

# The Hydrogen Molecular Ion Revisited

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The hydrogen molecular ion (HMI), the simplest molecular system, was studied in the early days of quantum mechanics. The demonstration that this species had, in agreement with experiment, a stable ground state corresponding to a bond between two atoms, was one of the early achievements of quantum theory. Classical mechanics could not predict a stable state for  $H_2^+$ .

The molecular orbital method, in the form of a linear combination of atomic orbitals (LCAO-MO method), was proposed at that time; its first application was to the HMI. Many other approximate treatments were then devised and applied to  $H_2^+$  (see e.g. ref 1).

Burrau (2) showed that the confocal elliptic coordinate system allowed the complete separation of the HMI Hamiltonian, thus paving the way toward an exact solution. This task was taken up by several investigators, including Burrau himself, Teller (3), Jaffé (4), and Hylleraas (5). They showed that the energy of any state of the HMI could be found by solving two coupled differential equations. Various methods of solution were proposed, all involving rather complicated expansions in series of associated Legendre functions. These led in turn to three term recurrence relations, from which intricate eigenvalue equations followed. In practice the energies could only be found numerically; formulas to compute the expansion coefficients were also given. More recently, electronic computers have replaced humans and the energy of the HMI can be obtained in this formalism to at least seven significant figures (6–9).

The analytical solution of the HMI problem is mentioned in most textbooks dealing with molecular structure, usually with few details. Notable exceptions are Pauling and Wilson (1), Slater (10), and Levine (11). The present-day student can only get a glimpse of the method used, unless he or she chooses to read the original literature, at the risk of being

drowned in a morass of complicated algebra. Further, in contrast to the LCAO-MO method, the analytical approach can hardly be generalized to other species. These facts explain why it is usually given short shrift in textbooks. Yet with the advent of powerful and inexpensive microcomputers, it should be possible for a student to repeat some of these computations and gain some feeling for the behavior of the HMI quantum system. It is the purpose of the present report to show that this goal is effectively within reach. We show here how the Schrödinger equation may be solved, keeping the required mathematics as simple as possible and letting the computer do most of the work. A similar point of view is taken by Press et al. (12). As we shall see, we will be able to obtain at once very accurate values of the wave function and of the energy and, in the process, learn how conserved quantities and quantum numbers are handled for a problem with cylindrical or  $D_{\infty h}$  symmetry.

This report should be of interest to advanced undergraduates in physical chemistry; it could be used as a starting point for a computational chemistry project. It may also be of historical interest to a wider audience.

## The Molecular Hamiltonian in Spheroidal Coordinates

The Schrödinger equation describing the motion of an electron in the field of two infinitely massive protons  $H_A$  and  $H_B$  located at points A and B, a distance  $D$  apart on the  $z$  axis (Fig. 1) is, in Slater's notation,

$$\left(-\nabla^2 - \frac{2}{r_A} - \frac{2}{r_B}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1)$$

where  $r_A$  and  $r_B$  are the distances from the electron to the two protons. Following Slater, we use a system of atomic units in which the unit of energy is the rydberg or 13.6 eV; the unit of length is the radius of the first Bohr orbit, 0.529 Å.

It is necessary to introduce prolate confocal elliptic coordinates,  $\xi = (r_A + r_B)/D$ ,  $\eta = (r_A - r_B)/D$ , and  $\varphi$ , which is the angle of rotation about the nuclear axis. The inverse relations are  $r_A = D(\xi + \eta)/2$  and  $r_B = D(\xi - \eta)/2$ ; we note that  $2/r_A = 4/[D(\xi + \eta)]$ ,  $2/r_B = 4/[D(\xi - \eta)]$ . The meaning of these definitions becomes clear when we examine elliptic coordinates in a plane. The lines of constant  $\xi$  are ellipses, which share foci A and B. The lines of constant  $\eta$  are hyperbolas, again with A and B as foci. These two families form an orthogonal system of curves (see Fig. 1). The variable  $\xi$  plays a role analogous to  $r$ , the distance to the origin, in the usual polar coordinate system. When  $\eta$  increases, the point  $(\xi, \eta)$  moves around the origin, so that this parameter is similar to the quantity  $\cos \theta$  in polar coordinates. The domains of each variable are  $-1 \leq \eta \leq 1$  and  $1 \leq \xi \leq \infty$ . On the part of the  $z$  axis that lies between A and B,  $r_A + r_B = D$ , so that  $\xi = 1$ , while  $-D \leq r_A - r_B \leq D$ , and  $-1 \leq \eta \leq 1$ . To the right of B ( $z \geq 1$ ),  $\eta = 1$ ; and  $\eta = -1$  to the left of A ( $z \leq -1$ ).

