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2004 J. Phys. A: Math. Gen. 37 10639

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Analytical evaluation of the short-range interaction energy for ground state H_2^+

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Received 14 July 2004, in final form 9 September 2004

Published 20 October 2004

Online at stacks.iop.org/JPhysA/37/10639

doi:10.1088/0305-4470/37/44/012

Abstract

This work aims at the extension of the power series in R and $\ln R$ of interaction energy k and separation constant A for the system of two protons and one electron in the Born–Oppenheimer approximation. The wave equation is separated into confocal elliptic coordinates, in order to obtain two one-dimensional problems. The approach that we present here is based upon our previous calculations, where a relation between A and k for the (outer) ξ -equation was obtained in two different but substantially equivalent ways: either by an integral equation representation of the solution or by a logarithmic-perturbative expansion, in powers of the energy difference k , from the united atom state. At variance with our previous work, we make use of the (inner) η -equation of a remarkably simple determinantal equation proposed long ago by Hylleraas for which we develop a recursive method of calculation. By combining the two procedures we obtain the solution of the problem by solving for the coefficients of the R and $\ln R$ expansion. We calculate in this way coefficients up to $O(R^7)$ and show how higher order coefficients may be evaluated recursively.

PACS number: 31.15.–p

1. Introduction

The short-range interaction energy for the hydrogen molecular ion H_2^+ , up to the united atom He^+ , is difficult to evaluate numerically because of the instabilities of the potential energy function in the vicinity of the attractive centres. Available numerical computations [1, 2] do not go beyond 0.1 au for the gerade ground state. It results in the need for precise analytical calculations of the electronic interaction energy which should be valuable in the very short

range of internuclear separations, while at the same time giving reliable results in the region of the chemical bond, which is at about 2 au of distance.

There have been several attempts to expand the potential energy of two protons bound by an electron in powers of their distance R , either by solving secular determinantal equations [3, 4] or by united atom symmetry-adapted perturbation theories [5, 6] or by fluctuation theory techniques [7] applied to wavefunction symmetrization. Most of these studies make use of variable separation in confocal elliptic (spheroidal) coordinates. The usefulness of these approaches is however limited by their range of validity, which does not exceed a few tenths of atomic units. For these reasons, we attempt here to extend the range of applicability of the calculations by adding higher powers of R in the expansion of the electronic interaction energy and separation constant (see section 2). We do this by combining the Hylleraas determinantal method [3] for solving the inner equation (equation (1.1') and section 3) with our integral equation method for the outer equation (equation (1.1), see section 4).

Moreover, it will be shown in section 5 that this method for obtaining a dispersion relation between separation constant and energy is equivalent to an even simpler perturbative JWKB method, which is therefore able to replace the Hylleraas determinantal approach for the outer problem, which appears awkward to solve. This is so because the outer equation does not involve symmetrization of the wavefunction (wf), which is therefore required only to satisfy the regularity conditions (see section 6). The required symmetry is therefore imposed through the inner determinantal equation, for which we found a recursive method of finding a solution (see the appendix).

By combining both the dispersion relations obtained from the regularity conditions imposed upon the solution of the outer equation, and from the Hylleraas determinantal secular equation for the inner equation, the expansion of the electronic interaction energy in powers of R is found in section 7 up to $O(R^7)$.

We summarize here the basic equations and the formalism that has been used in order to obtain their solution. The quantum mechanical wave equation for an electron in the static electric potential field of two protons separated by a distance R may be separated into the usual spheroidal coordinates ξ ($1 \leq \xi < +\infty$), η ($-1 \leq \eta \leq 1$) and ϕ ($0 \leq \phi \leq 2\pi$) [7-9]; equations in these variables are

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dX}{d\xi} \right] + \left(\frac{ER^2}{2} \xi^2 + 2R\xi + A - \frac{\Lambda^2}{\xi^2 - 1} \right) X(\xi) = 0 \quad (1.1)$$

$$\frac{d}{d\eta} \left[(1 - \eta^2) \frac{dY}{d\eta} \right] - \left(\frac{ER^2}{2} \eta^2 + A + \frac{\Lambda^2}{1 - \eta^2} \right) Y(\eta) = 0. \quad (1.1')$$

From [8] it can be realized that equation (1.1) is exactly the same as that for the system in which the whole charge is concentrated in one of the foci of the ellipse. In equations (1.1) and (1.1'), Λ^2 and A are separation constants, and E (the energy) is assumed to be negative, which corresponds to bound states.

