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

IV. New phase-integral quantization conditions, very accurate for arbitrary values of the magnetic quantum number, expressed in terms of complete elliptic integrals: survey of their accuracy

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New quantization conditions for the energy levels of a rigid diatomic dipole molecule in a homogeneous electric field of arbitrary strength, obtained by means of a phase-integral method involving phase-integral approximations of arbitrary order generated from two particular choices of the base function, are expressed in terms of complete elliptic integrals in the first, third and fifth order of the phase-integral approximation. Previous results, derived for one convenient choice of the parameter ξ_0 in the base function, namely $\xi_0 = \frac{1}{2}|m|$, where m is the magnetic quantum number, are used, and new formulas are derived for the other convenient choice $\xi_0 = 0$. The accuracy of the eigenvalues obtained from the quantization conditions is demonstrated in a number of diagrams.

1. Introduction

This paper is the fourth in a series concerning the energy levels of a rigid diatomic dipole molecule rotating in a homogeneous electric field. The previous three papers (this Volume) will be referred to as I, II and III. New quantization conditions, valid for arbitrary strengths of the electric field, were obtained in I by means of a phase-integral method involving a phase-integral approximation of arbitrary order generated from an *a priori* unspecified base function. The field-free case as well as the limiting cases of very weak and very strong fields were reviewed in II. With a particular choice of the base function, expected to be especially useful for sufficiently large absolute values of the magnetic quantum number m (but useful even for small values of $|m|$), some of the results in I were used in III, where a quantization condition was expressed in terms of complete elliptic integrals in the first, third and fifth order of the phase-integral approximation. The results in III are used in this paper to express a more general quantization condition in I, corresponding to the same choice of base function, and thus expected to be useful for all sufficiently large values of $|m|$, in terms of complete elliptic integrals. Quantization conditions, generated from another choice of the base function, appropriate for sufficiently small values of $|m|$, are also expressed in terms of complete elliptic integrals in the first, third and fifth order of the phase-integral approximation. The present paper thus completes the investigation in III.

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According to the equations (2.15) and (2.17) in I we have

$$\frac{\mathrm{d}^2 v}{\mathrm{d}z^2}+R(z)\,v=0, \tag{1.1}$$

where
$$R(z)=\frac{W+\omega z}{1-z^2}+\frac{1-m^2}{(1-z^2)^2}, \tag{1.2}$$

the dimensionless quantities W, ω and z being defined by equations (2.3), (2.10) and (2.12) in I, i.e.

$$W=\frac{2I}{\hbar^2}E, \tag{1.3}$$

$$\omega=\frac{2I}{\hbar^2}pF \quad (\geqslant 0), \tag{1.4}$$

$$z=\cos\vartheta, \tag{1.5}$$

where E is the energy, I is the moment of inertia about an axis through the centre of mass and perpendicular to the internuclear axis, p is the electric dipole moment, and F is the electric field strength with a direction corresponding to $\vartheta=0$ in spherical polar coordinates. We obtain the eigenvalues of W by solving the differential equation (1.1) with the boundary conditions

$$v(\pm 1)=0. \tag{1.6}$$

2. The base function

The phase-integral treatment of the eigenvalue problem (1.1) with (1.2) and (1.6) is given in I, where phase-integral quantization conditions of arbitrary order are given. Different quantization conditions arise for different choices of the base function, $Q(z)$, from which the phase-integral approximation of arbitrary order is generated. According to the equations (3.8) and (3.22) in I, a convenient choice for the square of the base function is

$$Q^2(z)=\frac{W+\frac{1}{4}+\omega z}{1-z^2}-\frac{4\xi_0^2}{(1-z^2)^2}, \tag{2.1}$$

where there are two natural choices for the constant ξ_0, namely $\xi_0=\frac{1}{2}|m|$ when $|m|$ is sufficiently large, and $\xi_0=0$ when $|m|$ is sufficiently small, both choices yielding the energy eigenvalues exactly for $\omega=0$.

The choice $\xi_0=\frac{1}{2}|m|>0$ was dealt with in III using the quantization condition (4.12*a*) in I, which is a limiting form of the more general quantization condition (4.11*a*) in I. The results were expected to be good for sufficiently large values of $|m|$, but they were shown to be useful even for $|m|=1$. The general quantization condition (4.11*b*) in I, pertaining to the case when $\xi_0=0$, and its limiting forms (4.12*a*) and (4.12*b*) in I were also investigated in III in the case when $m=0$. In this paper we extend the latter investigation to the case when m may be different from zero, thus completing the case when $\xi_0=0$. The general quantization condition (4.11*a*) in I is also investigated in a general way with the use of the results in III, thus completing the case when $\xi_0=\frac{1}{2}|m|>0$. In all cases the quantization conditions are

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expressed in terms of complete elliptic integrals, and the accuracy of the results is investigated.

(*a*) *The case when* $\xi_0 = \frac{1}{2}|m| > 0$ *and* $\omega > 0$

With $\xi_0 = \frac{1}{2}|m|$ the expression (2.1) takes the form

$$Q^2(z) = \frac{W+\frac{1}{4}+\omega z}{1-z^2} - \frac{m^2}{(1-z^2)^2}, \tag{2.2}$$

i.e. when $|m| > 0$ and $\omega > 0$,

$$Q^2(z) = \omega \frac{(a-z)(z-b)(z-c)}{(1-z^2)^2}, \tag{2.3}$$

where the zeros of $Q^2(z)$ are denoted a, b and c. When W is an eigenvalue, the zeros satisfy according to equation (2.5) in III the inequalities

$$c < -1 < b < a < +1, \quad |b| < a. \tag{2.4}$$

We make $Q(z)$ single-valued in the complex z-plane by introducing cuts along the real axis between $z = -\infty$ and $z = c$ and between $z = b$ and $z = a$, and we define $Q(z)$ to be positive on the upper lip of the latter cut (see figure 1).

(*b*) *The case when* $\xi_0 = 0$ *and* $\omega > 0$

With $\xi_0 = 0$ the expression (2.1) reduces to

$$Q^2(z) = \frac{W+\frac{1}{4}+\omega z}{1-z^2}, \tag{2.5}$$

i.e. when $\omega > 0$,

$$Q^2(z) = \omega(z-t)/(1-z^2), \tag{2.6}$$

where

$$t = -(W+\tfrac{1}{4})/\omega. \tag{2.7}$$

The function $Q^2(z)$ has a single zero at $z = t$ and two simple poles at $z = \pm 1$. It was shown in III that, when W is an eigenvalue, one has either $t < -1$ (figure 2) or $-1 < t < +1$ (figure 3). As can be seen from (2.7) and figure 11 in III, the case $t < -1$ corresponds to comparatively small values of ω, whereas the case $-1 < t < +1$ corresponds to comparatively large values of ω; see also the caption to figures 2 and 3 in I. We make $Q(z)$ single-valued in the complex z-plane by introducing convenient cuts. In the case $t < -1$ cuts are introduced along the real axis between $z = -\infty$ and $z = t$ and between $z = -1$ and $z = +1$, and $Q(z)$ is defined to be positive on the upper lip of the latter cut (see figure 2). In the case $-1 < t < +1$ cuts are introduced along the real axis between $z = -\infty$ and $z = -1$ and between $z = t$ and $z = +1$, and $Q(z)$ is defined to be positive on the upper lip of the latter cut (see figure 3).