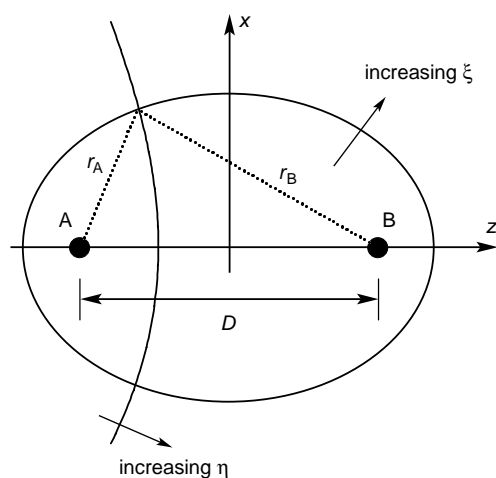


Figure 1. Definition of planar confocal elliptic coordinates

Prolate ellipsoidal coordinates in space are obtained by rotating the figure around the  $z$  axis. The ellipses generate a set of confocal ellipsoids, while the hyperbolas generate a family of hyperboloids with two sheets. Surface of constant  $\phi$  are half-planes through the  $x$  axis.

The derivation of the Laplacian operator in elliptic coordinates is found in several texts (10, 13, 14) and will not be repeated here. The volume element in spheroidal coordinates turns out to be

$$dV = \frac{D^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi \quad (2)$$

The Laplacian is

$$\nabla^2 = \frac{4}{D^2(\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} \left[ (\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \left[ \frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2}{\partial \phi^2} \right\} \quad (3)$$

Using the relation

$$\frac{1}{r_A} + \frac{1}{r_B} = \frac{4}{D} \frac{\xi}{\xi^2 - \eta^2}$$

Schrödinger's equation now reads, after some simple rearrangements

$$\frac{\partial}{\partial \xi} \left[ (\xi^2 - 1) \frac{\partial \psi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial \psi}{\partial \eta} \right] + \left[ \frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2 \psi}{\partial \phi^2} + [c^2(\xi^2 - \eta^2) + 2D\xi] \psi = 0 \quad (4)$$

with

$$c^2 = \frac{1}{4} ED^2 \quad (5)$$

According to the separation of variables method, we seek a solution of the form  $\psi = R(\xi)S(\eta)e^{im\phi}$ . By analogy with the atomic case, we have assumed an explicit form of the  $\phi$  dependence and introduced a so-called separation constant,  $m$ . Inserting in eq 4, putting  $\partial^2 \psi / \partial \phi^2 = -m^2 \psi$ , and dividing throughout by the product  $RS e^{im\phi}$ , we find that the various terms can be grouped in  $\xi$ - and  $\eta$ -dependent parts:

$$\left\{ \frac{1}{R} \left[ (\xi^2 - 1) R' \right]' - \frac{m^2}{\xi^2 - 1} + 2D\xi + c^2 \xi^2 \right\} + \left\{ \frac{1}{S} \left[ (1 - \eta^2) S' \right]' - \frac{m^2}{1 - \eta^2} - c^2 \eta^2 \right\} = 0 \quad (6)$$

In order for this equation to hold for any value of  $\xi$  and  $\eta$ , the expressions within the two braces must be constant and of opposite sign. Calling  $\Lambda$  the value of the  $\xi$ -dependent part, we see that the previous equation breaks into two:

$$\left[ (\xi^2 - 1) R' \right]' + \left[ 2D\xi + c^2 \xi^2 - \frac{m^2}{\xi^2 - 1} - \Lambda \right] R = 0 \quad (7)$$

$$\left[ (1 - \eta^2) S' \right]' + \left[ \Lambda - \frac{m^2}{1 - \eta^2} - c^2 \eta^2 \right] S = 0 \quad (8)$$

The parameter  $\Lambda$  is another separation constant. These are the two differential eigenvalue problems that we must solve to obtain the energies and eigenfunctions of the hydrogen molecular ion. In order that  $\psi$  be a continuous and single-valued function of  $\phi$ ,  $m$  must be an integer:  $m = 0, \pm 1, \pm 2, \dots$

The  $S(\eta)$  or angular equation has been studied in detail. Many of the properties of its solutions (the spheroidal wave functions) have been collected by, for example, Abramovitz and Stegun (15) and Flammer (16). Thompson has proposed an extremely accurate algorithm to compute them (17). Our notation is identical to that of Abramovitz and Stegun. The  $R(\xi)$  or radial equation only appears in the HMI problem. The quantity  $c^2$  can be positive or negative (in which case  $c$  is purely imaginary). We will restrict ourselves to bound states, with negative  $E$  and  $c^2$ . The corresponding  $S(\eta)$  functions are then called "oblate" spheroidal functions.