Following [4], we shall occasionally refer to the ξ -equation as the *outer* equation, and to the η -equation as the *inner* equation. By the variable transformation,

$$\xi = \tanh f, \quad \eta = \tanh g \quad (1.2)$$

where f is complex valued with constant imaginary part in the whole range of variation of ξ , while g is real, one can recast the two equations (for $\Lambda = 0$) into the following Hermitian

form:

$$\frac{d^2 X}{df^2} = \left(\frac{ER^2 \sinh^2 f}{2 \cosh^4 f} + 2R \frac{\sinh f}{\cosh^3 f} + \frac{A}{\cosh^2 f} \right) X(\tanh f) \quad (1.3)$$

$$\frac{d^2 Y}{dg^2} = \left(\frac{ER^2 \sinh^2 g}{2 \cosh^4 g} + \frac{A}{\cosh^2 g} \right) Y(\tanh g). \quad (1.3')$$

The quantities in parentheses are twice the potential energies $\frac{1}{2}\Delta_e(f)$, $\frac{1}{2}\varepsilon_e(g)$ of each one-dimensional problem. $\varepsilon_e(g)$ changes from the profile of a symmetrical double-well for positive real A to a single-well for real negative A . We use the subscript e to denote a special solution of equations (1.1) and (1.1'), which has been constructed perturbatively from the united atom solution, that is, a particular solution of the polarization equations which is not however the polarization function itself, because this is endowed with the proper boundary conditions that ensure convergence towards a state of symmetry required by the Hamiltonian operator [10–13]. Consequently, by taking as starting point the He^+ ground state, we have

$$X_e^{(0)}(\xi) = e^{-R\xi} \quad (1.4)$$

$$Y_e^{(0)}(\eta) = e^{-R\eta} \quad (1.4')$$

$$X_e^{(j)}(\xi) = \exp \{ i\varphi_e^{(0)}(\xi) + i\varphi_e^{(1)}(\xi) + \dots + i\varphi_e^{(j)}(\xi) \} \quad (1.5)$$

$$Y_e^{(j)}(\eta) = \exp \{ i\psi_e^{(0)}(\eta) + i\psi_e^{(1)}(\eta) + \dots + i\psi_e^{(j)}(\eta) \}. \quad (1.5')$$

The $\varphi_e^{(j)}(\xi)$, $\psi_e^{(j)}(\eta)$ are the perturbative solutions of order j for the action $\varphi_e(\xi)$, $\psi_e(\eta)$ relative to equations (1.1) and (1.1'). Then

$$p_e^{(j)}(\xi) = \frac{d\varphi_e^{(j)}}{df} = (1 - \xi^2) \frac{d\varphi_e^{(j)}}{d\xi} \quad (1.6)$$

$$q_e^{(j)}(\eta) = \frac{d\psi_e^{(j)}}{dg} = (1 - \eta^2) \frac{d\psi_e^{(j)}}{d\eta}. \quad (1.6')$$

2. Expansion of the constant A as a function of k up to terms $O(k^3)$

Recall that

$$k = E_e - E_k \quad (2.1)$$

where E_e is the energy of the reference state, E_k is the energy of the physical state that we are aiming to calculate. Thus, we are led to evaluate the expansion coefficients of

$$A_k = A_e + ak + bk^2 + ck^3 + \dots \quad (2.2)$$

having assumed the constant A_k to be analytical as a function of the energy difference k . This is a kind of dispersion relation, which holds between the coefficients of the outer differential equation, originating from the regularity conditions that the solutions must satisfy. A similar relation holds for the inner equation (see section 3). In our method [7, 9, 14], the boundary conditions are introduced through the formal solutions obtained from the iterative expansions of the integral equations, which solve equations (1.1) and (1.1').

3. Hylleraas method

Hylleraas [3] has deduced from the inner equation the following expansion, referring to the ground state with even parity (see the appendix, equation (A15)):

$$A_{00} = -A_k = -\frac{C}{3} - \frac{2}{135}C^2 - \frac{4}{8505}C^3 + \dots \quad (3.1)$$

