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# Rotation of a Rigid Diatomic Dipole Molecule in a Homogeneous Electric Field II. Energy Levels when the Field is Zero, very Weak or very Strong

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

## II. Energy levels when the field is zero, very weak or very strong

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The energy quantization problem for a rigid diatomic electric dipole molecule in a homogeneous static electric field is considered. The field-free case is treated in some detail, since it is difficult to find a comprehensive treatment in the literature. For the limiting case of very weak fields the available results of conventional perturbation theory are presented in lucid form. For the limiting case of very strong fields an easily surveyable perturbation calculation is performed.

### 1. Introduction

This paper is the second of a series (this Volume) concerning the rotation of a rigid diatomic dipole molecule in a homogeneous static electric field. The preceding paper will be referred to as I. The purpose of this paper is to collect and present in lucid form the available quantal energy level results for the case that the field is zero as well as for the limiting cases of very weak and very strong fields. For the cases of no field and very strong fields we have found it useful to give derivations that are comprehensive and easy to survey. For the background and the notations to be used we refer to §§1 and 2 in I. The results collected in this paper will be used in the following two papers (this Volume), which will be referred to as III and IV respectively.

### 2. The case of field-free space

It is well-known that the eigenvalues of a rigid diatomic molecule in field-free space are given by the formula

$$W = j(j+1), \quad j = |m|, \quad |m|+1, \quad |m|+2, \ldots . \tag{2.1}$$

Because this result is often quoted without full proof, and because we need it in §5 of I for the generalization that the real quantum number $m$ need not be an integer, we shall use a few lines for proving (2.1) under this general assumption.

By investigating the solutions of the differential equation (2.13) in I, with $U(z) = 0$, in the neighbourhood of $z = +1$ one finds that the solution which remains finite and single-valued at this point behaves as $(z-1)^{|m|/2}$ times a power series in $z-1$, the constant term of which is different from zero. For the solution which remains finite at $z = -1$ one finds a corresponding result. Thus the solution which remains finite at

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both points $z = \pm 1$ must be equal to $(1-z^2)^{|m|/2}$ times a single-valued and regular function. Therefore we insert

$$\psi = (1-z^2)^{|m|/2} \sum_{\nu=0}^{\infty} a_\nu z^\nu \tag{2.2}$$

into equation (2.13) in I, with $U(z) = 0$, getting the recurrence formula

$$(\nu+1)(\nu+2)\, a_{\nu+2} = [(\nu+|m|)(\nu+|m|+1) - W]\, a_\nu, \quad \nu = 0, 1, 2, \ldots . \tag{2.3}$$

By choosing ($a_0 \neq 0$, $a_1 = 0$) and ($a_0 = 0$, $a_1 \neq 0$), respectively, we obtain two solutions of opposite parity, which will be considered separately. Unless the coefficients $a_\nu$ are equal to zero for sufficiently large values of $\nu$, one finds from (2.3) that

$$\ln \frac{a_{\nu+2}}{a_\nu} = \frac{2(|m|-1)}{\nu} + O(1/\nu^2), \quad \nu \to \infty, \tag{2.4}$$

and therefore

$$\ln a_\nu = \exp\left(2(|m|-1) \sum_{\substack{\nu'=1 \\ \text{or } 2}}^{\nu} \frac{1}{\nu'} + O(1)\right), \quad \nu \to \infty, \tag{2.5}$$

where the sum over $\nu'$ contains only either even or odd values of $\nu'$, depending on whether $\nu$ is even or odd. Since

$$\sum_{\substack{\nu'=1 \\ \text{or } 2}}^{\nu} \frac{1}{\nu'} = \tfrac{1}{2} \ln \nu + O(1), \quad \nu \to \infty, \tag{2.6}$$

we obtain from (2.5)

$$a_\nu = \exp[O(1)]\, \nu^{|m|-1}, \quad \nu \to \infty. \tag{2.7}$$

When $m = 0$ the sum of the series

$$\sum_{\substack{\nu \text{ either} \\ \text{even or odd}}}^{\infty} a_\nu z^\nu \tag{2.8}$$

therefore tends to $\infty$ as $z \to \pm 1$, unless the coefficients $a_\nu$ are equal to zero for sufficiently large values of $\nu$.

To treat the case when $m \neq 0$ we first note that

$$(1-z^2)^{-|m|} = 1 + \frac{1}{\Gamma(|m|)\, 2^{|m|-1}} \sum_{\mu=1}^{\infty} \frac{\Gamma(\mu+|m|)}{\Gamma(\mu+1)\, \mu^{|m|-1}} (2\mu)^{|m|-1} z^{2\mu} \tag{2.9a}$$

and

$$z(1-z^2)^{-|m|} = z + \frac{1}{\Gamma(|m|)\, 2^{|m|-1}} \sum_{\mu=1}^{\infty} \frac{\Gamma(\mu+|m|)}{\Gamma(\mu+1)\, \mu^{|m|-1}} \left(\frac{1}{1+1/(2\mu)}\right)^{|m|-1} (2\mu+1)^{|m|-1} z^{2\mu+1}. \tag{2.9b}$$

