.9a)), and with due regard to the phase of $Q(z)$ shown in figures 1d and 2c, (3.5), (3.6a–c) and (3.7) with $\omega=0$ it follows that

$$Z_0\,Q(z)=\mathrm{i}\surd(C)/z+\ldots,\quad |z|\rightarrow\infty,\tag{4.13a}$$

$$Z_2\,Q(z)=\frac{\mathrm{i}(W+\frac{1}{4}-C)}{2\surd(C)\,z}+\ldots,\quad |z|\rightarrow\infty,\tag{4.13b}$$

$$Z_4\,Q(z)=-\frac{\mathrm{i}(W+\frac{1}{4}-C)^2}{8C^{\frac{3}{2}}z}+\ldots,\quad |z|\rightarrow\infty,\tag{4.13c}$$

and hence we obtain from (3.18)

$$\mathscr{L}^{(1)}=\pi\surd C,\tag{4.14a}$$

$$\mathscr{L}^{(3)}=\tfrac{1}{2}\pi\frac{W+\frac{1}{4}-C}{\surd C},\tag{4.14b}$$

$$\mathscr{L}^{(5)}=-\tfrac{1}{8}\pi\frac{(W+\frac{1}{4}-C)^2}{C^{\frac{3}{2}}}.\tag{4.14c}$$

Thus, with C given by (3.22), the right-hand members in (4.14b, c) become zero, and it can be shown quite generally that

$$\mathscr{L}^{(2s+1)}=0\quad\text{for}\quad s>0.\tag{4.15}$$

With $C=W+\frac{1}{4}$ we thus obtain from (3.17), (4.14a) and (4.15), for every possible value of N,

$$\mathscr{L}=\pi(W+\tfrac{1}{4})^{\frac{1}{2}},\tag{4.16}$$

and the quantization condition (4.12a) therefore gives $(W+\frac{1}{4})^{\frac{1}{2}}=j+\frac{1}{2}$, i.e.

$$W=j(j+1),\quad j=|m|,\quad |m|+1,\ldots,\tag{4.17}$$

since n in (4.10) is a non-negative integer. The values of W given by (4.17) are the exact eigenvalues of the differential equation (2.15) when $R(z)$ is given by (2.17) with $\omega = 0$ (see §2 in II).

5. Quantization condition obtained with the use of the Schrödinger equation for the free linear rigid rotator as comparison equation

For $\xi_0 > 0$ (figure 1) and for $\xi_0 = 0$ when figure 2 applies (but not for $\xi_0 = 0$ when figure 3 applies) one can use comparison equation technique (with the differential equation corresponding to $\omega = 0$ as the comparison equation) to derive an alternative quantization condition. The appropriate comparison equation technique is described in detail by Fröman & Fröman (1994). We shall therefore only specialize general formulas there to apply to our present problem with the Schrödinger equation for the free linear rigid rotator as the comparison equation.

Choosing the square of the base function to be given by (3.8), we consider instead of the original differential equation (3.1) the differential equation (2.2) in Fröman & Fröman (1994) with ψ replaced by v, i.e.

$$\frac{\mathrm{d}^2 v}{\mathrm{d}z^2} + \frac{1}{\lambda^2}(Q^2(z) + [R(z) - Q^2(z)]\,\lambda^2)\,v = 0, \tag{5.1}$$

which goes over into (3.1) when one puts $\lambda = 1$, as we shall finally do. We also consider the comparison equation (2.5) in Fröman & Fröman (1994), i.e.

$$\frac{\mathrm{d}^2 \Phi}{\mathrm{d}\varphi^2} + \frac{1}{\lambda^2}\Pi(\varphi)\,\Phi = 0, \tag{5.2}$$

where we choose

$$\Pi(\varphi) = \frac{D}{1-\varphi^2} + \frac{-4\xi_0^2 + (4\xi_0^2 + 1 - m^2)\,\lambda^2}{(1-\varphi^2)^2}, \tag{5.3}$$

