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Technical Report

New Approach for the Electronic Energies of the Hydrogen Molecular Ion

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Contents

Abstract

Herein, we present analytical solutions for the electronic energy eigenvalues of the hydrogen molecular ion H_2^+, namely the one-electron two-fixed-center problem. These are given for the homonuclear case for the countable infinity of discrete states when the magnetic quantum number m is zero i.e. for $^2\Sigma^+$ states. In this case, these solutions are the roots of a set of two coupled three-term recurrence relations. The eigensolutions are obtained from an application of *experimental mathematics* using Computer Algebra as its principal tool and are vindicated by numerical and algebraic demonstrations. Finally, the mathematical nature of the eigenenergies is identified.

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1 Introduction

Although, there are well established software packages in the area of quantum chemistry such as GAUSSIAN [1], MOLPRO [2] and GAMESS [3] which allow to obtain approximate numerical solutions to a number of fair sized molecules, the simplest molecule namely the hydrogen molecular ion, a quantum mechanical three-body problem, still remains mathematically intractable.

In the fixed nuclei approximation, it is well known that the Schrödinger wave equation - a second order partial differential equation (PDE) - of the problem of one electron moving in the field of two fixed nuclei can be separated in prolate-spheroidal coordinates [4]. These coordinates allow a separation of variables that results in two non-trivial ordinary differential equations (ODE), and hence two eigenparameters: the energy parameter p^2, and a separation constant A related to the total orbital angular momentum and the Runge-Lenz vector.

We note that asymptotic expansions for small or large internuclear distances R have been obtained. A very comprehensive presentation of the energy eigenvalues for the ground state and a number of exited states is shown in the work of Čížek *et al.* [9]. These could almost constitute analytical solutions but the resulting series are divergent though asymptotic [10] and therefore useful only at large internuclear distances. Another complication is that for the homonuclear case, every *gerade* energy E_g (wave function symmetric under exchange of nuclei) has a counterpart *ungerade* solution (wave function antisymmetric under exchange of nuclei) whose energy E_u has exactly the same $1/R$ expansion. This makes the calculation of exchange energy splittings $\Delta E = E_u - E_g$ very elusive to calculate at large R, although there are specialized methods for recovering these splittings (e.g. see [11]).

Even recently, there has been examination of series in small R limited to the ground state short-range interaction energy [12] but we still have no further insight into the actual mathematical nature governing the energy eigenvalues. We also cite the work of Demkov *et al.* [13] but their analytical solutions correspond to a peculiar charge ratio depending on the internuclear distance and therefore not physically useful.

Thus, complete analytical solutions of the eigenstates of H_2^+, in areas of molecular interest, such as e.g. the region near the equilibrium internuclear distance (bond length) of the ground state remain elusive.

A wide variety of *numerical* methods have been used to solve the H_2^+ problem in this case. For example, Bates, Ledsham and Stewart [5] used recursion and continued fractions. Hunter and Pritchard [6] used matrix methods and Rayleigh quotient iteration. Madsen and Peek [7] used power series and associated Legendre expansions to set up two equations whose simultaneous solution then gave the two eigenparameters. An accurate way to obtain energies and wavefunctions for the one-electron two-center problem is provided by the program ODKIL conceived by Aubert-Frécon *et al.* [14, 15] based on a method by Killingbeck. As of the 1980s, it was possible to calculate the eigenenergies and the eigenfunctions of the discrete states of H_2^+ with a rapid FORTRAN program. Yet, complete analytical solutions have so far remained elusive: the classical N-body problem cannot be solved in closed form for $N \geq 3$ and the quantum counterpart is even worse by virtue of being an eigenvalue problem.

The approach used here is called “experimental mathematics”, an unorthodox approach involving multi-disciplinary activities by which to find new mathematical patterns and conjectures. The goal in this context is to search and find mathematical structures and patterns to be re-examined with more “rigor” at a later stage. The level of rigor is of course relative: in dealing with a difficult problem in applied Mathematics, we cannot approach the level of rigor demanded in number theory.

Nonetheless, we desire demonstrations sufficiently convincing to the molecular physicist.

The present work will involve a combination of methods, results and procedures from different areas. We first start with results from what is called: *dimensional scaling*. It has been known for some time that the Schrödinger wave equation can be generalized to an arbitrary number of dimensions D which can be subsequently treated as continuous variable [17, 18]. In the limit as $D \to 1^+$, the hydrogen molecular ion becomes the double well Dirac Delta function model which can be solved exactly [25] in terms of the *Lambert W function* [19,20]. Dimensional scaling applied to H_2^+ has been studied at length by Hershbach's group [21–24], in particular, by Frantz [21], Loeser and Lopez-Cabrera [22, 23]. The latter work provides even more insight into the mathematical relationship between the real H_2^+ at $D = 3$ and its one-dimensional limit.

Next, armed with the information provided by dimensional scaling, we will return to the real three-dimensional formulation of Aubert *et al.* [15]. This formulation is re-examined using a Computer Algebra System (CAS) within the approach of experimental mathematics: patterns and results are obtained. The CAS used is Maple because it is readily available to us but the results could also be implemented on other systems. The resulting series expansions are verified numerically and algebraically. In particular, we will demonstrate that our results are independent of choice of basis and basis size and consequently completely general. The end-result will be then analytically compared with the one-dimensional result and put on a near equal footing allowing us to find the mathematical category to which belong the eigenvalues of H_2^+. In view of the type of solution obtained, a tentative "physical" picture is associated with the analytical solutions. A summary with concluding remarks is made at the end.

2 Preliminaries - Dimensional Scaling

The $D \to 1^+$ version of H_2^+ [17,18] is given by the double Dirac delta function model:

$$-\frac{1}{2}\frac{\partial^2\psi}{\partial x^2} - q[\delta(x) + \lambda\delta(x - R)]\psi = E(\lambda)\psi \tag{1}$$

where $Z_A = q$ and $Z_B = \lambda\, q$. The ansatz for the solution has been known since the work of Frost [26]:

$$\psi \;=\; Ae^{-d|x|} + Be^{-d|x-R|} \tag{2}$$

Matching of ψ at the peaks of the Dirac delta functions positioned at $x = 0, R$ when $(\lambda = 1)$ yields:

$$\begin{vmatrix} q - d & qe^{-dR} \\ qe^{-dR} & q - d \end{vmatrix} = 0 \tag{3}$$

and the energies are thus given by:

$$E_\pm = -d_\pm^2/2 \quad \text{where} \quad d_\pm = q[1 \pm e^{-d_\pm R}] \tag{4}$$

Although, the above has been known for more than half a century, it was not until Scott *et al.* [25] that the solution for $d_\pm$ was exactly found to be:

$$d_\pm = q + W(\pm qRe^{-qR})/R \tag{5}$$

where ± represent respectively the symmetric or *gerade* solution and the anti-symmetric or *ungerade* solution and W is the Lambert W function satisfying $W(t)e^{W(t)} = t$ [19,20]. This function first introduced by Johann Heinrich Lambert (1728-1777), a contemporary of Euler, has been "invented" and “re-invented” at various periods in history but its ubiquitous nature was not fully realized within the last decade or so.

For example, the W function appears in Wien’s Displacement Law of Blackbody radiation. In general, it has appeared in electrostatics, statistical mechanics, general relativity, radiative transfer, quantum chromodynamics, combinatorial number theory, fuel consumption and population growth etc... (e.g. see ref. [27] and references herein).

More recently, the Lambert W function has also appeared in “linear” gravity two-body problem [28] as a solution to the Einstein Field equations with one spatial dimension and one time dimension $(1+1)$. The present work also includes a generalization of the W function. Recent work [30] shows that the W function can be further generalized to express solutions to transcendental algebraic equations of the form:

$$\exp(\pm c\, x) \;=\; \frac{P_N(x)}{Q_M(x)} \tag{6}$$

where $P_N(x)$ and $Q_M(x)$ are polynomials in x of respectively degrees N and M and c is a constant. The standard W function applies for cases when $N = 1$ and $M = 0$ and expresses solutions for the case of equal charges for eq. (1) or equivalently the case of equal masses for the two-body $1 + 1$ linear gravity problem. The case of *unequal* charges or unequal masses corresponds to cases of higher N and M values. This form also expresses a subset of the solutions to the *three*-body linear gravity problem [29, 30] where one deals with transcendental equations of the form (6) where $M, N \to \infty$.

Some insight into the mathematical nature of the eigenenergies of H_2^+ is revealed by the fact that the eigensolutions for the electronic energies at $D \to 1^+$ and $D \to \infty$ actually bound the $D = 3$ ground state eigenenergy of H_2^+ [21, 22] as shown in Figure 1. Moreover, the latter can be estimated by a linear interpolation formula [23]:

$$E_3(R) \approx \frac{1}{3}E_1(\tfrac{R}{3}) \;+\; \frac{2}{3}E_\infty(\tfrac{2R}{3}) \tag{7}$$

This formula agrees with the numerically accurate eigenenergy (as given by program ODKIL or the work of D. Frantz) to within about 2 or 3 digits for the range of R near the bond length. The result at $D \to \infty$ involves the extrema of a Hamiltonian expression [23, eq.(58)]. We re-examined this result. One has to consider a region of R divided by $R_c = \frac{9}{8}\sqrt{3}$. For $R < R_c$, the root is determined by the root of a quartic polynomial [23] and the result for $R > R_c$ is determined by a sixth degree polynomial. Thus, the result at $D \to \infty$ is algebraic. On the other hand, the result at $D \to 1^+$ is in terms of an implicit special function, which is the Lambert W function. Given how well this interpolation formulation works, this already suggests what is the mathematical nature of the eigenenergies of the true hydrogen molecular ion $(D = 3)$.