3. Phase-integral quantization conditions

The energy eigenvalues of (1.1) are in the $(2N+1)$th-order phase-integral approximation obtainable from the quantization condition (4.11a) in I, when $\xi_0 = \frac{1}{2}|m| > 0$ and $|m|$ is sufficiently large, and from the quantization condition (4.11b) in

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I, when $\xi_0 = 0$ and $|m|$ is sufficiently small. These two quantization conditions, which will be recalled below, contain the common quantities given by the equations (3.17), (3.18), (4.3), (4.4) and (4.5) in I, i.e.

$$\mathscr{L} = \sum_{s=0}^{N} \mathscr{L}^{(2s+1)}, \tag{3.1}$$

where

$$\mathscr{L}^{(2s+1)} = \frac{1}{2}\int_{\Lambda} Z_{2s}\, Q(z)\, \mathrm{d}z, \tag{3.2}$$

and

$$\Delta = -\tfrac{1}{4}(|m|-1)\,\pi + \arg\Gamma(\tfrac{1}{2}|m| + \tfrac{1}{2} + \mathrm{i}\eta) - \xi_0(\operatorname{arctg}(\eta_0/\xi_0) - \tfrac{1}{2}\pi)$$
$$-\eta \ln(\xi_0^2 + \eta_0^2)^{\frac{1}{2}} + \sum_{s=0}^{N} \Delta^{(2s+1)}, \tag{3.3}$$

where

$$\eta = \sum_{s=0}^{N} \eta_{2s}, \tag{3.4}$$

with

$$\eta_{2s} = \frac{\mathrm{i}}{2\pi}\int_{\bar{\Lambda}} Z_{2s}\, Q(z)\, \mathrm{d}z, \tag{3.5}$$

where the first few Z_{2s} are obtained from the equations (3.6a–c) and (3.5) in I, with $R(z)$ given by (1.2) and $Q^2(z)$ given by (2.3) when $\xi_0 = \frac{1}{2}|m| > 0$ and by (2.6) with (2.7) when $\xi_0 = 0$. The closed contours of integration Λ and $\bar{\Lambda}$ in (3.2) and (3.5) depend on the choice of ξ_0 and, when $\xi_0 = 0$, also on the position of the zero t given by (2.7) (see figures 1, 2 and 3). The quantities $\Delta^{(2s+1)}$ are for $s = 0, 1, 2$ given in terms of the quantities η_{2s} by the equations (4.6a–c) and (4.7a–c) in I, pertaining to the case when $\xi_0 = \frac{1}{2}|m| > 0$ and the case when $\xi_0 = 0$ respectively.

As a consequence of the form of the expression (2.1) for $Q^2(z)$ the quantities $\mathscr{L}^{(2s+1)}$ and η_{2s} can be expressed in terms of complete elliptic integrals of the first kind, $K(k)$, the second kind, $E(k)$, and the third kind, $\Pi(\alpha^2, k)$, where k is the modulus and α^2 is the parameter of Π. The complementary modulus k', which will also be used, is related to k by the equation

$$k' = (1-k^2)^{\frac{1}{2}}. \tag{3.6}$$

(a) *The case when* $\xi_0 = \frac{1}{2}|m| > 0$ (*figure* 1)

The quantization condition is given by equation (4.11a) in I, i.e.

$$\mathscr{L} = (n + |m| + \tfrac{3}{4})\,\pi - \Delta, \quad n = 0, 1, 2, \ldots, \tag{3.7}$$

where $\mathscr{L}$ and Δ are given by (3.1) and (3.3) respectively. The quantities $\Delta^{(2s+1)}$ in Δ are for $s = 0, 1, 2$ given by the equations (4.6a–c) in I.

The phase Δ takes into account the possibility that the zero c may lie close to the pole at $z = -1$, and when this is the case (3.7) is expected to be more accurate than the quantization condition (4.12a) in I. When b moves away from -1, the phase Δ tends to the constant value $\frac{1}{4}\pi$ (cf. equation (4.8′) in I). We thus obtain equation (4.12a) in I as a limiting case of (3.7), i.e.

$$\mathscr{L} = (n + |m| + \tfrac{1}{2})\,\pi, \quad n = 0, 1, 2, \ldots, \tag{3.8}$$

which is preferable to use when b is well separated from the pole at $z = -1$.

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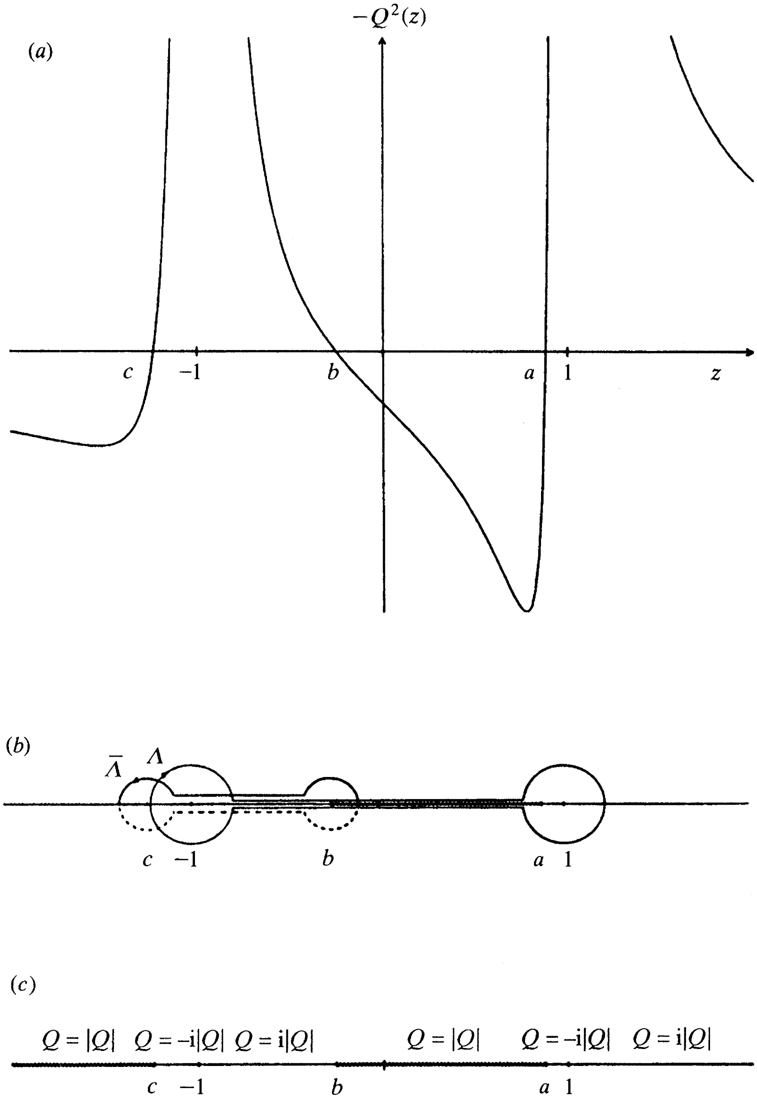

Figures 1–3. 1 (*a*). Graphical representation of $-Q^2(z)$, defined by (2.1), when $\xi_0 = \frac{1}{2}|m| > 0$ and $\omega > 0$. 2 (*a*). Graphical representation of $-Q^2(z)$, defined by (2.6), when $\xi_0 = 0$ and $t < -1$. 3 (*a*). Graphical representation of $-Q^2(z)$, defined by (2.6), when $\xi_0 = 0$ and $-1 < t < +1$. 1–3 (*b*) The contours of integration Λ and $\bar{\Lambda}$ in the complex z-plane. The whole of Λ and the part of $\bar{\Lambda}$ which lies in the complex z-plane under consideration is in each figure indicated by a solid line, and the part of $\bar{\Lambda}$ which lies on the adjacent Riemann sheet is in each figure indicated by a dashed line. 1–3 (*c*) Phase chosen for the base function $Q(z)$ in the complex z-plane under consideration. Cuts are denoted by wavy lines.