According to (2.7) the coefficients $a_\nu$ in the series (2.8) have for sufficiently large values of $\nu$ the same sign. When $m \neq 0$, and hence $1/\Gamma(|m|) \neq 0$, the corresponding assertion is true for the series (2.9$a$) as well as for the series (2.9$b$). Furthermore, with the aid of Stirling's formula we obtain

$$\lim_{\mu \to \infty} \frac{\Gamma(\mu+|m|)}{\Gamma(\mu+1)\, \mu^{|m|-1}} = 1. \tag{2.10}$$

Therefore, if $m \neq 0$ and the coefficients $a_\nu$ are not equal to zero for sufficiently large values of $\nu$, one can for $z \neq 0$ compare the terms in the series (2.8) with $\nu$ even or odd, respectively, with the corresponding terms in the power series expansion of $(1-z^2)^{-|m|}$ or $z(1-z^2)^{-|m|}$, respectively, when $\nu$ is sufficiently large. For $-1 < z < +1$ and $z \neq 0$ we thus get the estimates

$$\left| \sum_{\nu \text{ even}}^{\infty} a_\nu z^\nu \right| > \alpha (1-z^2)^{-|m|} > \alpha |z| (1-z^2)^{-|m|}, \tag{2.11a}$$

$$\left| \sum_{\nu \text{ odd}}^{\infty} a_\nu z^\nu \right| > \alpha |z| (1-z^2)^{-|m|}, \tag{2.11b}$$

where $\alpha$ is a positive constant. Hence we obtain from (2.2)

$$|\psi(z)| = (1-z^2)^{|m|/2} \left| \sum_{\substack{\nu \text{ either} \\ \text{even or odd}}}^{\infty} a_\nu z^\nu \right| > \alpha |z| (1-z^2)^{-|m|/2} \to \infty \quad \text{as} \quad z \to \pm 1. \tag{2.12}$$

Therefore $\psi(z)$ can remain finite as $z \to \pm 1$ only when the coefficients $a_\nu$ are equal to zero for sufficiently large values of $\nu$.

For $m = 0$ as well as for $m \neq 0$ the physically acceptable states are thus obtained from the requirement that $a_\nu \neq 0$ while $a_{\nu+2} = 0$. From the recurrence formula (2.3) one thus finds that the eigenvalues of $W$ are given by the formula

$$(\nu + |m|)(\nu + |m| + 1) - W = 0, \quad \nu = 0, 1, 2, \ldots, \tag{2.13}$$

which can also be written in the form (2.1).

## 3. The case of a very weak, homogeneous electric field

Several authors, mentioned in §1 of I, have calculated the energy levels of a permanent rigid diatomic dipole molecule in a very weak, homogeneous, electric field according to the Rayleigh–Schrödinger perturbation theory. In the $(2k)$th-order approximation of this perturbation theory the result can be written as

$$W = \sum_{\nu=0}^{k} W_{2\nu}(j, m)\, \omega^{2\nu}, \tag{3.1}$$

where $W$ and $\omega$ are defined by equations (2.3) and (2.10) in I, respectively, and $W_{2\nu}(j, m)$ are certain coefficients. Explicit analytical expressions for these coefficients are available up to $\nu = 6$ and can be found in Propin (1978*b*). We present these results in the following convenient form

$$W_0(j, m) = Z, \tag{3.2a}$$

$$W_2(j, m) = \frac{1}{2(4Z-3)} (1 - 3m^2/Z), \tag{3.2b}$$

$$W_4(j, m) = \frac{1}{8(4Z-3)^3 (4Z-15)} [(20Z+33) - (m^2/Z)(504Z-90) + (m^4/Z^3)(612Z^2+513Z-405)], \tag{3.2c}$$

$$W_6(j,m) = \frac{1}{32(4Z-3)^5(4Z-15)^2(4Z-35)}\Big[8(576Z^3+1840Z^2-12180Z-10575)$$
$$-(24m^2/Z)(14080Z^3-48752Z^2-25204Z+15715)$$
$$+(12m^4/Z^3)(118144Z^4-248992Z^3-1044680Z^2+1070450Z+93625)$$
$$-(6m^6/Z^5)(197120Z^5-11840Z^4-3280816Z^3+1376260Z^2$$
$$+2088725Z+587125)-\frac{918750\,m^2(1+2m/Z)^2(1-2m/Z)^2}{Z(Z-2)}\Big], \qquad (3.2d)$$

where
$$Z = j(j+1). \qquad (3.3)$$

For $j = 0$ one has $Z = 0$, and (3.2*b–d*), which contain inverse powers of $Z$, seem at first sight to break down. However, when $j = 0$ one necessarily has $m = j = 0$, and (3.2*b–d*) remain valid also in this case, provided that one puts $m/Z = j/Z = 1/(j+1) = 1$. For $j = 0$ and $m = 0$ one thus obtains

$$W_2(0,0) = -1/6, \qquad (3.2b')$$
$$W_4(0,0) = 11/1080, \qquad (3.2c')$$
$$W_6(0,0) = -47/34020. \qquad (3.2d')$$

We remark that the values (3.2*b*′) and (3.2*c*′) agree with the values originally given by Brouwer (1930, p. 36) and quoted by Kusch & Hughes (1959, equation (51.7)), while the values corresponding to (3.2*d*′) given by Brouwer and by Kusch & Hughes are not quite right.

