Eur. Phys. J. D **4**, 63–72 (1998)

THE EUROPEAN
PHYSICAL JOURNAL D

Expansions for the eigenvalues of three-term recurrence relations. Two applications in molecular physics

G. Hadinger[1], M. Aubert-Frécon[1,a], and G. Hadinger[2]

[1] Laboratoire de Spectrométrie Ionique et Moléculaire[b], CNRS et Université Lyon I, Bâtiment 205,
43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France
[2] Institut de Physique Nucléaire de Lyon, IN2P3-CNRS, Université Claude Bernard,
43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

Received: 30 January 1998 / Received in final form: 10 April 1998 / Accepted: 25 May 1998

Abstract. Approximate expressions for the eigenvalue of a three-term recurrence relation with a general form describing various physical problems are proposed. Their range of availability is examined by comparison with exact values for two different problems: the bound and continuum states of monoelectronic diatomic ions and the Schrödinger equation describing molecular alignment in intense laser fields. For each case, very good predictions have been obtained, which may be useful as initial values in iterative procedures for deriving exact solutions.

PACS. 31. Electronic structure of atoms, molecules and their ions: theory

1 Introduction

Many of the functions of interest in mathematical physics obey second order recurrence relations. For instance, when expanding the eigenfunctions of the Schrödinger equation of the one-electron two-centre problem as series of conveniently chosen basis functions, the corresponding expansion coefficients can be linked together by three-term recurrence relations involving the required eigenvalues. Several techniques are available for calculating exactly these eigenvalues, either numerically [1] or analytically by means of infinite continued fractions [2–4] or by means of a successive approximations procedure [3,5–8]. In a similar way, the Schrödinger equation proposed recently [9] to describe alignment and trapping of molecules in intense laser fields can also be reduced to a three-term recurrence relation from which exact solutions are obtained.

In the present paper, we use the Hill-determinant technique [10,11] to set up a scheme that yields analytic approximate expressions for the eigenvalues of a three-term recurrence relation which can be very easily determined by use of a symbolic algebraic manipulation language.

These expressions can be used successfully to calculate accurate initial values of the eigenvalues E and of their derivatives $\partial E/\partial x$ with respect to some variable x, requisite to initiate the numerical iterative processes [1,12] by which to obtain exact values.

The process by which to derive approximate expressions for the eigenvalue E entering a three-term recurrence relation is presented in some details in Section 2. In Section 3 these general formulas are applied to the specific case of monoelectronic diatomic ions, for bound and continuum states. In Section 4, approximations of the eigenenergy and squared alignment cosine are displayed for the problem of molecular alignment in intense laser fields. Some illustrative numerical results are presented in Section 5. In addition a lot of useful analytical formulas concerning eigensolutions for monoelectronic diatomic ions expanded on the various basis sets proposed in literature, are gathered in Tables 1 to 3.

2 Approximate analytic expressions for eigenvalues and their derivatives

2.1 Eigenvalues

Let us consider a three-term recurrence relation written as

$$\alpha_k a(k+1) + (E + h_k)a(k) + \beta_k a(k-1) = 0 \qquad (1)$$

with $k \geq 0$, $\alpha_k \neq 0$ and the boundary condition $a(-1) = 0$. E is the required eigenvalue. α_k, h_k and β_k are known coefficients for a given problem. Setting either

$$a(0) = F(0);\ a(-1) = F(-1) = 0$$

$$\text{and} \quad a(k) = F(k)/\prod_{t=0}^{k-1} \alpha_t \qquad (2a)$$

---

[a] e-mail: `frecon@in2p3.fr`

[b] UMR n° 5579

$$
\begin{aligned}
E_k^{(3)} = {} & Q_{k+2}(2,2)Q_{k+1}(1,1)\big[P_{k+3}(3,3) + P_{k+2}(2,1) - P_{k+1}(1,1) + P_k(1,1)\big] \\
& - Q_k(1,1)Q_{k-1}(1,2)\big[P_{k+1}(1,1) - P_k(1,1) + P_{k-1}(0,1) + P_{k-2}(1,3)\big] \\
& - Q^2_{k+1}(1,1)\big[3P_{(k+2)}(2,2) - 2P_{k+1}(1,1) + 3P_k(1,1)\big] + Q^2_k(1,1)\big[3P_{k+1}(1,1) - 2P_k(1,1) + 3P_{k-1}(1,2)\big] \\
& - Q_{k+1}(1,1)Q_k(1,1)\big[P_{k+2}(2,2) - 2P_{k+1}(1,1) + 2P_k(1,1) - P_{k-1}(1,2)\big] \\
& + S_{k+1}(1,1)P_k(1,1)\big[2P_{k+2}(2,2) + P_k(1,1)\big] - S_k(1,1)P_{k+1}(1,1)\big[P_{k+1}(1,1) + 2P_{k-1}(1,2)\big] \qquad (12)
\end{aligned}
$$

or

$$a(0) = G(0); \;\; a(-1) = G(-1) = 0$$

$$\text{and} \quad a(k) = G(k)/\prod_{t=1}^{k}\beta_t. \qquad (2b)$$

We get the following recurrence relations with a simplified form either

$$F(k+1) + (E + h_k)F(k) + f_k F(k-1) = 0 \qquad (3a)$$

or

$$f_{k+1}G(k+1) + (E + h_k)G(k) + G(k-1) = 0 \qquad (3b)$$

with $f_k = \alpha_{k-1}\beta_k$. The coefficients h_k and f_k are assumed to be real.

Such relations (3) are ordinary handled by a method of continued fractions or by means of successive approximations procedure. Nevertheless, as pointed out in reference [10], these recurrence relations can be looked upon as infinite sets of linear equations in $F(k)$ or in $G(k)$. For the self-consistency of these sets, the determinant $D(E)$ of the matrix of the coefficients of $F(k)$ or $G(k)$ must be zero: $D(E) = 0$, and the corresponding roots are the required eigenvalues E.