When  $c^2$  goes to zero, eq 8 becomes identical to the differential equation for the associated Legendre polynomials, which has the known eigenvalues  $\Lambda = \ell(\ell + 1)$ . One must be a little bit more careful when looking at the limit of eq 7. We can write  $\xi = 2u/D$ , change variables, and then let  $D \rightarrow 0$ , taking into account that  $c^2 \xi^2 = Eu^2$ . The result is

$$\left[ \left( u^2 - \frac{D^2}{4} \right) R' \right]' + \left[ 4u + Eu^2 - \Lambda - \frac{m^2 D^2}{4u^2 - D^2} \right] R = 0$$

which converges to the radial equation for the helium ion ( $Z=2$ )

$$-R'' - \frac{2}{u} R' - \frac{4}{u} R = ER$$

A consequence of these remarks is that the numerical treatment of eq 7 will be rather inaccurate in the region of small  $D$  because then  $c^2$  will be very small for every value of  $E$ .

There are some further differences between the present problem and the case of the hydrogen atom, the main one being that two eigenvalues are simultaneously involved:  $E$  and  $\Lambda$ . In a simple approach, one can solve one of eqs 7 or 8 to get a relation between  $c^2$  and  $\Lambda$  and then substitute in the other equation to determine the remaining parameter. A second difference is related to the physics of the problem. Because of the cylindrical symmetry,  $L_z$  is the sole conserved quantity apart from the energy, its eigenvalue being  $m$ ;  $\Lambda$ , which would seem to be analogous to  $\ell(\ell + 1)$  of the atomic case, is not the eigenvalue of any observable. In fact, its allowed values can be positive as well as negative. This raises the following question. Suppose that the two protons start moving toward each other and eventually coincide, to form a helium nucleus. The wave function must distort and end up being identical with a  $Z = 2$  atomic function. Is there a parameter that can help in classifying the molecular wave functions and retains its significance in the atomic limit? Yes, there is: the number of nodes of  $S(\eta)$ . As the molecular ion shrinks, the wave function deforms adiabatically, keeping the same number of nodal surfaces. This number is equal to  $\ell$  for atoms. The same reasoning applies to the radial factor. The number of nodes is conserved in the united atom limit, where it is equal to  $n - 1$ ,  $n$  being the atomic radial quantum number.

## Numerical Solution

We will attempt to solve eqs 7 and 8 by numerical means, without relying on much previous specialized knowledge. Some computational details are given in the Appendix.

### The Angular Function

We begin with eq 8. The factor  $(1 - \eta^2)$  vanishes at both ends of the domain of  $\eta$ . This means that we have to solve a singular Sturm–Liouville problem (12, 18, 19). Proceeding as explained (18), we put  $\eta = -1 + u$  and look at the behavior of  $S(\eta)$  close to the singular point at  $\eta = -1$ . After clearing denominators, the equation for  $S$  becomes

$$u^2(u-2)^2S'' + 2u(u-1)(u-2)S' + [c^2u(u-1)^2(u-2) - \Lambda u(u-2) - m^2]S = 0$$

Next we assume a series solution for  $S$  of the form

$$S = u^p(a_0 + a_1u + a_2u^2 + \dots)$$

where  $a_0 \neq 0$ . When we insert this expansion into the previous equation, we find that the term of lowest degree in  $u$  is proportional to  $u^p$ , with coefficient  $a_0(4p^2 - m^2)$ . The index  $p$  must therefore satisfy the indicial equation  $4p^2 = m^2$ . Bounded solutions will only be obtained for positive  $p$ ,  $p = |m|/2$ . A similar derivation holds for  $\eta$  close to 1, with the same index value. We now define a new unknown function,  $f(\eta)$ , by

$$S(\eta) = (1 - \eta^2)^{m/2}f(\eta) \quad (9)$$

where  $f$  will be well behaved over the whole domain of  $\eta$ . By direct substitution, it is found that  $f$  is a solution of the following problem:

$$(1 - \eta^2)f'' - 2(m+1)\eta f' - [m(m+1) - \Lambda + c^2\eta^2]f = 0 \quad (10)$$