We can state this in view of the work of Frantz *et al.* [21] who showed that the D-dimensional problem could be decoupled into two coupled ODEs for $2 \leq D < \infty$ and how a particular energy eigenvalue for a given D could exactly express the solution of another eigenvalue for an excited state at a dimension $D + 2$ through a precise re-scaling.

3 Three-dimensional H_2^+

3.1 Starting Formulation

The Schrödinger Wave Equation for H_2^+ in atomic units is given by:

$$\left[\Delta + 2\left(\frac{Z_A}{r_A} + \frac{Z_B}{r_B}\right) + 2E\right]\psi = 0 \tag{8}$$

As mentioned before, this is separable into prolate-spheroidal coordinates:

$$\begin{array}{rcl} \xi & = & (r_A + r_B)/R \quad , \quad 1 \le \xi < \infty \\ \eta & = & (r_A - r_B)/R \quad , \quad -1 \le \eta \le 1 \end{array}$$

$$0 \le \phi \le 2\pi$$

$$\begin{array}{rcl} \mathcal{Q}_1 & = & R(Z_A - Z_B) \\ \mathcal{Q}_2 & = & R(Z_A + Z_B) \end{array}$$

We can write the ansatz for the eigensolution:

$$\psi(\xi, \eta, \phi) = \Lambda(\xi) M(\eta, \phi) = \Lambda(\xi) G(\eta) e^{\pm i m \phi} \tag{9}$$

which allow us to obtain two coupled ODEs:

$$\left[\frac{\partial}{\partial\eta}\left((1-\eta^2)\frac{\partial}{\partial\eta}\right) - \frac{m^2}{1-\eta^2} + p^2\eta^2 - \mathcal{Q}_1\,\eta - A\right] M(\eta,\phi) = 0 \tag{10}$$

$$\left[\frac{\partial}{\partial\xi}\left((\xi^2-1)\frac{\partial}{\partial\xi}\right) - \frac{m^2}{\xi^2-1} - p^2\xi^2 + \mathcal{Q}_2\,\xi + A\right] \Lambda(\xi) = 0$$

where A is the separation constant and the eigenenergy E is expressed as:

$$E_{elec} \;=\; -\,2\,\frac{p^2}{R^2} \tag{11}$$

Note that:

$$\lim_{R\to 0} A \;=\; -\ell(\ell+1) \tag{12}$$

$$\lim_{R\to 0} p^2 \;=\; 0 \tag{13}$$

Although the set of quantum numbers (n, ℓ, m) - the *united* atom quantum numbers - can be used to identify the eigenstates, as is the case for e.g. program ODKIL, it must be emphasized that only the magnetic quantum number m is a good quantum number (resulting from the azimuthal symmetry of H_2^+ about its internuclear axis).

We follow the treatment of Aubert *et al.* [15] and consider the following basis expansion for the η coordinate:

$$M(\eta,\phi) = \sum_{k=m} f_k^m \, Y_k^m(\eta,\phi) \tag{14}$$

where Y_k^m are the Spherical Harmonics. Injection of the above basis into the ODE governing M in η leads to the creation of a symmetric matrix $\mathcal{F}$ whose determinant must vanish when p and A satisfy the eigenvalue problem:

$$[\mathcal{F}(p, A)]\,|f| = 0 \tag{15}$$

where

$$\begin{aligned}
F_{i,i}(p,A) &= -i(i+1) + p^2\left(\frac{2i^2-2m^2+2i-1}{(2i+3)(2i-1)}\right) - A,\\
F_{i+1,i}(p,A) &= -R\,\mathcal{Q}_1\left(\frac{(i+m+1)(i-m+1)}{(2i+1)(2i+3)}\right)^{1/2},\\
F_{i+2,i}(p,A) &= \frac{p^2}{(2i+3)}\left(\frac{(i+m+1)(i-m+1)(i+m+2)(i-m+2)}{(2i+1)(2i+5)}\right)^{1/2},
\end{aligned}$$

are the non-vanishing matrix elements of $\mathcal{F}$. If $\mathcal{Q}_1 = Z_A - Z_B = 0$ i.e. the homonuclear case, then the pentadiagonal matrix $\mathcal{F}$ divides in *even* and *odd* tridiagonal matrices in terms of x where $x = p^2$ with no *explicit* dependence on the internuclear distance R (although this is not true for the other ODE in ξ). For the ξ coordinate, we use a basis of Hylleraas functions, i.e. in terms of Laguerre polynomials:

$$\Lambda(\xi) = e^{-p(\xi-1)}[2p(\xi-1)]^{m/2}\sum_{n=m/2} C_{n-(m/2)}\,\mathcal{L}^{m}_{n-(m/2)}[2p(\xi-1)] \tag{16}$$

$$\begin{aligned}
[\mathcal{Y}(p,A)]\,|C| &= 0\\
[\mathcal{Y}(p,A)] &= [\mathcal{Q}(p,A)] \;+\; p\,m^2\,[\mathcal{B}(p)]^{-1}
\end{aligned} \tag{17}$$

where

$$\begin{aligned}
b_{i,i}(p) &= 4p + 2i + 1,\\
b_{i,i+1}(p) &= b_{i+1,i}(p) = -\left[(i-\frac{m}{2}+1)(i+\frac{m}{2}+1)\right]^{1/2}
\end{aligned}$$

and

$$\begin{aligned}
r_{i,i}(p,A) &= (2i+1)\left(\frac{R\,\mathcal{Q}_2}{2p} - i - 1 - 2p\right) + \frac{m^2}{4} + i + R\,\mathcal{Q}_2 - p^2 + A,\\
r_{i+1,i}(p,A) &= -\left[(i-\frac{m}{2}+1)(i+\frac{m}{2}+1)\right]^{1/2} \times \left(\frac{R\,\mathcal{Q}_2}{2p} - i - 1\right)\\
r_{i,i+1}(p,A) &= r_{i+1,i}(p,A)\,.
\end{aligned}$$

When $m = 0$, the matrix is tridiagonal. For $m \neq 0$, one has to consider the inverse of the matrix $\mathcal{B}$, which is not a band matrix.

Of course, we realize that this choice of basis is only one of several possible choices. The results obtained are valid provided the results are independent of the size of the basis and the choice of basis.

3.2 Recurrence Relations

The following relations apply to the homonuclear case and when $m = 0$ in which case, the band matrices are purely tridiagonal matrices. These are governed by recurrence relations namely $(A.1)$ and $(A.2)$ of reference [15]:

$$\begin{aligned}
\det[\mathfrak{M}_0] &= 1\\
\det[\mathfrak{M}_1] &= \mathfrak{m}_{1,1}\\
\det[\mathfrak{M}_k] &= \mathfrak{m}_{k,k}\det[\mathfrak{M}_{k-1}] \;-\; \mathfrak{m}_{k-1,k}\,\mathfrak{m}_{k,k-1}\det[\mathfrak{M}_{k-2}]
\end{aligned}$$

Thus for $m = 0$, we have the following:

$$\begin{aligned} \det(\mathcal{Y}_0) &= 1 \\ \det(\mathcal{Y}_1) &= \frac{R}{p} - 1 - 2\,p + 2\,R - p^2 + A \\ \det(\mathcal{Y}_{k+1}) &= \left((2\,k+1)\left(\frac{R}{p} - k - 1 - 2\,p\right) + k + 2\,R - p^2 + A\right)\det(\mathcal{Y}_k) \\ &\quad -k^2\left(\frac{R}{p} - k\right)^2 \det(\mathcal{Y}_{k-1}) \end{aligned} \tag{18}$$

For the even ℓ case, we have:

$$\begin{aligned} \det(\mathcal{F}\mathrm{e}_0) &= 1 \\ \det(\mathcal{F}\mathrm{e}_1) &= \frac{p^2}{3} - A \\ \det(\mathcal{F}\mathrm{e}_{k+1}) &= \left(-2\,k\,(2\,k+1) + \frac{p^2\left(8\,k^2 + 4\,k - 1\right)}{(4\,k-1)\,(4\,k+3)} - A\right)\det(\mathcal{F}\mathrm{e}_k) \\ &\quad -4\,\frac{p^4\,(2\,k-1)^2\,k^2\,\det(\mathcal{F}\mathrm{e}_{k-1})}{(4\,k-1)^2\,(4\,k-3)\,(4\,k+1)} \end{aligned} \tag{19}$$

Defining $\det(\mathcal{F}\mathrm{o}_i) = \det(\mathcal{F}(i))$ for the odd ℓ case, we have:

$$\begin{aligned} \det(\mathcal{F}\mathrm{o}_0) &= 1 \\ \det(\mathcal{F}\mathrm{o}_1) &= -2 + \frac{3p^2}{5} - A \\ \det(\mathcal{F}\mathrm{o}_{k+1}) &= \left(-(2k+1)(2k+2) + \frac{p^2\left(2\,(2k+1)^2 + 1 + 4k\right)}{(4k+5)\,(4k+1)} - A\right)\det(\mathcal{F}\mathrm{o}_k) \\ &\quad -4\,\frac{p^4 k^2\,(2k+1)^2\;\det(\mathcal{F}\mathrm{o}_{k-1})}{(4k+1)^2\,(4k-1)\,(4k+3)} \end{aligned} \tag{20}$$

Note that the radial equations for the hydrogen atom are governed by two-term recurrence relations. Thus, it suffices to find an eigenenergy such that the coefficient a_{k+1} of the basis of Laguerre functions is zero. This in effect truncates the infinite series into a polynomial and consequently closed form solutions for the eigenstates are obtained of the hydrogen atom. This is not possible for H_2^+ which is governed by *three*-term recurrence relations no matter what the choice of basis.

