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Exchange energy splitting for ground state H_2^+ from fluctuation theory

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Abstract

The quantum-mechanical energy splitting for a ground state hydrogen molecular ion has been computed as the complex-valued mean first-passage time across the potential barrier between two wells, by separating the Schrödinger equation using spheroidal coordinates and applying a subsequent transformation so as to obtain three one-dimensional Hermitian operator equations. One of these operators describes a particle oscillating between two wells separated by a potential barrier. The splitting is then calculated as the energy difference between the symmetry-adapted wavefunctions and a reference state whose probability density is concentrated on one side of the barrier. The eigenfunctions are calculated as the solutions of a Volterra integral equation, where the energy difference is the eigenvalue.

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1. Introduction

The quantum-mechanical exchange energies in a bistable potential have recently been calculated by us [1] by computing the complex-valued mean first-passage time across the potential barrier from a transient state, endowed with Smoluchowski boundary conditions [2], whose probability density is concentrated on one side of the barrier. An integral equation was derived, whose first iterate gives an approximate solution valid in the asymptotic region of large R .

In the present work, we apply this approach to the evaluation of the exchange energy splitting for the H_2^+ molecular ion after separating the eigenvalue equation by a coordinate transformation yielding two independent Hermitian Schrödinger equations. These equations are solved by a perturbative expansion assuming as unperturbed function a suitable solution of the polarization equations in spheroidal coordinates. Since this solution is not known in closed

analytical form, we use for it a second-order expansion in the nuclear potential perturbation. The first-mentioned perturbative expansion allows us to obtain an order-by-order evaluation of the energy splitting in terms of an integral equation explicating the resolvent of the Schrödinger operator. The first perturbation order is valid in the asymptotic region of large R , where it leads the mean first-passage time expression as the first iterative solution of the integral equation considered in our previous work. The first exponentially decreasing term of the energy splitting obtained with the two leading coefficients of the asymptotic series in $1/R$ is seen to coincide with the results obtained previously by different authors [3–5] by partitioning the coordinate space into different regions.

The paper is organized as follows. Sections 2 and 3 contain the Schrödinger equation in spheroidal coordinates which is subsequently separated into two equations, which, by a second coordinate transformation using hyperbolic functions, are reduced to Hermitian form [6]. This coordinate transformation is similar, but not identical, to that used in [7] in a similar context.

The two Schrödinger equations in Hermitian form are then used to derive evolution equations for transition density matrix elements. By appropriate linear combination of these equations the diffusion equations and the current operator in three-dimensional Euclidean space are reconstructed, entirely expressed in spheroidal coordinates.

In section 4, the perturbative scheme is set up in order to obtain the complete polarization function. The various perturbation orders of the logarithm of the wavefunction (the action) are distinguished by a perturbation parameter λ . The unperturbed wavefunction (wf) is hydrogenic, and the perturbation is the electric potential of the proton.

In section 5, the values of the constants E_e and A_e are determined through first order from the boundary conditions which are imposed on the wf as a function of ξ and η .

In section 6, we show the relationship between the first-order correction to the action and the first-order correction to the polarization wf as calculated by various authors [8–12]. The boundary conditions on the polarization wf as a function of the coordinate η can be chosen freely in the present method, so the way they are chosen is in order to make subsequent calculations easier. The same procedure is applied to second-order corrections to the action which are calculated fully to leading order in $1/R$.

Section 7 is the key to the paper. It is shown there how the wf endowed with the desired boundary conditions can be constructed by a Volterra-type integral equation where the full polarization function enters into the kernel. The eigenvalue of the integral equation is precisely the energy shift, to be determined by boundary conditions. The advantages of this approach are evident. The boundary conditions on the polarization function are to some extent arbitrary. Its logarithm, or the action, does not need to be determined within exponential precision (to leading order) and moreover there is no need to vary the indices of special functions in order to obtain the matching at the frontier between separate regions of the coordinate space. The variation is operated directly on the eigenvalue, and the varied eigenfunction is obtained by quadratures.

A systematic procedure [13] is given so as to solve the integral equation in powers of a perturbation parameter μ , which is associated with the exponentially decreasing factor, not analytic in $1/R$ (see appendix A). Only the first iterate is considered in this work, although the interest in higher-order terms has been pointed out in more recent developments [5]. This procedure of solution contains the iterative method of solution of the integral equation as a particular case [14].

Section 8 yields the values of the separation constant and of the energy for the symmetric and antisymmetric eigenstates of the Schrödinger operator of the hydrogen molecular ion, up to the first exponentially decreasing term. The separation constant is obtained from the

boundedness condition for the ξ -component of the wf, while the energy depends, as usual, on the boundary conditions, which involve here the η -coordinate.

Appendix B shows that the energy difference between the reference state and the symmetrized state is additive, in the sense that the result is independent of the assumed reference state.

2. Dynamical equations

The equation of motion for a quantum-mechanical wf $\Psi(x, y, z)$ of an electron in the static electric potential field of two protons separated by a distance R is the following [6]:

$$-\left(\frac{1}{2}\nabla^2 + \frac{1}{r_1} + \frac{1}{r_2}\right)\Psi(x, y, z) = i\frac{\partial\Psi}{\partial t} \quad (2.1)$$

where ∇^2 is the Laplacian operator, and r_1 and r_2 are the distances between the electron and the two fixed centres of attraction, x, y, z the Cartesian coordinates, i the imaginary unit and t the time. Atomic units³ are used throughout this paper, so that e (elementary charge) = m (electronic mass) = \hbar (Planck constant) = $4\pi\epsilon_0$ (vacuum permittivity) = 1.

Now it is convenient to separate this problem into three coupled one-dimensional equations by introducing, as usual, a system of spheroidal coordinates

$$\begin{cases} \xi = \frac{r_1 + r_2}{R} & \eta = \frac{r_2 - r_1}{R} \\ \varphi = \text{rotation angle around the axis joining the nuclei, measured from an arbitrary} \\ \text{reference plane.} \end{cases} \quad (2.2)$$

There follows [3, 4, 6, 9, 15, 16]

$$\nabla^2 = \frac{4}{R^2(\xi^2 - \eta^2)} \left[\frac{\partial}{\partial\xi}(\xi^2 - 1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1 - \eta^2)\frac{\partial}{\partial\eta} \right] + \frac{1}{R^2(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial\varphi^2}. \quad (2.3)$$

By (2.2) and (2.3), equation (2.1) can be transformed so as to yield two separate equations in the variables ξ and η , respectively:

$$\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dX}{d\xi} \right] + \left(\frac{ER^2}{2} \xi^2 + 2R\xi + A - \frac{\Lambda^2}{\xi^2 - 1} \right) X(\xi) = 0 \quad (2.4)$$

$$\frac{d}{d\eta} \left[(1 - \eta^2) \frac{dY}{d\eta} \right] - \left(\frac{ER^2}{2} \eta^2 + A + \frac{\Lambda^2}{1 - \eta^2} \right) Y(\eta) = 0 \quad (2.4')$$

where it is assumed that

$$\Psi(\xi, \eta, \varphi, t) = X(\xi)Y(\eta) e^{i\Lambda\varphi} e^{-iEt}. \quad (2.5)$$

A is a separation constant which depends upon the constants of the motion Λ (axial angular momentum) and E (energy), and a third constant of the motion. In practice, for given E and Λ , A plays the role of an eigenvalue common to both operators (2.4) and (2.4') (with opposite signs). Consequently, it must be determined from the condition that both functions $X(\xi)$ and $Y(\eta)$ satisfy the required boundary conditions of the problem.

³ Energies are given in hartree ($E_h = e^2(4\pi\epsilon_0 a_0)^{-1} = 4.359\,748 \times 10^{-18}$ J) provided lengths are in bohr ($a_0 = 4\pi\epsilon_0\hbar^2(me^2)^{-1} = 5.291\,772 \times 10^{-11}$ m).

3. Diffusion equations

The eigenvalue equations (2.4), (2.4') can be transformed into a couple of eigenvalue equations for Hermitian operators upon multiplication by $\xi^2 - 1$ and $1 - \eta^2$, respectively, provided the functions $X(\xi)$ and $Y(\eta)$ satisfy suitable conditions on the boundaries.

By the variable transformation

$$\xi = \tanh f \quad \eta = \tanh g \quad (3.1)$$

equations (2.4), (2.4') assume the more familiar form

$$\frac{d^2 X}{df^2} = \left(\frac{ER^2 \sinh^2 f}{2 \cosh^4 f} + \frac{2R \sinh f}{\cosh^3 f} + \frac{A}{\cosh^2 f} + \Lambda^2 \right) X(\tanh f) \quad (3.2)$$

$$\frac{d^2 Y}{dg^2} = \left(\frac{ER^2 \sinh^2 g}{2 \cosh^4 g} + \frac{A}{\cosh^2 g} + \Lambda^2 \right) Y(\tanh g). \quad (3.2')$$

Variable f is defined by

$$f = \tanh^{-1} \xi = \frac{1}{2} \ln \frac{1+\xi}{1-\xi} \quad 1 \leq \xi < +\infty \quad (3.3)$$

so that f is complex in the whole range of variation of ξ , with constant imaginary part $i(n + \frac{1}{2})\pi$, $n = 0, \pm 1, \pm 2$, etc. Variable g is obviously real, since $-1 \leq \eta \leq 1$.