For $j = 1$ one has $Z = 2$, and (3.2*d*), which contains $1/(Z-2)$, seems at first sight to break down. However, when $j = 1$ one necessarily has either $m = j-1$ or $m = j$, and the last term in the square brackets of (3.2*d*), which with the aid of (3.3) can be written as

$$-918750(j-1)(j^2+3j-2)^2(j^2-j+2)^2/[j^5(j+1)^5(j+2)]$$

for $m = j-1$ and as

$$-918750(j-1)j(j+3)^2/[(j+1)^5(j+2)]$$

for $m = j$, disappears for $j = 1$, and (3.2*d*) gives the correct result also in this case. Thus one obtains, for $j = 1$ and $m = 0$

$$W_6(1,0) = 3281/2362500, \qquad (3.2d'')$$

and for $j = 1$ and $m = 1$

$$W_6(1,1) = -1661\times10^{-5}/3024. \qquad (3.2d''')$$

## 4. The case of a very strong, homogeneous electric field

### (*a*) *Rewriting of the Schrödinger equation*

When the homogeneous electric field is very strong, the dipole is, classically speaking, vibrating very close to the direction $\vartheta = 0$. In this case we write the differential equation (2.11) in I as follows

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\vartheta^2}+(\omega+W+\tfrac{1}{4}-\tfrac{1}{3}B)-\frac{B}{\vartheta^2}-(\tfrac{1}{2}\omega+\tfrac{1}{15}B)\,\vartheta^2-(\tfrac{1}{2}\omega+\tfrac{1}{15}B)^{\frac{1}{2}}g(\vartheta)\right)u = 0, \qquad (4.1)$$




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where

$$B = m^2 - \tfrac{1}{4} = (|m| - \tfrac{1}{2})\,(|m| + \tfrac{1}{2}) \tag{4.2}$$

and

$$g(\vartheta) = -(\tfrac{1}{2}\omega + \tfrac{1}{15}B)^{-\frac{1}{2}}[\omega(\cos\vartheta - 1 + \tfrac{1}{2}\vartheta^2) - B(\cot^2\vartheta - 1/\vartheta^2 + \tfrac{2}{3} - \tfrac{1}{15}\vartheta^2)]. \tag{4.3}$$

Introducing instead of $\vartheta$ the variable

$$\rho = (\tfrac{1}{2}\omega + \tfrac{1}{15}B)^{\frac{1}{4}}\vartheta \tag{4.4}$$

and defining

$$c = \frac{\omega + W + \frac{1}{4} - \frac{1}{3}B}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{1}{2}}}, \tag{4.5}$$

we can write the differential equation (4.1) as follows

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + c - \rho^2 - \frac{B}{\rho^2} - g(\vartheta)\right)u = 0, \tag{4.6}$$

where $g(\vartheta)$ is to be expressed in terms of $\rho$ by means of (4.3) and (4.4).

The eigenvalues of $c$ in the differential equation (4.6) are to be determined from the requirement that the function $u$ be equal to zero for $\rho = 0$ and for $\rho = \pi\,(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{1}{4}}$. If the latter limit for $\rho$ is replaced by $+\infty$, this changes the eigenvalues of $c$ by only exponentially small quantities, while the replacement of a large value of $\omega$ by $+\infty$ has a much larger influence on the eigenvalues of $c$ (see Fröman *et al.* 1987). Therefore, we can determine the eigenvalues $c$ of the differential equation (4.6) by requiring the function $u$ to vanish for $\rho = 0$ and for $\rho = +\infty$.

When $\omega$ is sufficiently large, the quantity $g(\vartheta)$ in the differential equation (4.6) has the character of a small perturbation which it is reasonable to expand in powers of $\vartheta$. From (4.3) we thus obtain

$$\begin{aligned} g(\vartheta) = -\frac{1}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{1}{2}}}\big((\tfrac{1}{24}\omega - 2B/189)\,\vartheta^4 - (\omega/720 + B/675)\,\vartheta^6 \\ + (\omega/40\,320 - 2B/10\,395)\,\vartheta^8 - (\omega/3\,628\,800 + 1382B/58\,046\,625)\,\vartheta^{10} \\ + \text{higher powers of } \vartheta^2\big). \end{aligned} \tag{4.7}$$

With the aid of (4.4) we obtain from (4.7) the expansion

$$\begin{aligned} -g(\vartheta) = \frac{1}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{1}{2}}}\Bigg(\frac{\frac{1}{24}\omega - 2B/189}{\frac{1}{2}\omega + \frac{1}{15}B}\rho^4 - \frac{\omega/720 + B/675}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{3}{2}}}\rho^6 \\ + \frac{\omega/40\,320 - 2B/10\,395}{(\frac{1}{2}\omega + \frac{1}{15}B)^2}\rho^8 - \frac{\omega/3\,628\,800 + 1382B/58\,046\,625}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{5}{2}}}\rho^{10} \\ + \text{higher powers of } \frac{\rho^2}{(\frac{1}{2}\omega + \frac{1}{15}B)^{\frac{1}{2}}}\Bigg) \end{aligned} \tag{4.8}$$

from which it follows that

$$-g(\vartheta) = \frac{\rho^4}{6\sqrt{2}}\omega^{-\frac{1}{2}} - \frac{\rho^6}{180}\omega^{-1} - \left(\frac{143B\rho^4}{1890\sqrt{2}} - \frac{\rho^8}{5040\sqrt{2}}\right)\omega^{-\frac{3}{2}} - \left(\frac{B\rho^6}{225} + \frac{\rho^{10}}{453\,600}\right)\omega^{-2} + \ldots. \tag{4.9}$$