The band matrices for H_2^+ and their determinants have been injected into a computer algebra system. The determinants $\det(\mathcal{Y}_i)$ and $\det(\mathcal{F}_i)$ (even or odd) for $i = 1, 2, 3\ldots$ are multivariate polynomial-like in A and p. The determinants $\det(\mathcal{F}_i)$ are true polynomials in A and p^2. On the other hand, although $\det(\mathcal{Y}_i)$ is a polynomial in A, it has also negative powers for p and thus akin to a Laurent series (Laurent polynomial) in p.

It is possible to eliminate one of the unknowns by obtaining a *resultant* of the two determinants $\det(\mathcal{Y}_i)$ and $\det(\mathcal{F}_i)$. If a and b are polynomials over an integral domain, where et 2 (rational) polynomial equations in 2 unknowns A and p.

$$a = a_n \prod_{i=1}^{n}(x - \alpha_i) \quad b = b_m \prod_{i=1}^{m}(x - \beta_i)$$

Then

$$\mathrm{resultant}(a, b, x) = a_n^m b_m^n \prod_{i=1}^{n}\prod_{j=1}^{m}(\alpha_i - \beta_j)$$

This can be computed from the Euclidean algorithm or determinant of a *Sylvester* matrix and its roots will be common to those satisfying the original set of polynomials. Since both expressions are true polynomials in A only, the resultant must be in A. E.g. for $i = 2$ (i.e. 2×2 matrices)

$$\mathrm{resultant}(\det(\mathcal{Y}_i), \det(\mathcal{F}\mathrm{e}_i), A) \;=$$

$$\begin{aligned}
&64/1225\, p^8 + 512/245\, p^7 - 256/245\, (R - 27)\, p^6 - 128/245\, (56\, R - 369)\, p^5 \\
&+\; 64/245\, (2911 - 1037\, R + 27\, R^2)\, p^4 + 32/245\, (13580 - 9405\, R + 948\, R^2)\, p^3 \\
&-\; 32/245\, (140\, R^3 - 17780 + 24010\, R - 5571\, R^2)\, p^2 \;-\; 64/7\, (20\, R^3 - 224\, R^2 \\
&+\; 481\, R - 161)\, p - 4128/7\, R^3 \;+\; 19968/7\, R^2 \;+\; 16\, R^4 \;-\; 2880\, R \;+\; 304 \\
&+\; 16/7\, R\, (28\, R^3 - 347\, R^2 + 791\, R - 252)/p \;+\; 4\, R^2\, (20\, R^2 - 108\, R + 85)/p^2 \\
&+ 8\, R^3\, (4\, R - 9)/p^3 \;+\; 4\, R^4/p^4
\end{aligned}$$

i.e. a Laurent polynomial in p with coefficients in R only. When the size of the $i \times i$ increases, the size of the resulting expression increases dramatically (expression swell). However, from a numerical point of view, the most useful outcome comes from numerically solving the simultaneous expressions for $\det(\mathcal{Y}_i)$ and $\det(\mathcal{F}_i)$ since i must be sufficiently large to give a sufficiently good result near the bond length. In Maple, this can be done using the `fsolve` procedure. To find the minimum energy for the ground state, it is a matter of getting derivatives of these determinants with respect to R. Combining the latter with the condition:

$$\frac{\partial E_T}{\partial R} = 0 \quad \text{where} \quad E_T \;=\; E_{elec} + 1/R \tag{21}$$

we get five equations in the five unknowns R, A, p, $\frac{\partial A}{\partial R}$ and $\frac{\partial p}{\partial R}$. The result has been calculated using a small Maple program. In atomic units, these are:

$$\begin{aligned}
R &= 1.997193319969992\ldots \\
E_{minimum} &= -0.6026346191065398\ldots
\end{aligned}$$

Note that the electronic energy, evaluated at $R = 2.0$ a.u. for comparison, is as expected exactly the reference tabulated value of Madsen and Peek [7] i.e. -0.6026342144949. An indirect way of ascertaining the accuracy of electronic energies is to use these values in an adiabatic standard scheme to obtain vibrational energies which are directly comparable to highly accurate values provided by approaches that do not involve the separability of the electronic and nuclear motions (e.g. [31–33] and [34, 35]). This has been done [36] and comparisons with values from the literature are displayed in table 3.2.

In fact, given how heavy the nuclear centers are with respect to the electron, clamping the nuclear centers is a very good approximation for the quantum three-body problem represented by H_2^+ with the following caveat: the approximation that the nuclei are clamped fixed in space creates a symmetry under exchange of nuclei in the homonuclear case. A different picture arises when the movement of nuclei is considered. The mere movement of the nuclei breaks the symmetry under exchange of nuclei and thereby leads to a localization of the states. In this case, the work of Esry and Sadeghpour is instructive [37].

However, if one stopped here, there is no pattern from an analytical point of view. E.g. setting $x = p^2$ and examining $\det(\mathcal{F}\mathrm{e}_i)$ at low order in A, we have:

at $i = 2$:

$$1/35\, p^2(-70 + 3\, p^2) + (6 - 6/7\, p^2)A + O\left(A^2\right)$$

at $i = 3$:

$$\frac{5}{231}\, p^2\left(1848 - 126\, p^2 + p^4\right) + (-120 + \frac{244}{11}\, p^2 - \frac{5}{11}\, p^4)A + O\left(A^2\right)$$

Table 1: Ground State Vibrational Energies
Energies are in a.u., differences in cm^{-1} (1 a.u. = 219474.63 cm^{-1})
a) ref. [31], b) ref. [32], c) ref. [33], d) ref. [34], e) ref. [35]

System	Quantum Vibrational Number v	Present Adiabatic Values	Literature Values	Differences ΔE (cm^{-1})
H_2^+	0	-0.597138471	-0.597139055$^{a)}$	-0.13
			-0.597139063123$^{b)}$	-0.13
	1	-0.587154167	-0.587155679212$^{b)}$	-0.33
D_2^+	0	-0.598788594	-0.5987876(11)$^{a)}$	+0.22
			-0.598788784331$^{c)}$	-0.04
HD^+	0	-0.597897521	-0.5978979685$^{d)}$	-0.10
			-0.5978979686$^{e)}$	-0.10

at $i = 4$:

$$\frac{1}{1287}p^2\left(-2162160+173316p^2-2772p^4+7p^6\right)$$
$$+(5040-1032p^2+\frac{6356}{195}p^4-\frac{28}{143}p^6)A+O\left(A^2\right)$$

If we look at $A = 0$ and grab the leading coefficient p^2, we have the sequence $-70, 1848, -2162160\ldots$. Not only are the coefficients increasing dramatically in size, they also alternate in sign. Although the roots A, p of these determinants $\det(\mathcal{Y}_i)$ and $\det(\mathcal{F}_i)$ converge with increasing i, the actual coefficients of these determinants and especially those of the resultant increase in size becoming more and more cumbersome although a CAS can handle them (up to a point).

Moreover, we have made a particular choice of basis and the combined set of polynomial-like expressions for the determinants though numerically useful could be viewed more as a computational “model” rather than anything truly representative of the wave function. If we stop here, we see no pattern. Insight comes from *inverting* the problem.

3.3 Roots of Determinants

The three-term recurrence relations for $\det(\mathcal{Y}_i)$ or $\det(\mathcal{F}_i)$ cannot be solved in closed form. We start with $\det(\mathcal{F}_i)$ because it is easier and has no explicit dependence on R. Upon careful scrutiny of eqs. (19) and (20), the term in $\det(\mathcal{F}_{k-1})$ has a coefficient in p^4 whereas the term in $\det(\mathcal{F}_k)$ has terms at order p^2. Let us assume that p is small, which is indeed the case for small R. We can therefore neglect the last term in $\det(\mathcal{F}_{k-1})$ and the resulting two-term recurrence relation becomes trivial to solve. It is merely a matter of compounding the multiplicative terms of the recursion:

$$\det(\mathcal{F}\mathrm{e}_k) \;\approx\; (-1)^k\prod_{j=0}^{k-1}\left(2j(2j+1)+A-\frac{(8j^2+4j-1)\,p^2}{(4j-1)\,(4j+3)}\right) \tag{22}$$

Solving for A such that $\det(\mathcal{F}\mathrm{e}_k) = 0$ yields:

$$A \;=\; -\,2j\,(2j+1) \;+\; \frac{8j^2+4j-1}{(4j-1)(4j+3)}\,p^2 \;+\; O(p^4) \tag{23}$$

We can clearly identify the $R \to 0$ limit with $\ell = 2\,j$. Similarly, for the odd case, we have:

$$\det(\mathcal{F}\mathrm{o}_k) \;\approx\; (-1)^k \prod_{j=0}^{k-1} \left(2\,(j+1)(2\,j+1) \;+\; A - \frac{(8j^2+12j+3)p^2}{(4\,j+5)(4\,j+1)} \right) \tag{24}$$

$$A \;=\; -\,(2j+1)\,(2j+2) \;+\; \frac{8j^2+12j+3}{(4j+1)(4j+5)}\,p^2 \;+\; O(p^4) \tag{25}$$

We can clearly identify the $R \to 0$ limit with $\ell = 2\,j+1$. Thus, although ℓ is only a valid quantum number in the united atom limit, it is nonetheless feasible to use it to identify an eigenstate as an expansion for small p (and small R).