The limiting case (3.8) has been treated in III, and we shall use the expressions for $\mathscr{L}^{(2s+1)}$ obtained there to obtain expressions for the quantities η_{2s}.

The contour Λ in (3.2) encircles in the negative sense the poles of $Q^2(z)$ at $z = \pm 1$, but not the zero c. The integrals $\mathscr{L}^{(2s+1)}$ are for $s = 0, 1, 2$ given by the equations (3.21 *a*–*c*) in III, and the functions $g^{(2s+1)}(k, \alpha_1^2, \alpha_2^2)$ appearing in these equations are

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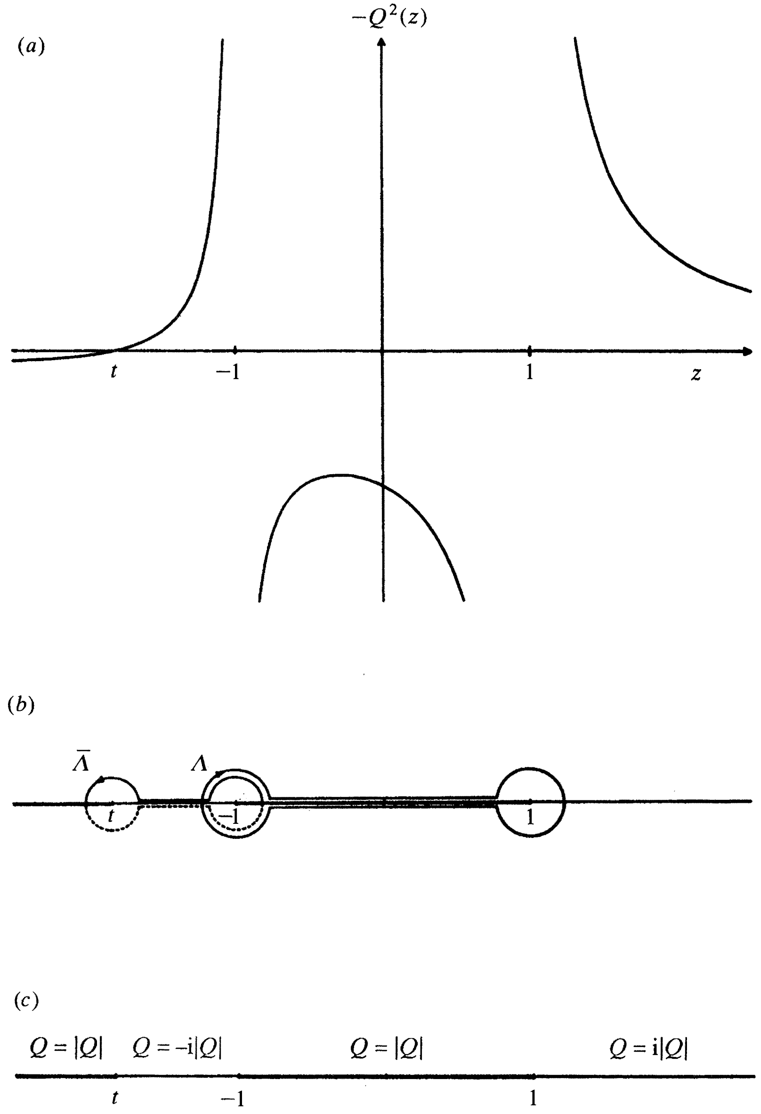

Figure 2. For details see figure 1 caption.

expressed in terms of complete elliptic integrals by the equations (3.19*a*–*c*) in III, with the square of the modulus, k^2, and the parameters α_1^2 and α_2^2 given by the equations (3.9) and (3.13*a*, *b*) in III. The contour $\bar{\Lambda}$ in (3.5) encircles in the positive sense the zeros b and c, but not the zero a (cf. figure 1). We can obtain the expressions for η_{2s} from the expressions for $\mathscr{L}^{(2s+1)}$ by making use of the appropriate values of the modulus k and the parameters α_1^2 and α_2^2. Thus we obtain

$$\eta_0 = -g^{(1)}(k, \alpha_1^2, \alpha_2^2)/\pi, \tag{3.9a}$$

$$\eta_2 = +g^{(3)}(k, \alpha_1^2, \alpha_2^2)/\pi, \tag{3.9b}$$

$$\eta_4 = -g^{(5)}(k, \alpha_1^2, \alpha_2^2)/\pi, \tag{3.9c}$$

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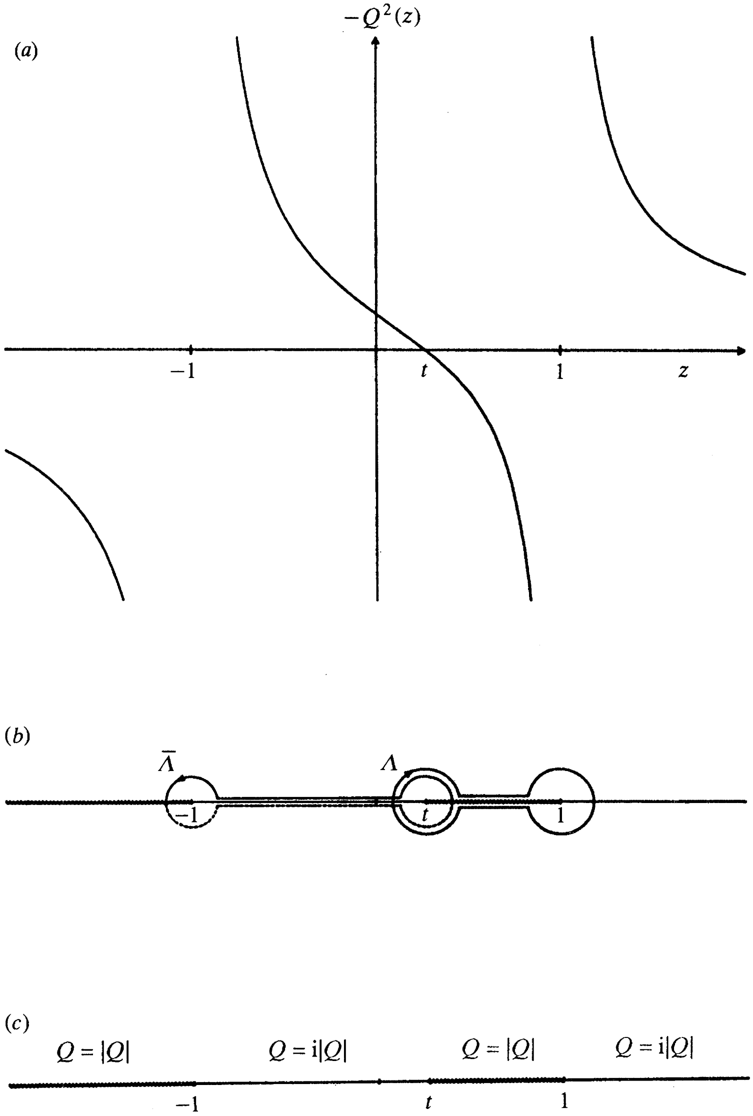

Figure 3. For details see figure 1 caption.

where the functions $g^{(2s+1)}(k, \alpha_1^2, \alpha_2^2)$ for $s = 0, 1, 2$ are defined by the equations (3.19*a–c*) in III with the square of the modulus, k^2, and the parameters α_1^2 and α_2^2 now given by

$$k^2 = (b-c)/(a-c), \tag{3.10a}$$

$$\alpha_1^2 = (b-c)/(1-c) \quad (>0), \tag{3.10b}$$

$$\alpha_2^2 = (b-c)/(-1-c) \quad (>0). \tag{3.10c}$$

For an alternative way of representing the integrals $\mathscr{L}^{(2s+1)}$ and η_{2s} we refer to Appendix A.