Now we put $\Lambda = 0$ and consider two solutions of each equation (3.2), (3.2'), which we label by the indices 0 and 1. Multiplying the equations labelled with index 0 by X_1, Y_1 , respectively, and the equations labelled with index 1 by X_0, Y_0 , and subtracting, one obtains after some manipulations

$$\frac{d^2}{df^2} X_1 X_0 = 2 \frac{d}{df} X_1 \frac{dX_0}{df} + \left[(E_1 - E_0) \frac{R^2 \sinh^2 f}{2 \cosh^4 f} + \frac{A_1 - A_0}{\cosh^2 f} \right] X_1(\tanh f) X_0(\tanh f) \quad (3.4)$$

$$\frac{d^2}{dg^2} Y_1 Y_0 = 2 \frac{d}{dg} Y_1 \frac{dY_0}{dg} + \left[(E_1 - E_0) \frac{R^2 \sinh^2 g}{2 \cosh^4 g} + \frac{A_1 - A_0}{\cosh^2 g} \right] Y_1(\tanh g) Y_0(\tanh g). \quad (3.4')$$

These are equations of diffusion type in the variables f and g separately. From them it is possible to reconstruct the three-dimensional diffusion-like equation in the Euclidean space (x, y, z) , thereby obtaining

$$\begin{aligned} & \frac{2}{R^2(\tanh^2 f - \tanh^2 g)} \left(\cosh^2 f \frac{\partial^2}{\partial f^2} - \cosh^2 g \frac{\partial^2}{\partial g^2} \right) \\ & \quad \times X_1(\tanh f) Y_1(\tanh g) X_0(\tanh f) Y_0(\tanh g) \\ & = \left[\frac{2}{R^2(\tanh^2 f - \tanh^2 g)} \left(\cosh^2 f \frac{\partial}{\partial f} \frac{\partial \ln X_0^2}{\partial f} - \cosh^2 g \frac{\partial}{\partial g} \frac{\partial \ln Y_0^2}{\partial g} \right) \right. \\ & \quad \left. + E_1 - E_0 \right] X_1(\tanh f) Y_1(\tanh g) X_0(\tanh f) Y_0(\tanh g). \end{aligned} \quad (3.5)$$

Converting back to variables ξ, η, φ , it can be recognized that equation (3.5) is equivalent to

$$\begin{aligned} & -i \left[\frac{1}{2} \nabla^2 - \frac{2}{R^2(\xi^2 - \eta^2)} \left(\frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial \ln X_0^2}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial \ln Y_0^2}{\partial \eta} \right) \right. \\ & \quad \left. + E_1 - E_0 \right] X_1(\xi) Y_1(\eta) X_0(\xi) Y_0(\eta) = 0 \end{aligned} \quad (3.5')$$

where use has been made of equation (2.3) with $\Lambda_1 = \Lambda_0 = 0$.

Equation (3.5') can be identified with the equation of motion for the elements of the density matrix of the system [1, 2] (actually, an off-diagonal matrix element). Consequently, the second term in the left-hand side (lhs) of this equation represents the divergence of the current expressed in spheroidal coordinates, and the equation can be interpreted as an equation for a probability density distribution for a hypothetical, or virtual, diffusion process [2, 17, 18].

4. Perturbative equations and their solutions through first order

We attempt now to solve equations (2.4), (2.4') or (3.2), (3.2') by perturbation theory (p.t.) choosing as zero order solutions the hydrogenic wavefunctions⁴

$$X_e^{(0)}(\xi) = \exp(i\phi_e^{(0)}(\xi)) = \exp\left(i\sqrt{E_e^{(0)}/2}\xi R\right) \quad (4.1)$$

$$Y_e^{(0)}(\eta) = \exp(i\psi_e^{(0)}(\eta)) = \exp\left(i\sqrt{E_e^{(0)}/2}\eta R\right) \quad (4.1')$$

which satisfy the zero-order hydrogenic equations in a one-centre potential [15]:

$$\frac{d^2 X_e^{(0)}}{df^2} = \left[-\frac{1}{2}E_e^{(0)} \frac{R^2}{\cosh^4 f} - i\sqrt{2E_e^{(0)}} \frac{R \sinh f}{\cosh^3 f} \right] X_e^{(0)}(\tanh f) \quad (4.2)$$

$$\frac{d^2 Y_e^{(0)}}{dg^2} = \left[-\frac{1}{2}E_e^{(0)} \frac{R^2}{\cosh^4 g} - i\sqrt{2E_e^{(0)}} \frac{R \sinh g}{\cosh^3 g} \right] Y_e^{(0)}(\tanh g). \quad (4.2')$$

We take as perturbation the difference between the actual two-centre potential and the one-centre hydrogenic potential, multiplied by λ which is the order parameter. Therefore, this perturbation is an analytic function of $1/R$ modulated by the charge of the second centre. Then we write⁵, leaving the proportionality constant unspecified

$$X_e(\xi) \propto \exp\{i\phi_e^{(0)}(\xi) + \lambda i\phi_e^{(1)}(\xi) + \lambda^2 i\phi_e^{(2)}(\xi) + \dots\} \quad (4.3)$$

$$Y_e(\eta) \propto \exp\{i\psi_e^{(0)}(\eta) + \lambda i\psi_e^{(1)}(\eta) + \lambda^2 i\psi_e^{(2)}(\eta) + \dots\} \quad (4.3')$$

and, in the same way

$$E_e = E_e^{(0)} + \lambda E_e^{(1)} + \lambda^2 E_e^{(2)} + \dots \quad (4.4)$$

$$A_e = A_e^{(0)} + \lambda A_e^{(1)} + \lambda^2 A_e^{(2)} + \dots \quad (4.5)$$

$$X_e^{(j)}(\xi) \propto \exp\{i\phi_e^{(0)}(\xi) + \dots + \lambda^j i\phi_e^{(j)}(\xi)\} \quad (4.6)$$

$$Y_e^{(j)}(\eta) \propto \exp\{i\psi_e^{(0)}(\eta) + \dots + \lambda^j i\psi_e^{(j)}(\eta)\} \quad (4.6')$$

where λ is a perturbation parameter, whose value will be put equal to 1, and j is a positive integer. The values of $E_e^{(0)}$ and $A_e^{(0)}$ may be calculated according to [15] which yields

$$E_e^{(0)} = -\frac{1}{2}, \quad A_e^{(0)} = -\frac{1}{2}E_e^{(0)}R^2. \quad (4.7)$$

This value can also be obtained from equations (2.4), (2.4') and using (4.1), (4.1') in the hydrogenic Schrödinger equation in spheroidal coordinates:

$$-\left[2\xi \frac{d \ln X_e^{(0)}}{d\xi}\right]_{\xi=1} = \frac{1}{2}E_e^{(0)}R^2 + R + A_e^{(0)} \quad (4.8)$$

⁴ The subscript 'e' denotes a reference state representing an equilibrium density.

⁵ We recall that all ϕ 's and ψ 's are complex functions, so that it is convenient to use $i\phi$'s and $i\psi$'s as a whole to denote real functions. For this reason we do not factorize the imaginary unit.

$$-\left[2\eta \frac{d \ln Y_e^{(0)}}{d\eta}\right]_{\eta=-1} = \frac{1}{2} E_e^{(0)} R^2 - R + A_e^{(0)}. \quad (4.8')$$

Now we substitute into equations (3.2), (3.2'), thus obtaining, to first order in λ (with $\lambda = 1$)

$$\begin{aligned} \frac{d^2 X_e^{(1)}}{df^2} = & \left[(E_e^{(0)} + \lambda E_e^{(1)}) \frac{R^2 \sinh^2 f}{2 \cosh^4 f} + i\sqrt{2E_e^{(0)}}(\lambda - 1) \frac{R \sinh f}{\cosh^3 f} \right. \\ & \left. + \frac{(A_e^{(0)} + \lambda A_e^{(1)})}{\cosh^2 f} + \lambda 2R \frac{\sinh f}{\cosh^3 f} \right] X_e^{(1)}(\tanh f) + O(\lambda^2) \end{aligned} \quad (4.9)$$

$$\begin{aligned} \frac{d^2 Y_e^{(1)}}{dg^2} = & \left[(E_e^{(0)} + \lambda E_e^{(1)}) \frac{R^2 \sinh^2 g}{2 \cosh^4 g} + i\sqrt{2E_e^{(0)}}(\lambda - 1) \frac{R \sinh g}{\cosh^3 g} \right. \\ & \left. + \frac{(A_e^{(0)} + \lambda A_e^{(1)})}{\cosh^2 g} \right] Y_e^{(1)}(\tanh g) + O(\lambda^2). \end{aligned} \quad (4.9')$$