Recalling that, in atomic units,

$$C = p^2 = -\frac{1}{2}ER^2 = -\frac{1}{2}(E_e - k)R^2 = \left(1 + \frac{k}{2}\right)R^2 \quad (3.2)$$

upon substituting C from (3.2) into (3.1) the following is obtained,

$$A_k = \left(\frac{1}{3}R^2 + \frac{2}{135}R^4 + \frac{4}{8505}R^6\right) + \left(\frac{1}{6}R^2 + \frac{2}{135}R^4 + \frac{6}{8505}R^6\right)k \\ + \left(\frac{1}{210}R^4 + \frac{3}{8505}R^6\right)k^2 + \frac{1}{17010}R^6k^3 + O(R^8) \quad (3.3)$$

which is the dispersion relation for the inner equation obtained by Hylleraas from the infinite determinantal equation arising from the expansion in associated Legendre polynomials. A similar determinant was introduced by Hylleraas for solving the outer equation, which could yield a similar dispersion relation involving A and E . However, in this case, the off-diagonal elements of that determinant are not all infinitesimal as $R \rightarrow 0$ (or $R \rightarrow \infty$), consequently, we decided to obtain the dispersion relation for the outer equation after representing the solution either by an integral expansion satisfying boundary conditions (section 4), or by a perturbative expansion of the action $\varphi(\xi)$, which is a sort of JWKB expansion [10] (see sections 5 and 6).

4. Evaluation of coefficients a, b, c from the outer equation with boundary conditions

Since the principles of our approach have been discussed to some extent in [7, 9, 14], we only need to recall here equation (8.1) of [9] or, more generally, equation (27) of [7]. Therefore, we use the integrability condition

$$\int_1^\infty dy \left[k \frac{R^2}{2} y^2 - (A_k - A_e) \right] X_e(y) X_k(y) = 0 \quad (4.1)$$

writing

$$k = \sum_{j=0}^{\infty} \mu^j k^{(j)} \quad (4.2)$$

$$X_k(\xi) = X_e(\xi) + \sum_{j=1}^{\infty} \mu^j X_k^{(j)}(\xi). \quad (4.2')$$

On substituting equations (4.2) and (4.2') into equation (4.1) and separating the orders in μ , an equation is deduced for each coefficient a, b, c, \dots of equation (2.2):

$$\int_1^\infty dy \left(k^{(1)} \frac{R^2}{2} y^2 X_e(y)^2 - a k^{(1)} X_e(y)^2 \right) = 0 \quad (4.3a)$$

$$\int_1^\infty dy \left(k^{(2)} \frac{R^2}{2} y^2 X_e(y)^2 - a k^{(2)} X_e(y)^2 \right) + \int_1^\infty dy \left(k^{(1)} \frac{R^2}{2} y^2 X_e(y) X_k^{(1)}(y) \right. \\ \left. - a k^{(1)} X_e(y) X_k^{(1)}(y) \right) - \int_1^\infty dy b (k^{(1)})^2 X_e(y)^2 = 0. \quad (4.3b)$$

The first integral vanishes because of (4.3a), so we obtain an equation for the coefficient b . Moreover,

$$\begin{aligned} \int_1^\infty dy \left(k^{(3)} \frac{R^2}{2} y^2 X_e(y)^2 - ak^{(3)} X_e(y)^2 \right) \\ + \int_1^\infty dy \left(k^{(2)} \frac{R^2}{2} y^2 X_e(y) X_k^{(1)}(y) - ak^{(2)} X_e(y) X_k^{(1)}(y) \right) \\ + \int_1^\infty dy \left(k^{(1)} \frac{R^2}{2} y^2 X_e(y) X_k^{(2)}(y) - ak^{(1)} X_e(y) X_k^{(2)}(y) \right) \\ - \int_1^\infty dy (c(k^{(1)})^3 + 2bk^{(1)}k^{(2)}) X_e(y)^2 \\ - \int_1^\infty dy b(k^{(1)})^2 X_e(y) X_k^{(1)}(y) = 0. \end{aligned} \quad (4.3c)$$

Upon substituting from equations (4.3a) and (4.3b) it is finally obtained that

$$\begin{aligned} \int_1^\infty dy \left(\frac{R^2}{2} y^2 - a \right) X_e(y) X_k^{(2)}(y) - \int_1^\infty dy bk^{(1)} X_e(y) X_k^{(1)}(y) \\ - \int_1^\infty dy (c(k^{(1)})^2 + bk^{(2)}) X_e(y)^2 = 0. \end{aligned} \quad (4.3'c)$$