By the implicit function theorem, $\det(\mathcal{F}_i) = 0 \;\Rightarrow\; A = A(p^2)$. Moreover, the structure of the recurrence relations for $\det(\mathcal{F}_i)$ and $\det(\mathcal{Y}_i)$ namely eqs. (19), (20) and (18) tell us that all these quantities are i^{th} degree polynomials in A. If one can find all the values of A such that these determinants are zero, the latter are clearly known by the fundamental theorem of algebra. If $\det(\mathcal{F}_i)$ as a formal series in x where $x = p^2$, we can use *reversion* of power series to obtain an analytical solution. This is the best possible analytical result. E.g. , we consider:

$$x \;=\; \cos(x) \quad\Rightarrow\quad x/\cos(x) \;=\; \lambda \quad \text{where} \quad \lambda \;=\; 1 \tag{26}$$

$$\begin{aligned} x \;+\; \frac{1}{2}x^3 \;+\; \frac{5}{24}x^5 \;+\; \ldots \;&=\; \lambda \\ \Rightarrow x \;&=\; \lambda \;-\; \frac{1}{2}\lambda^3 \;+\; \frac{13}{24}\lambda^5 \;+\; \ldots \end{aligned}$$

The reverted series of x in terms of λ can be obtained in a number of ways including Lagrange's method [4] and represents the best possible representation of an analytical solution to the root of eq. (26). Formally, the infinite series in λ is a complete solution. The issue of getting numbers for e.g. $\lambda = 1$ is a matter of a summation technique. Solutions by reversion of power series are possible via Maple's `solve` command. E.g. inverting $\det(\mathcal{F}\mathrm{e}_3)$ yields:

$$1/3\,x + \frac{2}{135}\,x^2 + O\left(x^3\right)\,, \quad -6 + \frac{11}{21}\,x - \frac{94}{9261}\,x^2 + O\left(x^3\right)\,,$$
$$-20 + \frac{39}{77}\,x - \frac{8}{1715}\,x^2 + O\left(x^3\right)$$

where $x \;=\; p^2$. To first order in x (or p^2), we recover the solutions in eq. (23) for respectively $\ell = 0, 2, 4$. The action of inverting $\det(\mathcal{F}\mathrm{e}_i)$ produces i solutions to order $O(x^i)$. E.g. if we isolate the $\ell = 0$ solution obtained from $\det(\mathcal{F}\mathrm{e}_i)$ for $i = 3, 4, 5, 6$, we obtain:

$$\begin{array}{ll} i=3: & 1/3\,x + \frac{2}{135}\,x^2 + O\left(x^3\right) \\ i=4: & 1/3\,x + \frac{2}{135}\,x^2 + \frac{4}{8505}\,x^3 + O\left(x^4\right) \\ i=5: & 1/3\,x + \frac{2}{135}\,x^2 + \frac{4}{8505}\,x^3 - \frac{26}{1913625}\,x^4 + O\left(x^5\right) \\ i=6: & 1/3\,x + \frac{2}{135}\,x^2 + \frac{4}{8505}\,x^3 - \frac{26}{1913625}\,x^4 - \frac{92}{37889775}\,x^5 + O\left(x^6\right) \\ & \quad\vdots \qquad\quad \vdots \qquad\quad \vdots \qquad\qquad \vdots \qquad\qquad\quad \vdots \\ i\to\infty: & 1/3\,x + \frac{2}{135}\,x^2 + \frac{4}{8505}\,x^3 - \frac{26}{1913625}\,x^4 - \frac{92}{37889775}\,x^5 + \ldots \end{array} \tag{27}$$

What is important to note is that the coefficients are *stable*! Letting $i \to i+1$ adds a term of order $O(x^{i+1})$ to the series and yields an extra solution for $\ell = 2\,(i+1)$. By re-injection of this solution to within order $O(x^i)$ into $\det(\mathcal{F}\mathrm{e}_i)$ with computer algebra, one can see that $\det(\mathcal{F}\mathrm{e}_i)$ is satisfied, term by term to within that same order. Conversely, the coefficients of A for a particular choice of ℓ even can be obtained from this simple algorithm:

1. Select value of j and $\ell \;=\; 2\,j$ and desired order N.
2. Set a_0 and a_1 according to eq. (23)

$$\begin{aligned} a_0 &= -\ell\,(\ell\,+\,1) \\ a_1 &= \frac{8j^2+4j-1}{(4j-1)(4j+3)}\,x \end{aligned}$$

3. For $i \;=\; 1$ to $(N-1)$
    (a) Let $A_{trial} \;=\; \sum_{k=0}^{i} a_k\,x^k + a_{i+1}\,x^{i+1}$. Note that a_{i+1} is symbolic and not yet determined.
    (b) Substitute A_{trial} into $\det(\mathcal{F}\mathrm{e}_{\ell+i+1})$.
    (c) Isolate coefficient for x^{i+1}.
    (d) Solve for a_{i+1} such that this coefficient is zero.

A counterpart result also holds for the odd case of ℓ i.e. for $\det(\mathcal{F}\mathrm{e}_i)$. This simple algorithm allows us to yield the series solution for A for any given choice of ℓ. At the same time, the solution of this algorithm implies that $\det(\mathcal{F}\mathrm{e}_i) = 0$ is formally solved.

It must be emphasized that increasing i merely means adding basis functions. There are no singularities between the two nuclei of H_2^+, and we can expect the wave function to be not only continuous but also continuously differentiable in that regime i.e. we expect no surprises with the basis functions as $i \;\to\; \infty$. As the estimates for A and p are closer and closer to the true values of the eigenparameters, the magnitude of the coefficients f_i of eq. (15) become smaller and smaller as $i \to \infty$. In this limit, the basis set is a valid representation of the true wave function.

The first 10 coefficients of the series for $A(x)$ where $x = p^2$ for $\ell = 0$ are:

$$\begin{aligned} A(x) \;=\; & 1/3\,x + \frac{2}{135}\,x^2 + \frac{4}{8505}\,x^3 - \frac{26}{1913625}\,x^4 - \frac{92}{37889775}\,x^5 \\ & - \frac{513988}{9050920003125}\,x^6 + \frac{122264}{11636897146875}\,x^7 + \frac{57430742}{6231558422151625}\,x^8 \\ & - \frac{26237052532}{15664268405762382656 25}\,x^9 - \frac{1550889714543116}{213229853673440433908203125}\,x^{10} \end{aligned} \tag{28}$$

and our computer algebra programs allow us to generate many more such coefficients. The first three non-vanishing terms of the Taylor series for $A(p^2)$ have already been published for cases of small p consistent with small internuclear distances R [38–40]. We now claim that the present algorithm provides a means of generating the Taylor series of A in small x where $x \;=\; p^2$, the result being valid as $i \;\to\; \infty$ and thus *independent* of the size of the truncated basis. Later, we will demonstrate it to be independent of the actual choice of basis. However, the first test concerns numerical vindication.

Table 2: Convergence of “Taylor series” of $\mathrm{A}(\mathrm{p}^2)$
Ground State: $1s\,\sigma_{\mathrm{g}}\quad(n=1,\ell=0,m=0)$

	ODKIL (accurate)		series (20 terms)
R	p	A	A
0	0	0	0
0.5	.46569679	.729927345e-1	.7299273577e-1
1.0	.851993637	.249946241	.2499467374
1.5	1.18537488	.498858904	.4988725127
] 2.0	1.48501462	.811729585	.8118596153
2.5	1.7622992	1.19023518	1.190951531
3.0	2.02460685	1.64100244	1.643819599
4.0	2.52362419	2.79958876	2.822919217
5.0	3.00919486	4.37769375	4.491055954
10.0	5.47986646	20.1332932	25.05609231
20.0	10.4882244	90.0528912	-1147.477000

Table 3: Convergence of “Taylor series” of $\mathrm{A}(\mathrm{p}^2)$
State: $2s\,\sigma_{\mathrm{g}}\quad(n=2,\ell=0,m=0)$

	ODKIL (accurate)		series (20 terms)
R	p	A	A
0	0	0	0
0.5	0.241110452	0.194282436e-1	0.1942824361e-1
1.0	0.459850296	0.711543142e-1	0.7115431427e-1
2.0	0.849546791	0.248466171	0.2484661714
3.0	1.19791141	0.510154273	0.5101542740
4.0	1.51924947	0.8535318	0.8535318053
5.0	1.82176362	1.28400188	1.284001886
10	3.19930169	5.12935962	5.127249696
15	4.51129751	12.4337232	-17315.20146

3.4 Numerical vindication of the Series for $\mathbf{A}(\mathbf{p^2})$

To vindicate the series, we obtain data entries of R, p and A from program ODKIL and inject the data entries of p into the series solutions for A. We then compare the latter with the value of A obtained from ODKIL for a given state. This is done for the ground state and a few excited states as shown in the following tables. The results for the ground state i.e. $1s\,\sigma_{\mathrm{g}}$ $(n=1,\ell=0,m=0)$ are shown in table 2 and those of state $2s\,\sigma_{\mathrm{g}}$ $(n=2,\ell=0,m=0)$ are shown in table 3 demonstrating that the same series of A for a given ℓ works for more than one state. The results for the excited state $2p\,\sigma_{\mathrm{u}}$ $(n=2,\ell=1,m=0)$ vindicate the series solution for $\ell=1$. The results for state $3d\,\sigma_{\mathrm{g}}$ $(n=3,\ell=2,m=0)$ vindicate the series solution for A for $\ell=2$.

