Short-range interaction energy for ground-state H$_2^+$

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Abstract

The analytical procedures previously developed by the authors (see references) in order to evaluate the short-range interaction energy of two protons bound by one electron are briefly reviewed. The Hamilton-Jacobi-Riccati outer equation is solved perturbatively up to fifth order in the perturbation parameter, where the zero-order function is the He$^+$ ground-state function. The inner equation is solved by expanding Hylleraas determinant. The results are consistent with those of similar treatments and with accurate numerical calculations.

1. Introduction

The evaluation of the coefficients arising in the short-range expansion of the interaction in ground state H$_2^+$ has been the object of many investigations [1–11]. In this paper we extend the calculations to the evaluation of the C$_{10}$ coefficient using our previous techniques. The main principles and assumptions on which they are founded are examined and refined calculations are presented. In [7] perturbation theory was applied in conjunction with first-passage time techniques in order to solve both the so-called [4] inner and outer equations, while in subsequent work [8, 10] it was found more suitable to make recourse to Hylleraas tridiagonal determinantal method [1] applied to the inner equation. This led straightforwardly to useful analytical results, although the physical picture of an electron stabilized by resonance in a double-well potential, which results from our transformed equations (2), (2') below, was somewhat hidden in that approach.

2. Methods

The separation of the 3-dimensional Schrödinger equation for H$_2^+$ in confocal elliptic (spheroidal) coordinates ($\xi$, $\eta$, $\varphi$) of the electron, with nuclei kept in fixed position [1–13], originates three one-dimensional differential equations, the outer $\xi$-equation, the inner $\eta$-equation and the $\varphi$-equation. The subsequent variable transformation:

$$\xi = \tanh f, \quad \eta = \tanh g$$

allows to write the two equations for $A = 0$ into the Hermitean form [13]:

$$\frac{d^2X}{df^2} = \left( \frac{E_fR^2 \sinh^2 f}{2 \cosh^2 f} + \frac{A}{\cosh^2 f} \right) X(\tanh f)$$

(2)

$$\frac{d^2Y}{dg^2} = \left( \frac{E_gR^2 \sinh^2 g}{2 \cosh^2 g} + \frac{A}{\cosh^2 g} \right) Y(\tanh g)$$

(2')

where A and $E_f$ are separation constants. In these equations, $f$ is complex in the whole range of variation of $\xi$ and $g$ obviously real. The profile of the 'potential' in equation (2') changes from a symmetrical double well for real positive A to a single well for real negative A.
Following [2] it is inferred that the X-equation depends only on the sum of the charges located at the foci of the elliptical co-ordinates, so that, increasing nuclear separation, the only varying parameters are the electronic energy shift from the united atom value\(^3\)

\[
\Delta E_e = E_e - E_{\text{u.a.}} = E_e + 2
\]

and the separation constant \(A\).

The regularity conditions upon the solutions of each separate equation in spheroidal co-ordinates yield two independent relations between the constants \(A\) and \(E_e\) that can be solved as a function of \(R\). The inner \(\eta\)-equation has been satisfactorily solved by Hylleraas [1] by a determinantal method, whose zeroes yield the required functional relation. The outer \(\xi\)-equation has been solved perturbatively by us [8–10, 13] in powers of the energy variation \(\Delta E_e\) which induces a variation in the ‘potential’ of the \(f\)-equation above. The perturbative solution of the Hamilton-Jacobi-Riccati (HJR) equation associated to this equation is expanded in powers of \(\Delta E_e\) and the regularity conditions imposed order by order so as to make the solution physically acceptable [10]. There results a relation between \(A\) and \(\Delta E_e\) which is independent of the distribution of the charge between the foci, being only dependent on the distance \(R\) and the sum of the charges. Similarly, boundary conditions imposed upon the iterative solution of an integral equation yield the desired relationship between the constants, order by order [8], under the assumption that \(A\) may be expanded into power series of \(\Delta E_e\).