It is now recalled from [7, 9] that the $X_k^{(j)}(\xi)$ are defined by iterating equation (5.1) below, using equations (2.2) and (4.2), and subsequently separating the orders in the variable μ . Therefore, by further introducing the complete expressions for $X_k^{(1)}(y)$ and $X_k^{(2)}(y)$, the variables $k^{(j)}$ can be eliminated from the equations so as to obtain, after dividing by $(k^{(1)})^2$, an equation which is solvable for the coefficient c :

$$\begin{aligned} c \int_1^\infty dy X_e(y)^2 = \int_1^\infty dy \left(\frac{R^2}{2} y^2 - a \right) X_e(y)^2 \int_1^y \frac{dx}{(1-x^2)X_e(x)^2} \\ \times \int_x^\infty dz \left(\frac{R^2}{2} z^2 - a \right) X_e(z)^2 \int_1^z \frac{du}{(1-u^2)X_e(u)^2} \\ \times \int_u^\infty dv \left(\frac{R^2}{2} v^2 - a \right) X_e(v)^2 - b \int_1^\infty dy \left(\frac{R^2}{2} y^2 - a \right) X_e(y)^2 \\ \times \int_1^y \frac{dx}{(1-x^2)X_e(x)^2} \int_x^\infty dz X_e(z)^2 - b \int_1^\infty dy X_e(y)^2 \\ \times \int_1^y \frac{dx}{(1-x^2)X_e(x)^2} \int_x^\infty dz \left(\frac{R^2}{2} z^2 - a \right) X_e(z)^2. \end{aligned} \quad (4.4)$$

The two expressions multiplying the coefficient b are seen to be equal by inverting the order of integration.

After somewhat lengthy calculations it is therefore obtained that

$$\begin{aligned} c = -\frac{3}{64}R + \frac{11}{128} + \frac{R}{4} \left(R - \frac{1}{2} \right) e^{4R} E_1(4R) \\ + \frac{R}{8} e^{8R} E_1(4R)^2 - \frac{R}{8} e^{4R} \int_1^\infty dx \frac{E_1(2R(1+x))}{1+x} \end{aligned} \quad (4.5)$$

while we recall from [7] that

$$a = \frac{1}{2} \left(R^2 + R + \frac{1}{2} \right), \quad b = -\frac{R}{16} - \frac{5}{32} + \frac{R}{4} e^{4R} E_1(4R). \quad (4.6)$$

5. The relationship between boundary conditions

We proceed now to elucidate the connection between the method of section 4 and the perturbative method which is shown below (see also section 6). Writing

$$X_k(\xi) = X_e(\xi) \left[1 + k \int_1^\xi \frac{dx}{(1-x^2)X_e(x)^2} \int_x^\infty dy X_e(y)X_k(y) \left(\frac{R^2}{2}y^2 - \frac{A_k - A_e}{k} \right) \right] \quad (5.1)$$

$$i\varphi_k(\xi) = \ln X_k(\xi) \quad (5.2)$$

it follows, from equations (5.1) and (5.2), that

$$ip_k(\xi) = \frac{d}{df} i\varphi_k(\xi) = (1 - \xi^2) \frac{d}{d\xi} i\varphi_k(\xi) \quad (5.2')$$

$$ip_k(\xi) = ip_e(\xi) + \frac{\frac{k}{X_e(\xi)^2} \int_\xi^\infty dy X_e(y)X_k(y) \left(\frac{R^2}{2}y^2 - \frac{A_k - A_e}{k} \right)}{1 + k \int_1^\xi \frac{dx}{(1-x^2)X_e(x)^2} \int_x^\infty dy X_e(y)X_k(y) \left(\frac{R^2}{2}y^2 - \frac{A_k - A_e}{k} \right)}. \quad (5.3)$$

Therefore condition (4.1) with vanishing $p_e(1)$ implies that

$$p_k(1) = 0. \quad (5.4)$$

This condition suffices to evaluate A_k to all orders in k .

We can prove now by a perturbative calculation that the expansion

$$ip_e(\xi) = ip_e^{(0)}(\xi) + \sum_{n=1}^{\infty} ip_e^{(n)}(\xi) \quad (5.5)$$

for an arbitrary variation of the parameter $E_e^{(1)}$ from the value of the energy $E_e^{(0)} = -2E_h$ pertaining to the united atom He^+ ,

$$E_e^{(1)} = -k, \quad (5.6)$$

yields the variation of the parameter A_e from the He^+ value $A_e^{(0)} = R^2$ as

$$A_e = R^2 + \sum_{n=1}^{\infty} (E_e^{(1)})^n A_e^{(n)} \quad (5.7)$$

where the $A_e^{(n)}$ may be calculated from the conditions

$$p_e^{(0)}(1) = p_e^{(1)}(1) = p_e^{(2)}(1) = \dots = p_e^{(n)}(1) = \dots = 0 \quad (5.8)$$

$$\lim_{\xi \rightarrow \infty} p_e^{(n)}(\xi) e^{-2R\xi} = 0. \quad (5.9)$$

The unexpected result is found that condition (5.8) can be fulfilled with free $A_e^{(n)}$, which are therefore subsequently calculated from the further requirement (5.9). Actually, the proper behaviour at infinity has been implicitly embodied in equation (5.1) by putting appropriate extrema to the integrals (see equation (5.3)); in fact, both boundary conditions (5.8) and (5.9) are needed to fix the value of the constant A .