In all cases, we can see that the series obtained for $A(p^2)$ works indeed like a Taylor series, working very well for small p. Beyond a certain value of R, the series solution rapidly degenerates. Nonetheless, e.g. for the ground state, the series solution works well near the bond length (around $R=2$ which is underlined) and beyond. Degradation of the series becomes apparent at $R=5$.

The question arises as to whether or not the series coefficients of $A(p^2)$ follow a pattern. We have found none so far. The pattern of the changing signs $+,-$ is not one of alternating series and thus

Table 4: Convergence of “Taylor series” of $\mathrm{A}(\mathrm{p}^2)$
State: $2p\,\sigma_{\mathrm{u}}\quad(n=2,\ell=1,m=0)$

R	ODKIL (accurate)		series (20 terms)
	p	A	A
0	0	-2	-2
0.5	.254186316	-1.96120498	-1.961204981
1.0	.53141962	-1.83001042	-1.830010419
2.0	1.15545177	-1.18688939	-1.186889387
4.0	2.35889913	1.53846448	1.538464473
6.0	3.43970785	5.92793017	5.927930398
8.0	4.4671459	12.0646853	12.07439611
9.0	4.97308004	15.8356448	16.60977070
10	5.476774	20.0920989	58.89905749
20	10.4882239	90.0528776	.7649129703e13

Table 5: Convergence of “Taylor series” of $\mathrm{A}(\mathrm{p}^2)$
State: $3d\,\sigma_{\mathrm{g}}\quad(n=3,\ell=2,m=0)$

R	ODKIL (accurate)		series (20 terms)
	p	A	A
0	-	-6	-6.
0.5	0.166934253	-5.98541087	-5.985410869
1.0	0.335547827	-5.94115241	-5.941152409
2.0	0.686698811	-5.75530105	-5.755301048
4.0	1.51188304	-4.86085811	-4.860858108
6.0	2.37168861	-3.43229937	-3.432299419
8.0	3.09069127	-2.07684281	-2.076688125
10	3.69538523	-0.874720469	2.071237971
20	6.12806789	7.31365225	5232651466.

this function is unlike all the special functions known in the literature (such as e.g. [41]).

Nonetheless, there is something of a pattern for a given series when modifying the quantum number ℓ, term by term. The first two terms a_0 and a_1 follow a pattern in ℓ according to e.g. (23) for even ℓ. No such simple pattern exists for the next term a_2. However, if one solves for a_2 in terms of a_0 and a_1 for a high value of ℓ, say $\ell = \ell_{max}$, one obtains a polynomial formula for a_2. If one then substitutes the general formulae in ℓ for a_0 and a_1 into this polynomial expression for a_2: it will correctly generate the coefficients a_2 not only for ℓ_{max} but for all $\ell = 0, 1, 2 \ldots \ell_{max}$. At some point, the resulting formula will break down for a value of $\ell > \ell_{max}$. This “triangular” relationship, - useful because one often does calculations within for a limited range of ℓ - indicates that:

$$a_2 \;\approx\; \lim_{\ell_{max}\to\infty} \frac{P_{\ell_{max}}(\ell)}{Q_{\ell_{max}}(\ell)}\,,$$

which places us beyond eq. (23) (or (25)) which determine a_0 and a_1 only. However, this is subject of further exploration elsewhere.

The range of the series solution can be considerably improved by modifying the recurrence relation for $\det(\mathcal{F}\mathrm{e})$ like so:

$$
\begin{aligned}
\det(\mathcal{F}\mathrm{e}_0) &= 1 && (29)\\
\det(\mathcal{F}\mathrm{e}_1) &= \frac{y}{3} - A && (30)\\
\det(\mathcal{F}\mathrm{e}_{k+1}) &= \left(-2\,k\,(2\,k+1) + \frac{y\,\left(8\,k^2-1+4\,k\right)}{(4\,k-1)\,(4\,k+3)} - A\right)\det(\mathcal{F}\mathrm{e}_k) && (31)\\
&\quad -4\,\frac{x\,y\,(2\,k-1)^2\,k^2}{(4\,k-1)^2\,(4\,k-3)\,(4\,k+1)}\det(\mathcal{F}\mathrm{e}_{k-1})
\end{aligned}
$$

where it is understood $x = y = p^2$ but it is only x which is treated as a perturbation. This is simply a different representation denoted $A = A(x, y)$ but which represents the same function $A(p^2)$. Modifying slightly our previous algorithm, we obtain e.g. a modified series solution for $A(x, y)$ for $\ell = 0$:

$$
\begin{aligned}
A = \frac{y}{3} - \frac{14}{15}\,\frac{y\,x}{(2\,y-63)} + \frac{14}{375}\,\frac{y^2\,P_1(y)\,x^2}{(2\,y-63)^3(2\,y-231)} \qquad (32)\\
-\frac{28}{121875}\,\frac{y^3\,P_3(y)\,x^3}{(2\,y-63)^5\,(2\,y-231)^2(2\,y-495)} + \ldots
\end{aligned}
$$

where the polynomials $P_k(y)$ of order k are given by:

$$
\begin{aligned}
P_1(y) &= 94\,y - 44121\\
P_3(y) &= 166376\,y^3 + 16398492\,y^2 + 131745081006\,y - 13685763372435
\end{aligned}
$$

Note that if we inject $y = x$ into the above and make a Taylor series expansion in x, we simply recover the series solution in $x = p^2$ obtained in eq. (27) for $\ell = 0$. Since the radius of convergence is determined by the closest singularity or branch point in the complex plane, we have

$$2\,y - 63 = (2\,p^2\ -\ 63) = 0 \Rightarrow p \approx 5.6$$

We note that the sequence of numbers 63, 231, 495, 855,... which appear in the denominator have a pattern which can be found using the `gfun` package [45]. This demonstrates that these numbers fit a holonomic function and it is found that these fit the pattern:

$$3\,(4\,j+3)(4\,j+7) \qquad (33)$$

We recognize it as one of the terms which appear in the recursion relations for $\det(\mathcal{F}\mathrm{e}_k)$ i.e. $(4k-1)(4k+3)$ with $k = j+1$. However, no pattern has (so far) been found for the polynomials $P_k(y)$. Nonetheless, our computer algebra routines allow us to generate this series to relatively high order.

Next, the sum can be calculated using non-linear transformations known as the Levin or Sidi transformations. The latter involves a series transformation by which one can accelerate the convergence of a series and even sum divergent series (e.g. see the work of [43,44]). We take the point of view that a Taylor or asymptotic series has all the desired “information”, getting numbers from the series is a matter of a summation technique. These transformations are available in the Maple system as `NonlinearTransformations`.

The best results for the ground state are obtained by applying a Sidi d transformation in x compounded with y as shown in table 6. Even when the modified series behaves badly, the result from the Sidi d transformation provides reliable numbers. The results hold up remarkably well all the way up to $R = 10$ and beyond. Beyond $R = 10$, the asymptotic series expansions as e.g. listed by Čížek *et al.* [9] are more useful. What is important in our case, is that our series solution works so well around the bond length and the intermediate regime.

Table 6: Convergence of Series A(x,y)
Ground State Revisited: $1s\,\sigma_{\mathrm{g}}$ $(n = 1, \ell = 0, m = 0)$

R	A		
	series (12 terms)	ODKIL (accurate)	Sidi-d
1	0.24994624090	0.2499462409	0.2499462410
$\underline{2}$	0.81172958404	0.8117295840	0.8117295850
3	1.6410024366	1.6410024369	1.6410024370
4	2.7995666114	2.7995887586	2.7995887590
5	3.9638237398	4.3776938960	4.3776937530
6	-4.6313683166e+03	6.4536051398	6.4536037430
8	-3.7137673759e+12	12.2262006172	12.2261746150
10	-1.5608159299e+33	20.1339450995	20.1332931780
15	1.0054600411e+15	48.8656127918	48.8223535290

3.5 Solution for $\mathbf{A(R, p)}$

Although we have eliminated one of the unknowns i.e. found $A(p^2)$ such that the determinantal conditions for $\det(\mathcal{F}_i)$ are satisfied, there is still the remaining determinant $\det(\mathcal{Y}_i)$ to address. The recurrence relations for $\det(\mathcal{Y}_i)$ of eq. (18) depend on the internuclear distance R and have more structure than those of $\det(\mathcal{F}\mathrm{e}_i)$ of eq. (19) or $\det(\mathcal{F}\mathrm{o}_i)$ of eq. (20). Nonetheless, we proceed in parallel to what we did for $A(p^2)$.