(*b*) *The unperturbed differential equation*

Neglecting in (4.6) the term $g(\vartheta)$, we get with the aid of (4.2) the unperturbed differential equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2}+c-\rho^2-\frac{(|m|-\frac{1}{2})\,(|m|+\frac{1}{2})}{\rho^2}\right)u=0, \tag{4.10}$$

which is expected to be approximately valid when $\omega\,(>0)$ is sufficiently large.

The differential equation (4.10) is the same as the radial Schrödinger equation for a two-dimensional, isotropic harmonic oscillator (see Pauling & Wilson 1935, pp. 105–111; Flügge 1974, pp. 107–110, problem 42).

Both the eigenvalues and the corresponding eigenfunctions of the unperturbed differential equation (4.10) are needed for the determination of the eigenvalues of the perturbed differential equation (4.6) by means of perturbation theory. According to equation (2.6) in I and (4.4) the physically acceptable solutions $u$ of (4.10) must vanish for $\rho=0$, and therefore such a solution is approximately equal to a constant times $\rho^{|m|+\frac{1}{2}}$ for small values of $\rho$. For large values of $\rho$ every physically acceptable solution of (4.10) is (except for a constant factor) approximately equal to $\exp(-\frac{1}{2}\rho^2)$ times a (possibly non-integer) power of $\rho$. Thus it is convenient to introduce instead of $u$ a new dependent variable $v$ by writing

$$u=\rho^{|m|+\frac{1}{2}}\mathrm{e}^{-\frac{1}{2}\rho^2}v. \tag{4.11}$$

(The function $v$ introduced here must not be confused with the function $v$ introduced by equation (2.14) in I.)

Instead of $\rho$ we introduce a new independent variable $r$ by writing

$$r=\rho^2. \tag{4.12}$$

By using (4.11) and (4.12), we can write the unperturbed differential equation (4.10) in the form of the confluent hypergeometric differential equation (often referred to as Kummer's equation)

$$r\frac{\mathrm{d}^2v}{\mathrm{d}r^2}+((|m|+1)-r)\frac{\mathrm{d}v}{\mathrm{d}r}+nv=0, \tag{4.13}$$

where by definition

$$n=\tfrac{1}{4}c-\tfrac{1}{2}(|m|+1). \tag{4.14}$$

The physically acceptable solution $v$ of (4.13) must tend to a finite constant as $r\to0$ and is therefore proportional to Kummer's function $M(-n,|m|+1,r)$ according to 13.1.2 in Abramowitz & Stegun (1972). In (4.11) we therefore put

$$v=\text{const.}\times M(-n,|m|+1,r), \tag{4.15}$$

getting with the aid of (4.12)

$$u=\text{const.}\times\rho^{|m|+\frac{1}{2}}\mathrm{e}^{-\frac{1}{2}\rho^2}\quad M(-n,|m|+1,\rho^2). \tag{4.16}$$

For large positive values of $\rho$ we have, according to 13.1.4 in Abramowitz & Stegun (1972), when $n$ is not a non-negative integer,

$$M(-n,|m|+1,\rho^2)=\frac{\Gamma(|m|+1)}{\Gamma(-n)}\rho^{-2[n+(|m|+1)]}\mathrm{e}^{\rho^2}\,(1+O(1/\rho^2)), \tag{4.17}$$

and therefore the function in the right-hand member of (4.16) tends to infinity as $\rho \to +\infty$, unless $n$ is a non-negative integer. A physically acceptable solution can thus exist only when $n$ is a non-negative integer, and when this is the case, the solution (4.16) is actually physically acceptable, since then $M(-n, |m|+1, \rho^2)$ is a polynomial in $\rho^2$ of the degree $n$. Solving (4.14) with respect to $c$, we obtain the corresponding eigenvalue

$$c = 2(|m|+1+2n), \quad n = 0, 1, 2, \ldots. \tag{4.18}$$

Because, according to 22.5.54 in Abramowitz & Stegun (1972), the Kummer functions are related to the generalized Laguerre polynomials as follows

$$M(-n, |m|+1, r) = \frac{\Gamma(|m|+1)\,\Gamma(1+n)}{\Gamma(|m|+1+n)} L_n^{(|m|)}(r), \quad n = 0, 1, 2, \ldots, \tag{4.19}$$

and because, according to 22.1.2 and 22.2.12 in Abramowitz & Stegun (1972), the generalized Laguerre polynomials satisfy the integral relation

$$\int_0^\infty \mathrm{e}^{-r} r^{|m|} (L_n^{(|m|)}(r))^2 \,\mathrm{d}r = \frac{\Gamma(|m|+1+n)}{\Gamma(1+n)}, \tag{4.20}$$

the normalized eigenfunctions (4.16) of the unperturbed differential equation (4.10) are (cf. (4.12))

$$u = \left(\frac{2\Gamma(1+n)}{\Gamma(|m|+1+n)}\right)^{\frac{1}{2}} \rho^{|m|+1/2} \mathrm{e}^{-\frac{1}{2}\rho^2} L_n^{(|m|)}(\rho^2), \quad n = 0, 1, 2, \ldots. \tag{4.21}$$