6. The perturbative solution

From the calculations reported in [8, 9] we find

$$ip_e^{(1)} = \frac{1}{4} E_e^{(1)} [R(1 - \xi^2) + 1 - \xi] \quad (6.1)$$

and, for $n > 1$,

$$ip_e^{(n)}(\xi) e^{-2R\xi} = ip_e^{(n)}(1) e^{-2R\xi} + \sum_{j=1}^{n-1} \int_1^\xi d\zeta \frac{p_e^{(j)}(\zeta) p_e^{(n-j)}(\zeta)}{1 - \zeta^2} e^{-2R\zeta} + A_e^{(n)} (E_e^{(1)})^n \int_1^\xi d\zeta e^{-2R\zeta} \quad (6.2)$$

$$ip_e^{(n)}(\xi) = - \sum_{j=1}^{n-1} \int_\xi^\infty d\zeta \frac{p_e^{(j)}(\zeta) p_e^{(n-j)}(\zeta) e^{-2R(\zeta-\xi)}}{1 - \zeta^2} + \sum_{j=1}^{n-1} \int_1^\infty d\zeta \frac{p_e^{(j)}(\zeta) p_e^{(n-j)}(\zeta) e^{-2R(\zeta-1)}}{1 - \zeta^2}. \quad (6.3)$$

Results thus obtained are

$$ip_e^{(2)}(\xi) = \frac{1}{16} (E_e^{(1)})^2 \left[\frac{R}{2} (1 - \xi^2) + \frac{3}{2} (1 - \xi) + 2e^{2R(1+\xi)} E_1(2R(1 + \xi)) - 2e^{4R} E_1(4R) \right] \quad (6.4)$$

$$ip_e^{(3)}(\xi) = \frac{1}{32} (E_e^{(1)})^3 \left[\frac{R}{4} (1 - \xi^2) + \frac{5}{4} (1 - \xi) + (3 - 2R(1 + \xi)) E_1(2R(1 + \xi)) e^{2R(1+\xi)} - (3 - 4R) E_1(4R) e^{4R} + 2e^{8R} E_1(4R)^2 - 2e^{4R} E_1(4R) e^{2R(1+\xi)} E_1(2R(1 + \xi)) + e^{2R(1+\xi)} \int_\xi^\infty dx \frac{E_1(2R(1+x))}{1+x} - 2e^{4R} \int_1^\infty dx \frac{E_1(2R(1+x))}{1+x} \right]. \quad (6.5)$$

By the same tool the coefficients $A_e^{(1)}$, $A_e^{(2)}$, $A_e^{(3)}$ are calculated, and are consistent with the results obtained from equation (4.1) (see [7, 9]).

7. Expansion coefficients a , b , c and interaction energy in powers of R

The coefficients a , b , c . . . thus obtained are exact to all orders in R , which is not true for those calculated from the Hylleraas method. Here their expansion in powers of R is however needed for calculation purpose. To this end, we expand the coefficients b and c in equation (2.2) in powers of the variables R and $\ln R$ by first expanding the function

$$e^{4R} E_1(4R) = -\gamma - \ln 4R + (1 - \gamma)4R - 4R \ln 4R + \left(\frac{3}{2} - \gamma\right) 8R^2 - 8R^2 \ln 4R + o(R^2). \quad (7.1)$$

The term represented by an integral may be expanded in the following manner by integrations by parts, so as to extract the logarithmic divergence from the integral sign:

$$\int_1^\infty dx \frac{E_1(2R(1+x))}{1+x} = \int_{2R}^\infty d\alpha \frac{E_1(2\alpha)}{\alpha} = -\ln 2R E_1(4R) - \frac{1}{2} (\ln 2R)^2 e^{-4R} + \int_{2R}^\infty d\alpha (\ln \alpha)^2 e^{-2\alpha}. \quad (7.2)$$

Then we have

$$\int_{2R}^\infty d\alpha (\ln \alpha)^2 e^{-2\alpha} = \int_0^\infty d\alpha (\ln \alpha)^2 e^{-2\alpha} + o(1). \quad (7.3)$$