To start with, we ignore the term $\det(\mathcal{Y}_{k-1})$ and solve the resulting two-term recurrence relation since all linear recurrence relations of this type are solvable in terms of the roots of the characteristic polynomial obtained by assuming a $\det(\mathcal{Y}_i) = f^i$ and then solving for f:

$$\det(\mathcal{Y}_i) \;=\; (-2)^k \, \frac{\Gamma((2\,k\,p + Y_+ + X/2p))\;\Gamma((2\,k\,p + Y_+ - X)/(2p))}{\Gamma(-(Y_- - X)/(2p))\;\Gamma(-(Y_- + X)/(2p))} \tag{34}$$

where

$$\begin{aligned} X &= \sqrt{2\,p^4 - p^2 + R^2 + 2\,A\,p^2} \\ Y_+ &= 2\,p^2 \,+\, p \,-\, R \\ Y_- &= 2\,p^2 \,-\, p \,+\, R \end{aligned}$$

and Γ is the Gamma function [41]. This result bears some resemblance with the outcome of solving the eigenvalue problem for the hydrogen atom. In this case, solutions to the ODE for the radial equation in the radius r can be expressed in terms of hypergeometric functions. Matching the asymptotic solution at $r \to \infty$ with the regular solution at $r \to 0$ necessitates the elimination of the irregular solution by forcing one of its coefficients - also expressed in terms of the Gamma function - to be zero (e.g. see [42]). In our case (as in the case of the hydrogen atom), it is a matter of ensuring that the arguments for one (or both) of the Gamma functions in the denominator of the expression above to be $-\jmath$ where $\jmath = 0, 1, 2 \ldots$ Thus, solving for A, we find that:

$$A(R,p) \;\approx\; p^2 \;+\; 2\,(1 + 2\jmath)\,p \;+\; 1 - 2\,R \;+\; 2\jmath \;+\; 2\jmath^2 - \frac{R\,(1 + 2\jmath)}{p}\,. \tag{35}$$

What remains is the identification of j. Next we treat term $\det(\mathcal{Y}_{k-1})$ as a perturbation formally by multiplying it by λ with the understanding that $(\lambda = 1)$. For $\jmath = 0$, the series solution for $A(R, p)$

Table 7: Convergence of A(R, p)
Ground State: $1s\,\sigma_{\mathrm{g}} \quad (n=1, \ell=0, m=0)$

R	ODKIL (accurate)		series (4 terms)
	p	A	A
0.5	0.46569679	0.729927345e-1	0.7299778055e-1
1.0	0.851993637	0.249946241	0.2499480309
2.0	1.48501462	0.811729585	0.8117297560
5.0	3.00919486	4.37769375	4.377693772
10	5.47986646	20.1332932	20.13329314
20	10.4882244	90.0528912	90.05289034
30	15.4919739	210.034597	210.0345960
40	20.4939187	380.025707	380.0257060
50	25.4951064	600.020452	600.0204512

is:

$$\begin{aligned} A(R,p) &= (p+1)^2 - 2\,R - \frac{R}{p} - \frac{(p-R)^2\lambda}{2\,p\,(2\,p^2+2\,p-R)} \\ &\quad - \frac{(p-R)^2\,P_4(R,p)\lambda^2}{(8\,p\,(2\,p+2\,p^2-R)^3\,(3\,p+2\,p^2-R))} \\ &\quad - \frac{(p-R)^2\,P_{10}(R,p)\lambda^3}{(16\,p\,(2p+2p^2-R)^5\,(3p+2p^2-R)^2\,(4p+2p^2-R))} \end{aligned} \tag{36}$$

where

$$\begin{aligned} P_4(R,p) &= 14p^4 + (13-12R)\,p^3 + R\,(2\,R-17)\,p^2 + 7\,pR^2 - R^3 \\ P_{10}(R,p) &= 584\,p^{10} - 8\,(116\,R-233)\,p^9 + 2\,(256\,R^2+969-1878\,R)\,p^8 \\ &\quad - 4\,(28\,R^3 - 722\,R^2 + 1184\,R - 165)\,p^7 \\ &\quad + R\,(8\,R^3 + 4678\,R - 1056\,R^2 - 1897)\,p^6 \\ &\quad + 2\,R^2\,(92\,R^2 - 1200\,R + 1145)\,p^5 \\ &\quad - R^3\,(12\,R^2 - 678\,R + 1513)\,p^4 - 2\,R^4(50\,R-297)\,p^3 \\ &\quad + R^5\,(6\,R-139)\,p^2 + 18\,R^6\,p - R^7 \end{aligned}$$

The series looks complicated and the presence of singularities at every $-R + i\,p + 2\,p^2 = 0$ for $i = 2, 3, \ldots$ already tell us that this function is unlike most special functions in the literature. However, the series gives very good results as shown in table 7 with only 4 terms. It does not need any convergence acceleration summation methods at large R. The results of Table 8 for state $2s\,\sigma_{\mathrm{g}}$ $(n=2, \ell=0, m=0)$ show us that $A(R,p)$ works well for large R but diverges for small R. Also shown in the table are the results of the Sidi d transformation which considerably improves the series solution for small R.

What remains is to identify the meaning of the number j. By checking the solution for excited states, we find out empirically that:

$$\jmath = n - \ell - 1 \tag{37}$$

where n is the united atom quantum number. This number $\jmath$ is a valid quantum number for the *separated* atom limit [8, eq.24,p.666]. Thus, just as we match the outward and inward radial solutions for the radial ODE for the hydrogen atom by which to determine the eigenvalue, the eigensolution for H_2^+ results from matching $A(p^2)$ governed by the united atom quantum number ℓ with $A(R,p)$ governed by the separated atom quantum number $\jmath = n - \ell - 1$.

Table 8: Convergence of $\mathrm{A(R,p)}$
State: $2s\,\sigma_{\mathrm{g}} \quad (n=2,\ell=0,m=0)$

R	ODKIL (accurate)		series (5 terms)	Sidi-d
	p	A	A	A
0	0	0	-	-
0.5	0.241110452	0.0194282436	-7.5860659805e+02	0.0211395500
1.0	0.459850296	0.0711543142	-2.1405738045	0.0718499907
2.0	0.849546791	0.2484661710	0.23871213039	0.2485999772
3.0	1.197911410	0.5101542730	0.50971077859	0.5101743643
4.0	1.519249470	0.853531800	0.85348392428	0.8535343888
5.0	1.821763620	1.28400188	1.2839939077	1.2840020996
10.	3.199301690	5.12935962	5.1293596329	5.1293596444
15.	4.511297510	12.4337232	12.433723259	12.4337232589
20.	5.805158110	23.1467952	23.146795143	23.1467951431
30.	8.359177000	54.1918175	54.191817437	54.1918174372
40.	10.8899708000	97.83692290	97.836923003	97.8369230031

As suggested by Table 8 the series behaves well for large p, it is found that $A(R,p)$ yields a stable series in powers of $1/p$. To within $O(1/p^7)$, the expansion for (36) is:

$$\begin{aligned}
A(R,p) \quad = \quad & (p+1)^2 - 2\,R - \frac{(4\,R+1)}{4\,p} + \frac{(2\,R+1)}{4\,p^2} - \frac{(16\,R^2+40\,R+23)}{64\,p^3} \\
+ \quad & \frac{(32\,R^2+68\,R+41)}{64\,p^4} - \frac{(64\,R^3+576\,R^2+1108\,R+681)}{512\,p^5} \\
+ \quad & \frac{(256\,R^3+1432\,R^2+2566\,R+1593)}{512\,p^6} \\
- \quad & \frac{(1280\,R^4+28160\,R^3+123680\,R^2+210448\,R+131707)}{16384\,p^7} \\
+ \quad & \frac{(8192\,R^4+95040\,R^3+358368\,R^2+587512\,R+371061)}{16384\,p^8} \\
- \quad & \frac{(7168\,R^5+313600\,R^4+2607232\,R^3+8854496\,R^2+14149364\,R+9039151)}{131072\,p^9} \\
+ \quad & \frac{(65536\,R^5+1366016\,R^4+9200576\,R^3+29011472\,R^2 45621790\,R+29559559)}{131072p^{10}} \,.
\end{aligned} \tag{38}$$

The coefficients up to $O(p^{-6})$ have been previously published [40] but our computer algebra programs allow us to go much further.

3.6 Other Bases - Algebraic Vindication

Although our previous results are apparently independent of the size of the chosen basis, we must consider other bases. For the η coordinate, we consider the Baber-Hassé and the Wilson bases [14] which are described as follows.

Baber-Hassé:

$$M(\eta,\phi) = e^{im\phi} e^{-q\eta} \sum_{\ell=m} a_\ell \, P_\ell^m(\eta) \tag{39}$$

The recurrence relation is given by:

$$\frac{(\ell+m+1)}{(2\ell+3)}[2p(\ell+1)+\mathcal{Q}_1]a_{\ell+1}+\alpha_1(k)a_\ell+\frac{(\ell-m)}{(2\ell-1)}(\mathcal{Q}_1-2p\ell)a_{\ell-1}=0 \tag{40}$$

where for $m=0$:

$$\begin{aligned}\alpha_1(k) &= A\ -\ p^2\ +\ \ell(\ell+1)\\ a_{-1} &= 0\,.\end{aligned}$$

Wilson:

$$M(\eta,\phi)=e^{im\phi}e^{q\eta}(1-\eta)^{m/2}\sum_{k=0}(-1)^k\,c_k\,(1-\eta)^k \tag{41}$$

The recurrence relation is:

$$2(k+1)\,(k+m+1)\,c_{k+1}+\sigma_1(k)\,c_k+2[\mathcal{Q}_1\ +\ p\,(k+m)\,c_{k-1}=0 \tag{42}$$

where

$$\begin{aligned}\sigma_1(k) &= A\ -\ p^2\ +\ (m+1)\,(m+2p)+\ k\,(k+2\,m+4\,p\ +\ 1)\\ c_{-1} &= 0\,.\end{aligned}$$

Both of these bases have been implemented into the Maple system. If we consider $\ell=0$, the coefficient a_N of Baber-Hassé basis is of order $O(1/p^N)$ and the coefficient c_N of Wilson basis is of order $O(p^0)$. However, if we inject our series solution for $A(p^2)$ into the series coefficients of both bases, we find that both a_N and c_N are *formally* zero to within order $O(p^N)$. This can be seen through a number of computer algebra demonstrations. Thus our series solution for $A(p^2)$ also *formally* satisfies the recurrence relations of these other bases, *order by order* in p.