We are now in a position to apply a numerical algorithm to the solution of eq 10. We will use a result from the mathematical theory: the parity of the functions  $S(\eta)$  and  $f(\eta)$  is that of  $(-1)^{n-m}$ , if  $n$  is the number of nodes. In practice we search for solutions of given axial symmetry (given  $m$ ) and assumed energy. Bonding states will have negative energies ( $c^2 \leq 0$ ) and we will encounter levels of alternating parity with increasing  $E$ . We use the shooting method (12, 19), with starting points  $\eta = \pm 1$ . We choose  $f(1) = 1$  and  $f(-1) = \pm 1$ , depending on the required parity. The limiting form of eq 10 when  $\eta \rightarrow \pm 1$  allows us to write

$$f'(1) = \frac{m(m+1) + c^2 - \Lambda}{2(m+1)}f(1) \quad (11)$$

$$f'(-1) = \pm \frac{m(m+1) + c^2 - \Lambda}{2(m+1)}f(1)$$

We require that  $f$  and its first derivative be continuous at  $\eta$ . For even functions, the first condition is always fulfilled, whereas the second is always true for odd solutions. The effective constraints are thus

$$f'(0 + \epsilon) = f'(0 - \epsilon), \text{ even } f; \quad f(0 + \epsilon) = f(0 - \epsilon), \text{ odd } f \quad (12)$$

We describe in detail the case of the lowest-energy, bonding state. The wave function will presumably be without any

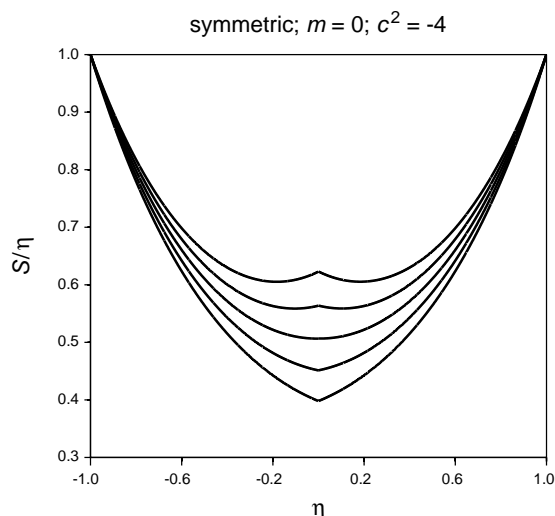


Figure 2. Shooting toward an eigenvalue of the angular equation: the symmetric case. Plots of  $S(\eta)$  are shown with, from top to bottom,  $\Lambda = -1.8, -1.7, -1.6, -1.5, -1.4$ . The best value is  $-1.59449$ .

node, so that we assume  $m = 0$ . When  $D = 1$ , we should be reasonably close to the united atom limit, with  $E = -Z^2/n^2 = -4$ . A trial-and-error process, using  $c^2 = -1$ , as implied by eq 5, converges to  $\Lambda = -0.3486$ . Figure 2 shows the first stages of such an iteration, as reflected by the shape of  $f(\eta)$ . We repeat the process for decreasing values of  $c^2$ . The search can be automated, using a simple root-seeking algorithm such as the bisection method. Since we intend to use the functional relation between  $c^2$  and  $\Lambda$  to solve the radial equation, we need about a dozen pairs of values of these parameters. While it would be possible to find the  $\Lambda$  that corresponds to an arbitrary value of  $c^2$  by interpolation, we find it more convenient to fit a fourth-degree polynomial to these data by a linear least squares method. In the united atom limit,  $D = 0$  so that  $c^2 = 0$  and  $\Lambda = 0$ , as befits an  $s$  state. Therefore, the fitting polynomial should appear as

$$\Lambda = a_1(c^2) + a_2(c^2)^2 + a_3(c^2)^3 + a_4(c^2)^4 \quad (13)$$

The coefficients, determined over the range  $-1 \geq c^2 \geq -35$ —which allows  $0 \leq D \leq 12$ , a convenient span of internuclear distances—are