As done for the infinite-dimensional characteristic Hill determinant, approximate expressions $E_k^{(n)}$ for the eigenvalue E can be obtained by expanding the finite dimensional $(2n+1) \times (2n+1)$ determinant $D_{2n+1}(E)$. The zero-order approximation $(n = 0)$ is given by

$$E_k^{(0)} = -h_k. \qquad (4)$$

The first order approximation $E_k^{(1)}$ is obtained from the expansion of $D_3(E)$ conveniently written around the central element $E_k^{(1)}$ [10,11]. From relation (3a) with $k \geq 1$, $D_3(E)$ has the following form

$$D_3(E) = \begin{vmatrix} E_k^{(0)} + h_{k-1} & 1 & 0 \\ f_k & E_k^{(1)} & 1 \\ 0 & f_{k+1} & E_k^{(0)} + h_{k+1} \end{vmatrix}. \qquad (5)$$

The condition $D_3(E) = 0$ leads to

$$E_k^{(1)} = P_{k+1}(1,1) - P_k(1,1) \qquad (6)$$

where for simplicity we have set:

$$
\begin{aligned}
& P_k(s,t) = f_k/g_k(s,t), \\
& P_k(s,t) = 0 \quad \text{for} \quad s > k, \qquad (7)
\end{aligned}
$$

with

$$g_k(s,t) = h_{k-s+t} - h_{k-s}. \qquad (8)$$

To proceed to a nth order of approximation, we consider the expansion of the $D_{2n+1}(E)$ (with $k \geq n$) about the central element $E_k^{(n)}$ while all the other E_k appearing on the diagonal are set equal to $\sum_{i=0}^{n-1} E_k^{(i)}$. Proceeding in this way and using the symbolic algebraic manipulation language MAPLE approximate analytic expression for the eigenvalues E have been determined in the present work up to the third order.

The eigenvalue E can be written as

$$E = E_k^{(0)} + E_k^{(1)} + E_k^{(2)} + E_k^{(3)} \qquad (9)$$

where $E_k^{(0)}$ and $E_k^{(1)}$ are given by equations (4, 6), respectively. The expression for $E_k^{(2)}$ is

$$
\begin{aligned}
E_k^{(2)} = {} & Q_{k+1}(1,1)[P_{k+2}(2,2) - P_{k+1}(1,1) + P_k(1,1)] \\
& - Q_k(1,1)[P_{k+1}(1,1) - P_k(1,1) + P_{k-1}(1,2)] \qquad (10)
\end{aligned}
$$

with

$$
\begin{aligned}
& Q_k(s,t) = P_k(s,t)/g_k(s,t) \\
& Q_k(s,t) = 0 \quad \text{for} \quad s > k. \qquad (11)
\end{aligned}
$$

The expression for $E_k^{(3)}$ is given by

see equation (12) above

with

$$
\begin{aligned}
& S_k(s,t) = Q_k(s,t)/g_k(s,t) \\
& S_k(s,t) = 0 \quad \text{for} \quad s > k. \qquad (13)
\end{aligned}
$$

It is obvious that the recurrence relation (3b) provides exactly the same expressions for the E_k.

2.2 Derivatives of the eigenvalues

In some physical problems [1,12] one must calculate the derivatives of the eigenvalue E_k with respect to a variable x of which the functions h_k and f_k are dependent. This is done in a straightforward way by differentiating equations (4, 6–13) with respect to x.

$$E_k^{(3)} = \frac{K_{\ell+1}}{2(\ell+1)}\left[\frac{K_{\ell+3}K_{\ell+2}}{12(2\ell+3)}+\frac{K_{\ell+2}^2}{8(\ell+1)}-\frac{(7\ell+10)}{4(2\ell+3)(\ell+1)}K_{\ell+2}K_{\ell+1}+\frac{(3\ell^2+2\ell-3)}{4(2\ell+3)(\ell+1)\ell}K_{\ell+2}K_\ell+\frac{K_{\ell+1}^2}{(\ell+1)}-\frac{(2\ell^2+1)}{2(\ell+1)\ell^2}K_{\ell+1}K_\ell\right]$$
$$-\frac{K_\ell}{2\ell}\left[\frac{K_{\ell-2}K_{\ell-1}}{12(2\ell-1)}+\frac{K_{\ell-1}^2}{8\ell}-\frac{(7\ell-3)}{4(2\ell-1)\ell}K_{\ell-1}K_\ell+\frac{(3\ell^2+4\ell-2)}{4(2\ell-1)(\ell+1)\ell}K_{\ell-1}K_{\ell+1}+\frac{K_\ell^2}{\ell}-\frac{(2\ell^2+4\ell+3)}{2\ell(\ell+1)^2}K_{\ell+1}K_\ell\right] \quad (19)$$

---

3 Application to the one-electron two-centre problem

Within the Born-Oppenheimer approximation, the Schrödinger equation for the one-electron two-centre problem with the fixed nuclear charges Z_A and Z_B is separable when introducing prolate spheroidal coordinates: $-1 \le \mu \le 1$, $1 \le \lambda < +\infty$ and $0 \le \phi \le 2\pi$. The corresponding diatomic eigenfunctions of the bound and continuous states can be factorized and written as:

$$\Psi(\mathbf{r}) = N \exp(im\phi) M(\mu) \Lambda(\lambda)$$

where N is the normalization constant.

The functions $M(\mu)$ and $\Lambda(\lambda)$ are solutions of the following pair of ordinary differential equations, "angular" and "radial", respectively

$$\left[\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial}{\partial\mu}-\frac{m^2}{(1-\mu^2)}+p^2\mu^2-R_1\mu-A\right]M(\mu)=0 \quad (14)$$

and

$$\left[\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda}-\frac{m^2}{(\lambda^2-1)}-p^2\lambda^2+R_2\lambda+A\right]\Lambda(\lambda)=0. \quad (15)$$

For the bound states the angular functions $M(\mu)$ and the radial functions $\Lambda(\lambda)$ can be expanded on appropriate sets of basis functions: Wilson [13], Baber and Hassé [2], or Power [4] basis for $M(\mu)$, and Hylleraas [14] or Jaffé [15] basis for $\Lambda(\lambda)$. For the continuum states $M(\mu)$ is expanded on the associated Legendre function $P_{m+k}^m(\mu)$ with $\mu \ge 0$ [16]. These expansions lead to solving three-term recurrence relations satisfied by expansion coefficients of the type investigated in the preceding section (Eqs. (3)). The required separation constant A is contained in the eigenvalue E.