The results (4.18) and (4.21) are valid also if $m$ is not an integer, and with appropriate changes of notation these results can therefore be used for obtaining the eigenvalues and the normalized eigenfunctions of the radial Schrödinger equation for a three-dimensional, isotropic harmonic oscillator (with a dimensionless independent radial variable $\rho$) (see Flügge 1974, pp. 166–168, solution to problem 65; Flügge & Marschall 1952, pp. 99–101, Aufgabe 35; ter Haar 1964, p. 217, solution to problem 5).

Now that we know the eigenvalues (4.18) and eigenfunctions (4.21) of the unperturbed differential equation (4.10), we shall determine the eigenvalues of the differential equation (4.6) with (4.2) and (4.3) by perturbation theory.

### (*c*) *The perturbed differential equation*

(i) *The eigenvalues of c*

The perturbation $-g(\vartheta)$ in the differential equation (4.6) is according to (4.9) a series in powers of the small parameter $1/\sqrt{\omega}$. By inserting this expression for $-g(\vartheta)$ into the Rayleigh–Schrödinger perturbation series, which is obtained by making approximate expansions of the denominators of the general formula (9.1.15) on p. 1005 in Morse & Feshbach (1953), and collecting terms by groups in powers of $1/\sqrt{\omega}$, we get for the eigenvalue of $c$ corresponding to the fixed quantum number $m$ (which we suppress in the notation) and the quantum number $n$ the formula

$$c = \sum_{\nu=0}^{\infty} c_\nu^n \, \omega^{-\nu/2}, \tag{4.22}$$

where

$$c_0^n = 2(|m|+1+2n), \tag{4.23a}$$

$$c_1^n = -\langle\rho^4\rangle/(6\sqrt{2}), \tag{4.23b}$$

$$c_2^n = \frac{1}{180}\langle\rho^6\rangle + \frac{1}{72}\sum_{n'\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2}{c_0^n - c_0^{n'}}, \tag{4.23c}$$

$$\begin{aligned} c_3^n = {} & \frac{143B}{1890\sqrt{2}}\langle\rho^4\rangle - \frac{1}{5040\sqrt{2}}\langle\rho^8\rangle - \frac{1}{540\sqrt{2}}\sum_{n'\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^6|n\rangle}{c_0^n - c_0^{n'}} \\ & - \frac{1}{432\sqrt{2}}\sum_{n',\,n''\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^4|n''\rangle\langle n''|\rho^4|n\rangle}{(c_0^n - c_0^{n'})(c_0^n - c_0^{n''})} \\ & + \frac{1}{432\sqrt{2}}\langle\rho^4\rangle\sum_{n'\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2}{(c_0^n - c_0^{n'})^2}, \end{aligned} \tag{4.23d}$$

$$\begin{aligned} c_4^n = {} & \frac{B}{225}\langle\rho^6\rangle + \frac{1}{453\,600}\langle\rho^{10}\rangle + \frac{1}{32\,400}\sum_{n'\neq n}\frac{|\langle n|\rho^6|n'\rangle|^2}{c_0^n - c_0^{n'}} \\ & - \frac{143B}{11\,340}\sum_{n'\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2}{c_0^n - c_0^{n'}} + \frac{1}{30\,240}\sum_{n'\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n|\rho^8|n'\rangle}{c_0^n - c_0^{n'}} \\ & + \frac{1}{6480}\sum_{n',\,n''\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^4|n''\rangle\langle n''|\rho^6|n\rangle}{(c_0^n - c_0^{n'})(c_0^n - c_0^{n''})} \\ & + \frac{1}{12\,960}\sum_{n',\,n''\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^6|n''\rangle\langle n''|\rho^4|n\rangle}{(c_0^n - c_0^{n'})(c_0^n - c_0^{n''})} \\ & - \frac{1}{6480}\langle\rho^4\rangle\sum_{n'\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n|\rho^6|n'\rangle}{(c_0^n - c_0^{n'})^2} - \frac{1}{12\,960}\langle\rho^6\rangle\sum_{n'\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2}{(c_0^n - c_0^{n'})^2} \\ & + \frac{1}{5184}\langle\rho^4\rangle^2\sum_{n'\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2}{(c_0^n - c_0^{n'})^3} - \frac{1}{5184}\sum_{n',\,n''\neq n}\frac{|\langle n|\rho^4|n'\rangle|^2|\langle n|\rho^4|n''\rangle|^2}{(c_0^n - c_0^{n'})^2(c_0^n - c_0^{n''})} \\ & - \frac{1}{2592}\langle\rho^4\rangle\sum_{n',\,n''\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^4|n''\rangle\langle n''|\rho^4|n\rangle}{(c_0^n - c_0^{n'})^2(c_0^n - c_0^{n''})} \\ & + \frac{1}{5184}\sum_{n',\,n'',\,n'''\neq n}\frac{\langle n|\rho^4|n'\rangle\langle n'|\rho^4|n''\rangle\langle n''|\rho^4|n'''\rangle\langle n'''|\rho^4|n\rangle}{(c_0^n - c_0^{n'})(c_0^n - c_0^{n''})(c_0^n - c_0^{n'''})}, \end{aligned} \tag{4.23e}$$