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(*b*) *The case when* $\xi_0 = 0$ (*figures* 2 *and* 3)

The quantization condition is given by equation (4.11*b*) in I, i.e.

$$\mathscr{L} = (n+\tfrac{1}{2}|m|+\tfrac{3}{4})\,\pi - \varDelta, \quad n = 0, 1, 2, \ldots, \tag{3.11}$$

where $\mathscr{L}$ and $\varDelta$ are given by (3.1) and (3.3) respectively. The quantities $\varDelta^{(2s+1)}$ in $\varDelta$ are for $s = 0, 1, 2$ now given by the equations (4.7*a*–*c*) in I.

The phase $\varDelta$ takes into account the possibility that the zero t may lie close to the pole at $z = -1$, and when this is the case (3.11) is expected to be more accurate than the quantization conditions (4.12*a*) and (4.12*b*) in I. When t in figures 2 and 3 moves far away from -1 the phase $\varDelta$ tends to the limiting values $(\frac{1}{4}-\frac{1}{2}|m|)\,\pi$ and $\frac{1}{4}\pi$ respectively; see equations (4.8′) in I. Thus, when $t < -1$, we obtain from (3.11) the quantization condition (4.12*a*) in I, i.e.

$$\mathscr{L} = (|m|+n+\tfrac{1}{2})\,\pi, \quad n = 0, 1, 2, \ldots, \tag{3.12}$$

and when $-1 < t < +1$ we obtain from (3.11) the quantization condition (4.12*b*) in I, i.e.

$$\mathscr{L} = (\tfrac{1}{2}|m|+n+\tfrac{1}{2})\,\pi, \quad n = 0, 1, 2, \ldots. \tag{3.13}$$

The quantization condition (3.11) and its limiting forms (3.12) and (3.13) have been treated in III only in the case when $m = 0$. The investigation in III is in the present paper extended to the case when m may be different from zero.

The procedure for evaluating the integrals $\mathscr{L}^{(2s+1)}$ and η_{2s} in terms of complete elliptic integrals consists essentially in decomposing the integrands into partial fractions until integrals of the types given in Byrd & Friedman (1971) appear (cf. §3 in III).

(i) *The subcase to* $\xi_0 = 0$ *when* $t < -1$ (*figure* 2)

The contour $\varLambda$ in (3.2) encircles in the negative sense the poles ± 1, but not the zero t (see figure 2*b*). The results are

$$\mathscr{L}^{(1)} = 2\left(\frac{2\omega}{k^2}\right)^{\frac{1}{2}} E(k), \tag{3.14a}$$

$$\mathscr{L}^{(3)} = \frac{1-3m^2}{12k'^2}\left(\frac{k^2}{2\omega}\right)^{\frac{1}{2}}((2-k^2)\,[K(k)-E(k)]-k^2K(k)), \tag{3.14b}$$

$$\begin{aligned}\mathscr{L}^{(5)} = \frac{1}{2880k'^6}\left(\frac{k^2}{2\omega}\right)^{\frac{3}{2}} &[((120m^4-240m^2+56)\,k^8+(-105m^4+570m^2-145)\,k^6\\ &+(-135m^4-450m^2+129)\,k^4+(480m^4-240m^2+32)\,k^2\\ &+(-240m^4+120m^2-16))\,[K(k)-E(k)]\\ &-((60m^4-120m^2+28)\,k^6+(-45m^4+270m^2-69)\,k^4\\ &+(225m^4-450m^2+105)\,k^2+(-120m^4+60m^2-8))\,k^2K(k)],\end{aligned} \tag{3.14c}$$

where
$$k = (2/(1-t))^{\frac{1}{2}}. \tag{3.15}$$

When we put $m = 0$ in (3.14*a*–*c*), we obtain the equations (3.22*a*–*c*) in III.

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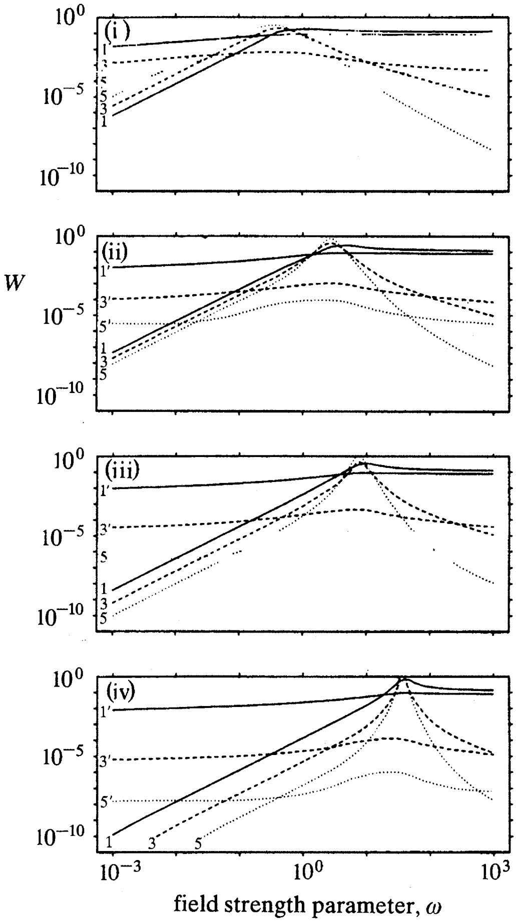

Figures 4–9. Envelope curves representing the magnitude of the absolute error in the approximate energy eigenvalues W against ω. These envelopes are constructed such that the absolute value of the error is less than or equal to the error indicated by the envelopes (cf. figures 4 and 7*c* in III). Figures 4–9 refer to the quantum numbers $|m| = 0, 1, 2, 3, 4$ and 5 respectively. Figures 5–9 consist of two columns of diagrams, where the left column (*a*) refers to the case when $\xi_0 = \frac{1}{2}|m| > 0$, i.e. to the quantization conditions (3.7) and (3.8), whereas the right column (*b*) refers to the case when $\xi_0 = 0$, i.e. to the quantization conditions (3.11) and (3.12) or (3.13). Since we are thus left with only one possible choice, namely $\xi_0 = 0$, when $m = 0$, figure 4 consists of only one column of diagrams. For each value of $|m|$, the error in the eigenvalue W obtained in the first (solid line), third (dashed line) and fifth (dotted line) order of the phase-integral approximation is shown for the quantum numbers $n = 0$ (i), 1 (ii), 2 (iii) and 5 (iv). The curves denoted by the digits 1′, 3′, 5′ and 1, 3, 5 in the figures refer to the order of the phase-integral approximations in the cases when the eigenvalues are obtained from the quantization conditions (3.7) and (3.11), and in the cases when the eigenvalues are obtained from the quantization conditions (3.8), (3.12) and (3.13) respectively.