In Table 1, expansions for the bound states angular $M(\mu)$ and radial $\Lambda(\lambda)$ eigenfunctions are recalled, together with the expressions for the corresponding eigenvalues E. For the continuum wavefunctions only the angular function $M(\mu)$ can be considered. In Table 1, $P_{m+k}^m(\mu)$ is the associated Legendre polynomial of the first kind, $\Phi(\alpha,\beta;y)$ the confluent hypergeometric function and $L_k^m(y)$ the orthogonal Laguerre polynomial [17]. p is the energy parameter ($\varepsilon = -2p^2/R^2$) in terms of the internuclear distance R, $R_1 = R(Z_A - Z_B)$ and $R_2 = R(Z_A + Z_B)$. For the continuum, the nonnegative energy is defined by $c^2 = -p^2$ [18]. The three-term recurrence relations obtained for these different basis sets are listed in Table 2, together with the asymptotic behaviour of the dominant $a^{(1)}(k)$ and subdominant $a^{(2)}(k)$ corresponding solutions, worked out by the method described in reference [19]. The corresponding expressions for the functions f_k, $g_k(s,t)$ (Eq. (8)) and h_k are given in Table 3. Since the variation ∂k is exponentially small in p, Power [4] sets $\partial k = 0$ when calculating the angular eigenvalues E_k, consequently Power's recurrence relation and Power's functions f_k, $g_k(s,t)$ and h_k are given after setting $\partial k = 0$.

3.1 Approximate analytic expressions for the eigenvalue E deduced from the angular equation

In the case where the angular function $M(\mu)$ is expressed in accordance with the model proposed by Baber and Hassé [2] for the bound states, or by Rankin and Thorson [16] for the continuum, the functions $P_k(s,t)$, $Q_k(s,t)$ and $S_k(s,t)$ (Eqs. (7, 11, 13), respectively) take the general form $p^2\left[\chi_k\left(\frac{R_1}{2p}\right)^2-\rho_k\right]$ or $c^2\left[\chi_k\left(\frac{R_1}{2p}\right)^2+\rho_k\right]$ and provide terms in p^{2j} or c^{2j} with $j=1$ for $E_k^{(1)}$ (Eq. (6)), $j=2$ for $E_k^{(2)}$ (Eq. (10)), and with $j=3$ for $E_k^{(3)}$ (Eq. (12)). The contracted expression E_k (Eq. (9)) provides an approximate analytic expression suitable for p or c small and easily computed with an algebraic manipulation language such as MAPLE. We obtain:

$$E_k^{(0)} = -\ell(\ell+1) \quad (16)$$

$$E_k^{(1)} = K_{\ell+1} - K_\ell \quad (17)$$

$$E_k^{(2)} = \frac{K_{\ell+1}}{4(\ell+1)}[K_{\ell+2}-2K_{\ell+1}-K_\ell/\ell] - \frac{K_\ell}{4\ell}[K_{\ell-1}-2K_\ell+K_{\ell+1}/(\ell+1)] \quad (18)$$

see equation (19) above

with $\ell = m + k$ for the bound states, and

for $t > 0$

$$K_{\ell+t} = 4p^2\frac{((\ell+t)^2-m^2)}{(4(\ell+t)^2-1)(2\ell+t+1)}\left(\left(\frac{R_1}{2p}\right)^2-(\ell+t)^2\right), \quad (20a)$$

and for $t \le 0$

$$K_{\ell+t} = 4p^2\frac{((\ell+t)^2-m^2)}{(4(\ell+t)^2-1)(2\ell+t)}\left(\left(\frac{R_1}{2p}\right)^2-(\ell+t)^2\right). \quad (20b)$$

Table 1. Expressions for the diatomic eigenfunctions and eigenvalues for some basis.

	Basis	Diatomic eigenfunctions*	Eigenvalues E
Angular bound states $M(\mu)$	Baber Hassé	$\exp(-p\mu)\sum_{k=0} a(k)P^m_{m+k}(\mu)$	$A-p^2$
	Wilson	$\exp(-p\mu)(1-\mu^2)^{m/2}\sum_{k=0}(-1)^k a(k)(1+\mu)^k$	$A-p^2-R_1+(m+1)(m+2p)$
	Power	$\exp(-p(1+\mu))(1-\mu^2)^{m/2}$ $\times\sum_{k=0} a(k)\Phi(-(k+\delta k),m+1;2p(1+\mu))$	$A-p^2-R_1+(m+1)(2p-1+R_1/2p)$
Angular continuous states $M(\mu)$	Rankin Thorson	$\exp(-ic\mu)\sum_{k=0} a(k)P^m_{m+k}(\mu)$	$A+c^2$
Radial bound states $\Lambda(\lambda)$	Hylleraas	$\exp(-p(\lambda-1))(\lambda^2-1)^{m/2}\sum_{k=0} a(k)L^m_k(2p(\lambda-1))$	$A-p^2+R_2-(m+1)(2p+1-R_2/2p)$
	Jaffé	$\exp(-p\lambda)(\lambda^2-1)^{m/2}(\lambda+1)^{-m-1+R_2/2p}$ $\times\sum_{k=0} a(k)\left[\frac{\lambda-1}{\lambda+1}\right]^k$	$A-p^2+R_2-(m+1)(2p+1-R_2/2p)$

*m is a positive integer.

For the continuum p^2 must be replaced by $(-c^2)$ in the above expressions. As expected, formulas (16) to (19) remain unchanged when changing ℓ into $-(\ell+1)$. Of course, the sum $E_k^{(0)}+E_k^{(1)}+E_k^{(2)}$ gives the known expressions of Abramov and Slavyanov [7] up to p^4, of Abramov *et al.* [8] up to c^4 and of Baber and Hassé [2] up to p^4 for the case $\ell=m=0$, and the sum $E_k^{(0)}+E_k^{(1)}+E_k^{(2)}+E_k^{(3)}$ reproduces the first terms of the results given by Flammer [3] in the particular case $R=0$ $(R_1=0,\ R_2=0)$.

For the derivatives E'_k with respect to R we obtain terms in p^j or c^j with $j=1$ from ${E'}_k^{(1)}$, with $j=3$ from ${E'}_k^{(2)}$, and with $j=5$ from ${E'}_k^{(3)}$. We can write

$$ {E'}_k^{(0)} = 0 \tag{21a} $$

$$ {E'}_k^{(1)} = {K'}_{\ell+1} - {K'}_{\ell} + O(p^2) \tag{21b} $$

$$ \begin{aligned} {E'}_k^{(2)} = {} & \frac{{K'}_{\ell+1}}{4(\ell+1)}[K_{\ell+2}-2K_{\ell+1}-K_\ell/\ell] \\ & + \frac{K_{\ell+1}}{4(\ell+1)}[{K'}_{\ell+2}-2{K'}_{\ell+1}-{K'}_\ell/\ell] \\ & - \frac{{K'}_\ell}{4\ell}[K_{\ell-1}-2K_\ell-K_{\ell+1}/(\ell+1)] \\ & - \frac{K_\ell}{4\ell}[{K'}_{\ell-1}-2{K'}_\ell-{K'}_{\ell+1}/(\ell+1)] + O(p^3) \end{aligned} \tag{21c} $$

and consequently

$$ \begin{aligned} \frac{\partial E_k}{\partial R} = 4p\Bigg[& \frac{((\ell+1)^2-m^2)}{(4(\ell+1)^2-1)(2\ell+2)}\left[\frac{R_1}{2p}(Z_A-Z_B)\right. \\ & \left. -2(\ell+1)^2\frac{\partial p}{\partial R}\right] - \frac{(\ell^2-m^2)}{(4\ell^2-1)(2\ell+1)} \\ & \times\left[\frac{R_1}{2p}(Z_A-Z_B)-2\ell^2\frac{\partial p}{\partial R}\right]\Bigg] + O(p^2). \end{aligned} \tag{22} $$