D being an unspecified quantity depending on λ but not on φ. So that equation (2.6) in Fröman & Fröman (1994) be fulfilled, the coefficient of $1/(1-\varphi^2)^2$ in the second member of (5.3) has been chosen to be equal to the coefficient of $1/(1-z^2)^2$ in the expression (cf. (5.1))

$$Q^2(z) + [R(z) - Q^2(z)]\,\lambda^2 = \frac{(C + \omega z) + (W - C)\,\lambda^2}{1 - z^2} + \frac{-4\xi_0^2 + (4\xi_0^2 + 1 - m^2)\,\lambda^2}{(1-z^2)^2}, \tag{5.4}$$

which has been obtained from (3.7) and (3.8).

Formula (5.3) can be written in the form of equations (2.9a–c) in Fröman & Fröman (1994), i.e.

$$\Pi(\varphi) = \sum_{n=0}^{\infty} A_n \varphi^n \Big/ \sum_{q=0}^{\infty} B_q \phi^q, \tag{5.5}$$

where

$$A_0 = D - 4\xi_0^2 + (4\xi_0^2 + 1 - m^2)\,\lambda^2, \quad A_1 = 0, \tag{5.6a, b}$$

$$A_2 = -D, \quad A_n = 0 \quad \text{for} \quad n > 2, \tag{5.6c, d}$$

$$B_0 = 1, \quad B_1 = 0, \tag{5.7a, b}$$

$$B_2 = -2, \quad B_3 = 0, \tag{5.7c, d}$$

$$B_4 = 1, \quad B_q = 0 \quad \text{for} \quad q > 4. \tag{5.7e, f}$$

We assume all coefficients B_q to be independent of λ as in Fröman & Fröman (1994). Assuming D to be expanded as follows

$$D = \sum_{\beta=0}^{\infty} D_{2\beta}\lambda^{2\beta}, \qquad (5.8)$$

where $D_0, D_2, D_4, \ldots$ are constants (independent of λ), we expand the coefficients A_n in powers of λ according to equation (2.12) in Fröman & Fröman (1994), i.e.

$$A_n = \sum_{\beta=0}^{\infty} A_{n,2\beta}\lambda^{2\beta}, \qquad (5.9)$$

where according to (5.6*a*–*d*) with (5.8)

$$A_{0,2\beta} = D_{2\beta} - 4\xi_0^2\,\delta_{2\beta,0} + (4\xi_0^2 + 1 - m^2)\,\delta_{2\beta,2}, \qquad (5.10a)$$

$$A_{1,2\beta} = 0, \quad A_{2,2\beta} = -D_{2\beta}, \quad A_{n,2\beta} = 0 \quad \text{for} \quad n > 2. \qquad (5.10b\text{–}d)$$

From equations (2.16*a*–*c*) in Fröman & Fröman (1994), where the function $P^2(\varphi_0)$ is defined, we obtain with the aid of (5.10*a*–*d*) and (5.7*a*–*f*)

$$P^2(\varphi_0) = \frac{D_0 - 4\xi_0^2 - D_0\varphi_0^2}{1 - 2\varphi_0^2 + \varphi_0^4} = \frac{D_0}{1-\varphi_0^2} - \frac{4\xi_0^2}{(1-\varphi_0^2)^2}. \qquad (5.11)$$

If $\xi_0 \neq 0$ the function $P^2(\varphi_0)$ has second-order poles at $\varphi_0 = \pm 1$ and zeros at $\varphi_0 = \pm(1 - 4\xi_0^2/D_0)^{\frac{1}{2}}$. So that these zeros lie on the real axis between the poles ± 1 we require that $D_0 > 4\xi_0^2$. If $\xi_0 = 0$ the function $P^2(\varphi_0)$ has first-order poles at $\varphi_0 = \pm 1$ and no zeros. In order that $P^2(\varphi_0)$ be positive on the real axis between the poles we require that $D_0 > 0$. From (5.11) one obtains the function $P(\varphi_0)$, the phase of which is assumed to be chosen according to figure 1*f* or figure 2*e*, respectively.