The contour $\bar{\Lambda}$ in (3.5) encircles in the positive sense the zero t and the pole -1, but not the pole $+1$ (see figure 2*b*). The results are

$$\eta_0 = -\frac{2}{\pi}\left(\frac{2\omega}{k'^2}\right)^{\frac{1}{2}}[K(k)-E(k)], \tag{3.16a}$$

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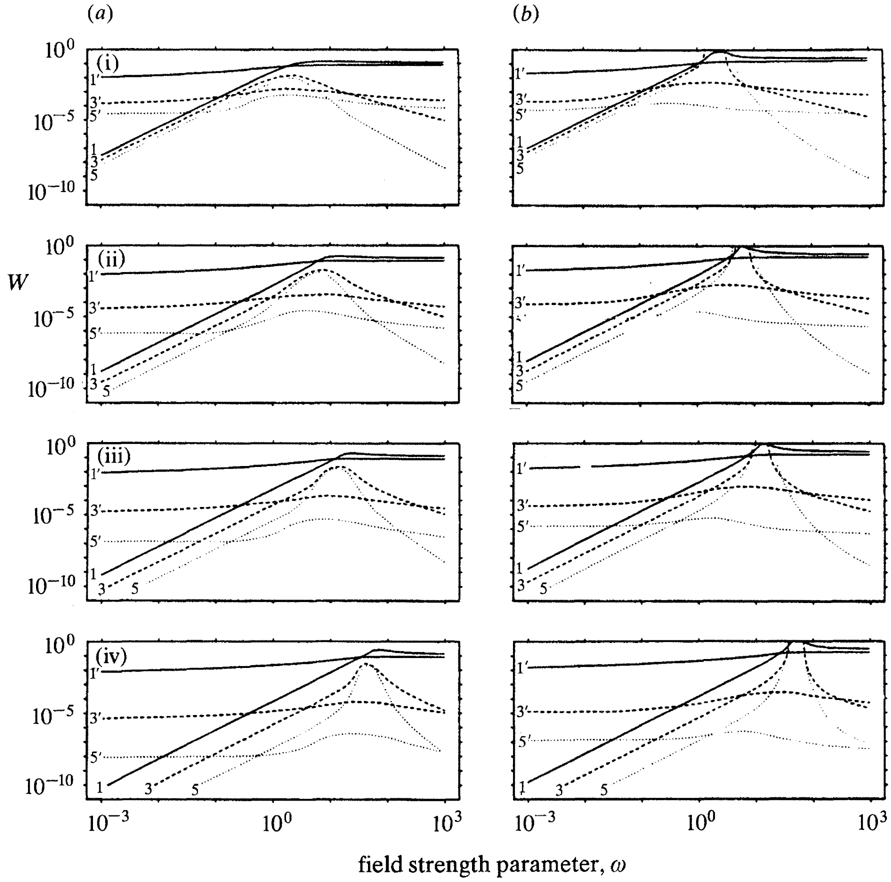

Figure 5. For details see figure 4 caption.

$$\eta_2 = \frac{1-3m^2}{12\pi k^2}\left(\frac{k'^2}{2\omega}\right)^{\frac{1}{2}}((k^2+1)\,[K(k)-E(k)]-2k^2K(k)), \tag{3.16b}$$

$$\begin{aligned}\eta_4 = \frac{1}{2880\pi k^6}\left(\frac{k'^2}{2\omega}\right)^{\frac{3}{2}}&[((120m^4-240m^2+56)\,k^8+(-375m^4+390m^2-79)\,k^6\\&+(270m^4-180m^2+30)\,k^4+(-375m^4+390m^2-79)\,k^2\\&+(120m^4-240m^2+56))\,[K(k)-E(k)]\\&-((60m^4-120m^2+28)\,k^6+(-180m^4+180m^2-36)\,k^4\\&+(-180m^4+180m^2-36)\,k^2+(60m^4-120m^2+28))\,k^2K(k)],\end{aligned} \tag{3.16c}$$

where
$$k=((t+1)/(t-1))^{\frac{1}{2}}. \tag{3.17}$$

When we put $m=0$ in (3.16*a*–*c*), we obtain the equations (3.30*a*–*c*) in III.

For an alternative way of representing the results in this subsection we refer to Appendix B.

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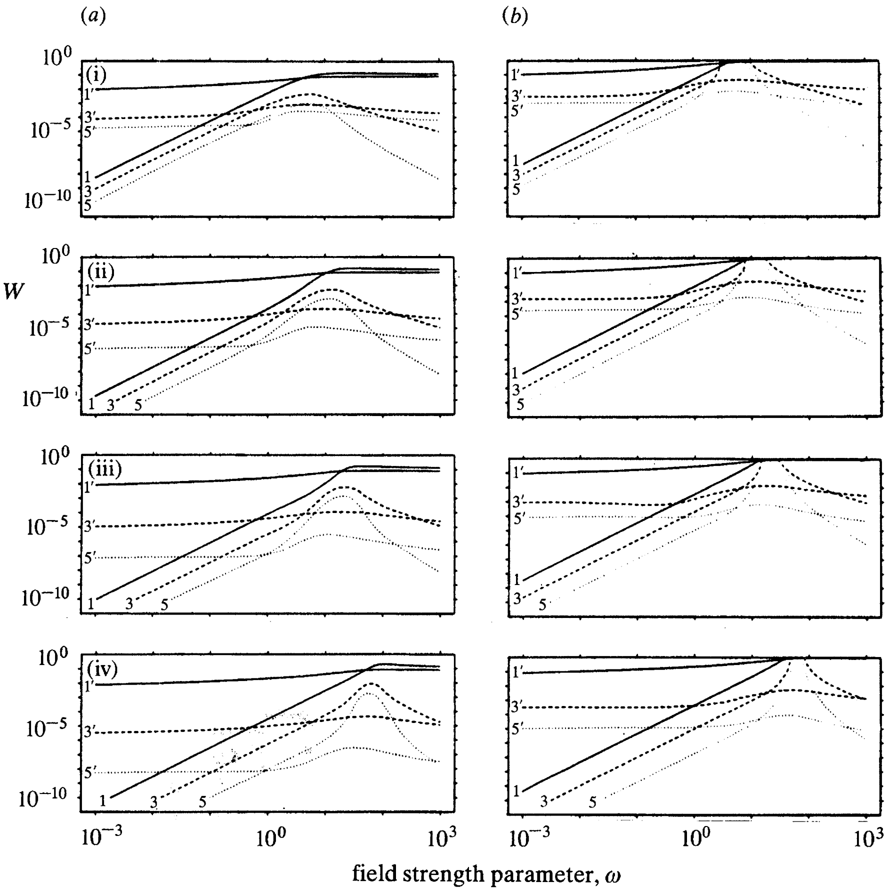

Figure 6. For details see figure 4 caption.

(ii) *The subcase to* $\xi_0 = 0$ *when* $-1 < t < \pm 1$ (*figure* 3)

The contour Λ in (3.2) encircles in the negative sense the pole $+1$ and the zero t, but not the pole -1 (see figure 3*b*). Defining the functions

$$h^{(1)}(k) = 2(2\omega)^{\frac{1}{2}}(-[K(k)-E(k)]+k^2K(k)), \tag{3.18a}$$

$$h^{(3)}(k) = \frac{1-3m^2}{12k^2k'^2(2\omega)^{\frac{1}{2}}}((1-2k^2)[K(k)-E(k)]+k^2K(k)), \tag{3.18b}$$

$$\begin{aligned} h^{(5)}(k) = \frac{1}{2880k^6k'^6}\frac{1}{(2\omega)^{\frac{3}{2}}}[((240m^4-120m^2+16)\,k^8 \\ +(-480m^4+240m^2-32)\,k^6+(135m^4+450m^2-129)\,k^4 \\ +(105m^4-570m^2+145)\,k^2+(-120m^4+240m^2-56))\,[K(k)-E(k)] \\ -((120m^4-60m^2+8)\,k^6+(-225m^4+450m^2-105)\,k^4 \\ +(45m^4-270m^2+69)\,k^2+(-60m^4+120m^2-28))\,k^2K(k)], \end{aligned} \tag{3.18c}$$