3. The perturbative solution

The solution of the complete outer equation in \(X(\xi)\) is approximated through an expansion of the action\(^4\) \(\varphi(\xi)\) in powers of the energy difference \(\Delta E_e\), the \(\kappa\)-th order solution being

\[
X_\kappa(\xi) = \exp \left\{ i \varphi_\kappa(\xi) \right\}, \quad \kappa = 0, 1, 2, 3 \ldots
\]

where it is recalled that all the \(\varphi_\kappa^\lambda\), \(\lambda = 0, 1, 2 \ldots \kappa\) are imaginary functions so that the \((i \varphi_\kappa^\lambda(\xi))\) are real as a whole, for real \(\xi\). Thus

\[
p_\kappa^\lambda(\xi) = \frac{d \varphi_\kappa^\lambda}{df} = (1 - \xi^2) \frac{d \varphi_\kappa^\lambda}{d \xi}
\]

\[
p_\kappa(\xi) = (1 - \xi^2) \frac{d \varphi_\kappa}{d \xi} = \sum_{\lambda=0}^{\infty} p_{\kappa}^\lambda(\xi)
\]

the last equality being true in the domain of convergence of the series. The corresponding \(\varphi_\kappa^\lambda\) are obtained by integration from the \(p_{\kappa}^\lambda\) which are the solutions to the expanded Riccati equation given in [10, 13]. The complete Riccati equation for the derivative of the action over \(f\) is:

\[
(\xi - 1)p_{\kappa} = (\xi - 1) \left[ E(1 - \xi^2) - \frac{1}{2}kR^2\xi^2 + 2R\xi + A_k - A_0 \right] - \frac{p_{\kappa}^2}{1 + \xi}
\]

To get corrections up to \(O(R^{10})\) it is necessary to calculate \(p_{\kappa}^\lambda\) up to \(O(\Delta E_e^\lambda)\) with the appropriate boundary conditions:

\[
p_\kappa(1) = 0, \quad \lim_{\xi \to \infty} p_\kappa(\xi) \exp \{-2R\xi\} = 0
\]

These boundary conditions yield a kind of dispersion relation\(^5\) between the constants \(A\) and \(E_e\):

\[
A_k - A_0 = \sum_{\kappa=1}^{\infty} A_\kappa (\Delta E_e)^{\kappa} = ak + bk^2 + ck^3 + dk^4 + ek^5 + O(k^6)
\]

with \(k = -\Delta E_e, A_0 = A(R, k = 0)\). The solutions to the expanded HJR equation are linear in \(A_\kappa\) and therefore it is possible to solve for this parameter which would depend in a complicated (non-analytic) way on \(R\), although the solutions were analytic in \(R\) in the limit \(R \to 0\). There results [10], if \(\kappa \geq 2\).

\(^3\) Atomic units are used throughout this work. Energy (Hartree): \(E_0 = e^2(4\pi\varepsilon_0\rho_0)^{-1} = 4.395 \ 748 \times 10^{-18} \) J; length (Bohr): \(a_0 = \frac{\hbar^2(\pi m e^2)}{\varepsilon_0} = 5.291 \ 772 \times 10^{-11} \) m.

\(^4\) The action is here the solution of the time-independent Riccati equation obtained by separating time and co-ordinate variables in the full Hamilton-Jacobi-Riccati equation. It is the quantum analogue of the classical ‘reduced’ action [14].

\(^5\) Dispersion relations establish the law of variation of wave velocity with wavelength [15]. The role of squared wavenumber is played here by the constant \(A\), which goes into squared angular momentum for vanishing \(R\). A proof for the analyticity of dispersion relations is mentioned in [6].
A_{\xi}^{\alpha} = -\frac{2R}{(\Delta E_{\alpha})^\kappa} \sum_{\lambda=1}^{\kappa-1} \int_{\lambda}^{+\infty} d\zeta \frac{P_{\lambda}^{\alpha}(\zeta) P_{\lambda-1}^{\alpha}(\zeta)}{1 - \zeta^2} \exp \{-2R(\zeta - 1)\} \tag{8} 

The solutions to the expanded HJR equation up to \(\kappa = 5\) are reported in [10]. Equation (5) exhibits a singularity in the point \(\xi = 1\), consequently there are analytical and non-analytical solutions in the environment of this point. In [2] the analytical solution for \(X(\xi)\) was retained, the total charge being concentrated in one focus of the ellipse. The solution that was evaluated in [8–10] by perturbative series expansion of the HJR equation with boundary conditions⁶ (6) is analytical in the environment of \(\xi = 1\).