Next we expand the interaction energy given by equation (2.1),

$$k = k_2 R^2 + k_3 R^3 + k_4 R^4 + k_5 R^5 + \dots \quad (7.4)$$

where the coefficients k_j up to $j = 5$ have been evaluated in [7] (see also [4]). Equating now the expansion of the constant $A[k(R)]$ in powers of R and $\ln R$ obtained from equations (3.1), (3.2) and (7.4) according to Hylleraas calculations, with that we have deduced from the outer equation with boundary conditions (equations (2.2), (4.5), (4.6), (7.4) and [7]), we obtain the following equation, where only those terms have been retained which bear a factor R^6 or R^7 :

$$\begin{aligned} & \frac{4}{8505} R^6 + \frac{1}{6} R^2 (k_4 R^4 + k_5 R^5) + \frac{2}{135} R^4 (k_2 R^2 + k_3 R^3) \\ &= \frac{1}{2} R^2 (k_4 R^4 + k_5 R^5) + \frac{1}{2} R (k_5 R^5 + k_6 R^6) + \frac{1}{4} (k_6 R^6 + k_7 R^7) \\ & \quad - \frac{R}{16} (2k_2 k_3 R^5 + ((k_3)^2 + 2k_2 k_4) R^6) - \frac{5}{32} (((k_3)^2 + 2k_2 k_4) R^6 \\ & \quad + 2(k_2 k_5 + k_3 k_4) R^7) - \frac{R}{4} (\gamma + \ln 4R) (2k_2 k_3 R^5 + ((k_3)^2 + 2k_2 k_4) R^6) \\ & \quad + R^2 (1 - \gamma - \ln 4R) ((k_2)^2 R^4 + 2k_2 k_3 R^5) + R^3 (3 - 2\gamma - 2 \ln 4R) (k_2)^2 R^4 \\ & \quad + \frac{11}{128} ((k_2)^3 R^6 + 3(k_2)^2 k_3 R^7) + \frac{1}{16} R \left[-\frac{3}{4} + 2\gamma + 2 \ln 4R + 2(\gamma + \ln 4R)^2 \right. \\ & \quad \left. - 2 \ln 2R (\gamma + \ln 4R) + (\ln 2R)^2 - 2 \int_0^\infty d\alpha (\ln \alpha)^2 e^{-2\alpha} \right] (k_2)^3 R^6. \quad (7.5) \end{aligned}$$

By solving equation (7.5) for the coefficients of the terms proportional to R^6 and R^7 it is obtained that

$$\begin{aligned} k_6 = & \frac{16}{8505} - \frac{4}{3} k_4 + \frac{8}{135} k_2 - 2\kappa_5 + \frac{1}{2} k_2 k_3 - 4(k_2)^2 - \frac{11}{32} (k_2)^3 + \frac{5}{8} ((k_3)^2 + 2k_2 k_4) \\ & + \left(-\frac{128}{9} + 2k_2 k_3 + 4(k_2)^2 \right) (\gamma + \ln 4R) = \frac{310816}{8505} - \frac{128}{9} (\gamma + \ln 4R) \quad (7.6) \end{aligned}$$

$$\begin{aligned} k_7 = & -\frac{32}{8505} - \frac{16}{135} k_2 + \frac{8}{135} k_3 + \frac{8}{3} k_4 + \frac{8}{3} \kappa_5 - 4k_2^2 - 9k_2 k_3 \\ & - k_3^2 - 2k_2 k_4 + \frac{5}{4} (k_2 \kappa_5 + k_3 k_4) + \frac{7}{8} (k_2)^3 - \frac{33}{32} k_2^2 k_3 \\ & + \left(\frac{512}{27} + \frac{80}{9} k_2 + 4k_2 k_3 + (k_3)^2 + 2k_2 k_4 - \frac{1}{2} (k_2)^3 \right) (\gamma + \ln 4R) \\ & - \left(\frac{1}{2} (\gamma + \ln 4R)^2 + \frac{1}{4} (\ln 2R)^2 - \frac{1}{2} \ln 2R (\gamma + \ln 4R) \right. \\ & \left. - \frac{1}{2} \int_0^\infty d\alpha e^{-2\alpha} (\ln \alpha)^2 \right) (k_2)^3 = -\frac{87392}{8505} - \frac{3968}{405} (\gamma + \ln 4R) \\ & + \frac{256}{27} \left[(\gamma + \ln 4R)^2 + \frac{1}{2} (\ln 2R)^2 - \ln 2R (\gamma + \ln 4R) \right] \\ & - \frac{128}{27} \left[\frac{\pi^2}{6} + (\gamma + \ln 2)^2 \right] \quad (7.7) \end{aligned}$$

where the rational numerical part of k_j has been renamed κ_j , and γ is the Euler constant [15]:

$$\gamma = - \int_0^\infty e^{-t} \ln t \, dt.$$

8. Summary and conclusions

In this paper, the expansion of the separation constant in powers of the internuclear distance R has been calculated for the system of two fixed protons interacting through a single electron. The potential energy which is effective for the electron motion depends upon energy E and separation constant A , which are therefore required to satisfy the conditions of stability of the motion.