$\langle n|\rho^{2p}|n'\rangle$ being the matrix element of $\rho^{2p}$ between the states $n$ and $n'$ of the unperturbed differential equation (4.10).

(ii) *The matrix elements* $\langle n|\rho^{2p}|n'\rangle$

Recalling (4.21) and (4.12), we obtain

$$\langle n|\rho^{2p}|n'\rangle = \left(\frac{\Gamma(1+n)}{\Gamma(|m|+1+n)}\right)^{\frac{1}{2}}\left(\frac{\Gamma(1+n')}{\Gamma(|m|+1+n')}\right)^{\frac{1}{2}}\int_0^\infty r^{|m|+p}\,\mathrm{e}^{-r}L_n^{(|m|)}(r)\,L_{n'}^{(|m|)}(r)\,\mathrm{d}r. \tag{4.24}$$




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With the aid of the generating function for the generalized Laguerre polynomials (see 22.9.15 in Abramowitz & Stegun (1972)) one obtains from (4.24) the explicit formula

$$\langle n|\rho^{2p}|n'\rangle = \left(\frac{n!\,n'!}{(|m|+n)!\,(|m|+n')!}\right)^{\frac{1}{2}} \times \sum_{k=\max(n,n')-p}^{\min(n,n')} (-1)^{n+n'} \binom{p}{n-k}\binom{p}{n'-k}\frac{(|m|+p+k)!}{k!}, \quad (4.25)$$

$\langle n|\rho^{2p}|n'\rangle$ being equal to zero unless $\max(n,n')-p \leqslant \min(n,n')$. From (4.25) the matrix element $\langle n|\rho^{2p}|n'\rangle$ can be calculated for non-negative values of the integers $p$, $|m|$, $n$ and $n'$. In this connection we remark that Shaffer (1944), amongst a number of matrix elements occurring in the theory of perturbations in polyatomic molecules, also has given the matrix elements of $\rho$, $\rho^2$, $\rho^3$ and $\rho^4$.

(iii) *The eigenvalues of W*

Solving (4.5) with respect to $W$, we obtain

$$W = -\omega + \tfrac{1}{3}B - \tfrac{1}{4} + \frac{\omega^{\frac{1}{2}}}{\sqrt{2}}\left(1+\frac{2B}{15\omega}\right)^{\frac{1}{2}} c. \quad (4.26)$$

Inserting (4.22) into (4.26), and expanding in powers of $1/\sqrt{\omega}$, we obtain

$$W = -\omega + \tfrac{1}{\sqrt{2}}c_0^n\,\omega^{\frac{1}{2}} + (\tfrac{1}{\sqrt{2}}c_1^n + \tfrac{1}{3}B - \tfrac{1}{4}) + (c_2^n + \tfrac{1}{15}Bc_0^n)\tfrac{1}{\sqrt{2}}\omega^{-\frac{1}{2}} + (c_3^n + \tfrac{1}{15}Bc_1^n)\tfrac{1}{\sqrt{2}}\omega^{-1} + (c_4^n + \tfrac{1}{15}Bc_2^n - B^2c_0^n/450)\tfrac{1}{\sqrt{2}}\omega^{-\frac{3}{2}} + \ldots. \quad (4.27)$$

Calculating the matrix elements appearing in (4.23*a–e*) by means of (4.25), and inserting the expressions for $c_\nu^n$ thus obtained into (4.27), and recalling (4.2), we obtain after long and tedious (though algebraically simple) calculations, which are highly facilitated with the aid of formula manipulations on a computer by means of the algebraic programming system REDUCE, the following formula for the eigenvalue of $W$ corresponding to the quantum numbers $m$ and $n$

$$W = \sum_{\nu=-2}^{\infty} \bar{W}_\nu(N,|m|)\,\omega^{-\nu/2}, \quad (4.28)$$

where

$$\bar{W}_{-2}(N,|m|) = -1, \quad (4.29a)$$

$$\bar{W}_{-1}(N,|m|) = N\sqrt{2}, \quad (4.29b)$$

$$\bar{W}_0(N,|m|) = \tfrac{1}{8}(3(m^2-1)-N^2), \quad (4.29c)$$

$$\bar{W}_1(N,|m|) = \frac{N}{64\sqrt{2}}(3(3m^2-1)-N^2), \quad (4.29d)$$

$$\bar{W}_2(N,|m|) = \frac{1}{2048}(-3(11m^4-14m^2+3)+34(3m^2-1)N^2-5N^4), \quad (4.29e)$$

$$\bar{W}_3(N,|m|) = \frac{N}{32768\sqrt{2}}(-3(271m^4-574m^2+135)+410(3m^2-1)N^2-33N^4), \quad (4.29f)$$

with

$$N = |m|+1+2n. \quad (4.30)$$

A quantum number also denoted by $N$ is defined in another way (namely $N = |m|+2n$) by von Meyenn (1970). The use of our definition (4.30) makes the expressions (4.29*a–f*) simpler. The coefficients $\bar{W}_\nu(N,|m|)$ have previously been obtained by