4. Solution by integral equation

Omitting for short the index \(e\), it is written [8, 13]

\[
X_k(\xi, 1) = X_0(\xi) \left[ 1 + \int_1^\xi \frac{dx}{(1-x^2)X_0(x)^2} \int_x^{+\infty} dyX_0(y)X_k(y, 1) \right. \\
\times \left. \left( \frac{k}{2} R^2 y^2 - A_k + A_0 \right) \right]
\tag{9}
\]

there follows

\[
i\varphi_k(\xi) = \ln X_k(\xi, 1)
\tag{9'}
\]

consequently, since \(p_0(1) = 0\), it is obtained that the following condition should be necessarily satisfied [8]:

\[
\int_{-\infty}^{+\infty} dyX_0(y)X_0(y, 1) \left( \frac{k}{2} R^2 y^2 - A_k + A_0 \right) = 0
\tag{10}
\]

In equation (9) the lower limit of integration has been put equal to 1, but it is at large extent arbitrary. In fact, using equation (4.1) of [16] (see appendix A), there results

\[
X_k(\xi, \alpha) = X_0(\xi) \left[ 1 + \int_0^\xi \frac{dx}{(1-x^2)X_0(x)^2} \int_x^{+\infty} dyX_0(y)X_k(y, \alpha) \right. \\
\times \left. \left( \frac{k}{2} R^2 y^2 - A_k + A_0 \right) \right]
\tag{12}
\]

Consequently, the condition requiring the derivative over \(\xi\) to vanish [8] is independent of the lower extremum of integration, provided the factor multiplying the rhs of equation (12) is different from zero.

5. Expansion of coefficients \(a, b, c, d, e\) in powers of \(R\)

The coefficients \(a, b, c, d, e\) were evaluated in [8, 10]⁷. The expanded form of these coefficients is the following, where it has been made use of appendix B:

\[
a = \frac{1}{4} + \frac{R}{2} \frac{1}{2} + \frac{R^2}{2} \tag{13}
\]

⁶ The first of these boundary conditions ensures that also \(p_0(\xi)/\left(1 - \xi^2\right)\) and consequently \(\varphi(\xi), X(\xi)\) are analytical in the environment of \(\xi = 1\).

⁷ These coefficients were also evaluated in [17]. The present calculations of the expanded form are consistent with the results of that reference.
\[ b = -\frac{5}{32} - \left[ \frac{1}{16} + \frac{1}{4} (\gamma + \ln 4R) \right] R + \left[ 1 - (\gamma + \ln 4R) \right] R^2 + \left[ 3 - 2(\gamma + \ln 4R) \right] R^3 + \left[ \frac{44}{9} - \frac{8}{3} (\gamma + \ln 4R) \right] R^4 + \left[ \frac{1096}{225} - \frac{32}{15} (\gamma + \ln 4R) \right] R^6 + \text{h.o.t.} \] (13')

\[ c = \frac{11}{128} + \left[ -\frac{\pi^2}{24} + \frac{3}{4} (\gamma + \ln 4R) + \frac{3}{4} (\gamma + \ln 4R)^2 \right] R + \left[ \frac{13}{4} - \frac{\pi^2}{12} - 7(\gamma + \ln 4R) + \frac{7}{2} (\gamma + \ln 4R)^2 \right] R^3 + \left[ \frac{424}{27} - \frac{\pi^2}{9} - \frac{230}{9} (\gamma + \ln 4R) + 10(\gamma + \ln 4R)^2 \right] R^4 + \text{h.o.t.} \] (13'')

\[ d = -\frac{93}{2048} + \left[ \frac{43}{1024} + \frac{7}{768} \pi^2 - \frac{5}{96} \zeta(3) \right] R + \left[ -\frac{7}{256} + \frac{\pi^2}{192} \right] (\gamma + \ln 4R) - \frac{7}{128} (\gamma + \ln 4R)^2 - \frac{1}{96} (\gamma + \ln 4R)^3 R + \left[ \frac{9}{64} - \frac{3}{192} \pi^2 - \frac{23}{48} \zeta(3) \right] R^2 + \text{h.o.t.} \] (13'''')

\[ e = \frac{193}{8192} + \text{h.o.t.} \] (13''''')

The nonexpanded form of coefficients may be found in [8, 10].