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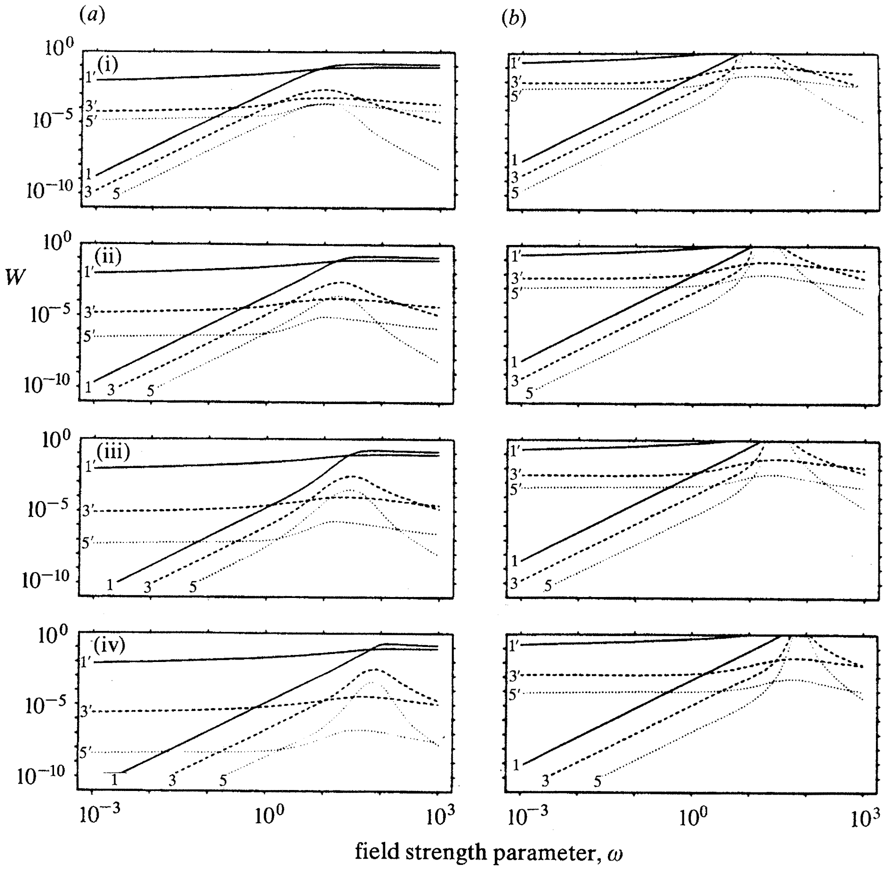

Figure 7. For details see figure 4 caption.

we obtain

$$\mathscr{L}^{(1)} = h^{(1)}(k), \tag{3.19a}$$

$$\mathscr{L}^{(3)} = h^{(3)}(k), \tag{3.19b}$$

$$\mathscr{L}^{(5)} = h^{(5)}(k), \tag{3.19c}$$

where

$$k = (\tfrac{1}{2}(1-t))^{\frac{1}{2}}. \tag{3.20}$$

When we put $m = 0$ in (3.19*a*–*c*) with (3.18*a*–*c*) and (3.20), we obtain the equations (3.24*a*–*c*) in III.

The contour $\bar{\Lambda}$ in (3.5) encircles in the positive sense the pole -1 and the zero t, but not the pole $+1$ (see figure 3*b*). We can obtain the expressions for η_{2s} from the expressions for $\mathscr{L}^{(2s+1)}$ by making use of the appropriate value of the modulus k. The results are

$$\eta_0 = +h^{(1)}(k)/\pi, \tag{3.21a}$$

$$\eta_2 = -h^{(3)}(k)/\pi, \tag{3.21b}$$

$$\eta_4 = +h^{(5)}(k)/\pi, \tag{3.21c}$$

where

$$k = (\tfrac{1}{2}(1+t))^{\frac{1}{2}}. \tag{3.22}$$

When we put $m = 0$ in (3.21*a*–*c*) with (3.18*a*–*c*) and (3.22), we obtain the equations (3.32*a*–*c*) in III.

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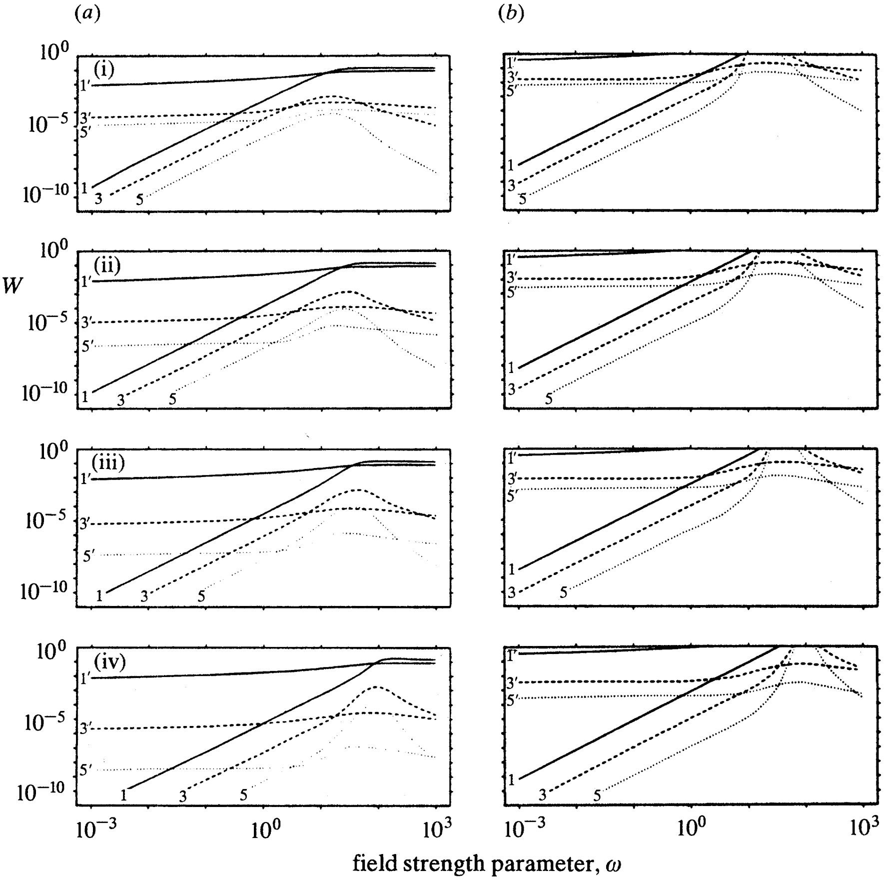

Figure 8. For details see figure 4 caption.

For an alternative way of representing the results in this subsection we refer to Appendix B.

4. Investigation of the accuracy: conclusions

The accuracy of the eigenvalues W obtained from the quantization condition (3.7), pertaining to the case when $\xi_0 = \frac{1}{2}|m| > 0$, and the quantization condition (3.11), pertaining to the case when $\xi_0 = 0$, and their limiting forms (3.8) and (3.12) or (3.13), respectively, is demonstrated in figures 4–9 for $m = 0$, 1, 2, 3, 4, 5 from which it is seen that the quantization conditions and their limiting forms become better with increasing order of the phase-integral approximation (at least up to order 5) with only a few minor exceptions.

The magnitude of the absolute error in W obtained from the two quantization conditions which include the phase Δ, is almost independent of the values of ω; see the curves denoted by primed digits in figures 4–9. The error in W obtained from the limiting forms of the quantization conditions is small for small values of ω and (except for the first order of the phase-integral approximation) also for large values of ω, while the error for intermediate values of ω is larger, giving rise to a pronounced peak; see the curves denoted by unprimed digits in figures 4–9.