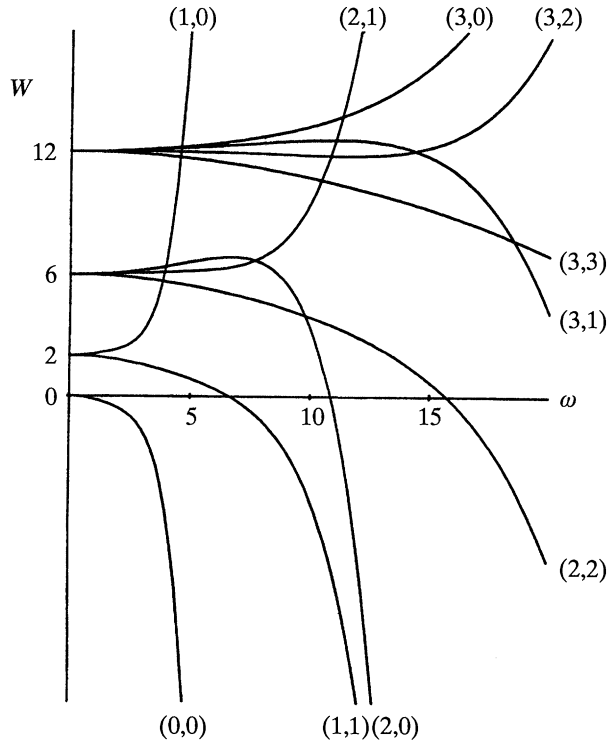


Figure 1. The first ten approximate energy levels, obtained from the weak-field Rayleigh–Schrödinger perturbation series (3.1) in the sixth-order approximation, are plotted versus the dimensionless field strength parameter $\omega$. Each energy level is denoted by the appropriate pair of quantum numbers $(j, |m|)$.

Peter & Strandberg (1957) up to $\nu = 1$, by Gaponov *et al.* (1965) up to $\nu = 0$, by von Meyenn (1970) up to $\nu = -1$, and by Propin (1978*a*) up to $\nu = 2$. Gaponov *et al.* (1965) and von Meyenn (1970) were obviously not aware of the work by their predecessors. For a few sets of quantum numbers exact values of the coefficient $\bar{W}_3(N, |m|)$ can be obtained numerically from Propin (1978*a*). These numerical results are fully reproduced with the aid of (4.29*f*). For the same few sets of quantum numbers numerical approximations of the coefficients $\bar{W}_\nu(N, |m|)$ for $\nu = 4, 5, \ldots, 15$ can be obtained from Propin (1978*a*). After having completed the calculations resulting in (4.28) with (4.29*a–f*) and (4.30) we became aware of the paper by Cohen & Feldmann (1982), where a series equivalent to (4.28) up to $\nu = 4$ is given. The expressions for their coefficients up to $\nu = 3$ are equivalent to (4.29*a–f*), and their coefficient corresponding to $\nu = 4$ is in our notation

$$\bar{W}_4(N, |m|) = (9/262\,144)\,(2(41m^6 - 157m^4 + 143m^2 - 27) - 3(165m^4 - 450m^2 + 109)N^2 + 140(3m^2 - 1)N^4 - 7N^6). \quad (4.29g)$$

The state $(j, |m|)$ at very weak fields is unambiguously connected with the state $(N, |m|)$ with $N = 2j - |m| + 1$ at very strong fields; see von Neumann & Wigner (1929).

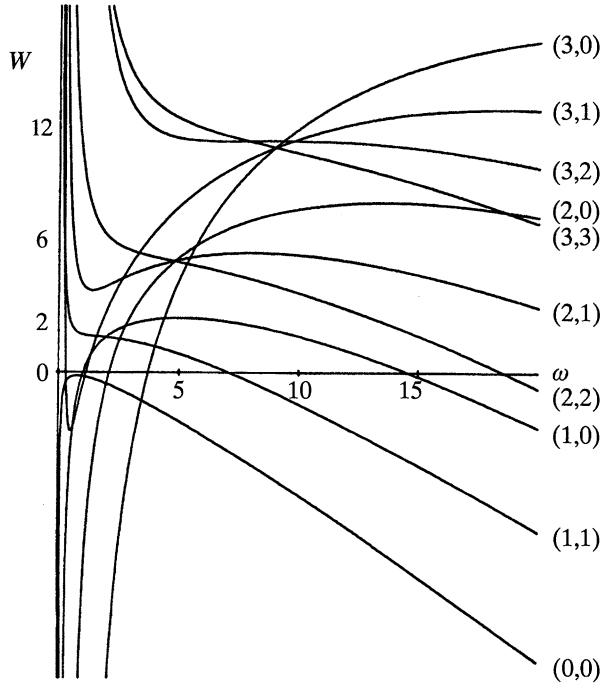


Figure 2. The first ten approximate energy levels, obtained from the strong-field Rayleigh–Schrödinger perturbation series (4.28) in the fourth-order approximation, are plotted versus the dimensionless field strength parameter $\omega$. Each energy level is denoted by the appropriate pair of quantum numbers $(j, |m|)$.