3.2 Asymptotic analytic expressions for the eigenvalue E deduced from the radial equation

The radial eigenfunction $\Lambda(\lambda)$ expanded in accordance with either the Hylleraas [14] or the Jaffé [15] basis functions leads to the same simplified recurrence relation (see Tab. 3). Since the corresponding function $g_k(s,t)$ depends on p, the expression for E_k (Eq. (9)) provides an analytic approximation when p and R_2 are large, in an asymptotic form obtained when expanding the functions $P_k(s,t)$, $Q_k(s,t)$ and $S_k(s,t)$ (Eqs. (7, 11, 13), respectively) as Taylor's series in $1/p$, without deriving the $(R_2/2p)$ terms.

We obtain the following asymptotic expansion directly from equations (6, 10, 12), by use of the language MAPLE:

$$ E_k = -h_k + \sum_{t=1}^{6} b_t/p^t + O(1/p^7) \tag{23} $$

Table 2. Recurrence relations and asymptotic behaviour of the solutions*.

Basis	Recurrence relations and solutions $a^{(1)}(k)$ et $a^{(2)}(k)$
Baber Hassé	$\frac{(2m+k+1)}{(2m+2k+3)}(2p(m+k+1)+R_1)a(k+1)+(E+(m+k)(m+k+1))a(k)$ $+\frac{k}{(2m+2k-1)}(R_1-2p(m+k))a(k-1)=0$ $a^{(1)}(k)\approx(-1/p)^{(m+k)}(m+k)^{(-m-1/2-R_1/2p)}(m+k)!$ $a^{(2)}(k)\approx p^{(m+k)}(m+k)^{(-m-1/2-R_1/2p)}/(m+k)!$
Wilson	$2(k+1)(m+k+1)a(k+1)+(E+k(2m+k+4p+1))a(k)+(2p(m+k)-R_1)a(k-1)=0$ $a^{(1)}(k)\approx(-1/2)^k k^{(m-1)}$ $a^{(2)}(k)\approx(-2p)^k k^{(-m-1-R_1/2p)}/k!$
Power	$(k+1)(k+1-\frac{R_1}{2p})a(k+1)+(E-2k(m+k+1-2p-\frac{R_1}{2p}))a(k)+(m+k)(m+k-\frac{R_1}{2p})a(k-1)=0$ $\lvert a^{(1)}(k)\rvert=\lvert a^{(2)}(k)\rvert$ $a(k)\approx k^{m-3/4}\exp[\pm i4(pk)^{1/2}]$
Rankin Thorson	$\frac{(2m+k+1)}{(2m+2k+3)}(2ic(m+k+1)+R_1)a(k+1)+(E+(m+k)(m+k+1))a(k)$ $+\frac{k}{(2m+2k-1)}(R_1-2ic(m+k))a(k-1)=0$ $a^{(1)}(k)\approx(1/c)^{(m+k)}(m+k)^{(-m-1/2)}(m+k)!\exp[i((m+k)\frac{\pi}{2}+\frac{R_1}{2c}\mathrm{Ln}(m+k)]$ $a^{(2)}(k)\approx c^{(m+k)}(m+k)^{(-m-1/2)}\frac{1}{(m+k)!}\exp[i((m+k)\frac{\pi}{2}+\frac{R_1}{2c}\mathrm{Ln}(m+k)]$
Hylleraas	$(m+k+1)(k+1-\frac{R_2}{2p})a(k+1)+(E-2k(m+k+2p+1-\frac{R_2}{2p}))a(k)+k(m+k-\frac{R_2}{2p})a(k-1)=0$ $a^{(1)}(k)\approx k^{-1/4}\exp[2((4p+1))k)^{1/2}]$ $a^{(2)}(k)\approx k^{-1/4}\exp[-2((4p+1))k)^{1/2}]$
Jaffé	$(m+k+1)(k+1)a(k+1)+(E-2k(m+k+2p+1-\frac{R_2}{2p}))a(k)+(k-\frac{R_2}{2p})(m+k-\frac{R_2}{2p})a(k-1)=0$ $a^{(1)}(k)\approx k^{(-3/4-R_2/2p)}\exp[4(pk)^{1/2}]$ $a^{(2)}(k)\approx k^{(-3/4-R_2/2p)}\exp[-4(pk)^{1/2}]$

* $a^{(1)}(k)$ and $a^{(2)}(k)$ are the dominant and subdominant solutions respectively: $|a^{(1)}(k)|>|a^{(2)}(k)|$.

where

$$b_1=\frac{1}{4}\left[f_k-f_{k+1}\right]$$

$$b_2=\frac{1}{4}\left[(\sigma_k+1)f_{k+1}-\sigma_k f_k\right]$$

$$\begin{aligned}b_3=\frac{1}{128}\big[&-f_{k+2}f_{k+1}+2f_{k+1}^2-32(\sigma_k+1)^2f_{k+1}\\&-2f_k^2+f_kf_{k-1}+32\sigma_k^2f_k\big]\end{aligned}$$

$$\begin{aligned}b_4=\frac{1}{128}\big[&(3\sigma_k+7/2)f_{k+2}f_{k+1}-6(\sigma_k+1)f_{k+1}^2\\&+2f_{k+1}f_k+32(\sigma_k+1)^3f_{k+1}+6\sigma_kf_k^2\\&-(3\sigma_k-1/2)f_kf_{k-1}-32\sigma_k^3f_k\big]\end{aligned}$$

with

$$\sigma_k=1/2[m+2k-R_2/2p]. \qquad (24)$$

Table 3. Expressions for the functions f_k, $g_k(s,t)$ and h_k.