6. Solution of the inner equation by Hylleraas determinantal method

The inner \( \eta \)-equation is solved by putting

\[ Y(\eta) = \sum_{\ell=0}^{\infty} c_{\ell} P_{\ell}^{\eta}(\eta) \]

where \( P_{\ell}^{\eta}(\eta) \) are associated Legendre polynomials, which for \( R = 0, \eta = \cos \vartheta \) yield exact solutions of the inner equation with \( c_{\ell} = \delta_{\ell,\ell} \). By direct substitution into the inner equation it is obtained a linear system whose finite determinant must vanish. Battezzati and Magnasco [8] have shown that for \( \ell = 0 \)

\[
\begin{bmatrix}
-A - E_e R^2/6 & -E_e R^2/15 & 0 \\
-A - E_e R^2/3 & -A - 6 - 11E_e R^2/42 & -2E_e R^2/21 \\
0 & -6E_e R^2/35 & -A - 20 - 39E_e R^2/154
\end{bmatrix} = O(R^{12})
\]

(15)

There follows the expansion of the inner separation constant \( A_k \) (see also [1, 12, 17]):

\[ A_k = \frac{1}{3} C + \frac{2}{135} C^2 + \frac{4}{8505} C^3 = \frac{26}{1913625} C^4 = \frac{92}{37889775} C^5 + O(C^6) \]

(16)

\[ C = \left( 1 + \frac{k}{2} \right) R^2 \]

(16')

This expansion has been obtained from the solution \( A = 0 \) which makes the determinant (15) to vanish for \( C = 0 \). It is not an expansion in powers of \( k \), but the expansion of \( A \) in powers of \( k \) may be deduced from it with numerical coefficients involving powers of \( R \) which are exact up to \( O(R^{11}) \). From the position

\[ k = \sum_{\alpha=0}^{\infty} k_{\alpha} R^\alpha \]

(17)
from equation (16) it is deduced the expansion of $A_k$ into powers of $R$, which was calculated in [10]:

$$A_k = \frac{1}{3} R^2 + \left( \frac{2}{135} + \frac{1}{2} k_2 \right) R^3 + \frac{1}{8} k_3 R^4 + \left( \frac{4}{8505} + \frac{2}{135} k_2 + \frac{1}{6} k_4 \right) R^5$$

$$+ \left( \frac{2}{135} k_1 + \frac{1}{6} k_2 \right) R^3 \right) + \left[ - \frac{26}{1913625} + \frac{1}{2} k_2 k_3 + \frac{2}{135} \right] R^6$$

$$+ \left\{ - \frac{1}{6} k_6 \right\} R^7 + \left\{ 2 \frac{2835}{1913625} \right\} k_5 + \frac{1}{2} \left( k_2 + \frac{1}{6} k_7 \right) R^8$$

$$+ \left\{ \frac{92}{37889775} - \frac{52}{1913625} k_2 + \frac{2}{2835} \left( k_4 + \frac{1}{2} k_5 \right) \right\} R^9$$

$$+ \left\{ \frac{2}{135} \left( k_6 + \frac{1}{4} k_3 + \frac{1}{2} k_2 k_4 \right) + \frac{1}{6} k_8 \right\} R^{10} + O(R^{11})$$

(18)

From equation (18) the $A_k$ are evaluated recursively using the corresponding $k_k$, which are obtained from equations (7), (13)–(15), (17), (18) (see [10] for details).