$$a_1 = 0.3127477; \quad a_2 = -0.0231669$$

$$a_3 = -0.0005110; \quad a_4 = -0.0000045$$

The first excited state will again be axially symmetric, but will have an odd  $f$ . At large internuclear separation, its energy should be close to that of a  $1s$  hydrogen atom ( $E \cong -1$ ) while tending to that of a  $2p$  state ( $E \cong -1$ ) in the united atom limit ( $\ell = 1$ , one node). The electronic energy should thus be rather insensitive to  $D$ . Using  $c^2 = -1$ , we discover a solution for  $\Lambda = 1.393205$ . A typical search for an eigenvalue is shown in Figure 3. We track this root for decreasing  $c^2$  and finally fit a polynomial to the results. The constant term must be  $a_0 = 2$ , since  $\Lambda$  converges to the value  $\ell(\ell + 1)$  of a  $2p$  state.  $\Lambda$  is observed to be an almost linear function of  $c^2$ , so

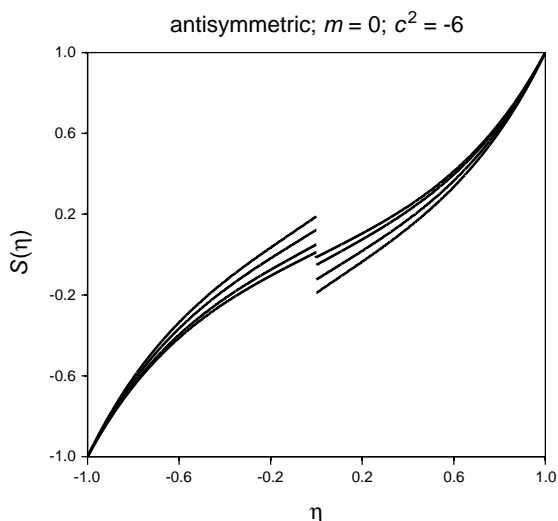


Figure 3. Search for an eigenvalue of the angular equation: the antisymmetric case.  $S$  as function of  $\eta$  with, from outside to inside,  $\Lambda = -1.3, -1.5, -1.7, -1.8$ . The most accurate value is  $-1.83105$ .

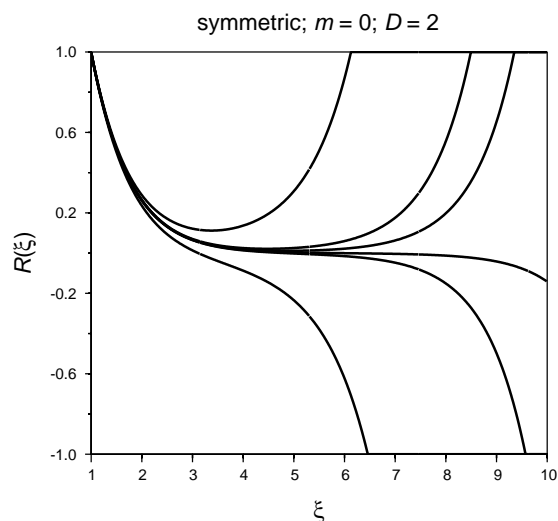


Figure 4. Searching for an eigenvalue of the radial equation. Function  $R(\xi)$  with, from bottom to top,  $E = -2.1, -2.2, -2.202, -2.205, -2.21, -2.3$  Ry. The best value is  $-2.20218$  Ry.

that a cubic was chosen. The coefficients for the range  $-1 \geq c^2 \geq -35$  are

$$\begin{aligned} a_0 &= 2.000000; & a_1 &= 0.6043499 \\ a_2 &= -0.0061888; & a_3 &= 0.0000589 \end{aligned}$$

The angular part of the wave function for any other state of the HMI can be found using this procedure. In order to gain time, values of  $c^2$  and  $\Lambda$  could be read from the tables of Abramowitz and Stegun, the computer being used only to obtain the wave function.