The coefficients $D_0, D_2, D_4, \ldots$, will soon be determined from consistency conditions in the successive orders of the phase-integral approximation.

As already mentioned, the case in figure 3 cannot be treated with the aid of the comparison equation used in the present section. Therefore, we are now considering only the cases in figures 1 and 2. The poles $z = \pm 1$ of $Q^2(z)$ correspond to the poles $\varphi_0 = \pm 1$ of $P^2(\varphi_0)$, while the zero t_0 (figure 1) or t (figure 2) of $Q^2(z)$ has no counterpart for $P^2(\varphi_0)$. Therefore, according to equations (2.24′) and (2.59*a*, *b*) in Fröman & Fröman (1994) and the comments (concerning the contours of integration) made below equations (2.24′) and (2.58) in that paper, we have the following consistency conditions, valid both for $\xi_0 \neq 0$ and for $\xi_0 = 0$,

$$\frac{1}{2}\int_A P(\varphi_0)\,\mathrm{d}\varphi_0 = \frac{1}{2}\int_A Y_0\,Q(z)\,\mathrm{d}z, \qquad (5.12a)$$

$$\frac{1}{2}\int_A \tfrac{1}{2}hP(\varphi_0)\,\mathrm{d}\varphi_0 = \frac{1}{2}\int_A Y_2\,Q(z)\,\mathrm{d}z, \qquad (5.12b)$$

$$\frac{1}{2}\int_A \left(-\tfrac{1}{8}h^2 + \frac{S_4/T}{2P^2}\right)P(\varphi_0)\,\mathrm{d}\varphi_0 = \frac{1}{2}\int_A Y_4\,Q(z)\,\mathrm{d}z, \qquad (5.12c)$$

where h is defined by equation (2.34) in Fröman & Fröman (1994), i.e.

$$h = P^{-\frac{3}{2}}\frac{\mathrm{d}^2 P^{-\frac{1}{2}}}{\mathrm{d}\varphi_0^2} + \frac{S_2/T}{P^2}, \qquad (5.13)$$

and $S_{2\beta}$ and T are defined by equations (2.31) and (2.16c) in Fröman & Fröman (1994), which with the aid of (5.10a–d) and (5.7a–f) give

$$\frac{S_2}{T} = \frac{D_2 + (4\xi_0^2 + 1 - m^2) - D_2\varphi_0^2}{1 - 2\varphi_0^2 + \varphi_0^4} = \frac{D_2}{1-\varphi_0^2} + \frac{4\xi_0^2 + 1 - m^2}{(1-\varphi_0^2)^2}, \tag{5.14a}$$

$$\frac{S_4}{T} = \frac{D_4 - D_4\varphi_0^2}{1 - 2\varphi_0 + \varphi_0^4} = \frac{D_4}{1-\varphi_0^2}. \tag{5.14b}$$

From (5.11), with due regard to the phase of $P(\varphi_0)$ shown in figures 1f and 2e, it is seen that for large values of $|\varphi_0|$ the function $P(\varphi_0)$ can be expanded in Laurent series with the result

$$P(\varphi_0) = \mathrm{i}\,(\surd D_0)/\varphi_0 + O(1/\varphi_0^3), \quad \varphi_0 \to \infty, \tag{5.15}$$

where $\surd D_0$ denotes the positive square root of D_0. Hence,

$$\frac{1}{2}\int_A P(\varphi_0)\,\mathrm{d}\varphi_0 = \pi\surd D_0. \tag{5.16}$$