Evaluating derivatives to first order in λ , using the zero-order equations (4.2), (4.2') and dividing by $\exp\{i\phi_e^{(1)}\}$, $\exp\{i\psi_e^{(1)}\}$, multiplying by $\exp\{i\phi_e^{(0)}(f)\}$, $\exp\{i\psi_e^{(0)}(g)\}$, respectively, leads to the result

$$\begin{aligned} \left[i \frac{dp_e^{(1)}}{df} - 2p_e^{(0)}(f)p_e^{(1)}(f) \right] \exp\{2i\phi_e^{(0)}(f)\} = & \left[\frac{1}{2} E_e^{(1)} R^2 \frac{\sinh^2 f}{\cosh^4 f} + \frac{A_e^{(1)}}{\cosh^2 f} \right. \\ & \left. + \left(2 + i\sqrt{2E_e^{(0)}} \right) R \frac{\sinh f}{\cosh^3 f} \right] \exp\{2i\phi_e^{(0)}(f)\} \end{aligned} \quad (4.10)$$

$$\begin{aligned} \left[i \frac{dq_e^{(1)}}{dg} - 2q_e^{(0)}(g)q_e^{(1)}(g) \right] \exp\{2i\psi_e^{(0)}(g)\} = & \left[\frac{1}{2} E_e^{(1)} R^2 \frac{\sinh^2 g}{\cosh^4 g} + \frac{A_e^{(1)}}{\cosh^2 g} \right. \\ & \left. + i\sqrt{2E_e^{(0)}} R \frac{\sinh g}{\cosh^3 g} \right] \exp\{2i\psi_e^{(0)}(g)\} \end{aligned} \quad (4.10')$$

$$p_e^{(j)} = \frac{d\phi_e^{(j)}}{df} \quad q_e^{(j)} = \frac{d\psi_e^{(j)}}{dg}. \quad (4.11)$$

Returning to variables ξ , η , the solutions to the equations above are

$$\begin{aligned} ip_e^{(1)}(\xi) = ip_e^{(1)}(1) \exp\left(i\sqrt{2E_e^{(0)}}R(1-\xi)\right) - & \left[\frac{2 + i\sqrt{2E_e^{(0)}}}{i\sqrt{2E_e^{(0)}}} + \frac{1}{2} E_e^{(1)} \left(\frac{R}{i\sqrt{2E_e^{(0)}}} + \frac{1}{E_e^{(0)}} \right. \right. \\ & \left. \left. - \frac{1}{i\sqrt{2E_e^{(0)}}E_e^{(0)}R} \right) + \frac{A_e^{(1)}}{i\sqrt{2E_e^{(0)}}R} + \frac{2 + i\sqrt{2E_e^{(0)}}}{2E_e^{(0)}R} \right] \exp\left(i\sqrt{2E_e^{(0)}}R(1-\xi)\right) \\ & + \frac{1}{2} E_e^{(1)} \left(\frac{\xi^2 R}{i\sqrt{2E_e^{(0)}}} + \frac{\xi}{E_e^{(0)}} - \frac{1}{i\sqrt{2E_e^{(0)}}E_e^{(0)}R} \right) + \frac{A_e^{(1)}}{i\sqrt{2E_e^{(0)}}R} \\ & + \xi \frac{2 + i\sqrt{2E_e^{(0)}}}{i\sqrt{2E_e^{(0)}}} + \frac{2 + i\sqrt{2E_e^{(0)}}}{2E_e^{(0)}R} \end{aligned} \quad (4.12)$$

$$\begin{aligned} iq_e^{(1)}(\eta) = iq_e^{(1)}(-1) \exp\left(-i\sqrt{2E_e^{(0)}}R(1+\eta)\right) + & \left[1 - \frac{1}{2} E_e^{(1)} \left(\frac{R}{i\sqrt{2E_e^{(0)}}} + \frac{1}{E_e^{(0)}} \right. \right. \\ & \left. \left. - \frac{1}{i\sqrt{2E_e^{(0)}}E_e^{(0)}R} \right) - \frac{A_e^{(1)} - 1}{i\sqrt{2E_e^{(0)}}R} \right] \exp\left(-i\sqrt{2E_e^{(0)}}R(1+\eta)\right) \end{aligned}$$

$$+ \frac{1}{2} E_e^{(1)} \left(\frac{\eta^2 R}{i\sqrt{2E_e^{(0)}}} + \frac{\eta}{E_e^{(0)}} - \frac{1}{i\sqrt{2E_e^{(0)}} E_e^{(0)} R} \right) + \eta + \frac{A_e^{(1)} - 1}{i\sqrt{2E_e^{(0)}} R}. \quad (4.12')$$

5. Constant evaluation for the ξ -equation

Equations (4.12), (4.12') depend upon the four unspecified constants $E_e^{(1)}$, $A_e^{(1)}$, $p_e^{(1)}(1)$, $q_e^{(1)}(-1)$. Now $E_e^{(1)}$ is easily determined by ordinary Rayleigh–Schrödinger (RS) perturbation theory [9] with the appropriate boundary conditions⁶, which do not need to be fulfilled here at all orders. We find easily

$$\frac{1}{2} \nabla^2 X_e^{(1)}(\xi) Y_e^{(1)}(\eta) = \left[E_e^{(0)} + \lambda E_e^{(1)} + (\lambda - 1) \frac{i\sqrt{2E_e^{(0)}}}{R} \frac{\xi - \eta}{\xi^2 - \eta^2} + \frac{2\lambda\xi}{R(\xi^2 - \eta^2)} \right] \times X_e^{(1)}(\xi) Y_e^{(1)}(\eta) + O(\lambda^2). \quad (5.1)$$

Multiplying now both members of this equation on the left by $X_e^{(1)}(\xi) Y_e^{(1)}(\eta)$, and integrating both members of the resulting equation over all space there results, upon expansion of the wfs through first order in λ , the familiar expansion of the energy functional in powers of the perturbation parameter from which follows [9]

$$E_e^{(1)} = -\frac{1}{R} + \left(1 + \frac{1}{R}\right) e^{-2R}. \quad (5.2)$$

This procedure can be generalized to all perturbation orders.

Equation (4.12) is considered multiplied by $\exp\{i\sqrt{2E_e^{(0)}}\xi\}$. Then we assume

$$\lim_{\xi \rightarrow +\infty} p_e^{(1)}(\xi) \exp\{i\sqrt{2E_e^{(0)}}R\xi\} = 0 \quad (5.3)$$

$$p_e^{(1)}(1) = \left. \frac{d\phi_e^{(1)}}{d\xi} (1 - \xi^2) \right|_{\xi=1} = 0. \quad (5.4)$$

There follows

$$\begin{aligned} A_e^{(1)} &= -\left(2 + i\sqrt{2E_e^{(0)}}\right) R + \frac{1}{2} E_e^{(1)} \left(-R^2 \pm i\sqrt{\frac{2}{E_e^{(0)}}} R + \frac{1}{E_e^{(0)}} \right) \pm i\sqrt{\frac{2}{4E_e^{(0)}}} \left(2 + i\sqrt{2E_e^{(0)}}\right) \\ &= -\frac{R}{2} + \frac{1}{R} - \frac{1}{2} \left(1 + \frac{1}{R}\right) e^{-2R} (R^2 + 2R + 2). \end{aligned} \quad (5.5)$$

The upper sign refers to a negative numerator under the square root, the lower sign to a negative denominator.

From equation (5.5) it follows that

$$\frac{dA_e^{(1)}}{dE_e^{(1)}} = -\frac{1}{2} (R^2 + 2R + 2). \quad (5.6)$$

A similar relation can be deduced for any perturbative order. By writing, for n positive integer > 1 , from equations (3.2), (4.6)

$$\begin{aligned} &\left[i \frac{dp_e^{(n)}}{df} - 2p_e^{(0)}(f) p_e^{(n)}(f) \right] \exp\{2i\phi_e^{(0)}(f)\} \\ &= \left[\sum_{\substack{j,k=1 \\ j+k=n}}^{n-1} p_e^{(j)}(f) p_e^{(k)}(f) + \frac{1}{2} E_e^{(n)} R^2 \frac{\sinh^2 f}{\cosh^4 f} + \frac{A_e^{(n)}}{\cosh^2 f} \right] \exp\{2i\phi_e^{(0)}(f)\} \end{aligned} \quad (5.7)$$

⁶ The boundary conditions are the proper behaviour of the functions at the boundaries.