These conditions are expressed through two relations between E and A , one for each equation that the motion is bound to satisfy on a plane (the rotational motion around the internuclear axis is separated out).

In order to formulate the desired stability conditions for the two-centre problem, the one-centre wf of this problem is taken as a starting point, from which a two-centre reference state, denoted by the subscript e , is constructed through the calculation of its wf $\Psi_e(\xi, \eta)$, by a JWKB expansion [10, 16].

The stability conditions on the wf are now translated into three different but largely equivalent schemes:

- (i) By expansion of the wf $\Psi_e(\xi, \eta)$ in a suitable united atom basis, each differential equation is recast into the form of an infinite linear system whose unknowns are the coefficients, whose determinant is put equal to zero.
- (ii) The reference state $\Psi_e(\xi, \eta) = X_e(\xi)Y_e(\eta)$, which is a solution of equations (1.1) and (1.1'), is allowed to vary at will, with free parameters E_e and A_e , therefore the physical state $\Psi_k(\xi, \eta)$ is constructed by iterative solution of an integral equation, whose kernel contains Ψ_e . In order that the method be effective, Ψ_e should be a tight approximation to Ψ_k so as to ensure rapid convergence of the iteration procedure. So it is required that $\Psi_k(\xi, \eta) \rightarrow \Psi_e(\xi, \eta)$ locally as $R \rightarrow 0$. The stability requirements (boundary conditions and symmetry) are then translated into integral conditions.
- (iii) The proper behaviour may be required on the function $\Psi_e(\xi, \eta)$ by imposing appropriate relations among the parameters entering into it: in this case, $\Psi_e(\xi, \eta)$ is the required solution. This approach works satisfactorily on the outer equation (see sections 5 and 6), and it has been proved above to be entirely equivalent to the integral method. It does not appear to have been used for the inner equation, except in Rayleigh–Schroedinger perturbation theory, which requires an infinite-order summation so as to obtain the desired symmetry properties (see, however, [16]).

While in previous works [7, 9, 14] the present authors preferred method (ii) for the purpose of testing its potentialities, in the present study this is only retained to calibrate the outer equation, but in parallel conjunction with method (iii), which appears by far the most expeditious.

On the other hand, method (i), borrowed from [3], implemented with the calculations reported in the appendix which allow us to estimate its precision, appears to be the most efficient for obtaining a dispersion relation from the inner equation.

Calculations along these lines are now in hand in order to obtain higher coefficients in the expansion of A and E in powers of R .

Acknowledgment

Financial support by the University of Genoa is gratefully acknowledged.

Appendix. Evaluation of Hylleraas determinant for the inner equation

Let us consider the matrix $\|d_{i,j}\|$ where the i, j are integers, $i, j \geq 1$, and

$$d_{i,j} = 0, \quad \text{if } j \neq i, i \pm 1. \tag{A1}$$

Then we denote by $D_{n,m}$ the cofactor of the element $d_{n,m}$. The determinantal (secular) equation is

$$D_0 = \det\|d_{i,j}\| = 0, \tag{A2}$$

therefore upon expanding D_0 around the element $d_{n,n}$ according to Kramer's rule we obtain, for $n > 1$,

$$D_0 = d_{n,n}D_{n,n} + d_{n,n-1}D_{n,n-1} + d_{n,n+1}D_{n,n+1}. \tag{A3}$$

It is now defined as

$$\begin{cases} D_n^+ = \det\|d_{i,j}\|, & i, j > n \\ D_n^- = \det\|d_{i,j}\|, & i, j < n \end{cases} \tag{A4}$$

$$\begin{cases} C_n^+ = \det\|d_{i,j}\| & \text{with } i > n, j \geq n, j \neq n+1 \\ C_n^- = \det\|d_{i,j}\| & \text{with } i < n, j \leq n, j \neq n-1. \end{cases} \tag{A5}$$