### The Radial Equation

We seek solutions of eq 7, using a process similar to that of the last section. Here again, the equation seems to blow up at  $\xi = 1$ . The cure should by now be familiar. We shift the origin, putting  $\xi = 1 + u$ , and look for a solution of the form  $R(\xi) = \xi^p(a_0 + a_1\xi + a_2\xi^2 + \dots)$ . The indicial equation is the same as previously and the index  $p$  is equal to  $|m|/2$ . Introducing the new function  $g(\xi)$  by

$$R(\xi) = g(\xi)(\xi^2 - 1)^{m/2} \quad (14)$$

we find that  $g(\xi)$  must be a solution of

$$(\xi^2 - 1)g'' + 2(m+1)\xi g' + [2D\xi + c^2\xi^2 + m(m+1) - \Lambda]g = 0 \quad (15)$$

We again solve this differential eigenvalue problem by the shooting method. Boundary conditions at  $\xi = 1$  are  $g(1) = 1$ , which ensures a smooth joining of  $S$  and  $R$  along the  $\xi$  axis, and a value of  $g'(1)$  derived from the differential equation

$$g'(1) = -\frac{2D + c^2 + m(m+1) - \Lambda}{2(m+1)} \quad (16)$$

We first choose a value of  $D$ . Then, we replace  $\Lambda$  by one of the polynomial expressions in  $c^2$  found in the previous subsection. Equations 15 and 16 now comprise a single unknown parameter,  $c^2$  or  $E$ . The domain of  $\xi$  being infinite, we choose a cutoff distance,  $\xi_{\max} \cong 10$ , where we require that

$|g(\xi_{\max})| \cong 0$ . The progress of a typical search is shown graphically in Figure 4, as plots of the functions  $g(\xi)$ .

The process is repeated for several  $D$  values in order to build an energy versus internuclear distance curve, and for the two lower states, symmetric and antisymmetric.

### Accuracy

A general theory of the accuracy of shooting algorithms is available (19), but is beyond the scope of this paper. We will limit ourselves to some empirical remarks. The computations were run in double precision (roughly 13-digit accuracy). For the angular equation, we recover the results tabulated by Abramowitz and Stegun (15) (6-digit accuracy) provided the integration step is not larger than  $10^{-4}$ . The least-squares fit introduces some error ( $2 \times 10^{-4}$  energy units or 3 meV). If necessary, this error can be reduced by interpolating on a finer grid. The eigenvalues of the radial equation are not so well defined, mainly because we use a cutoff distance. Tests with increasing cutoffs show that the energy should be accurate to four digits if an exact value of  $\Lambda$  is used.

### Some Results

The symmetric, lowest-energy state is usually designated as the molecular  $1\sigma_g$  state. The correlated state in the united atom limit (1s) may also be mentioned. The antisymmetric wave function belongs to the  $1\sigma_u$  state (sometimes called  $2p\sigma_u$ ).

The energies of these levels are shown as functions of  $D$  in Figure 5. We recall that the limiting values for  $D \rightarrow 0$  are  $-4$  and  $-1$  Ry, respectively and  $-1$  Ry for  $D \rightarrow \infty$ . The total molecular energy is obtained by adding the coulombic repulsion between the nuclei ( $2/D$ ) to the previous quantities. This is shown in Figure 6. The  $1\sigma_g$  state has a minimum for  $D = D_c \cong 2$ , with a binding energy of  $-1.2$  Ry. The very accurate calculations of Schaad and Hicks (9) give  $D_c = 1.9972$ , for a total energy of  $-1.205269238$  Ry. In contrast, the energy of the  $2p\sigma_u$  level is seen to be monotonically decreasing; this state is nonbonding or dissociative.

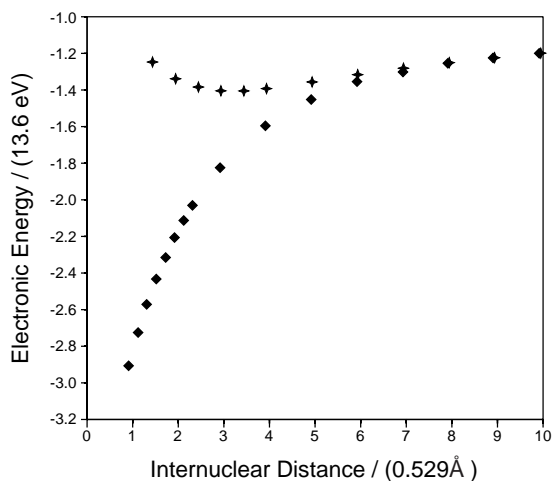


Figure 5. Electronic energy of the HMI (in units of 13.6 eV) as a function of the internuclear distance (in units of 0.529 Å). Diamonds: bonding  $\sigma_g$  state, stars: antibonding  $\sigma_u$  state.