Using the values of $k_k$ which have been calculated in [9, 10] up to $O(R^8)$ it is obtained the expansion of $A_k$ up to $O(R^8)$:

$$A_k = \frac{1}{3} R^2 - \frac{178}{135} R^4 + \frac{8}{9} R^5 - \frac{4028}{8505} R^6 + \left[ \frac{392}{135} + \frac{32}{27} (\gamma + \ln 4R) \right] R^7$$

$$+ \left[ \frac{77532}{127575} - \frac{26}{1913625} - \frac{64}{27} (\gamma + \ln 4R) \right] R^8$$

$$+ \left[ \frac{265264}{127575} - \frac{32}{243} \gamma^2 - \frac{1856}{1215} (\gamma + \ln 4R) + \frac{64}{81} (\gamma + \ln 4R)^2 \right] R^9$$

$$+ \left[ - \frac{15935932}{1148175} + \frac{11552}{18944875} - \frac{128}{243} \gamma^2 + \frac{19072}{1215} (\gamma + \ln 4R) \right] R^{10}$$

$$- \frac{256}{81} (\gamma + \ln 4R)^2 R^{10} + h.o.t.$$ (19)

The wavefunctions may be obtained by a perturbative expansion [7]

$$Y^\xi_n(\eta) \propto \exp \{ i \psi^\xi_n(\eta) + i \psi^\xi_1(\eta) + \ldots + i \psi^\xi_s(\eta) \}$$

(20)

with $A_0 = R^2$, the zero-order value of the separation constant:

$$Y^\xi_0(\eta) \propto \exp \{ - R \eta \}$$ (20′)

$$q^\xi_n(\eta) = \frac{d \psi^\xi_n}{d \eta} = (1 - \eta^2) \frac{d \psi^\xi_n}{d \eta}$$ (21)

The solution (20) has been calculated up to $\kappa = 5$ in [7] with the boundary condition $q_n(-1) = 0$, the result being:

$$\sum_{k=0}^5 i q_n^\xi(\eta) = \frac{1}{3} R^2 (1 + \eta)^2 (2 - \eta) + \frac{R^4}{9} \left[ \left( 1 + \eta \right)^2 \left( 1 + \eta \right)^2 \left( 1 + \eta \right)^2 \left( 1 + \eta \right)^2 \right]$$

$$+ (1 + \eta)^2 + 4(1 + \eta) + 8 \ln \left( \frac{1 - \eta}{2} \right) + h.o.t.$$ (22)

the result being an even function of $R$ to this order. Retaining terms up to $\kappa = 3$ there follows upon integration [7]:

$$Y^\xi_3(\eta) \propto (1 - \eta)^{-2R/3} \exp \left\{ \frac{R^2}{6} \eta^2 \right\}$$ (23)

This function is consistent with the general form of solutions of a second-order ordinary differential equation whose lower order coefficients are singular in the point $\eta = 1$ [18], which is therefore an algebraic critical point of the solution. The rhs. of equation (22) also exhibits a logarithmic singularity in the same point.
Dispersion relations may be derived by imposing appropriate boundary conditions to the solution modified by the integral equation method [7, 8, 13], which allows to represent the correctly symmetrized solution, while keeping into account variation of $A_k$ from the united atom value $A_0$.

7. Evaluation of coefficients $C_{\kappa}$

Upon substituting equation (17) into (7), there follows $A_k - A_0$ expanded in powers of $R$ [10]. Thus, using (18) and equating coefficients of equal powers of $R$, equal powers of $R$ multiplied by $\ln 4R$, $(\ln 4R)^2$, $(\ln 4R)^3$ the $k_{\kappa}$ are obtained recursively up to $O(R^{10})$. The result is

$$
C_2 = \frac{8}{3} , C_3 = -\frac{16}{3} , C_4 = \frac{352}{135} , C_5 = \frac{2416}{135} - \frac{64}{9} (\gamma + \ln 4R)
$$

$$
C_{6} = -\frac{310816}{8505} + \frac{128}{9} (\gamma + \ln 4R)
$$

$$
C_7 = \frac{87392}{8505} + \frac{64}{81} \pi^2 + \frac{3968}{405} (\gamma + \ln 4R) - \frac{128}{27} (\gamma + \ln 4R)^2
$$

$$
C_8 = 4 \left\{ \frac{398534}{18225} + \frac{26}{1913625} - \frac{64}{81} \pi^2 - \frac{9664}{405} (\gamma + \ln 4R)
$$

$$
+ \frac{128}{27} (\gamma + \ln 4R)^2 \right\}
$$

$$
C_9 = 4 \left\{ -\frac{38312}{945} - \frac{52}{1913625} + \frac{1104}{1215} \pi^2 - \frac{640}{243} \zeta(3) \right\} + \frac{5261968}{127575} + \frac{64}{243} \pi^2 (\gamma + \ln 4R) - \frac{736}{135} (\gamma + \ln 4R)^2
$$