there follows by integration

$$\begin{aligned} ip_e^{(n)}(\xi) \exp \left\{ i\sqrt{2E_e^{(0)}} R\xi \right\} &= ip_e^{(n)}(1) \exp \left\{ i\sqrt{2E_e^{(0)}} R \right\} \\ &+ \sum_{j=1}^{n-1} \int_1^\xi d\zeta \frac{p_e^{(j)}(\zeta) p_e^{(n-j)}(\zeta)}{1-\zeta^2} \exp \left\{ i\sqrt{2E_e^{(0)}} R\zeta \right\} \\ &+ \frac{1}{2} E_e^{(n)} R^2 \int_1^\xi d\zeta \zeta^2 \exp \left\{ i\sqrt{2E_e^{(0)}} R\zeta \right\} + A_e^{(n)} \int_1^\xi d\zeta \exp \left\{ i\sqrt{2E_e^{(0)}} R\zeta \right\}. \end{aligned} \quad (5.8)$$

Now, evaluating the integrals by successive integrations by parts taking the exponential as integral factor, every $p_e^{(n)}(f)$ results to be representable by a Laurent series in the variable R . The first term on the rhs of (5.8) vanishes by assumption. The second term on the rhs is $O\left(\frac{1}{R}\right)$ for $n=2$ and higher order with increasing n by induction, if the boundary condition (5.3) is extended to every positive integer n . There follows

$$\begin{aligned} ip_e^{(n)}(\xi) &= \sum_{j=1}^{n-1} \int_{+\infty}^\xi d\zeta \frac{p_e^{(j)}(\zeta) p_e^{(n-j)}(\zeta)}{1-\zeta^2} \exp \left\{ i\sqrt{2E_e^{(0)}} R(\zeta - \xi) \right\} \\ &+ \frac{1}{2} E_e^{(n)} \left(\frac{\xi^2 R}{i\sqrt{2E_e^{(0)}}} + \frac{\xi}{E_e^{(0)}} - \frac{1}{i\sqrt{2E_e^{(0)}} E_e^{(0)} R} \right) + \frac{A_e^{(n)}}{i\sqrt{2E_e^{(0)}} R} \end{aligned} \quad (5.9)$$

from which follows

$$\delta A_e = - \left(\frac{R^2}{2} + R + 1 \right) (\lambda \delta E_e^{(1)} + \lambda^2 \delta E_e^{(2)} + \dots) + \frac{2}{R} \lambda^2 \delta E_e^{(1)} + O\left(\frac{1}{R^2}\right). \quad (5.10)$$

It is remarkable that this result, which is deduced from the boundary condition (5.3) and its generalizations to higher orders, is coincident with that calculated in equation (8.3) from a condition of boundedness for $X_k(\xi)$, which is of a different nature. In fact, neither condition is strictly necessary for the functions to be normalizable.

6. Boundary conditions for the η -equation: comparison with the first-order polarization function

6.1. First-order corrections

The solutions that we have found are of course related to the first-order RS polarization function which is calculated, for instance, by Robinson [9]. Putting

$$F(\xi, \eta) = \frac{i}{2} (\phi_e^{(1)}(\xi) + \psi_e^{(1)}(\eta)) \quad (6.1)$$

multiplying equations (4.10), (4.10') by $\cosh^2 f$ and $\cosh^2 g$, respectively, and subtracting, there results, after dropping the exponential factor

$$\begin{aligned} -\frac{\partial}{\partial \xi} (1 - \xi^2) \frac{\partial i\phi_e^{(1)}}{d\xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial i\psi_e^{(1)}}{d\eta} - i\sqrt{2E_e^{(0)}} R \left[\frac{\partial i\phi_e^{(1)}}{\partial \xi} (1 - \xi^2) - \frac{\partial i\psi_e^{(1)}}{\partial \eta} (1 - \eta^2) \right] \\ = -\frac{1}{2} E_e^{(1)} R^2 (\xi^2 - \eta^2) - (2 + i\sqrt{2E_e^{(0)}}) R\xi + i\sqrt{2E_e^{(0)}} R\eta \end{aligned} \quad (6.2)$$

which, by equation (6.1), is manifestly identical to the first-order polarization equation given in [9]. Now, integrating equation (4.12) under the assumptions (5.3) and (5.4) and substituting $A_e^{(1)}$ from equation (5.5) and $E_e^{(1)}$ from equation (5.2), we obtain

$$i\phi_e^{(1)}(\xi) = -\frac{1}{2}\xi + \left(1 - \frac{1}{R}\right) \ln(1 + \xi) + \frac{1}{2} \left(1 + \frac{1}{R}\right) e^{-2R} [R\xi + 2 \ln(1 + \xi)] + \text{const} \quad (6.3)$$

where $E_e^{(0)}$ has been substituted from equation (4.7). In the same way we can obtain the analogous expression for the action in the variable η :

$$\begin{aligned} i\psi_e^{(1)}(\eta) &= \frac{1}{2}B^{(1)}[\text{Ei}\{R(1+\eta)\} - \text{Ei}\{R\} - e^{2R}\text{Ei}\{-R(1-\eta)\} - \text{Ei}\{-R\}] \\ &\quad + \frac{1}{2}E_e^{(1)}[R\eta + 2\ln(1+\eta)] - \ln(1-\eta) + \frac{1}{R}\ln\frac{1+\eta}{1-\eta} + C^{(1)} \\ &= \frac{1}{2}B^{(1)}[\text{Ei}\{R(1+\eta)\} - \text{Ei}\{R\} - e^{2R}\text{Ei}\{-R(1-\eta)\} - \text{Ei}\{-R\}] \\ &\quad - \frac{1}{2}\eta - \left(1 + \frac{1}{R}\right)\ln(1-\eta) + \frac{1}{2}\left(1 + \frac{1}{R}\right)e^{-2R}[R\eta + 2\ln(1+\eta)] + C^{(1)} \end{aligned} \quad (6.3')$$

where $\text{Ei}(x)$ is the exponential integral function [19], and $B^{(1)}$, $C^{(1)}$ are arbitrary constants. Equation (4.12') relates $B^{(1)}$ to the derivative of $\psi_e^{(1)}$ at a fixed point. Now, on putting

$$B^{(1)} = 0 \quad (6.4)$$

there results the full expression for the wavefunctions (4.6), (4.6') corrected to first order in λ , for all values of R :

$$X_e^{(1)}(\xi) \propto \exp\left\{-\frac{1}{2}(R+1)(1-e^{-2R})\xi\right\} \times (1+\xi)^{(1+e^{-2R})-\frac{1}{R}(1-e^{-2R})} \quad (6.5)$$

$$Y_e^{(1)}(\eta) \propto \exp\left\{-\frac{1}{2}(R+1)(1-e^{-2R})\eta\right\} \times (1-\eta)^{-(1+\frac{1}{R})}(1+\eta)^{(1+\frac{1}{R})e^{-2R}}. \quad (6.5')$$

Equations (6.5), (6.5') yield acceptable solutions to the first-order polarization equation (5.1) in the region

$$1 \leq \xi < +\infty \quad -1 \leq \eta \leq 0.$$

Equations (4.9), (4.9') and, consequently, the two-dimensional equation (5.1) (we recall that $\Lambda = 0$), yield the multiplicative corrections to the wavefunction whose logarithm is exact to first order in λ . Upon expansion of the exponential function it may be ascertained that these corrections, being multiplied by $\Psi_e^{(0)}$, the hydrogenic wf, yield exactly the first-order RS polarization function, up to an additive constant.

The second constant of integration $B^{(1)}$ is related to the derivatives of the polarization function at some fixed point. Indeed, from equation (4.12'), putting $\eta = -1$ it follows that

$$\begin{aligned} q_e^{(1)}(-1) &= \left.\frac{d\psi_e^{(1)}}{d\eta}(1-\eta^2)\right|_{\eta=-1} \\ &= B^{(1)} + \frac{A_e^{(1)} - 1}{i\sqrt{2E_e^{(0)}}R} + \frac{1}{2}E_e^{(1)}R^2 \left(\frac{1}{i\sqrt{2E_e^{(0)}}R} - \frac{1}{E_e^{(0)}R^2} - \frac{1}{i\sqrt{2E_e^{(0)}}E_e^{(0)}R^3}\right) - 1. \end{aligned} \quad (6.6)$$

Equating $q_e^{(1)}(-1)$ to zero, yields, instead of equation (6.4):

$$B^{(1)} = \frac{E_e^{(1)}}{E_e^{(0)}} + \left(1 + \frac{i}{\sqrt{2E_e^{(0)}}R}\right) \frac{2 + i\sqrt{2E_e^{(0)}}}{i\sqrt{2E_e^{(0)}}} + \frac{1}{i\sqrt{2E_e^{(0)}}R} + 1 = -2\left(1 + \frac{1}{R}\right)e^{-2R}. \quad (6.7)$$

With this value of $B^{(1)}$, we recover the regular solution to the first-order polarization equation, given by Dalgarno and Lynn [8] and Robinson [9]. Neglecting overlap terms in equation (6.6) leads to equation (6.4).