## 5. Accuracy of the energy eigenvalues obtained in Rayleigh–Schrödinger perturbation theory for very weak and very strong fields

In this section we consider the qualitative dependence of the dimensionless energy parameter $W$ on the quantum numbers $(j, |m|)$ and on the dimensionless field strength parameter $\omega$ and the applicability of the Rayleigh–Schrödinger perturbation series (3.1) and (4.28) pertaining to very weak and very strong fields respectively. The values of $j$, $|m|$ and $\omega$ for which these series break down depend strongly on the order of approximation used. We restrict the following discussion to the sixth order for the weak-field series (3.1) and to the fourth order for the strong-field series (4.28), since these are the highest orders for which explicit expressions are available. In figure 1 we have plotted the first ten approximate energy levels $W$ obtained from the sixth-order Rayleigh–Schrödinger perturbation series (3.1) pertaining to sufficiently weak fields. Comparing this figure with figure 3 (which depicts the first ten exact energy eigenvalues $W$), we see that, for fixed $j$, the range of validity of (3.1) in general seems to increase towards larger values of $\omega$ when $|m|$ increases. In figure 2 we have plotted the first ten approximate energy levels $W$ obtained from the fourth-order Rayleigh–Schrödinger perturbation series (4.28) pertaining to sufficiently strong fields. Comparing this figure with figure 3, we see that, for fixed $j$, the range of validity of (4.28) in general seems to increase towards smaller values of $\omega$ when $|m|$ increases. In figure 3 we have plotted the first ten exact energy levels $W$ (obtained as described in the beginning of §5 in III) and indicated where the approximate energy levels $W$ of figures 1 and 2 cease to be useful, if we wish to obtain




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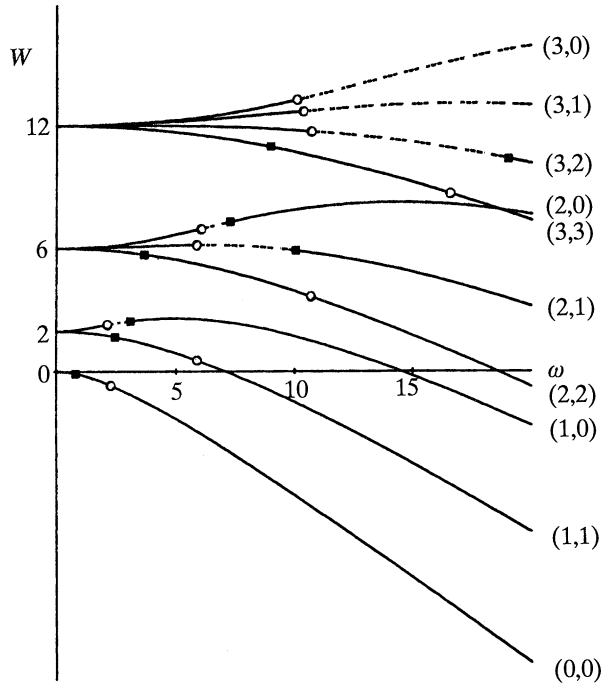


Figure 3. The first ten exact energy levels, obtained by one of the authors (K.L.) by numerical solution of the eigenvalue problem, are plotted against the dimensionless field strength parameter $\omega$. Each energy level is denoted by the appropriate pair of quantum numbers $(j, |m|)$. For a prescribed absolute error of at the most 0.1 for each energy level, the weak-field sixth-order perturbation series (3.1) is useful only to the left of the small open circle, and the strong-field fourth-order perturbation series (4.28) is useful only to the right of the small filled square. The part of each energy level curve which cannot be obtained, with the above-mentioned accuracy, from the sixth order of (3.1) or the fourth order of (4.28) is drawn as a dashed line. The curve (3, 0) of figure 2 accidentally crosses the curve (3, 0) of figure 3 for $\omega$ roughly equal to 15, but the interval around this crossing value of $\omega$ in which the fourth order of (4.28) can be used with the prescribed accuracy is very small and has therefore not been indicated.

approximations to the energy levels $W$ with an absolute error of at the most 0.1. Figure 3 indicates that, if sufficiently accurate approximations for the energy levels are required, there are ranges of $\omega$-values in which neither the weak-field approximation nor the strong-field approximation is useful. The extension of such a range of $\omega$-values, which depends on the prescribed maximum absolute error of $W$ and on the energy level involved, seems to increase with increasing value of $j$. Because of the existence of the intermediate range of $\omega$-values, where neither (3.1) nor (4.28) is applicable, it is highly desirable to obtain analytical formulas from which accurate energy eigenvalues can be obtained efficiently for all values of $\omega$. This can be achieved by means of the phase-integral quantization conditions in I, as will be demonstrated in the following two papers (III and IV) in this series.

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