Basis	f_k	$g_k(s,t)$	h_k
Baber Hassé	$4p^2((m+k)^2-m^2)$ $\times[(\frac{R_1}{2p})^2-(m+k)^2]/(4(m+k)^2-1)$	$t(2m+2k-2s+t+1)$	$(m+k)(m+k+1)$
Wilson	$k(m+k)(4p(m+k)-2R_1)$	$t(2m+2k-2s+t+4p+1)$	$k(2m+k+4p+1)$
Power	$k(m+k)(k-\frac{R_1}{2p})(m+k-\frac{R_1}{2p})$	$-2t(m+2k-2s+t+1-2p-\frac{R_1}{2p})$	$-2k(m+k+1-2p-\frac{R_1}{2p})$
Rankin Thorson	$4c^2((m+k)^2-m^2)[(\frac{R_1}{2c})^2$ $+(m+k)^2]/(4(m+k)^2-1))$	$t(2m+2k-2s+t+1)$	$(m+k)(m+k+1)$
Hylleraas Jaffé	$k(m+k)(k-\frac{R_2}{2p})(m+k-\frac{R_2}{2p})$	$-2t(m+2k-2s+t+1+2p-\frac{R_2}{2p})$	$-2k(m+k+1+2p-\frac{R_2}{2p})$

$$\begin{aligned}\frac{\partial E_k}{\partial R} &= 4k\frac{\partial p}{\partial R}-\frac{k}{p}\left(Z_A+Z_B-\frac{R_2}{p}\frac{\partial p}{\partial R}\right)\\ &+\frac{1}{4p^2}\left[(k+1)(m+k+1)\left(k+1-\frac{R_2}{2p}\right)\left(m+k+1-\frac{R_2}{2p}\right)-k(m+k)\left(k-\frac{R_2}{2p}\right)\left(m+k-\frac{R_2}{2p}\right)\right]\frac{\partial p}{\partial R}\\ &+\frac{1}{8p^2}\left[\frac{1}{2}\left(Z_A+Z_B-\frac{R_2}{p}\frac{\partial p}{\partial R}\right)\left[(k+1)(m+k+1)\left(m+2k+2-\frac{R_2}{p}\right)-k(m+k)\left(m+2k-\frac{R_2}{p}\right)\right]\right]+O(1/p^3).\end{aligned} \tag{26}$$

The expressions for the coefficients b_5 and b_6 are given in Appendix.

$E_k^{(1)}$ provides all the terms up to $1/p^2$, the sum $E_k^{(1)}+E_k^{(2)}$ provides all the terms up to $1/p^4$ and the sum $E_k^{(1)}+E_k^{(2)}+E_k^{(3)}$ provides all the terms up to $1/p^6$.

Taking into account the expressions for the functions f_k, $g_k(s,t)$ and h_k corresponding to the Power [4] and Hylleraas [14] or Jaffé [15] basis (see Tab. 3), it is obvious that Power's expression for E_k can be directly deduced from relation (23) by changing R_2 into $(-R_1)$ and p into $(-p)$. Expression (23) contains the results of Baber and Hassé [2] given up to $1/p^3$ for $k=0$ and $R=0$, and up to $1/p^3$ for $m=0$ and $R_2\neq 0$, those of Flammer [3] for the spheroidal wavefunctions ($R=0$) up to $1/p^5$, those of Power [4] up to $1/p^5$ and those of Komarov *et al.* [6] up to $1/p^4$. Let us remark that when starting from the Wilson [13] recurrence relation the asymptotic analytic expression for the eigenvalues is exactly the same as Power's equations (23) but contains terms only up to $1/p^2$.

For the derivatives E'_k with respect to R we obtain:

$$\begin{aligned}\frac{\partial E_k}{\partial R} &= -\frac{\partial h_k}{\partial R}+\frac{1}{4p}\left(\frac{\partial f_k}{\partial R}-\frac{\partial f_{k+1}}{\partial R}\right)\\ &-\frac{1}{4p^2}(f_k-f_{k+1})\frac{\partial p}{\partial R}+O(1/p^3)\end{aligned} \tag{25}$$

and consequently:

see equation (26) above.

4 Application to alignment and trapping of molecules

According to the recent work of Friedrich and Herschbach [9] on alignment and trapping of molecules in intense laser fields, let us consider a linear rotor subject to radiation with electric field strength $\varepsilon=\varepsilon_0\cos(2\pi\nu t)$. For a permanent dipole moment μ along the internuclear axis, when taking into account the interaction potential V_α in terms of the polarizability components α_1 and α_2, parallel and perpendicular to the axis respectively, and the interaction potential V_μ, the Schrödinger equation is

$$[B\tilde{\mathbf{J}}^2+V_\alpha(\theta)+V_\mu(\theta)]\Psi=E\Psi \tag{27}$$

where

$$\begin{aligned}V_\mu(\theta)&=-\mu\varepsilon\cos\theta,\\ V_\alpha(\theta)&=-\varepsilon^2(\alpha_1\cos^2\theta+\alpha_2\sin^2\theta)/2.\end{aligned}$$

B is the rotational constant, $\tilde{\mathbf{J}}$ the angular momentum vector, θ the polar angle between the molecular axis and the electric field direction and E the eigenenergy. When neglecting the interaction V_μ the normalized eigenfunctions $\Psi(z,\varphi)$ for linear molecules ($\alpha_1>\alpha_2$) satisfy the following Schrödinger equation:

$$\left[\frac{\partial}{\partial z}(1-z^2)\frac{\partial}{\partial z}-\frac{M^2}{1-z^2}+c^2z^2+\lambda_{JM}\right]\Psi(z,\varphi)=0 \tag{28}$$

where M (positive integer) is the projection of $\tilde{\mathbf{J}}$ on the internuclear axis and

$$\begin{aligned} z &= \cos\theta, \\ \omega_{1,2} &= (\alpha_{1,2}\varepsilon_0^2/4B), \\ c^2 &= \omega_1 - \omega_2, \\ \lambda_{JM} &= \omega_2 + E/B. \end{aligned}$$

The expectation value of the squared alignment cosine is evaluated from the Hellman-Feyman theorem (see Killingbeck [20]):

$$\langle\cos^2\theta\rangle = -\frac{\partial\lambda_{JM}}{\partial c^2}\cdot \tag{29}$$

4.1 Approximate analytic expression for the eigenvalues λ_{JM} for c small

In the case of c small the function Ψ_{JM} can be expressed as a Baber and Hassé eigenfunction (see Eq. (14) and Tab. 1) with $R_1 = 0$, $p^2 = c^2$ and $A = -\lambda_{JM}$:

$$\Psi_{JM}(z,\varphi) = \exp(-iM\varphi)\exp(-cz)\sum_{J=M} a(J)P_J^M(z). \tag{30}$$