For the ξ coordinate, apart from the used Hylleraas basis, there is also the Jaffé basis.

Jaffé:

$$\Lambda(\xi)=(\xi^2-1)^{m/2}(\xi+1)^{-m-1+\mathcal{Q}_2/2p}\,e^{-p\xi}\sum_{k=0}D_k\left(\frac{\xi-1}{\xi+1}\right)^k \tag{43}$$

The recurrence relation is:

$$(k+1)\,(k+m+1)\,D_{k+1}+\gamma_1(k)\,D_k+(k-\frac{\mathcal{Q}_2}{2p})(k+m-\frac{\mathcal{Q}_2}{2p})D_{k-1} \tag{44}$$

where

$$\begin{aligned}\gamma_1(k) &= A\ -\ p^2+\mathcal{Q}_2\ -\ (m+1)\,(2p+1-\frac{\mathcal{Q}_2}{2p})\\ &\quad -\ 2k\,(k+m+2p+1-\frac{\mathcal{Q}_2}{2p})\\ D_{-1} &= 0\,.\end{aligned}$$

Similarly, it can be algebraically demonstrated that e.g. for $\jmath=n-\ell-1=0$, the $1/p$ series expansion of $A(R,p)$ formally satisfies the coefficients of the Jaffé basis for negative powers of p just as they satisfy the Hylleraas basis. This demonstration allows us to consider another basis of importance for the η coordinate, namely the Power basis:

Power:

$$M(\eta,\phi) = e^{im\phi} e^{-q(1+\eta)} (1-\eta)^{m/2} \sum_{k=0} d_k \, \mathbf{M}(-(k+\delta k), m+1, 2p(1+\eta)) \tag{45}$$

The recurrence relation is:

$$(k+\delta k+1)\,(k+\delta k+1-\frac{\mathcal{Q}_1}{2p})\, d_{k+1} + \chi_1(k)\, d_k \tag{46}$$

$$+\,(k+\delta k+m)(k+\delta k+m-\frac{\mathcal{Q}_1}{2p})\, d_{k-1}$$

where

$$\begin{aligned} \chi_1(k) &= A \,-\, p^2 - \mathcal{Q}_1 \,+\, (m+1)\,(2p-1+\frac{\mathcal{Q}_1}{2p}) \\ &- \; 2(k+\delta k)(k+\delta k+m+1-2p-\frac{\mathcal{Q}_1}{2p}) \\ d_{-1} &= 0\,, \end{aligned}$$

and δk is an exponentially vanishing term in R and consequently we do not make the same demonstration as for the Wilson and Baber-Hassé bases. However, when we let $R \to \infty$ then $\delta k \to 0$ and we can make a similar demonstration as for the Jaffé basis using the $1/p$ expansion of $A(R,p)$.

Granted, we have not proven this for *all* bases. Nonetheless, we emphasize that e.g. the Wilson basis is very different from the Baber-Hassé basis or the Power Basis and the basis of spherical harmonics we used as a starting point for this analysis. Moreover, the Hylleraas basis is also very different from the Jaffé basis. These demonstrations strongly suggest basis independent results for $A(p^2)$ and $A(R,p)$.

This analysis herein exploits the fundamental theorem of algebra i.e. that if one knows all the N roots of a given polynomial say $P_N(x)$, the latter is completely defined within a scaling factor namely the coefficient of its highest power in x. The three-term recurrence relations of eqs. (19), (20) and (18) have a linear dependence on A for the term in d_k but *no* dependence of A for the third term in d_{k-1}. Thus, $\det(\mathcal{F}\mathrm{e}_i)$, $\det(\mathcal{F}\mathrm{o}_i)$ and $\det(\mathcal{Y}_i)$ are i^{th} degree polynomials in A regardless of whether or not the third term in d_{k-1} is neglected. This allows us to completely account and identify the the eigenparameters of the matrices $\mathcal{F}$ and $\mathcal{Y}$ for every discrete state.

3.7 Mathematical Classification of Solutions

So far, we have identified the functions implied by the determinants $\det(\mathcal{F}_i)$ and $\det(\mathcal{Y}_i)$, namely $A(p^2)$ and $A(R,p)$ respectively for *all* discrete states where $m = 0$ for the homonuclear case. In view of previous and recent work on the $D \to 1$ version of H_2^+ and the findings in this work concerning the $D = 3$ version of H_2^+, we are now equipped with the means to make the following analytical comparison. Here, we can put the $D \to 1$ and the $D = 3$ versions of H_2^+ on the same "canonical" footing:

D → 1: To reiterate the results of section 2, the energy eigenvalue is governed by an equation of the form:

$$\exp(-2\,R\,d) = P_2(d)_{\{P_N(d)\}} \quad \text{where} \quad E = -\frac{d^2}{2} \tag{47}$$

When the second order polynomial $P_2(d)$ factors into a product of first order polynomials, both sides of eq. (47) factors and the solution for d is a (standard) Lambert W function

[19, 20]. When it does not factor, the solution is a generalization of the W function reported in the work of [28]. When the right side is a polynomial, the solution is a *generalized* Lambert W function [30]. The subscript $P_N(d)$ reminds us that our generalization for the W function can accommodate a polynomial with rational coefficients of arbitrary degree on the right side of eq. (47).

The exponential term on the left side is a reflection of the fact that outside the Dirac delta function wells, the basis of the particle is a combination of free particle solutions which required matching at the Dirac delta function peaks.

D=3: To summarize the results of the past few sections, the eigenparameter p, which plays an analogous role to the parameter d of the $D \to 1$ version of H_2^+ is determined from the equation:

$$A(R,p) = A(p^2)_{\{P_N(p)\}} \quad \text{where} \quad E = -2\,\frac{p^2}{R^2} \tag{48}$$

The subscript $P_N(p)$ reminds us that we have a Taylor series for $A(p^2)$ with rational coefficients which exactly matches the generalized right-hand side form of eq. (47). However, the left-side of (48) looks very different than the left side of (47); it is the function implied by $\det(\mathcal{Y}_i)$ and is associated with the separated quantum number $\jmath = n - \ell - 1$. Nonetheless, like $\exp(-2Rd)$, this function is well-defined asymptotically for large R. The right side of eq. (48) is implied from $\det(\mathcal{F}_i)$ for even or odd ℓ which is a united atom quantum number.

So far, the functions $A(R,p)$ and $A(p^2)$ appear in the literature as expansions in terms of p^{-k} and p^k respectively, restricted to $k = 6$ and for specific cases of large and small values of R [38–40]. We can obtain series representations of both to a much greater extent in view of our computer algebra implementations. We have also seen that $A(p^2)$ can be represented as an infinite series in x where $x = p^2$ and is consequently polynomial-like.

Note that if $m \neq 0$, the governing equation has the same form as eq. (48) but the left side is more complicated and more difficult to get, as the determinant $\det(\mathcal{Y}_i)$ is no longer governed by a simple recurrence relation. However, in principle, eq. (48) governs the entire homonuclear case.

Mathematically, in both cases, the right side of the governing equation is expressed in terms of only one of the eigenparameters whereas the left side requires the parameter and the value of the internuclear distance R which is determined on input.

We therefore come to the conclusion that the eigenparameter p, like its $D \to 1$ counterpart d, is also determined by a special function which is an *implicit* function, an even greater generalization of the Lambert W function. So far, the functions $A(R,p)$ and $A(p^2)$ do not appear in the literature. However, we can obtain series representations of both to the extent of getting reliable numbers, as demonstrated by our tables of values.

On the subject of implicit functions or implicit equations, these are seen in a number of specific contexts:

Retardation Effects: Equations of form $e^{-c\,\lambda} = P_2(\lambda)$ and more generally $e^{-c\lambda} = P_2(\lambda)/Q_1(\lambda)$ express the solutions of a huge class of *delayed* differential equations [46, eq.(3)].

Bondi's K-calculus: It is well known in the area of special relativity that the Lorentz transformation can be derived from the theory of implicit functions with minimal assumptions of continuity [47]. Here one seeks the function $f(t)$ satisfying $f(f(t)) = k^2 t$ and the requirements that it be monotone increasing and continuous. The unique solution is:

$$f(f(t)) = k^2 t \quad \text{where} \quad v/c = k^2 - 1/k^2 \quad \rightarrow \quad f(t) = k\, t$$

GRT/QFT: As we mentioned before, the Lambert W function and its generalization appear in General Relativity as solutions to respectively the two-body and three-body linear $(1+1)$ gravity problems via dilaton theory [28, 29].