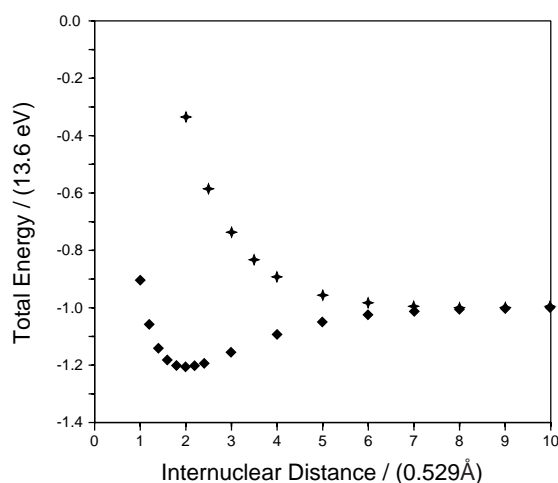


Figure 6. Total energy of the HMI; units and conventions are those of Figure 5.

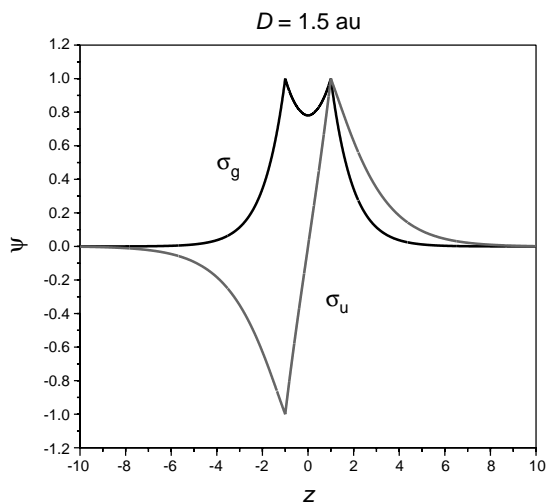


Figure 7. A cross section along the internuclear axis of the wave functions for  $D = 1.5$ . Black line:  $\sigma_g$  symmetric state. Gray line:  $\sigma_u$  antisymmetric state.

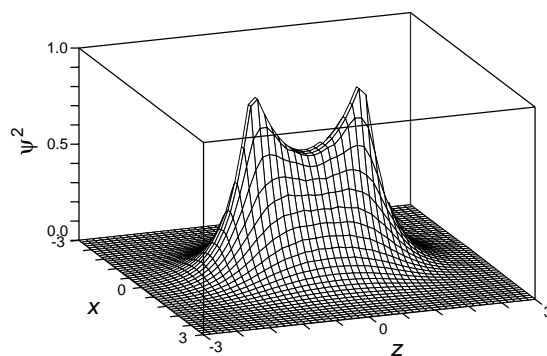


Figure 8. Plot of the electron density  $|\psi|^2$  (normalized to  $\psi(1,1) = 1$ ) for the  $\sigma_g$  bonding state. Coordinates in units of 0.529 Å.

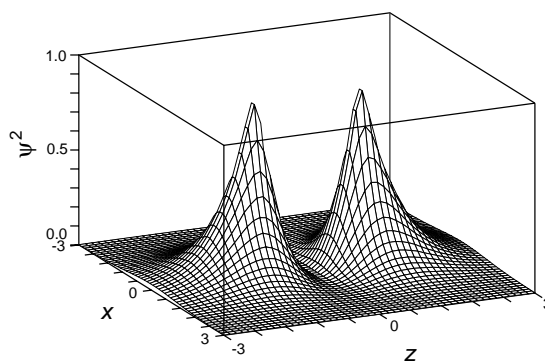


Figure 9. Plot of the electron density  $|\psi|^2$  (normalized to  $\psi(1,1) = 1$ ) for the  $\sigma_u$  antibonding state. Coordinates in units of 0.529 Å.

The complete wave functions are products of the relevant  $R(\xi)$  and  $S(\eta)$  factors. Along the molecular axis, as explained previously,  $\psi = R(\xi)$  on the right of B,  $\psi = S(\eta)$  between A and B, and  $\psi = \pm R(\xi)$  to the left of A, the sign being chosen according to the state symmetry. Figure 7 shows  $\psi$  for  $D = 1.5$ . Rather than displays of  $\psi(\xi, \eta)$ , we find it more informative to plot the electron density,  $|\psi|^2$ , as in Figures 8 and 9. These demonstrate rather strikingly the surplus of negative charge in the internuclear region, responsible for bonding, and the nodal plane of the antibonding orbital.