Then it is proved that

$$D_0 = d_{n,n}D_n^+D_n^- - d_{n,n-1}D_n^+C_n^- - d_{n,n+1}D_n^-C_n^+ \tag{A6}$$

$$D_0 = d_{n,n}D_n^+D_n^- - d_{n,n-1}d_{n-1,n}D_n^+D_{n-1}^- - d_{n,n+1}d_{n+1,n}D_{n+1}^+D_n^- \tag{A6'}$$

with each term of the rhs of (A6') being equal to the corresponding term of equation (A3). The equality of the first rhs terms is almost evident. In order to prove the equality of the second terms we write the cofactor extensively as

$$D_{n,n-1} = -1 \times \tag{A7}$$

$d_{1,1}$	$d_{1,2}$	0		
$d_{2,1}$	$d_{2,2}$	$d_{2,3}$		
0	$d_{3,2}$	$d_{3,3}$		
.....	$d_{n-3,n-4}$	$d_{n-3,n-3}$	$d_{n-3,n-2}$	0	0	0
.....	0	$d_{n-2,n-3}$	$d_{n-2,n-2}$	0	0	0
0	0	0	$d_{n-1,n-2}$	$d_{n-1,n}$	0	0
0	0	0	0	$d_{n+1,n}$	$d_{n+1,n+1}$	$d_{n+1,n+2}$
0	0	0	0	0	$d_{n+2,n+1}$	$d_{n+2,n+2}$	$d_{n+2,n+3}$
0	0	0	0	0	0	$d_{n+3,n+2}$	$d_{n+3,n+3}$
0

$$= -d_{n-1,n} \times$$

Next we use equations (A8) and both equations (A9) in order to substitute into the second and the third term respectively. This results in

$$D_0 = (d_{n,n}d_{n+1,n+1} - d_{n,n+1}d_{n+1,n})D_{n+1}^+ D_n^- - d_{n,n+1}d_{n+1,n}d_{n+1,n+2}d_{n+2,n+1} \frac{D_{n+1}^+ D_{n+2}^+ D_n^-}{D_n^+} \\ - d_{n,n-1}d_{n-1,n}d_{n+1,n+1}D_{n+1}^+ \frac{D_n^- + d_{n-1,n-2}C_{n-1}^-}{d_{n-1,n-1}}. \quad (\text{A12})$$

Then, upon substituting C_{n-1}^- from equation (A8) we finally obtain the secular equation in the form

$$\frac{D_{n+1}^+}{d_{n-1,n-1}D_n^+} \left[D_n^+ D_n^- (d_{n-1,n-1}d_{n,n}d_{n+1,n+1} - d_{n-1,n-1}d_{n,n+1}d_{n+1,n} - d_{n,n-1}d_{n-1,n}d_{n+1,n+1}) \right. \\ \left. - D_{n+2}^+ D_n^- d_{n-1,n-1}d_{n,n+1}d_{n+1,n}d_{n+1,n+2}d_{n+2,n+1} \right. \\ \left. - D_n^+ D_{n-2}^- d_{n+1,n+1}d_{n,n-1}d_{n-1,n}d_{n-1,n-2}d_{n-2,n-1} \right] = 0. \quad (\text{A13})$$

The quantity enclosed in square brackets is invariant under the interchange of the plus and minus signs in superscripts and subscripts as well. The operations that have been done necessitate that D_n^+ , as well as $d_{n-1,n-1}$, do not vanish.

The matrix that Hylleraas [3] has calculated from the inner equation in order to obtain its eigenvalues, has the form of equation (A1), where the off-diagonal elements are $O(R^2)$, while those in the principal diagonal are $O(R^0)$. Consequently, equation (A13) may be written as

$$\frac{D_{n+1}^+ D_n^-}{d_{n-1,n-1}} \begin{vmatrix} d_{n-1,n-1} & d_{n-1,n} & 0 \\ d_{n,n-1} & d_{n,n} & d_{n,n+1} \\ 0 & d_{n+1,n} & d_{n+1,n+1} \end{vmatrix} = O(R^8) \quad (\text{A14})$$

which allows us to evaluate the n th eigenvalue to $O(R^8)$. A still higher precision is obtained for the first eigenvalue ($n = 1$), which may be obtained from the equation

$$\begin{vmatrix} d_{1,1} & d_{1,2} & 0 \\ d_{2,1} & d_{2,2} & d_{2,3} \\ 0 & d_{3,2} & d_{3,3} \end{vmatrix} = d_{1,2} d_{2,1} d_{2,3} d_{3,2} d_{3,4} d_{4,3} \frac{D_4^+}{D_1^+} = O(R^{12}) \quad (\text{A15})$$

from which the root given by equation (3.1) is evaluated up to $O(C^5)$.

Note that equation (A13) is still meaningful for small n , because the matrix $\|d_{i,j}\|$ may be bordered suitably by the addition of a finite number of rows and columns, such that the value of the determinant and the off-diagonal properties (A1) are preserved.

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