The above-mentioned regions of intermediate values of ω, where the quantization

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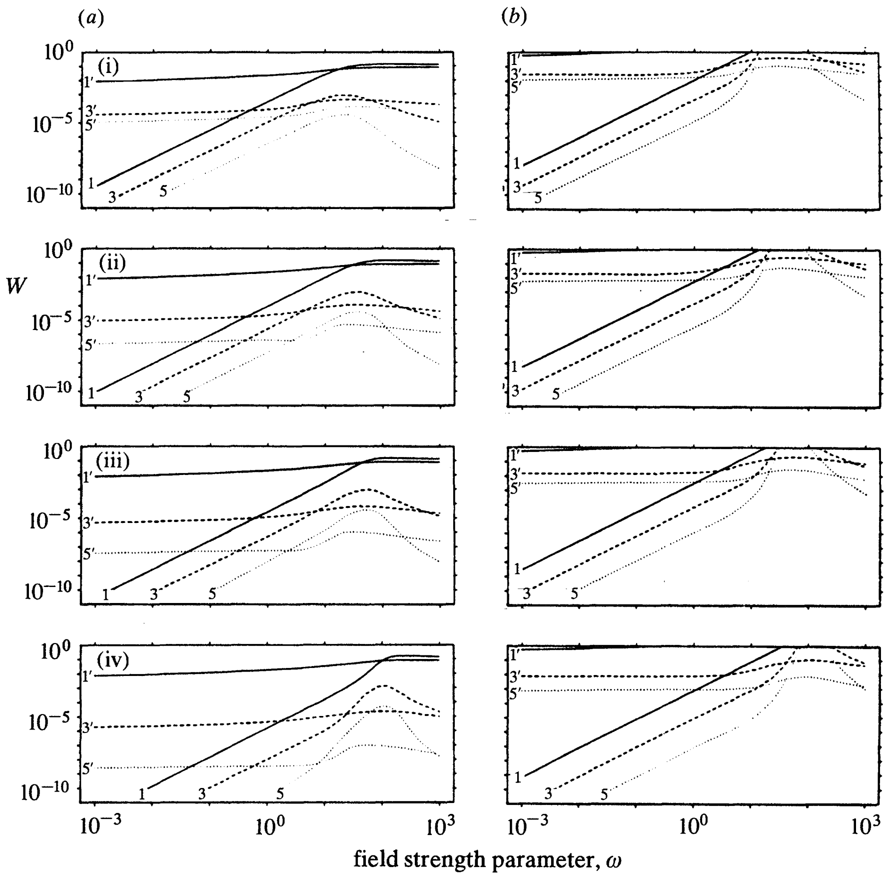

Figure 9. For details see figure 4 caption.

conditions (3.7) and (3.11) usually are more accurate than their corresponding limiting forms, i.e. (3.8) and (3.12, 13), respectively, are empirically seen from the figures 5–9 to coincide for both choices of base function and the same set of values of $|m|$ and n. In the case $\xi_0 = 0$ (figure 4 and the right columns of figures 5–9) no solution to the limiting forms (3.12) or (3.13) of the quantization condition might even exist when the zero denoted t lies close to the pole -1, which case corresponds to the situation when ω is close to $W+\frac{1}{4}$ according to (2.7). The simple quantization condition (3.12), which is valid when $t < -1$, is applicable to the left of the peak of each curve, and the simple quantization condition (3.13), which is valid when $-1 < t < +1$, is applicable to the right of the peak of each curve.

In the first-order approximation, (3.7) will yield fairly poor accuracy of W for all values of n, $|m|$ and ω, while (3.11) will cease to be useful for $|m| > 1$ in the region of intermediate and large values of ω. If we wish to obtain the energy eigenvalue W with a reasonable accuracy for all values of ω by means of one of the two quantization conditions (3.7) or (3.11), we should therefore exclude the results of the first-order phase-integral approximation. In the first, third and fifth order of the phase-integral approximation, the accuracy of W obtained by means of (3.11) will slowly decrease for fixed value of n, when $|m|$ increases from the value 2. On the other hand, if we choose $\xi_0 = 0$, the quantization condition (3.11) must be used for $|m| = 0$ and $n > 1$

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as well as for $|m| > 0$ and arbitrary values of n in the intermediate region of values of ω, where the limiting forms of this quantization condition, i.e. (3.12) or (3.13), become useless. For both quantization conditions (3.7) and (3.11) the accuracy of the third- and fifth-order approximations of W increases for fixed value of $|m|$, when the value of n increases.

If we ask the question which quantization condition gives the best approximation of the eigenvalue W, the following rules apply. If we compare the quantization condition (3.7) with the quantization condition (3.11) and compare the limiting form (3.8) with the limiting form (3.12) or (3.13), and make this comparison order by order, we observe that for $|m| = 1$ the accuracy of the eigenvalues obtained are comparable, apart from the regions of intermediate values of ω where (3.12) and (3.13) become useless, while for $|m|$ larger than 1, the quantization conditions which pertain to the case when $\xi_0 = \frac{1}{2}|m| > 0$, i.e. (3.7) and (3.8), are preferable. The quantization condition (3.7) should be used in the region where the curves pertaining to the quantization condition (3.8) has a peak, i.e. in the region around the point where the relation $\omega = W + \frac{1}{4}$ holds. Outside this region the quantization condition (3.8) should be used. When $|m|$ is large and n is at the same time small, the gain in accuracy achieved by the use of the quantization condition (3.7) decreases; e.g. when $|m| \geqslant 3$ and $n = 0$ the limiting form (3.8) should be used in the fifth order of the phase-integral approximation for all values of ω.

The least and the next least accurate energy eigenvalues are obtained in the centre of the intermediate region for $|m| = n = 0$ and for $|m| = 1$, $n = 0$ respectively (see figures 4 and 5). The highest accuracy we can get there for these quantum numbers is obtained by means of the quantization condition (3.11) in the fifth order of the phase-integral approximation, which yields an absolute error of less than 0.01 and 0.001 respectively. In most cases, however, and especially when $|m| > 1$, the absolute error in the eigenvalues obtained from the quantization condition (3.7) in the centre of the intermediate region, and its limiting form (3.8) on both sides of the intermediate region, in the fifth order of the phase-integral approximation is considerably less.

Thus we have shown that the phase-integral method is capable of giving good, and often extremely good energy eigenvalues for a rigid diatomic molecule in a homogeneous electric field of arbitrary strength, for all values of the quantum numbers m and n.

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Appendix A

The integrals $\mathscr{L}^{(2s+1)}$ and η_{2s} given in §3*a* and pertaining to the case when $\xi_0 = \frac{1}{2}|m| > 0$ can be presented in more condensed form when the modulus k and the parameters α_1^2 and α_2^2 are chosen in other ways. Thus, defining

$$f^{(1)}(k,\alpha_1^2,\alpha_2^2) = \frac{2}{kk'}\left(\frac{2\omega(\alpha_1^2-k^2)(k^2-\alpha_2^2)}{(\alpha_1^2-\alpha_2^2)^3}\right)^{\frac{1}{2}}((\alpha_1^2-\alpha_2^2)E(k)-(1-\alpha_1^2)(k^2-\alpha_2^2)\,\Pi(\alpha_1^2,k)$$
$$+(1-\alpha_2^2)(k^2-\alpha_1^2)\,\Pi(\alpha_2^2,k)), \quad (\mathrm{A}\,1a)$$