The HMI may also be studied within the LCAO–MO formalism. The simplest wave function, a linear combination of 1s atomic orbitals, leads to a binding energy of  $-1.13$  Ry. It is only when about 100 basis functions are included that the energy accuracy becomes comparable to that of the present approach. Ready-made software for these computations may be found on the Internet (20, 21).

## Conclusion

We have shown how a well-known but rather involved quantum mechanical problem can be completely solved numerically, using free software and a desktop computer. We found that the main difficulty in this undertaking was the comprehension of the equations and of the respective roles of

the various parameters. Running the programs for different values of  $D$ ,  $\Lambda$ , and  $E$  provides valuable insight. Several extensions of these calculations are possible. Higher states of the HMI can be investigated. As shown by Wilson and Gallup (22), heteronuclear diatomic ions are amenable to this formalism. The HMI is currently the subject of active theoretical (23) and experimental investigations (24). Some conclusions of the simple treatment have been proven to be incorrect. Particularly, the  $2p\sigma_u$  state is now known to possess a shallow long-range potential minimum (24).

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## Appendix: Computational Details

All computations reported in this article were done using the free software Scilab (25), which incorporates routines to solve initial value problems and to plot graphs of functions of one or several variables.

Algorithms for solving differential equations operate on first-order equations or systems of equations. The first task in computing  $R(\xi)$  and  $S(\eta)$  consists in transforming the relevant second-order equations into systems of two first-order equations. This is easily done at the price of a change of function. Consider the case of  $R$ ; it is determined through the auxiliary function  $g(\xi)$ . We introduce the vector of unknowns  $[z_1(\xi), z_2(\xi)]$  defined as  $z_1(\xi) = g(\xi)$  and  $z_2(\xi) = g'(\xi)$ . Equation 15 takes the form

$$\begin{aligned} z_1(\xi)' &= z_2(\xi) \\ z_2(\xi)' &= \frac{-\{2(m+1)\xi z_2(\xi) + [2D\xi + c^2\xi^2 + m(m+1) - \Lambda]z_1(\xi)\}}{\xi^2 - 1} \end{aligned}$$

The program operates on discrete values. We choose a step size,  $h$ , and initial and final values of  $\xi$  and create a vector of abscissas  $\{X_k\}$ , numbered from 1 to  $n$ . The program will generate approximations to  $z_1$  and  $z_2$ , in the form of two arrays  $Z_{1,k}$  and  $Z_{2,k}$ ,  $k = 1, \dots, n$ . The program should start at  $X_1 = 1$ , where the initial conditions (see eq 16) apply. This leads to a division by zero in eq 15, so that we start the actual computation at  $X_2 = h$ , using the known slope at  $X_1$  to set the values of  $Z_{1,2}$  and  $Z_{2,2}$ . At the end, we insert the correct values of  $Z_{1,1}$  and  $Z_{2,1}$ .

The definition and solving of eq 15 are taken care of in a few lines of code by Scilab. A double slash (//) indicates a comment. If  $z$  is a vector,  $z'$  is the transposed vector. Input and output statements have been deleted.

```
//radial equation in terms of vector z
deff("[zdot]=g(x,z)",...
"zdot=[z(2); (-2*(m+1)*x*z(2)-(2*D*x+m*(m+1)-
L+c2*x*x)*z(1))/(x*x-1)]")
step = 0.001;
x0=1+step;
x=x0:step:10; //abscissas, starting at point next to 1.
c2=D*D*E/4;
//L(c) for an antisymmetric f
L=(((-6.373E-7*c2-0.0001053)*c2-
0.0071351)*c2+0.5992722)*c2+1.9994397;
//initial conditions
slope = -(-L+m*(m+1)+2*D+c2)/(m+1)/2;
z0=[1+step*slope,slope]';
//solve differential equation
z=ode(z0,x0,x,g);
//compute R from z
temp=x.*x-1;
temp=temp.^(m/2);
//extract values of g
zz=temp.*z(1,:);
//insert missing values
zz=[1,zz];xt=[1,x];
```

According to the shooting method, we run this program for various values of  $E$  while watching  $Z_{1,n}$ . We stop when this quantity is smaller than a prescribed threshold.

The code needed to solve the angular eq 10 is quite similar, except that the two cases of even and odd  $l$  must be considered separately and we shoot from both ends of the interval, inward, and try to comply with eq 12.

The same software incorporates a least-squares fitting routine, allowing an easy computation of the polynomial regression of  $\Lambda$  versus  $c^2$ .