From equations (16) to (20) with $\ell = J$ an approximate analytic expression for the eigenvalues is obtained:

$$\lambda_{JM} = -c^2 - [E_{JM}^{(0)} + E_{JM}^{(1)} + E_{JM}^{(2)} + E_{JM}^{(3)}]. \tag{31}$$

Consequently for the first terms

$$\lambda_{JM} = \sum_{i=0}^{I}\gamma_{2i}c^{2i} + O(c^{2I+2}) \tag{32a}$$

with

$$\begin{aligned} \gamma_0 &= J(J+1) \\ \gamma_2 &= -\frac{1}{2}\left[1 - \frac{(4M^2-1)}{(2J-1)(2J+3)}\right] \\ \gamma_4 &= -\frac{1}{2}\left[\frac{((J+1)^2-M^2)((J+2)^2-M^2)}{(2J+1)(2J+3)^3(2J+5)}\right. \\ &\quad \left. - \frac{((J-1)^2-M^2)(J^2-M^2)}{(2J-3)(2J-1)^3(2J+1)}\right] \\ \gamma_6 &= (4M^2-1) \end{aligned} \tag{32b}$$

$$\begin{aligned} &\times\left[\frac{((J^2-M^2)((J-1)^2-M^2)}{(2J-5)(2J-3)(2J-1)^5(2J+1)(2J+3)}\right. \\ &\quad \left. - \frac{((J+1)^2-M^2)((J+2)^2-M^2)}{(2J-1)(2J+1)(2J+3)^5(2J+5)(2J+7)}\right]\cdot \end{aligned} \tag{32c}$$

Note that the coefficients γ_{2i} are similar to the ones obtained by Flammer [3] and given in Abramowitz and Segun [21].

From relations (29, 32) one obtains

$$\langle\cos^2\theta\rangle = -\sum_{i=1}^{I} i\gamma_{2i}c^{2(i-1)} + O(c^{2I}). \tag{33}$$

The previously published [9] limiting values (in $O(c^4)$) of eigenenergy and squared alignment cosine are contained in equations (32, 33) respectively.

4.2 Asymptotic analytic expression for the eigenvalues λ_{JM} for c large

In the case of c large the function Ψ_{JM} can be expressed as a Power eigenfunction (see Eq. (14) and Tab. 1) with $R_1 = 0$, $p_2 = c_2$ and $A = -\lambda_{JM}$:

$$\begin{aligned} &\Psi_{JM}(z,\varphi) = \exp(-iM\varphi)\exp(-c(1+z)) \\ &\times(1-z^2)^{M/2}\sum_{J=M} a(J)\Phi(-J+M,\ M+1;\ 2c(1+z)). \end{aligned} \tag{34}$$

An asymptotic expression, similar to the one for Power's functions (Eq. (23)) with $M + k = J$ is obtained

$$\lambda_{JM} = -c^2 + (2c-1)(M+1) - \sum_{i=0}^{3} E_{JM}^{(i)} \tag{35}$$

which can be written as follows:

$$\begin{aligned} \lambda_{JM} &= -c^2 + 2c(2J+1-M) \\ &\quad - \frac{1}{2}\Big[(2J+1-M)^2 + 1 - M^2\Big] \\ &\quad + \sum_{t=1}^{T}\frac{b_t}{(-c)^t} + O\left(\frac{1}{(-c)^{T+1}}\right) \end{aligned} \tag{36}$$

with for the first terms

$$\begin{aligned} b_1 &= \frac{1}{8}(2J+1-M)\left[(2J+1-M)^2 + 1 - M^2\right] \\ b_2 &= -\frac{1}{64}\left[(2J+1-M)^2(5(2J+1-M)^2 + 10 - 6M^2)\right. \\ &\quad \left. + (M^2-1)^2\right]. \end{aligned}$$

Further coefficients b_t are obtained from relations (24) for b_3 and b_4 and from relations (A.1, A.2) for b_5 and b_6, using

$$\begin{aligned} \sigma_k &= \frac{1}{2}(M+2k) \\ f_k &= k^2(M+k)^2 \end{aligned}$$

with $k = J - M$.

Table 4. Approximate values A_μ and A_λ (see Sect. 5) of the separation constant A for some states of H_2^+ and HeH^{2+}.

		H_2^+			HeH^{2+}		
state	$R(a_0)$	A	A_μ	A_λ	A	A_μ	A_λ
$1s\sigma_{(g)}$	1	0.24994624	0.24995051	0.24995286	0.75426151	0.75637554	0.75426339
	10	20.133293	36.103906	20.133294	95.025720	742.87761	95.025710
	100	2450.0101	7895597.3	2450.0101	9950.0025	26850773	9950.0028
$3d\pi_{(g)}$	1	− 5.9520464	− 5.9520464	− 28.173460	− 5.9043225	− 5.9043228	− 8.1939321
	10	− 1.0644557	− 1.0568713	− 1.0644865	− 1.2933656	− 2.8867318	− 1.2934018
	100	573.09378	6489.8173	573.09376	991.66928	2058848.1	991.66924
$4f\delta_{(u)}$	1	− 11.979158	− 11.979158	− 1396.2592	− 11.953209	− 11.953209	− 184.04015
	10	− 9.9601420	− 9.9600532	− 9.9657878	− 8.7076776	− 8.9358754	− 8.7089717
	100	222.16910	787.97600	222.16910	517.76337	52884.458	517.76337

From relations (29, 35–36) one obtains

$$\begin{aligned}\langle\cos^2\theta\rangle = 1 &- \frac{1}{c}(2J+1-M)\\ &- \frac{1}{16c^3}(2J+1-M)[(2J+1-M)^2+1-M^2]\\ &+ \frac{1}{16c^4}\left[(2J+1-M)^2(5(2J+1-M)^2\right.\\ &\left.+10-6M^2)+(M^2-1)^2\right]+O(1/c^5).\end{aligned} \tag{37}$$

The previously published [9] limiting values of eigenenergy (in $O(1/c)$) and squared alignment cosine (in $O(1/c^2)$) are contained in equations (35, 36) respectively, setting $2J = \tilde{J} + M$ for $(\tilde{J} + M)$ even and $2J = \tilde{J} + M - 1$ for $(\tilde{J} + M)$ odd.

5 Some illustrative results

The availability of the various approximate expressions displayed in the present work for eigenvalues is examined by comparison with exact values. Such exact eigenvalues can be obtained in a rather simply way from a Killingbeck-type procedure [1,12,22,23] used to solve the coupled pair of differential equations (14, 15) describing the one-electron two-centre problem as well as the differential equation (28) corresponding to alignment of molecules in intense laser fields [9]. Killingbeck's procedure works also well to obtain accurate expectation values, other than eigenvalues, such as the squared alignment cosine.