Using (3.18), with $s = 0$ and $Y_0 = 1$, (5.12a) and (5.16), we obtain

$$\mathscr{L}^{(1)} = \pi\surd D_0. \tag{5.17}$$

Solving (5.17) with respect to D_0, we obtain

$$D_0 = (\mathscr{L}^{(1)}/\pi)^2. \tag{5.18}$$

From (5.13), (5.14a) and (5.15) we obtain

$$h = \frac{D_2 + \frac{1}{4}}{D_0} + O(1/\varphi_0^2), \quad \varphi_0 \to \infty. \tag{5.19}$$

Therefore we obtain from (5.15)

$$\tfrac{1}{2}hP = \frac{\mathrm{i}(D_2 + \frac{1}{4})}{2\surd(D_0)\,\varphi_0} + O(1/\varphi_0^3), \quad \varphi_0 \to \infty, \tag{5.20}$$

and hence

$$\frac{1}{2}\int_A \tfrac{1}{2}hP(\varphi_0)\,\mathrm{d}\varphi_0 = \pi\frac{D_2 + \frac{1}{4}}{2\surd D_0}. \tag{5.21}$$

Using (3.18) with $s = 1$, (5.12b) and (5.21), we obtain

$$\mathscr{L}^{(3)} = \pi\frac{D_2 + \frac{1}{4}}{2\surd D_0}. \tag{5.22}$$

Solving (5.22) with respect to $D_2 + \frac{1}{4}$ and using (5.17), we get

$$D_2 + \tfrac{1}{4} = 2\,(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(3)}/\pi). \tag{5.23}$$

From (5.14b), (5.15) and (5.19) we obtain

$$\left(-\tfrac{1}{8}h^2 + \frac{S_4/T}{2P^2}\right)P = \left[D_4 - \left(\frac{D_2 + \frac{1}{4}}{2\surd D_0}\right)^2\right]\frac{\mathrm{i}}{2\,(\surd D_0)\,\varphi_0} + O(1/\varphi_0^3), \quad \varphi_0 \to \infty, \tag{5.24}$$

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and hence

$$\frac{1}{2}\int_{\Lambda}\left(-\tfrac{1}{8}h^2+\frac{S_4/T}{2P^2}\right)P(\varphi_0)\,\mathrm{d}\varphi_0=\frac{\pi}{2\sqrt{D_0}}\left[D_4-\left(\frac{D_2+\frac{1}{4}}{2\sqrt{D_0}}\right)^2\right]. \tag{5.25}$$

Using (3.18) with $s=2$, (5.12c) and (5.25), we obtain

$$\mathscr{L}^{(5)}=\frac{\pi}{2\sqrt{D_0}}\left[D_4-\left(\frac{D_2+\frac{1}{4}}{2\sqrt{D_0}}\right)^2\right]. \tag{5.26}$$

Solving (5.26) with respect to D_4 and using (5.18) and (5.23), we obtain

$$D_4=(\mathscr{L}^{(3)}/\pi)^2+2\,(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(5)}/\pi). \tag{5.27}$$

From (5.8), (5.18), (5.23) and (5.27) we obtain the formula

$$\begin{aligned}D+\tfrac{1}{4}\lambda^2&=D_0+(D_2+\tfrac{1}{4})\,\lambda^2+D_4\,\lambda^4+\dots\\&=(\mathscr{L}^{(1)}/\pi)^2+2(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(3)}/\pi)\,\lambda^2\\&\quad+[(\mathscr{L}^{(3)}/\pi)^2+2(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(5)}/\pi)]\,\lambda^4+\dots,\end{aligned} \tag{5.28}$$

the origin of which is the consistency conditions (5.12a–c).