Implicit functions often appear in problems with retardation effects, relativistic or otherwise. Thus, with some reservations, we associate with this mathematical category a tentative "physical picture":

Although the hydrogen molecular ion H_2^+ in the context of the Schrödinger wave equation is *not* a relativistic formulation, the eigensolutions we obtain nonetheless suggests something akin to a *retardation* or *delay* effect. This is not the case for a one center problem like the hydrogen atom but this characteristic appears for a two-center problem. However, this statement must be tempered with the fact that e.g. the Lambert W function also appears in many other types of problems with no relationship to retardation effects.

4 Summary/Conclusions

Through experimental Mathematics using computer algebra as a tool, we have identified the mathematical *structures* governing the energy spectrum of the hydrogen molecular ion H_2^+ for the two-center one-electron problem.

In the present work, we started with a particular choice of basis and expressed the determinantal conditions by which the eigenparameters p and A are obtained. From one of the two determinants, we inverted the problem to obtain a series representation of the separation constant $A(p^2)$ associated with the united atom quantum number ℓ. We applied a similar approach to obtain $A(R,p)$ from the remaining determinant and associated with the separated atom quantum number $\jmath = n - \ell - 1$. where n is a united quantum number. We then demonstrated that the results were independent of the size and even the choice of basis.

The eigenparameter p for which $E = -2p^2/R^2$ is obtained by matching $A(p^2) = A(R,p)$ and found to be the solution of an implicit function, with features similar to that of the Lambert W function *and* its recent generalizations [30]. This allowed us to mathematically categorize the eigenvalues (or rather make us realize what they are not) and even to associate a tentative "physical picture" to the solutions. While we made no pretense at rigor, the solutions were nonetheless vindicated numerically and by algebraic demonstrations with computer algebra.

The results express analytical solutions for the ground state and the countable infinity of discrete states of H_2^+ for the homonuclear case when the magnetic quantum number $m = 0$. From the discussion below eq. (48), we anticipate that the eigensolutions for $m \neq 0$ for the homonuclear case to be qualitatively similar though admittedly this remains to be proven. We emphasize that although the basis and approach used here were ideal for $m = 0$ and the homonuclear case. the computer algebra methods shown are directly applicated to the heteronuclear case with $m \neq 0$. For $m \neq 0$, one should work directly from the recurrence relations of the chosen basis now that we understand how these basis coefficients behave with better and better accuracy for the series expansions of $A(p^2)$ in p and the asymptotic series expansions for $A(R,p)$ in $1/p$.

However, we make no pronouncements concerning the nature or mathematical category of the solutions for the heteronuclear case or when the nuclei are allowed to move. We note that for $m = 0$, the matrix for $\det(\mathcal{Y}_i)$ remains tridiagonal while the band matrix for $\det(\mathcal{F}_i)$ is pentadiagonal and consequently governed by nested recurrence relations [15] suggesting that the analysis shown herein is possible.

A number of issues arise from this result. In a sense, the result is both overdue and premature. It is overdue because of our present capacity to find solutions to fair-sized molecules using computational chemistry. On the other hand, it is premature. The functions we found $A(p^2)$ and $A(R,p)$ do not seem to resemble anything we have seen in the literature. The apparent singularities or "resonances" at $2p^2 = 3\,(4\,j+3)(4\,j+7)$ for $A(p^2)$ and $R = (j+2)\,p + 2\,p^2$ for $A(R,p)$ for $j = 0, 1, 2, \ldots$ do not constitute a problem since the eigenparameters p and A for a given R are never found on these resonances. Once a value of R is injected into $A(p^2) = A(R,p)$, solving for p numerically did not create any problems in the test cases examined so far. At any rate, the tables shown herein merely illustrate the convergence properties of the functions $A(p^2)$ and $A(R,p)$ we have identified: solving the coupled set of polynomials $\det(\mathcal{F}_i)$ and $\det(\mathcal{Y}_i)$ for p and A at a given distance R involves no resonances and is still the most useful method from a computational point of view. In principle, the latter can go further than any FORTRAN program.

We have ordered series representations to relatively high order of both of these functions $A(p^2)$ and $A(R,p)$ and we can generate reliable numbers for a number of discrete quantum states. We have also demonstrated that we could use these series beyond their radius of convergence using techniques for handling divergent series.

From here, one could explore and seek alternate representations of these functions with better convergence properties especially at low R for $A(R,p)$ and large R for $A(p^2)$ but the results from the Sidi transformations are already very promising. At any rate, the hydrogen molecular ion for clamped nuclei can be entirely contained within simple computer algebra sessions, not much more complicated than those of the hydrogen atom[1].

The exploratory and roundabout way by which we found our solutions, suggests there is something missing in the mathematical physics or the methods for obtaining the eigenvalues of the Schrödinger wave equation. There is hardly any existing "technology" for solving quantum chemistry problems involving implicit functions. Our use of a basis is certainly valid to demonstrate or prove a result. Furthermore, the convergence of the bases used here has been confirmed by determining the asymptotic behavior of the expansion coefficients of the wavefunctions for the various basis sets considered [40]. Nonetheless, a more direct way of generating the functions of $A(p^2)$ and $A(R,p)$ would be instructive.

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[1] Maple CAS programs are available upon request.

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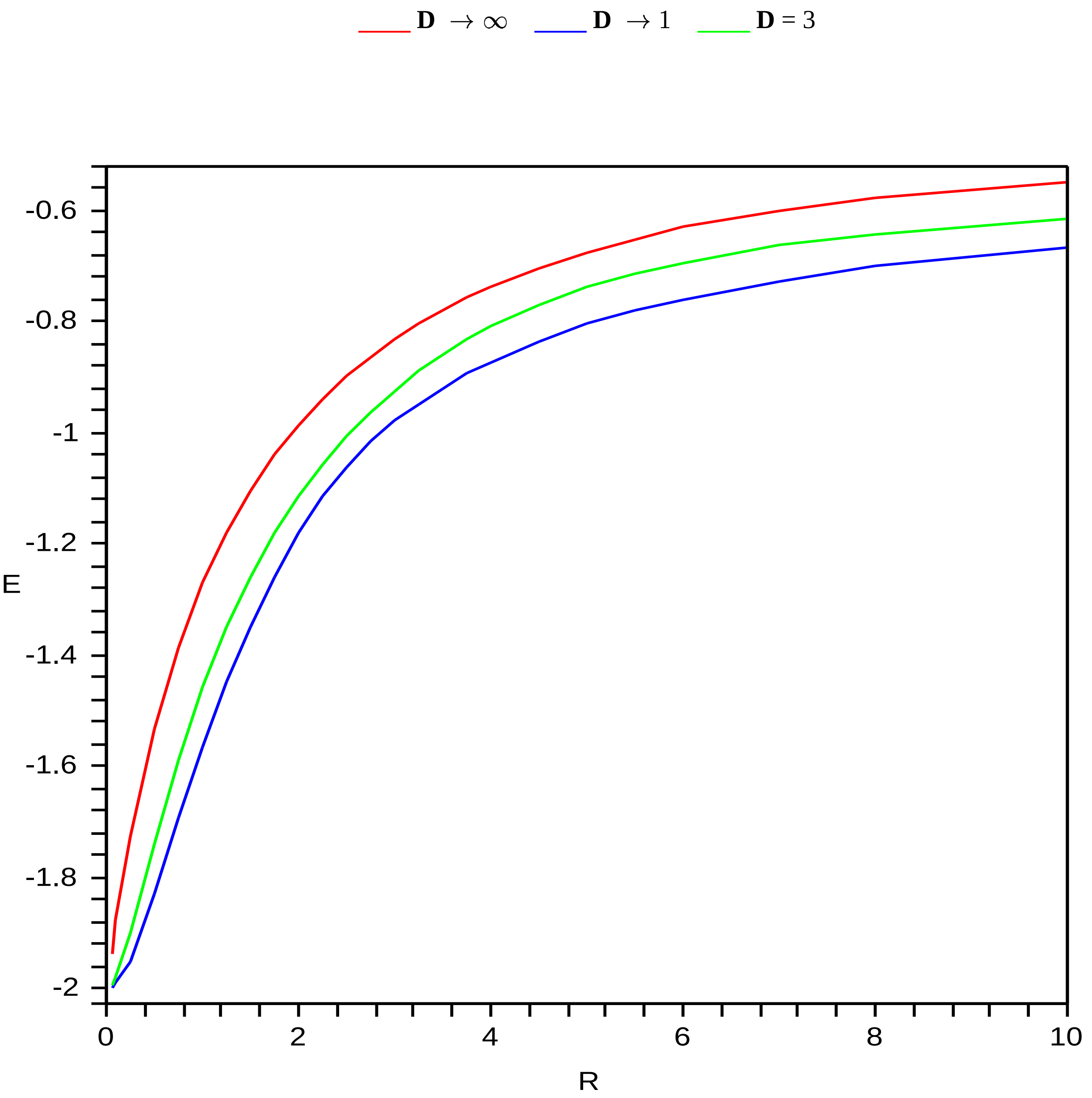
Energy vs. R for H_2^+ (a.u.)



$$\mathbf{E}_3\,(R) \approx \frac{1}{3}\mathbf{E}_1\,\left(\tfrac{R}{3}\right) \,+\, \frac{2}{3}\mathbf{E}_\infty\,\left(\tfrac{2\,R}{3}\right)$$

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