$$
- \frac{128}{243} (\gamma + \ln 4R)^3 \right\}
$$

$$
C_{10} = 4 \left\{ \frac{21563664}{1148175} - \frac{14984}{189448875} + \frac{512}{243} \zeta(3) + \frac{3584}{1215} \pi^2
$$

$$
+ \frac{1410784}{127575} - \frac{512}{243} \pi^2 (\gamma + \ln 4R) - \frac{9088}{405} (\gamma + \ln 4R)^2
$$

$$
+ \frac{1024}{243} (\gamma + \ln 4R)^3 \right\}
$$

where the $C_{\kappa} = -k_{\kappa}$ are the coefficients of the expansion of $\Delta E_{\kappa}$ in powers of the internuclear distance $R$.

This result matches those obtained in [7–10] up to $O(R^8)$, and that reported in [17] up to $O(R^{10})$.

8 Numerical calculations were performed by Sharp EL-520W scientific calculator.

8. Summary and conclusions

Previous calculations of short-range interactions in ground-state $H_2^+$ are extended up to the evaluation of the $C_{10}$ coefficient.

Recently analytical methods for evaluation of $H_2^+$ interaction energies were used extensively with the help of computer algebra and combined with highly accurate numerical calculations [12, 17]. They contribute to shed light on the structure and properties of the solutions. In [17] a variant of the present approach was developed in order to check numerical data, from which exact values of h.o. coefficients of the expansion were inferred by numerical interpolation.

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Appendix A. Proof of equation (12)

Equation (12) is proved by writing

\[ X_k(\xi, \alpha) = X_\alpha(\xi) \left[ 1 + \int_\alpha^\beta \frac{dx}{(1 - x^2)X_\alpha(x)^2} \int_x^{+\infty} \frac{dyX_\alpha(y)X_k(y, \alpha)}{y^2 - A_k + A_0} \right] \times \left( \frac{kR\gamma^2}{2} - A_k + A_0 \right) + \int_\beta^{+\infty} \frac{dx}{(1 - x^2)X_\alpha(x)^2} \int_x^{+\infty} \frac{dyX_\alpha(y)X_k(y, \alpha)}{y^2 - A_k + A_0} \right] \]

(A.1)

and then iterating. After every step the factor

\[ \left[ 1 + \int_\alpha^\beta \frac{dx}{(1 - x^2)X_\alpha(x)^2} \int_x^{+\infty} \frac{dyX_\alpha(y)X_k(y, \alpha)}{y^2 - A_k + A_0} \right] \]

can be factorized out from the expansion of \( X_k(\xi, \beta) \).

Appendix B. Expansion of integrals

The following integral identities have been proved with the help of [19] in order to expand the coefficients \( c, d \) in powers of \( R \) and \( \ln R \):

\[ \int_1^{+\infty} dx \frac{E_1(2R(x + 1))}{x + 1} = R \int_1^{+\infty} dx \left( \frac{\ln x + 1}{2} \right)^2 \exp\left\{ -2R(x + 1) \right\} = \frac{\pi^2}{12} + \frac{1}{2}\left( \gamma + \ln 4R \right)^2 - 4R + 2R^2 - \frac{32}{27}R^3 + \text{h.o.t.} \]  

(B.1)

\[ \int_1^{+\infty} dx E_1(4Rx) \frac{\ln x}{x} = \frac{1}{R} \int_1^{+\infty} dx (\ln x)^3 \exp\left\{ -4Rx \right\} = -\frac{1}{6}\left( \gamma + \ln 4R \right)^3 - \frac{\pi^2}{12}\left( \gamma + \ln 4R \right) - \frac{1}{4}\zeta(3) + 4R + \text{h.o.t} \]  

(B.2)

\[ \int_0^{+\infty} dx \ln x \exp\left\{ 2x \right\} E_1(2x)^2 = -\frac{\pi^2}{12}(\gamma + \ln 2) - \frac{3}{2}\zeta(3) \]  

(B.3)

where \( \zeta(n) \) is Riemann zeta function of argument \( n \) [19]. The remaining integrals are easily evaluated [10] by series expansion to the desired order of approximation.