In Table 4 we present some results for the separation constant A (see Eqs. (14, 15) and Tab. 1) for three molecular states $1s\sigma_{(g)}$, $3d\pi_{(g)}$ and $4f\delta_{(u)}$ of the ions H_2^+ and HeH^{2+}, chosen as examples. For $R = 1a_0$, the approximate values A_μ deduced from the angular equation (using exact value of p) are seen to be very good approximations of the true values A, for the three states considered here. For increasing values of R (increasing value of p) the agreement becomes poorer and for $R = 100\,a_0$, values of A_μ are meaningless as approximations of A.

The approximate values A_λ deduced from the radial equation (using the exact value of p) which are seen to be meaningless as approximation of A for $R = 1a_0$ (except for the $1s\sigma$ states) become good approximations with increasing values of R and reproduce quasi-exactly A for $R = 100\,a_0$. These variations with R (*i.e.* with p) were expected but it is interesting to see that, for any value of R there is always a very good approximation A_μ or A_λ of the separation constant, *i.e.* for small values of R, A can be approximated by A_μ while for large values of R, A can be approximated by A_λ. This is illustrated in Figure 1 where are drawn A, A_μ and A_λ for the $3d\pi_g$ state of H_2^+. Advantage may be taken of this remark to provide useful guess values in iterative procedures used for exact solutions, such as Killingbeck-type methods.

In Table 5 we present some results for the eigenenergy λ_{00} of the Schrödinger equation for molecular alignment. In Figure 2 are drawn the variation with c^2 of λ_{00} and of its approximations provided by equations (32, 35). Approximate formulas (Eq. (32)) are seen to provide good approximations of λ_{00} for small values of c^2 (up to $c^2 \approx 10$) while formulas (35) approximate very well the exact eigenenergies for large values of c^2 (from $c^2 \approx 4$). A same quality of prediction is observed for the squared alignment cosine $\langle\cos^2\theta\rangle$. From Table 5 it should be noted that when the expansions (32, 35) are good approximations of λ_{00}, they display a smooth convergence. This may be used to provide useful guess values in iterative procedures for exact solutions.

6 Conclusion

A procedure by which to determine approximate expressions for the eigenvalues and for their derivatives with respect to some variable of problems described by three-term recurrence relations, has been proposed. Two applications have been performed. One concerns the bound and

Table 5. Convergence of the two expansions, equations (32, 35), for the eigenenergy λ_{00} of the alignment equation.

	c^2	1	16	60
	λ_{00}	− 0.34860240	− 9.1507934	− 45.545685
Approximate expression				
equation (32) I	0	0	0	0
	1	− 0.33333333	− 5.3333333	− 20.0
	2	− 0.34814815	− 9.1259259	− 73.333333
	3	− 0.34861846	− 11.052322	− 174.92063
equation (35) T	1	− 0.25000000	− 9.0625000	− 45.540341
	2	− 0.50000000	− 9.0781250	− 45.544508
	3	− 0.85937500	− 9.0837402	− 45.545281
	4	− 1.5000000	− 9.0862427	− 45.545459
	5	− 2.8300781	− 9.0875416	− 45.545507
	6	− 5.9414062	− 9.0883012	− 45.545521
$\langle\cos^2\theta\rangle$	exact	0.364307	0.735263	0.870516
	equation (32)	0.364374		
	equation (35)		0.747070	0.870536

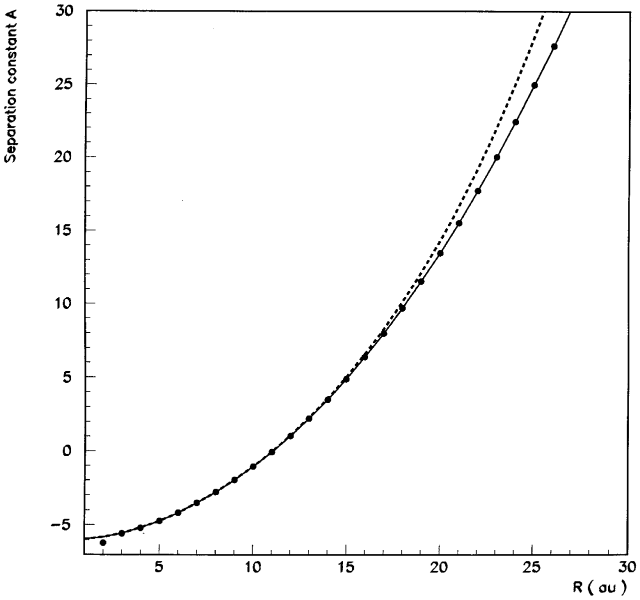

Fig. 1. Variation with R of separation constant A for the $3d\pi_{(g)}$ state of H_2^+. Full line exact value, dashed line (- - -) approximate value A_μ and points • approximate values A_λ.

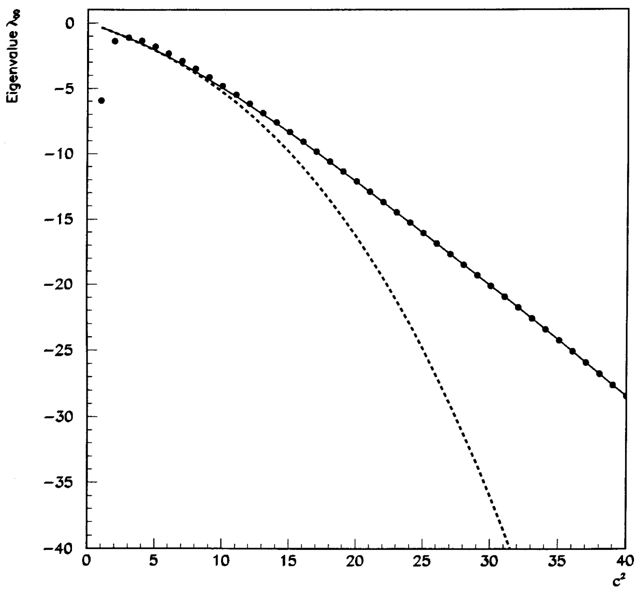

Fig. 2. Variation with the interaction parameter c^2 of the eigenvalue λ_{00} for molecular alignment. Full line exact value, dashed line (- - -) approximate value from equation (32) and points • approximate values from equation (35).

continuum eigenstates for monoelectronic diatomic ions. Six of the more often used basis sets have been explicitly worked out, *i.e.* the Baber and Hassé, Wilson, Power, Rankin and Thorson, Hylleraas and Jaffé basis functions. Useful material such as the recurrence relations and the asymptotic behaviour of the corresponding dominant and subdominant solutions not at disposal in the literature to the best of our knowledge is displayed. For any value of the internuclear distance R, at least one of the two approximate formulas proposed predicts very accurate values of the separation constant A for molecular states of H_2^+ and HeH^{2+}.