6.2. Second-order corrections

The functions $X_e^{(2)}(\tanh f)$, $Y_e^{(2)}(\tanh g)$ defined by equations (4.6), (4.6'), respectively, satisfy the following second-order ordinary homogeneous differential equations

$$\frac{d^2 X_e^{(2)}}{df^2} = \left[(E_e^{(0)} + \lambda E_e^{(1)} + \lambda^2 E_e^{(2)}) \frac{R^2 \sinh^2 f}{2 \cosh^4 f} + i\sqrt{2E_e^{(0)}}(\lambda - 1)R \frac{\sinh f}{\cosh^3 f} + \frac{A_e^{(0)} + \lambda A_e^{(1)} + \lambda^2 A_e^{(2)}}{\cosh^2 f} + \lambda 2R \frac{\sinh f}{\cosh^3 f} \right] X_e^{(2)}(\tanh f) + O(\lambda^3) \quad (6.8)$$

$$\frac{d^2 Y_e^{(2)}}{dg^2} = \left[(E_e^{(0)} + \lambda E_e^{(1)} + \lambda^2 E_e^{(2)}) \frac{R^2 \sinh^2 g}{2 \cosh^4 g} + i\sqrt{2E_e^{(0)}}(\lambda - 1) \frac{\sinh g}{\cosh^3 g} + \frac{A_e^{(0)} + \lambda A_e^{(1)} + \lambda^2 A_e^{(2)}}{\cosh^2 g} \right] Y_e^{(2)}(\tanh g) + O(\lambda^3). \quad (6.8')$$

Now, using equations (4.6), (4.6'), multiplied by an appropriate integrating factor, there follows

$$\left[i \frac{dp_e^{(2)}}{df^2} - 2p_e^{(0)}(f)p_e^{(2)}(f) \right] \exp(2i\phi_e^{(0)}(f)) = \left[p_e^{(1)}(f)^2 + E_e^{(2)} \frac{R^2 \sinh^2 f}{2 \cosh^4 f} + \frac{A_e^{(2)}}{\cosh^2 f} \right] \exp(2i\phi_e^{(0)}(f)) \quad (6.9)$$

$$\left[i \frac{dq_e^{(2)}}{dg^2} - 2q_e^{(0)}(g)q_e^{(2)}(g) \right] \exp(2i\psi_e^{(0)}(g)) = \left[q_e^{(1)}(g)^2 + E_e^{(2)} \frac{R^2 \sinh^2 g}{2 \cosh^4 g} + \frac{A_e^{(2)}}{\cosh^2 g} \right] \exp(2i\psi_e^{(0)}(g)). \quad (6.9')$$

Equations (6.9) and (6.9') are easily solved by quadratures, and, after transforming again to variables ξ , η , yield

$$ip_e^{(2)}(\xi) \exp(i\sqrt{2E_e^{(0)}}R\xi) = ip_e^{(2)}(1) \exp(i\sqrt{2E_e^{(0)}}R) - \int_1^\xi d\zeta \frac{(\zeta - 1)^2}{1 - \zeta^2} \left[\frac{1}{2} E_e^{(1)} \left(\frac{R}{i\sqrt{2E_e^{(0)}}}(\zeta + 1) + \frac{1}{E_e^{(0)}} \right) + \frac{2 + i\sqrt{2E_e^{(0)}}}{i\sqrt{2E_e^{(0)}}} \right] \exp(i\sqrt{2E_e^{(0)}}R\zeta) + E_e^{(2)} \frac{R^2}{2} \int_1^\xi d\zeta \zeta^2 \exp(i\sqrt{2E_e^{(0)}}R\zeta) + A_e^{(2)} \int_1^\xi d\zeta \exp(i\sqrt{2E_e^{(0)}}R\zeta). \quad (6.10)$$

The above expression can be easily evaluated, by repeated integration by parts, which yields an expansion in powers of $1/R$. The initial condition must be put equal to zero, as in the first-order calculation (equation (5.4) and related comments). By making $\xi \rightarrow \infty$ (see equation (5.3)), $A_e^{(2)}$ is deduced. It can be recognized by a first integration by parts that

$$A_e^{(2)} = O\left(\frac{1}{R}\right) \quad (6.11)$$

since $E_e^{(2)} = O\left(\frac{1}{R^4}\right)$, because only the dipole moment of the hydrogen atom and the higher moments interact with the point charge of the proton. In the same way one obtains

$$iq_e^{(2)}(\eta) \exp(i\sqrt{2E_e^{(0)}}R\eta) = - \int^\eta d\chi \left[\frac{1}{2} E_e^{(1)} \frac{R}{i\sqrt{2E_e^{(0)}}}(\chi^2 - 1) + \chi - \frac{2 + i\sqrt{2E_e^{(0)}}}{i\sqrt{2E_e^{(0)}}} \right]$$

$$\begin{aligned}
& + \frac{1}{2} \frac{E_e^{(1)}}{E_e^{(0)}} (\chi - 1) - \frac{1}{R} \left(\frac{2 + i\sqrt{2E_e^{(0)}}}{2E_e^{(0)}} + \frac{1}{i\sqrt{2E_e^{(0)}}} \right) \Big]^2 \frac{\exp(i\sqrt{2E_e^{(0)}}R\chi)}{1 - \chi^2} \\
& + \frac{R^2}{2} E_e^{(2)} \int^\eta d\chi \chi^2 \exp(i\sqrt{2E_e^{(0)}}R\chi) + A_e^{(2)} \int^\eta d\chi \exp(i\sqrt{2E_e^{(0)}}R\chi).
\end{aligned} \tag{6.10'}$$

The lower limits of the integrals have been left unspecified in order to avoid a divergent denominator. Using equations (4.7), (5.2), (6.10), (6.10') there results that

$$\begin{aligned}
ip_e^{(2)}(\xi) = \frac{1 - \xi}{i\sqrt{2E_e^{(0)}}R} \left[\frac{R^2}{8} \frac{E_e^{(1)2}}{E_e^{(0)}} (1 + \xi) + \frac{RE_e^{(1)}}{2E_e^{(0)}} (2 + i\sqrt{2E_e^{(0)}}) \right. \\
\left. + \frac{(2 + i\sqrt{2E_e^{(0)}})^2}{2E_e^{(0)}} \frac{1}{1 + \xi} \right] + O(1/R^2)
\end{aligned} \tag{6.12}$$

$$\begin{aligned}
iq_e^{(2)}(\eta) = \frac{1}{R} \left[\frac{R^2}{8} \frac{E_e^{(1)2}}{E_e^{(0)}i\sqrt{2E_e^{(0)}}} (1 - \eta^2) + \frac{1}{i\sqrt{2E_e^{(0)}}} \left(\frac{-\eta^2}{1 - \eta^2} \right) \right. \\
+ \frac{(2 - i\sqrt{2E_e^{(0)}})^2}{2E_e^{(0)}} \frac{1}{1 - \eta^2} - \frac{E_e^{(1)}R}{2E_e^{(0)}} \eta + \frac{E_e^{(1)}R(2 + i\sqrt{2E_e^{(0)}})}{2E_e^{(0)}i\sqrt{2E_e^{(0)}}} \\
\left. - \frac{2(2 + i\sqrt{2E_e^{(0)}})}{2E_e^{(0)}} \frac{\eta}{1 - \eta^2} \right] + B^{(2)} \exp(-i\sqrt{2E_e^{(0)}}R\eta) + O\left(\frac{1}{R^2}\right).
\end{aligned} \tag{6.12'}$$

From equations (6.12), (6.12') the second-order corrections to the action are deduced:

$$i\phi_e^{(2)}(\xi) = \frac{1}{R} \left[\frac{1}{4}\xi - \ln(1 + \xi) - \frac{1}{(1 + \xi)} \right] + \text{const} + O\left(\frac{1}{R^2}\right) \tag{6.13}$$

$$i\psi_e^{(2)}(\eta) = \frac{1}{R} \left[\frac{1}{4}\eta + \ln(1 - \eta) + \frac{1}{(1 - \eta)} \right] + \text{const} + O\left(\frac{1}{R^2}\right) \tag{6.13'}$$

where the constant $B^{(2)}$ has been put equal to zero, while the remaining constants have been substituted from equations (4.7), (5.2), (6.11). The evaluation of all the corrections to $O\left(\frac{1}{R^2}\right)$ would require the calculation of third-order terms in λ ; consequently, we have omitted it here, since it is beyond the scope of this work.

Inserting now equations (4.6), (4.6') there results the expression corrected to second order of the 'polarization' wfs, with the particular boundary conditions being chosen as

$$X_e^{(2)}(\xi) \propto \exp \left\{ -\frac{1}{2} \left(R + 1 - \frac{1}{2R} \right) \xi - \frac{1}{R(1 + \xi)} \right\} (1 + \xi)^{1-2/R} \tag{6.14}$$

$$Y_e^{(2)}(\eta) \propto \exp \left\{ -\frac{1}{2} \left(R + 1 - \frac{1}{2R} \right) \eta + \frac{1}{R(1 - \eta)} \right\} \frac{1}{1 - \eta} \tag{6.14'}$$

where we have equally omitted terms which are exponentially as small as e^{-2R} , in the action.