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$$\begin{aligned} f^{(3)}(k,\alpha_1^2,\alpha_2^2) = {} & \frac{kk'}{12}\left(\frac{\alpha_1^2-\alpha_2^2}{2\omega(\alpha_1^2-k^2)^3\,(k^2-\alpha_2^2)^3}\right)^{\frac{1}{2}}[((2k^2-1)\,\alpha_1^2\,\alpha_2^2-(k^2+1)\,(\alpha_1^2+\alpha_2^2) \\ & -(k^2-2))\,[K(k)-E(k)]+(-\alpha_1^2\,\alpha_2^2+2(\alpha_1^2+\alpha_2^2)-1)\,k^2K(k)], \end{aligned} \tag{A 1b}$$

$$\begin{aligned} f^{(5)}(k,\alpha_1^2,\alpha_2^2) = {} & \frac{k^3k'^3}{2880}\left(\frac{\alpha_1^2-\alpha_2^2}{2\omega(\alpha_1^2-k^2)^3\,(k^2-\alpha_2^2)^3}\right)^{\frac{3}{2}}[((1008k^8-1650k^6+768k^4 \\ & -1650k^2+1008)\,\alpha_1^2\,\alpha_2^2(\alpha_1^2+\alpha_2^2)+(-1792k^8+3584k^6-2082k^4 \\ & +290k^2+2)\,\alpha_1^6\,\alpha_2^6+(2k^8+290k^6-2082k^4+3584k^2-1792) \\ & +(2688k^8-5112k^6+2727k^4-309k^2)\,\alpha_1^4\,\alpha_2^4(\alpha_1^2+\alpha_2^2) \\ & +(-309k^6+2727k^4-5112k^2+2688)\,(\alpha_1^2+\alpha_2^2)+(-1680k^8 \\ & +3096k^6-1644k^4+234k^2-168)\,\alpha_1^4\,\alpha_2^4 \\ & +(-168k^8+234k^6-1644k^4+3096k^2-1680)\,\alpha_1^2\,\alpha_2^2+(-1008k^8 \\ & +1752k^6-804k^4+66k^2-42)\,\alpha_1^2\,\alpha_2^2(\alpha_1^2+\alpha_2^2)^2+(-42k^8+66k^6 \\ & -804k^4+1752k^2-1008)\,(\alpha_1^2+\alpha_2^2)^2+(56k^8-79k^6 \\ & +30k^4-79k^2+56)\,(\alpha_1^2+\alpha_2^2)^3)\,[K(k)-E(k)] \\ & +((-504k^6+762k^4+762k^2-504)\,\alpha_1^2\,\alpha_2^2(\alpha_1^2+\alpha_2^2)+(-28k^6+36k^4 \\ & +36k^2-28)\,(\alpha_1^2+\alpha_2^2)^3+(896k^6-1680k^4+873k^2-91)\,\alpha_1^6\,\alpha_2^6 \\ & +(-91k^6+873k^4-1680k^2+896)+(-1344k^6+2388k^4 \\ & -1128k^2+90)\,\alpha_1^4\,\alpha_2^4(\alpha_1^2+\alpha_2^2)+(90k^6-1128k^4+2388k^2-1344) \\ & \times(\alpha_1^2+\alpha_2^2)+(840k^6-1443k^4+681k^2+84)\,\alpha_1^4\,\alpha_2^4+(84k^6+681k^4 \\ & -1443k^2+840)\,\alpha_1^2\,\alpha_2^2+(504k^6-813k^4+324k^2+21) \\ & \times\alpha_1^2\,\alpha_2^2(\alpha_1^2+\alpha_2^2)^2+(21k^6+324k^4-813k^2+504)(\alpha_1^2+\alpha_2^2)^2)\,k^2K(k)], \end{aligned} \tag{A 1c}$$

we have

$$\mathscr{L}^{(1)} = f^{(1)}(k,\alpha_1^2,\alpha_2^2)+|m|\,\pi, \tag{A 2a}$$

$$\mathscr{L}^{(3)} = f^{(3)}(k,\alpha_1^2,\alpha_2^2), \tag{A 2b}$$

$$\mathscr{L}^{(5)} = f^{(5)}(k,\alpha_1^2,\alpha_2^2), \tag{A 2c}$$

with

$$\alpha_1^2 = \frac{(a-b)\,(1-c)}{(a-c)\,(1-b)} = k^2\frac{1-c}{1-b} \quad (>0), \tag{A 2d}$$

$$\alpha_2^2 = \frac{(a-b)\,(1+c)}{(a-c)\,(1+b)} = k^2\frac{1+c}{1+b} \quad (<0), \tag{A 2e}$$

$$k^2 = \frac{a-b}{a-c}, \tag{A 2f}$$

and

$$\eta_0 = +f^{(1)}(k,\alpha_1^2,\alpha_2^2)/\pi, \tag{A 3a}$$

$$\eta_2 = -f^{(3)}(k,\alpha_1^2,\alpha_2^2)/\pi, \tag{A 3b}$$

$$\eta_4 = +f^{(5)}(k,\alpha_1^2,\alpha_2^2)/\pi, \tag{A 3c}$$

with

$$\alpha_1^2 = \frac{(b-c)\,(1+a)}{(a-c)\,(1+b)} = k^2\frac{1+a}{1+b} \quad (>0), \tag{A 3d}$$

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$$\alpha_2^2 = \frac{(b-c)(1-a)}{(a-c)(1-b)} = k^2\frac{1-a}{1-b} \quad (>0), \tag{A 3e}$$

$$k^2 = \frac{b-c}{a-c}. \tag{A 3f}$$

Appendix B

The integrals $\mathscr{L}^{(2s+1)}$ and η_{2s} given in §3*b*(i), (ii) and pertaining to the case when $\xi_0 = 0$ can be written in the more condensed form

$$\mathscr{L}^{(2s+1)} = C^{(2n+1)}(a^{(2n+1)}E(k') + b^{(2n+1)}K(k')), \quad t < -1, \tag{B 1}$$

$$\mathscr{L}^{(2s+1)} = C^{(2n+1)}\left[a^{(2n+1)}\left(k'E(1/k') + k^2\frac{K(1/k')}{k'}\right) + b^{(2n+1)}\frac{K(1/k')}{k'}\right], \quad -1 < t < +1, \tag{B 2}$$

$$\eta_{2s} = \frac{C^{(2n+1)}}{\pi}(a^{(2n+1)}[E(k) - K(k)] - b^{(2n+1)}K(k)), \quad t < -1, \tag{B 3}$$

$$\eta_{2s} = \frac{C^{(2n+1)}}{\pi}\left[a^{(2n+1)}\left(k'E(\mathrm{i}k/k') - \frac{K(\mathrm{i}k/k')}{k'}\right) - b^{(2n+1)}\frac{K(\mathrm{i}k/k')}{k'}\right], -1 < t < +1, \tag{B 4}$$

where

$$k = ((t+1)/(t-1))^{\frac{1}{2}}, \tag{B 5a}$$

$$k' = (1-k^2)^{\frac{1}{2}}, \tag{B 5b}$$

$$C^{(2n+1)} = \frac{2}{(n+1)!\,(2n+1)!\,(2k^2)^{n(n+1)/2}}\left(\frac{2\omega}{k'^2}\right)^{\frac{1}{2}-n}, \quad n = 0, 1, 2, \tag{B 6}$$

$$a^{(1)} = 1, \tag{B 7a}$$

$$a^{(3)} = (k^2+1)(3m^2-1), \tag{B 7b}$$

$$a^{(5)} = (-8k^8 + k^6 + 6k^4 + k^2 - 8)(15m^4 - 30m^2 + 7) + 72(k^6 - k^4 + k^2)(5m^4 - 5m^2 + 1), \tag{B 7c}$$

$$b^{(1)} = 0, \tag{B 8a}$$

$$b^{(3)} = -2k^2(3m^2-1), \tag{B 8b}$$

$$b^{(5)} = 4(k^8 + k^2)(15m^4 - 30m^2 + 7) - 36(k^6 + k^4)(5m^4 - 5m^2 + 1). \tag{B 8c}$$

When $-1 < t < +1$, (B 3) remains valid, but the argument of the complete elliptic integrals is not real. With this exception the arguments of the complete elliptic integrals in (B 1), (B 2), (B 3) and (B 4) are real and lie between 0 and 1.

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