The other application has been chosen from the recent literature and concerns the Schrödinger equation for a linear rotor subject to radiation, describing alignment of molecules in intense laser fields. Approximate expressions for the eigenenergy and for the squared alignment cosine have been displayed including the previously published limiting values. For any value of the interaction parameter one of the two approximate formulas proposed reproduces very well the exact values for both energy and squared alignment cosine.

It is worth while to note that such approximations can be useful to initiate iterative processes for exact solving of corresponding differential equations.

Appendix: Expressions for the coefficients b_5 and b_6

$$\begin{aligned}
b5 = \frac{1}{12288}\Big[&- f_{k+3}f_{k+2}f_{k+1} - 3f_{k+2}^2 f_{k+1} + 21 f_{k+2}f_{k+1}^2 - 9 f_{k+2}f_{k+1}f_k - 96\left(6\sigma_k^2 + 14\sigma_k + \frac{33}{4}\right) f_{k+2}f_{k+1} \\
&- 24 f_{k+1}^3 + 24 f_{k+1}^2 f_k + 1152(\sigma_k+1)^2 f_{k+1}^2 - 24 f_{k+1}f_k^2 + 9 f_{k+1}f_k f_{k-1} - 384(2\sigma_k+1) f_{k+1}f_k - 3072(\sigma_k+1)^4 f_{k+1} \\
&+ 24 f_k^3 - 21 f_k^2 f_{k-1} - 1152\sigma_k^2 f_k^2 + 3 f_k f_{k-1}^2 + f_k f_{k-1} f_{k-2} + 96\left(6\sigma_k^2 - 2\sigma_k + \frac{1}{4}\right) f_k f_{k-1} + 3072\sigma_k^4 f_k \Big]. \qquad \text{(A.1)}
\end{aligned}$$

$$\begin{aligned}
b_6 = \frac{1}{12288}\Big[&(5\sigma_k+7) f_{k+3}f_{k+2}f_{k+1} + 3(5\sigma_k+6) f_{k+2}^2 f_{k+1} - 3(35\sigma_k+39) f_{k+2}f_{k+1}^2 \\
&+ 3(15\sigma_k+16) f_{k+2}f_{k+1}f_k + 12(80\sigma_k^3 + 280\sigma_k^2 + 330\sigma_k + 131) f_{k+2}f_{k+1} + 120(\sigma_k+1) f_{k+1}^3 \\
&- 24(5\sigma_k+4) f_{k+1}^2 f_k - 1920(\sigma_{k+1})^3 f_{k+1}^2 + 24(5\sigma_k+1) f_{k+1}f_k^2 - 3(15\sigma_k-1) f_{k+1}f_k f_{k-1} \\
&+ 192(10\sigma_k^2 + 10\sigma_k + 3) f_{k+1}f_k + 3072(\sigma_k+1)^5 f_{k+1} - 120\sigma_k f_k^3 + 3(35\sigma_k-4) f_k^2 f_{k-1} + 1920\sigma_k^3 f_k^2 \\
&- 3(5\sigma_k-1) f_k f_{k-1}^2 - (5\sigma_k-2) f_k f_{k-1} f_{k-2} - 12(80\sigma_k^3 - 40\sigma_k^2 + 10\sigma_k - 1) f_k f_{k-1} - 3072\sigma_k^5 f_k \Big]. \qquad \text{(A.2)}
\end{aligned}$$

References

1. G. Hadinger, M. Aubert-Frécon, G. Hadinger, J. Phys. B: At. Mol. Opt. Phys. **22**, 697 (1989).
2. W.G. Baber, H.R. Hassé, Proc. Camb. Soc. **31**, 564 (1935).
3. C. Flammer, *Spheroidal wave functions* (Stanford University Press, California, 1957).
4. J.D. Power, Philos. Trans. R. Soc. Lond. A **274**, 663 (1973).
5. I.V. Komarov, S.Yu. Slavyanov, J. Phys. B **1**, 1066 (1968).
6. I.V. Komarov, L.I. Ponomarev, S.Yu. Slavyanov, *Spheroidal and Coulomb Spheroidal functions* (Nauka, Moscow, 1976).
7. D.I. Abramov, S.Yu. Slavyanov, J. Phys. B: At. Mol. Phys. **11**, 2229 (1978).
8. D.I. Abramov, A.Ya. Kasakov, L.I. Ponomarev, S.Yu. Slavyanov, L.N. Somov, J. Phys. B: At. Mol. Phys. **12**, 1761 (1979).
9. B. Friedrich, D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
10. E.H. Kerner, Phys. Rev. **83**, 71 (1951).
11. K. Banerjee, J.K. Bhattacharjee, Phys. Rev. D **29**, 1111 (1984).
12. A. Yanacopoulo, G. Hadinger, M. Aubert-Frécon, J. Phys. B: At. Mol. Opt. Phys. **22**, 2427 (1989).
13. A.H. Wilson, Proc. Roy. Soc. Lond. A **118** 617, 635 (1928).
14. E.A. Hylleraas, Z. Phys. **71**, 739 (1931).
15. G. Jaffé, Z. Phys. **87**, 535 (1934).
16. J. Rankin, W.R. Thorson, J. Comput. Phys. **32**, 437 (1979).
17. I.S. Gradshtein, I.M. Ryzhik, *Tables of Integrals, Series and Products* (Academic Press, New-York and London, 1965).
18. L.I. Ponomarev, L.N. Somov, J. Comput. Phys. **20**, 183 (1976).
19. A. Hautot, M.T. Ploumhans, Bull. Soc. Math. Belg. **26**, 133 (1979).
20. J.P. Killingbeck, J. Phys. B: Math. Gen. **18**, 245 (1985).
21. M. Abramowitz, I.A. Segun, *Handbook of Mathematical Functions* (Dover, New-York, 1965).
22. J.P. Killingbeck, *Microcomputer Algorithms. Action from Algebra* (Hilger, Bristol, 1991).
23. G. Hadinger, M. Aubert-Frécon, G. Hadinger, J. Phys. B: At. Mol. Opt. Phys. **29**, 2951 (1996).