It can be ascertained that these terms originate from the overlap contributions to the energy. By neglecting these contributions, a special solution to the polarization equations is constructed whose energy is given by the asymptotic series in $1/R$, deprived of exponential terms, as pointed out in [20].

7. Solution of the two-dimensional Schrödinger equation with prescribed boundary conditions

Equations (6.5), (6.5'), (6.14), (6.14') yield approximate solutions to equations (3.2), (3.2'), with $\Lambda = 0$, and the boundary condition (6.4). This last condition can, however, be replaced by (6.7), thus leading to solutions regular over the whole domain of variation of the coordinates. The constants E and A have equally been calculated to first-order, through equations (4.7), (5.2), (5.5). We now want solutions to the same equations which satisfy prescribed boundary conditions so as to obtain acceptable eigenfunctions endowed with the required normalization and symmetry properties, and the related eigenvalues. The solutions to equations (3.2), (3.2') are, therefore, constructed in the following form

$$X_k(\tanh f) = X_e(\tanh f) \left[1 - k \int_{\tanh f}^{+\infty} \frac{df}{dx} \frac{dx}{P_e(x)} \right. \\ \left. \times \int_x^{+\infty} \frac{df}{dy} dy P_k(y) \left(\frac{R^2}{2} y^2 (1 - y^2) - a(1 - y^2) \right) \right] \quad (7.1)$$

$$Y_k(\tanh g) = Y_e(\tanh g) \left[1 - k \int_{-1}^{\tanh g} \frac{dg}{dx} \frac{dx}{Q_e(x)} \right. \\ \left. \times \int_{-1}^x \frac{dg}{dy} dy Q_k(y) \left(\frac{R^2}{2} y^2 (1 - y^2) - a(1 - y^2) \right) \right] \quad (7.1')$$

with (see equations (4.3) and (4.3'))

$$P_e(x) = X_e(x)^2 \quad (7.2)$$

$$Q_e(x) = Y_e(x)^2 \quad (7.2')$$

$$P_k(y) = X_k(y) X_e(y) \quad (7.3)$$

$$Q_k(y) = Y_k(y) Y_e(y) \quad (7.3')$$

where k and a are parameters to be determined by boundary conditions. By straightforward differential calculus we obtain

$$\frac{d^2 X_k}{df^2} = \left[\frac{1}{X_e(\tanh f)} \frac{d^2 X_e}{df^2} - k \frac{R^2}{2} \tanh^2 f (1 - \tanh^2 f) + ak(1 - \tanh^2 f) \right] X_k(\tanh f) \\ = \left[(E_e - k) \frac{R^2}{2} \tanh^2 f (1 - \tanh^2 f) + 2R \tanh f (1 - \tanh^2 f) \right. \\ \left. + (A_e + ak)(1 - \tanh^2 f) \right] X_k(\tanh f) \quad (7.4)$$

$$\frac{d^2 Y_k}{dg^2} = \left[\frac{1}{Y_e(\tanh g)} \frac{d^2 Y_e}{dg^2} - k \frac{R^2}{2} \tanh^2 g (1 - \tanh^2 g) + ak(1 - \tanh^2 g) \right] Y_k(\tanh g) \\ = \left[(E_e - k) \frac{R^2}{2} \tanh^2 g (1 - \tanh^2 g) + (A_e + ak)(1 - \tanh^2 g) \right] Y_k(\tanh g). \quad (7.4')$$

In order to solve equations (7.4), (7.4') the energy variation k , as well as the wavefunctions $X_k(\xi)$, $Y_k(\eta)$, is expanded in power series of a parameter μ [13]

$$k = \mu k^{(1)} + \mu^2 k^{(2)} + \dots \quad (7.5)$$

$$X_k(\xi) = X_e(\xi) + \mu X_k^{(1)}(\xi) + \mu^2 X_k^{(2)}(\xi) + \dots \quad (7.6)$$

$$Y_k(\eta) = Y_e(\eta) + \mu Y_k^{(1)}(\eta) + \mu^2 Y_k^{(2)}(\eta) + \dots \quad (7.6')$$

$X_e(\tanh f)$ and $Y_e(\tanh g)$ satisfy equations (3.2) and (3.2'), respectively, with parameters E_e and A_e ; consequently, from (7.4), (7.4') it follows that

$$\begin{aligned} \frac{d^2 X_k^{(1)}}{df^2} = & \left[-k^{(1)} \frac{R^2}{2} \tanh^2 f (1 - \tanh^2 f) + ak^{(1)} (1 - \tanh^2 f) \right] X_e(\tanh f) \\ & + \left[E_e \frac{R^2}{2} \tanh^2 f (1 - \tanh^2 f) + 2R \tanh f (1 - \tanh^2 f) \right. \\ & \left. + A_e (1 - \tanh^2 f) \right] X_k^{(1)}(\tanh f) \end{aligned} \quad (7.7)$$

$$\begin{aligned} \frac{d^2 Y_k^{(1)}}{dg^2} = & \left[-k^{(1)} \frac{R^2}{2} \tanh^2 g (1 - \tanh^2 g) + ak^{(1)} (1 - \tanh^2 g) \right] Y_e(\tanh g) \\ & + \left[E_e \frac{R^2}{2} \tanh^2 g (1 - \tanh^2 g) + A_e (1 - \tanh^2 g) \right] Y_k^{(1)}(\tanh g) \end{aligned} \quad (7.7')$$

with the solutions

$$X_k^{(1)}(\xi) = -k^{(1)} X_e(\xi) \int_{\xi}^{+\infty} \frac{df}{dx} \frac{dx}{P_e(x)} \int_x^{+\infty} \frac{df}{dy} dy P_e(y) (1 - y^2) \left(\frac{R^2}{2} y^2 - a \right) \quad (7.8)$$

$$Y_k^{(1)}(\eta) = -k^{(1)} Y_e(\eta) \int_{-1}^{\eta} \frac{dg}{dx} \frac{dx}{Q_e(x)} \int_{-1}^x \frac{dg}{dy} dy Q_e(y) (1 - y^2) \left(\frac{R^2}{2} y^2 - a \right). \quad (7.8')$$

These solutions fit into a theoretical perturbative scheme which leads to the full symmetry-adapted eigenfunctions. This has been sketched in appendix A.

The boundary conditions can be assigned to every perturbative order as requested by the problem. Actually, each perturbative equation contains the corresponding coefficient of the eigenvalue expansion (7.5) at most linearly, so that it can be easily solved as a function of lower-order coefficients.

On the other hand, if it is required that all the coefficients on the rhs of (7.5) are zero except for the first, then the iterative solutions of the integral equations (7.1), (7.1') are obtained [1, 2, 21]. In this alternative scheme, it is however difficult to impose the desired boundary conditions in the higher iterative orders.

Here, the first-order equations (7.7), (7.7') will be solved, which result to be the same in the two procedures. Then, the required boundary conditions will be imposed on the function approximating the solution up to first order in μ , thus calculating $k^{(1)}$. Subsequent orders of approximation could be added at will by imposing the boundary conditions successively (see [13]), though separately for each perturbation order.

8. Evaluation of the constants a and $k^{(1)}$ from boundary conditions

8.1. Evaluation of a

We put the upper limit of integration over dx equal to plus infinity in equation (7.8). Any other choice will not affect the result, since it will merely add a term proportional to $X_e(\xi)$. Consequently, the integral over dy must also extend to plus infinity, because it must vanish in this limit for x . Then, the request that $X_k^{(1)}(1)$ should be bounded, leads to the following

$$\int_1^{+\infty} dy X_e(y)^2 \left(\frac{R^2}{2} y^2 - a \right) = 0. \quad (8.1)$$

This condition is necessary, provided that $P_e(x)$ does not diverge for $x \rightarrow 1$. After neglecting exponentially small terms in $\phi_e(y)$, substitution of $X_e^{(2)}(y)$, which has been calculated in section 6 for $X_e(y)$, leads to the following equation

$$\int_1^{+\infty} dy \exp \left\{ - \left(R + 1 - \frac{1}{2R} \right) y - \frac{2}{R(1+y)} \right\} (1+y)^{2-4/R} \left(\frac{R^2}{2} y^2 - a^{(2)} \right) = 0. \quad (8.2)$$

By repeated integration by parts, we get

$$\begin{aligned} a^{(2)} &= \frac{2R^2 + \frac{6R^2-3R}{R+1-1/2R} + \frac{13R^2-18R+8+2/R-3/R^2}{(R+1-1/2R)^2}}{4 + \frac{4-6/R}{R+1-1/2R} + \frac{2-10/R+9/R^2}{(R+1-1/2R)^2}} + O\left(\frac{1}{R}\right) \\ &= a^{(1)} + O(1/R) = \frac{1}{2}R^2 + R + 1 + O(1/R) \end{aligned} \quad (8.3)$$

where terms of order $1/R$ are neglected, and where the constant $a^{(j)}$ has been evaluated using in equation (8.1) the density $P_e^{(j)} = X_e^{(j)2}$.