Appendix C. Behaviour of wavefunction at large distances

Defining

\[ i\rho_\xi(\xi) = -R(1 - \xi^2) + i\rho(\xi) \]  

(C.1)

upon substitution into equation (5) it is obtained by formal solution of that equation:

\[ i\rho(\xi) = -\frac{1}{4}kR \left[ \exp\left\{ 2R(\xi - 1) \right\} \left( 1 + \frac{1}{R} + \frac{1}{2R^2} \right) - \left( \xi^2 + \frac{\xi}{R} + \frac{1}{2R^2} \right) \right] \]

\[ + (A_k - A_0) \exp\left\{ 2R(\xi - 1) \right\} - 1 + \int_0^\xi \frac{(i\rho(\xi))^2}{\xi^2 - 1} \exp\left\{ -2R(\xi - \xi) \right\} d\xi \]  

(C.2)

After multiplication of both members of this equation by \( \exp\{ -2R\xi \} \) and evaluation of the limit for \( \xi \to +\infty \), \( A_k - A_0 \) can be evaluated from the condition that this limit is zero. This yields

\[ A_k - A_0 = \frac{1}{2}kR \left[ \xi^2 + 1 + \frac{1}{R}(\xi - 1) \right] - 2R \exp\left\{ 2R \right\} \int_1^{+\infty} \frac{(i\rho(\xi))^2}{\xi^2 - 1} \exp\left\{ -2R(\xi - \xi) \right\} d\xi \]  

(C.3)

\[ i\rho(\xi) = \frac{1}{4}kR \left[ \xi^2 + 1 + \frac{1}{R}(\xi - 1) \right] - \int_1^{+\infty} \frac{(i\rho(\xi))^2}{\xi^2 - 1} \exp\left\{ -2R(\xi - \xi) \right\} d\xi \]  

(C.3')

Since the argument of integrals is positive semidefinite for real \( i\rho(\xi) \), there follows that for large \( \xi \)

\[ i\rho(\xi) < \frac{1}{4}kR(\xi^2 - 1) \]  

(C.4)
\[
\begin{align*}
\imath \varphi(\xi) &> -R \xi + \frac{1}{4} \Delta E \xi
\end{align*}
\]

there follows that a real wavefunction \(X(\xi)\) would certainly diverge at infinity if \(\Delta E > 2\). More precisely, it can be ascertained by inspection of equations (9)–(13) of [10], or even proved to finite order by induction, that \(\imath \varphi(\xi)\) diverges at infinity \(\propto \xi^4\) with negative coefficient \(\varepsilon\). From equation (C.3') follows

\[
\varepsilon \xi^2 = \frac{1}{4} k R \xi^2 - \varepsilon^2 \int_0^{+\infty} \xi \exp\left(\frac{-2(\xi - \xi)}{\xi - 1}\right) + o(\xi^2)
\]

\[
= \left(\frac{1}{4} k R - \frac{\varepsilon^2}{2 R}\right) \xi^2 + o(\xi^2)
\]

There follows

\[
\varepsilon^2 + 2 R \varepsilon - \frac{1}{2} k R^2 = 0
\]

\[
\varepsilon = -R \left(1 \mp \sqrt{1 - \frac{\Delta E}{2}}\right)
\]

\(\varepsilon\) is real and negative for \(\Delta E < 2\), or \(-R\) for \(\Delta E = 2\). It assumes two complex-conjugate values if \(\Delta E > 2\), that yield to \(X(\xi)\) the form of free travelling waves at large distances from the nuclei. \(\varepsilon\) may be evaluated from the perturbation expansion to fifth order reported in [10], which yields \(\varepsilon = -0.753 906 25 \times R\) for \(\Delta E = 2\), and \(\varepsilon = -0.292 358 393 \times R\) for \(\Delta E = 1\), compared with the value \(\varepsilon = -0.292 893 218 \times R\) from equation (C.6'). The value \(\Delta E = 2\) is a branch-point of the solution, where the perturbation expansion in powers of \(\Delta E\) cannot converge.

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