From (5.3) we obtain

$$\frac{\Pi(\varphi)}{\lambda^2}=\frac{D/\lambda^2}{1-\varphi^2}+\frac{1-M^2}{(1-\varphi^2)^2}, \tag{5.29}$$

where by definition

$$M^2=4\xi_0^2/\lambda^2+m^2-4\xi_0^2 \tag{5.30}$$

and hence

$$|M|=(4\xi_0^2/\lambda^2+m^2-4\xi_0^2)^{\frac{1}{2}}. \tag{5.31}$$

The comparison equation (5.2) can therefore be written

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\varphi^2}+\left(\frac{D/\lambda^2}{1-\varphi^2}+\frac{1-M^2}{(1-\varphi^2)^2}\right)\Phi=0. \tag{5.32}$$

Whether the real quantity M is an integer or not, the eigenvalues of (5.32) are (see §2 in II)

$$D/\lambda^2=J(J+1), \tag{5.33}$$

where

$$J=|M|+n,\quad n=0,1,2,\dots. \tag{5.34}$$

From (5.28), (5.33) and (5.34) we obtain the quantization condition

$$\begin{aligned}&[(\mathscr{L}^{(1)}/\pi)^2]\,\lambda^{-2}+[2(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(3)}/\pi)]\,\lambda^0+[(\mathscr{L}^{(3)}/\pi)^2+2(\mathscr{L}^{(1)}/\pi)\,(\mathscr{L}^{(5)}/\pi)]\,\lambda^2+\dots\\&\qquad=(J+\tfrac{1}{2})^2,\quad J=|M|,\,|M|+1,\,|M|+2,\dots.\end{aligned} \tag{5.35}$$

Since in the derivation of this quantization condition the whole region of the real axis from a point well to the left of -1 to a point well to the right of $+1$ is treated by means of one and the same comparison equation (which, however, does not take account of the transition point to the left of -1), the quantization condition in question is expected to be valid also if the turning points t_1 and t_2 of figure 1 or the poles -1 and $+1$ of figure 2 lie close together, provided that the transition point to the left of -1 lies far away from -1.

When C is given by (3.22), i.e. when $C=W+\frac{1}{4}$, and $\omega=0$, we obtain from (4.14a–c)

$$\mathscr{L}^{(2s+1)}=\pi(W+\tfrac{1}{4})^{\frac{1}{2}}\,\delta_{s,0},\quad \omega=0, \tag{5.36}$$

and hence the quantization condition (5.35) with (5.31) and $\lambda = 1$ leads to the exact formula (4.17) for the energy levels.

When all terms are retained in the left-hand member of (5.35), this quantization condition can also be written as

$$\frac{1}{\pi^2\lambda^2}[\mathscr{L}^{(1)}+\mathscr{L}^{(3)}\lambda^2+\mathscr{L}^{(5)}\lambda^4+\ldots]^2 = (J+\tfrac{1}{2})^2, \quad J = |M|, |M|+1, |M|+2, \ldots, \tag{5.37}$$

i.e. as

$$\frac{1}{\lambda}(\mathscr{L}^{(1)}+\mathscr{L}^{(3)}\lambda^2+\mathscr{L}^{(5)}\lambda^4+\ldots) = (J+\tfrac{1}{2})\,\pi, \quad J = |M|, |M|+1, |M|+2, \ldots. \tag{5.38}$$

When we truncate the infinite series in (5.35) and (5.38), use (5.31) and put $\lambda = 1$, we obtain phase-integral quantization conditions for the original differential equation (3.1) with (3.7). The quantization condition thus obtained from (5.38) agrees with (4.12*a*), while that obtained from (5.35) has the more complicated form

$$[(\mathscr{L}^{(1)}/\pi)^2]+2[(\mathscr{L}^{(1)}/\pi)(\mathscr{L}^{(3)}/\pi)]+[(\mathscr{L}^{(3)}/\pi)^2+2(\mathscr{L}^{(1)}/\pi)(\mathscr{L}^{(5)}/\pi)]+\ldots$$
$$= (j+\tfrac{1}{2})^2, \quad j = |m|, \quad |m|+1, \quad |m|+2, \ldots. \tag{5.39}$$

In the left-hand member of this quantization condition the contributions from the successive orders of approximation are placed within square brackets. One may expect that (5.39) is more accurate than (4.12*a*) in the situations discussed below (5.35).

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