8.2. Evaluation of $k^{(1)}$

The evaluation of the ‘rate constant’ (actually multiplied by $-i$) is obtained by equation (7.1) after expansion to first order by requiring the appropriate boundary conditions on the plane surface defined by the value of the coordinate $\eta = 0$. For the antisymmetric state (triplet state for nuclei) there results, putting $\mu = 1$

$$\begin{aligned} \frac{1}{k^{(1)(-)}} &= \int_{-1}^0 \frac{dx}{(1-x^2)Q_e(x)} \int_{-1}^x dy Q_e(y) \left(\frac{R^2}{2} y^2 - a \right) \\ &\cong \int_{-1}^0 dx \frac{\left(\exp \left(\left(R + 1 - \frac{1}{2R} \right) x - \frac{2}{R(1-x)} \right) \right) (1-x)}{1+x} \\ &\quad \times \int_{-1}^x dy \frac{\left(\exp \left(- \left(R + 1 - \frac{1}{2R} \right) y + \frac{2}{R(1-y)} \right) \right) \left(\frac{R^2}{2} y^2 - a \right)}{(1-y)^2} \end{aligned} \quad (8.4)$$

where $Y_e(\eta)$ has been approximated by its second-order approximant, given by equation (6.14), and terms which are $O(e^{-2R})$ have been neglected in the exponents. The integral over dx in the rhs of equation (8.4) may be evaluated asymptotically by the method of Laplace [22]. We define

$$\begin{aligned} F(x) &= \frac{e^{-2/R(1-x)}}{1+x} (1-x) \int_{-1}^x dy \frac{\exp \left(- \left(R + 1 - \frac{1}{2R} \right) y + \frac{2}{R(1-y)} \right)}{(1-y)^2} \left(\frac{R^2}{2} y^2 - a \right) \\ &= e^{-2/R} \int_{-1}^0 dy \frac{\exp \left(- \left(R + 1 - \frac{1}{2R} \right) y + \frac{2}{R(1-y)} \right)}{(1-y)^2} \left(\frac{R^2}{2} y^2 - a \right) \\ &\quad + \left[e^{-2/R} \left(-\frac{2}{R} - 2 \right) \int_{-1}^0 dy \frac{\exp \left(- \left(R + 1 - \frac{1}{2R} \right) y + \frac{2}{R(1-y)} \right)}{1-y} \right. \\ &\quad \left. \times \left(\frac{R^2}{2} y^2 - a \right) - a \right] x + O(x^2) = F(0) + F'(0)x + O(x^2). \end{aligned} \quad (8.5)$$

Consequently, by retaining only terms growing exponentially with R

$$\int_{-1}^0 dx \exp \left(\left(R + 1 - \frac{1}{2R} \right) x \right) F(x, R) \cong \frac{F(0, R)}{R + 1 - \frac{1}{2R}} - \frac{F'(0, R)}{\left(R + 1 - \frac{1}{2R} \right)^2}$$

$$\begin{aligned}
& + O\left(\frac{1}{R^3}\right) F''(0, R) = e^{-2/R} \int_{-1}^0 dy \frac{\exp\left(-\left(R+1-\frac{1}{2R}\right)y + \frac{2}{R(1-y)}\right)}{(1-y)^2} \\
& \times \left(R^2 \frac{y^2}{2} - a\right) \left[\frac{1}{\left(R+1-\frac{1}{2R}\right)} + \frac{\frac{2}{R}+2}{\left(R+1-\frac{1}{2R}\right)^2} + \text{h.o.t.} \right]. \quad (8.6)
\end{aligned}$$

Now, in the same way the following equation is deduced

$$\begin{aligned}
& \int_{-1}^0 dy \frac{\exp\left(-\left(R+1-\frac{1}{2R}\right)y + \frac{2}{R(1-y)}\right)}{(1-y)^2} \left(\frac{R^2}{2}y^2 - a^{(2)}\right) \\
& = - \int_{-1}^0 dy \exp\left(-\left(R+1-\frac{1}{2R}\right)y\right) \left[\frac{R+1}{4} \right. \\
& \quad + \frac{1}{8} \left(2R^2 + 2R + 3 + \frac{1}{R}\right) (y+1) + \frac{1}{8} \left(R^2 + \frac{5}{2}R + 3 \right. \\
& \quad \left. \left. + \frac{7}{4R} + \frac{1}{4R^2}\right) (y+1)^2 + O(y+1)^3 \right] e^{1/R} \cong -\exp\left(R+1+\frac{1}{2R}\right) \\
& \times \left[\frac{R+1}{4\left(R+1-\frac{1}{2R}\right)} + \frac{R(R+1)}{4\left(R+1-\frac{1}{2R}\right)^2} + \frac{R^2+\frac{5}{2}R}{4\left(R+1-\frac{1}{2R}\right)^3} + O\left(\frac{1}{R^2}\right) \right]. \quad (8.7)
\end{aligned}$$

Substituting equation (8.7) into equation (8.6) one now obtains

$$\begin{aligned}
& \int_{-1}^0 dx \exp\left(\left(R+1-\frac{1}{2R}\right)x\right) F(x, R) = -\frac{R+1}{4\left(R+1-\frac{1}{2R}\right)^2} \exp(-3/2R + R+1) \\
& \times \left[1 + \frac{R}{R+1-\frac{1}{2R}} + \frac{1}{R} + \text{h.o.t.} \right] \left[1 + \frac{2\left(1+\frac{1}{R}\right)}{R+1-\frac{1}{2R}} + \text{h.o.t.} \right] \\
& \cong -\frac{R+1}{2\left(R+1-\frac{1}{2R}\right)^2} \exp(-3/2R + R+1) \left(1 + \frac{2}{R}\right). \quad (8.8)
\end{aligned}$$

Equation (8.8) and the preceding ones allow us to evaluate the energy difference as a function of boundary conditions. By straightforward computation one obtains

$$k^{(1)(-)} = -2R \exp(3/2R - R - 1) \left(1 - \frac{1}{R} + \text{h.o.t.}\right) \quad (8.9)$$

while the appropriate boundary condition for the wf symmetric under permutation of nuclear coordinates yields

$$\frac{1}{k^{(1)(+)}} = \frac{1}{k^{(1)(-)}} + \frac{2}{\left(dQ_e^{(2)}/d\eta\right)_0} \int_{-1}^0 dx Q_e^{(2)}(x) \left(\frac{R^2}{2}x^2 - a\right) \quad (8.10)$$

which corresponds to the vanishing of the derivative over $d\eta$ of the wf, in the plane orthogonal to the axis joining the nuclei, situated at $\eta = 0$ (or $r_1 = r_2$).

From equations (6.14'), (8.4)–(8.7) it follows that

$$\begin{aligned}
\frac{1}{k^{(1)(+)}} \cong & - \left\{ \left[\frac{1}{R+1-\frac{1}{2R}} + \frac{2\left(\frac{1}{R}+1\right)}{\left(R+1-\frac{1}{2R}\right)^2} \right] e^{-2/R} + \frac{2e^{-2/R}}{\left(-R+1+\frac{5}{2R}\right)} \right\} \left\{ \{R+1\} \right. \\
& \left. + \frac{R(R+1)}{R+1-\frac{1}{2R}} + \frac{R^2+\frac{5}{2}R+3+\frac{7}{4R}+\frac{1}{4R^2}}{\left(R+1-\frac{1}{2R}\right)^2} \right\} \frac{\exp(R+1+1/2R)}{4\left(R+1-\frac{1}{2R}\right)} + \text{h.o.t.} \quad (8.11)
\end{aligned}$$

from which the symmetric result to equation (8.9) follows

$$k^{(1)(+)} = 2 \operatorname{Re} e^{3/2R-R-1} \left(1 - \frac{1}{R} + \text{h.o.t.} \right). \quad (8.12)$$

9. Conclusions

Our perturbation series, equations (4.3)–(4.5), have been expanded into powers of λ , where each perturbation order has been in turn expanded in powers of $1/R$, which grow accordingly to powers of λ (see equation (5.8)). Consequently, each coefficient of the $1/R$ expansion is a polynomial in λ [20] and, therefore, becomes infinitesimal as $R \rightarrow \infty$. Even if it is well known [3–5, 9, 20] that the resulting series in $1/R$ is an asymptotic expansion when overlap is neglected, nonetheless it defines the related polarization functions in a unique way [5, 20]. Having defined the polarization energy from [20], we seek the solution of the Schrödinger equation corresponding to that value of the energy. This solution, as well as its logarithm, is supposed to be analytical in λ , which is a physical parameter (the nuclear charge). Then, the different terms of the expansion of the logarithm are given by the solution of the corresponding perturbation equation. The logarithm of the wavefunction can be represented by Borel summable series [23], in every open interval between two zeros of the wavefunction. This series becomes eventually asymptotically divergent outside the radius of convergence [24] in the complex variable λ . However, the expansion is equally valuable for calculation purposes (see, for instance, equation (3.13) in [25] and [23]).

The novelty of our approach is essentially that, in the preliminary step of the polarization function calculation, we are free from the constraints of those boundary conditions, which are introduced in a second step through the second perturbation expansion in powers of the splitting constants k (see appendices A and B). Since we are essentially calculating a normalized flux of particles across the boundary, it is evident that the accuracy of our results will rely upon the precision attained in the natural logarithm of the wavefunction. However, our main scope here is to show that with the simplest approximation to the polarization function obtainable through the λ -expansion we are able to reach high accuracy in the asymptotic exchange energy splitting.

Our approximate solution to the Schrödinger equations is similar in form, though not identical, to the expansion used in [3] for the solution in the intermediate region of the η variable, but we do not need to match the solution with the nuclear region, where an expansion in Laguerre polynomials was used by the previous authors [3–5, 26, 27].

Reference [5] reproduces the singular Hamiltonian of [4] (see also [20, 27]) which is then solved in terms of Whittaker functions, whose argument solves a differential equation of Riccati-type. The matching condition in the intermediate region between the wells then necessitates the evaluation of the solutions with high precision, which is not obtainable by the more commonly used WKB expansion [5].

It is, however, obvious that different types of expansion could be used in the framework of the present approach to represent the polarization function; however, we have proved that the most simple procedure that we have adopted is thoroughly sufficient to yield reliable results, without introducing the more sophisticated methods of calculation, involving variation of indices of special functions which are needed to fulfil the complete boundary conditions. In fact, we have calculated exactly, together with the first exponentially decreasing term, two terms of the related asymptotic series in $1/R$ and four terms of the separation constant.

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Appendix A. A system perturbed by boundary conditions

We write equations (3.2), (3.2') in the abbreviated form

$$\left[\frac{d^2}{df^2} + \Delta_e(f) \right] X_e(\tanh f) = 0 \quad (\text{A1})$$

$$\left[\frac{d^2}{dg^2} + \varepsilon_e(g) \right] Y_e(\tanh g) = 0. \quad (\text{A1}')$$

Assuming the 'potentials' $\Delta_e(f)$, $\varepsilon_e(g)$ to be varied, it is aimed to find the corresponding variations of the eigenfunctions, according to (7.6), (7.6'). The varied potentials are

$$\Delta_k(f) = \Delta_e(f) - k \frac{R^2}{2} \tanh^2 f (1 - \tanh^2 f) + (A_k - A_e)(1 - \tanh^2 f) = \Delta_e(f) + \delta_k(f) \quad (\text{A2})$$

$$\varepsilon_k(g) = \varepsilon_e(g) - k \frac{R^2}{2} \tanh^2 g (1 - \tanh^2 g) + (A_k - A_e)(1 - \tanh^2 g) = \varepsilon_e(g) + \varepsilon_k(g). \quad (\text{A2}')$$

The analyticity of the 'potential' in k is postulated so as to obtain

$$\delta_k(f) = \mu \delta_k^{(1)}(f) + \mu^2 \delta_k^{(2)}(f) + \dots \quad (\text{A3})$$

$$\varepsilon_k(g) = \mu \varepsilon_k^{(1)}(g) + \mu^2 \varepsilon_k^{(2)}(g) + \dots \quad (\text{A3}')$$

and the perturbative equations

$$\left[\frac{d^2}{df^2} + \Delta_e(f) \right] X_k^{(1)}(\tanh f) + \delta_k^{(1)}(f) X_e(\tanh f) = 0$$

$$\left[\frac{d^2}{df^2} + \Delta_e(f) \right] X_k^{(2)}(\tanh f) + \delta_k^{(1)}(f) X_k^{(1)}(\tanh f) + \delta_k^{(2)}(f) X_e(\tanh f) = 0 \quad (\text{A4})$$

....

$$\left[\frac{d^2}{dg^2} + \varepsilon_e(g) \right] Y_k^{(1)}(\tanh g) + \varepsilon_k^{(1)}(g) Y_e(\tanh g) = 0$$

$$\left[\frac{d^2}{dg^2} + \varepsilon_e(g) \right] Y_k^{(2)}(\tanh g) + \varepsilon_k^{(1)}(g) Y_k^{(1)}(\tanh g) + \varepsilon_k^{(2)}(g) Y_e(\tanh g) = 0 \quad (\text{A4}')$$

....

In order to solve equations (A4), (A4') we observe that the operators in equations (A1), (A1') enclosed in square brackets, admit a right inverse in the form used in equations (7.1), (7.1'). More precisely, we have the result

$$\left[\frac{d^2}{df^2} + \Delta_e(f) \right] X_e(\tanh f) \int_f^\infty \frac{df'}{X_e(\tanh f')^2} \int_{f'}^\infty df'' X_e(\tanh f'') T(\tanh f'') = T(\tanh f) \quad (\text{A5})$$

$$\left[\frac{d^2}{dg^2} + \varepsilon_e(g) \right] Y_e(\tanh g) \int_{-1}^s dg' \frac{1}{Y_e(\tanh g')^2} \int_{-1}^{g'} dg'' Y_e(\tanh g'') T(\tanh g'') = T(\tanh g) \quad (\text{A5'})$$

for every function T in the given intervals. It can, however, be ascertained that the operators in square brackets do not commute with their right inverse.

Appendix B. Energy difference between two solutions of the Schrödinger operator

Let us proceed now to elucidate the relationship between the values of the energy splittings referred to different eigenstates of the Hamiltonian operators (3.2), (3.2'). Since the eigenfunction $Y_\ell(\eta)$ satisfies equation (3.2'), and is regular, it must also be a solution of the integral equation:

$$Y_\ell(\eta) = Y_e(\eta) \left[1 - \ell \int_{-1}^{\eta} \frac{dg}{d\mu} \frac{d\mu}{Q_e(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_\ell(v) \right] \quad (\text{B1})$$

and therefore, in the proximity of $\eta = -1$, can be approximated by

$$Y_\ell(\eta) \cong Y_e(\eta) \left[1 - \ell \int_{-1}^{\eta} \frac{dg}{d\mu} \frac{d\mu}{Q_e(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_e(v) \right] \quad (\text{B2})$$

and in the same way

$$Y_k(\eta) \cong Y_\ell(\eta) \left[1 - (k - \ell) \int_{-1}^{\eta} \frac{dg}{d\mu} \frac{d\mu}{Q_\ell(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_\ell(v) \right] \quad (\text{B3})$$

where $Q_\ell(\eta)$ is now the density $Y_\ell(\eta)^2$ associated with the eigenfunction $Y_\ell(\eta)$. Substituting now from equation (B2) into (B3) follows:

$$Y_k(\eta) \cong Y_e(\eta) \left[1 - \ell \int_{-1}^{\eta} \frac{dg}{d\mu} \frac{d\mu}{Q_e(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_e(v) - (k - \ell) \int_{-1}^{\eta} \frac{dg}{d\mu} \frac{d\mu}{Q_\ell(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_\ell(v) \right] \quad (\text{B4})$$

where terms which are $O(k^2, \ell^2, k\ell)$ have been neglected. Now $\frac{dg}{d\mu} = \frac{1}{1-\mu^2}$, therefore

$$Y_k(-1) = Y_e(-1) \quad (\text{B5})$$

$$\left(\frac{dY_k}{d\eta} \right)_{-1} = \left(\frac{dY_e}{d\eta} \right)_{-1} - k \frac{1}{2} \left(\frac{R^2}{2} - a \right) Y_e(-1). \quad (\text{B5'})$$

Now $Y_k(\eta)$ can also be obtained from equations (B1), (B2) by putting $\ell = k$, and the values of the function and its first derivative are coincident with equations (B5), (B5'); therefore, equation (B3) is the same as equation (7.1'). There follows that the expression of k obtained by imposing the suitable boundary conditions on (7.1') is the same as that obtained by equation (B3).

From equation (B2) the following expression for the energy difference ℓ between two solutions of equation (3.2') results, to first order:

$$-\ell^{(1)} = \frac{\frac{Y_k(0)}{Y_e(0)} - 1}{\int_{-1}^0 \frac{dg}{d\mu} \frac{d\mu}{Q_e(\mu)} \int_{-1}^{\mu} dv \left(\frac{R^2}{2} v^2 - a \right) Q_e(v)} \quad (\text{B6})$$

so that it follows:

$$-\ell^{(1)} = k^{(1)(-)} \left(\frac{Y_\ell(0)}{Y_e(0)} - 1 \right) \approx k^{(1)(-)} (\ln Y_\ell(0) - \ln Y_e(0)) \cong ik^{(1)(-)} \left(\psi_\ell^{(1)}(0) - \psi_e^{(1)}(0) \right). \quad (B6')$$

Taking now as Y_ℓ and Y_e two approximate regular solutions corresponding to the values of the constant $B^{(1)}$ given by equations (6.7) and (6.4), respectively, with the normalization condition (B5) (for $k = \ell$), there follows that $\ell^{(1)} = k^{(1)(-)} \times O(e^{-R})$.

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