

Highly accurate calculation of the energy levels of the H_2^+ molecular ion

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Received 14 July 1997

Abstract. In this paper we present a new numerical method for the calculation of energy levels of the non-relativistic molecular ion H_2^+ , which is ‘exact’, i.e. beyond the Born–Oppenheimer approximation. It relies on the choice of a suitable basis using the dynamical symmetries of the system, in which the Hamiltonian is a sparse banded matrix. The numerical diagonalization of the Hamiltonian produces well converged energy levels, with a typical accuracy of 10^{-12} , and also highly accurate wavefunctions.

The H_2^+ molecular ion is the simplest molecular ion: it involves three particles interacting mainly through Coulomb forces. As a first step, the electron being about 2000 times lighter than the protons, the Born–Oppenheimer approximation can be used. The lowest electronic energy curve has a minimum supporting several bound states (20 vibrational states for zero total angular momentum). Such states have extremely long lifetimes, as they can only decay to a similar ro-vibrational state with a lower energy by spontaneous emission, a process whose probability is low because the frequency of the emitted photons is low (the motion of the nuclei is slow) and because single-photon decay is forbidden by selection rules. Hence, optical transitions between two ro-vibrational states of the H_2^+ , or similar molecular ions such as D_2^+ , should have extremely narrow linewidths and are potentially good candidates for frequency standards in the infrared region. The difficulty is that these optical transitions are strongly forbidden with one photon: they are only allowed as multiphotonic transitions involving intermediate electronic excited states. As the latter lies at a much higher energy, the multiphoton processes are far from resonance, which explains why only a very few spectroscopic measurements on H_2^+ have been reported [1].

In the Born–Oppenheimer approximation, the energy difference between, for example, the vibrational $v = 0$ and 1 states is proportional to the square root of the ratio m/M of the electron mass to the proton mass. It is about 2000 cm^{-1} for H_2^+ . Hence, from the frequency of an optical transition, one could deduce the ratio m/M . The latter is known by direct measurements in a ion trap [2], with an accuracy of 2×10^{-9} , which is rather modest compared to the accuracy of the better frequency measurements in the infrared and visible spectra [3].

However, if one wants to extract the value of m/M from a highly accurate spectroscopic measurement in H_2^+ , one needs accurate *ab initio* calculations at the same level of accuracy. Obviously, this is far beyond the standard Born–Oppenheimer approximation (see below). In this paper, we present a new method for calculating energy levels of the non-relativistic

H_2^+ molecular ion with arbitrary accuracy and show that it can be used for the lowest energy levels on an ordinary workstation, producing energy levels with a relative accuracy of better than one part in 10^{12} .

The non-relativistic Hamiltonian of a general three-body Coulomb system is

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + \frac{\mathbf{p}_3^2}{2m_3} + \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_2}{r_{12}} + \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_3}{r_{13}} + \frac{e^2}{4\pi\epsilon_0} \frac{Z_2 Z_3}{r_{23}} \quad (1)$$

where \mathbf{p}_i is the momentum of particle i ($i = 1, 2, 3$) with mass m_i and charge $Z_i e$ and r_{ij} is the distance between particles i and j .

In the following, we assume, as in H_2^+ , that particles 1 and 2 are identical (same charge Z , same mass M)[†] and particle 3 has mass m and charge Z' . As the total momentum $\mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3$ is a constant, the Hamiltonian can be written in the frame where the centre of mass is at rest, measuring the positions of particles 1 and 2 with respect to particle 3 by $r_1 = r_{13}$ and $r_2 = r_{23}$:

$$H = \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2)(m + M)}{2mM} + \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{m} + \frac{Z^2 e^2}{4\pi\epsilon_0 r_{12}} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_1} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_2}. \quad (2)$$

This Hamiltonian is well suited when particle 3 is much heavier than particles 1 and 2 ($m \gg M$). Indeed, the term $\mathbf{p}_1 \cdot \mathbf{p}_2/m$ can be treated as a perturbation, the rest of the Hamiltonian being the Hamiltonian for an infinitely massive particle 3 and reduced mass $\mu = mM/(m + M)$ for particles 1 and 2. This is, for example, the case for the helium atom ($Z = -1$; $Z' = 2$) or the H^- ion ($Z = -1$; $Z' = 1$). $\mathbf{p}_1 \cdot \mathbf{p}_2/m$ is then the term responsible for the so-called 'specific mass shift'.

On the other hand, the H_2^+ molecular ion is such that $m \ll M$; the $\mathbf{p}_1 \cdot \mathbf{p}_2/m$ is comparable to the other terms of the Hamiltonian. However, the Hamiltonian can be rewritten as

$$H = \frac{(\mathbf{p}_1 + \mathbf{p}_2)^2(m + 2M)}{4mM} + \frac{(\mathbf{p}_1 - \mathbf{p}_2)^2}{4M} + \frac{Z^2 e^2}{4\pi\epsilon_0 r_{12}} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_1} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_2} \quad (3)$$

where the term $(\mathbf{p}_1 - \mathbf{p}_2)^2/4M$ can now be treated as a small perturbation. This is nothing but the Born–Oppenheimer approximation. Indeed, $(\mathbf{p}_1 - \mathbf{p}_2)/2$ represents the relative momentum of the two nuclei, while $-(\mathbf{p}_1 + \mathbf{p}_2)$ is the momentum of the electron with respect to the middle of the internuclear axis. Hence the idea is to freeze the internuclear distance r_{12} at a fixed value, solve the electronic equation for the Hamiltonian with two fixed Coulomb centres:

$$H_{\text{electronic}} = \frac{(\mathbf{p}_1 + \mathbf{p}_2)^2(m + 2M)}{4mM} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_1} + \frac{ZZ' e^2}{4\pi\epsilon_0 r_2} \quad (4)$$

and finally treat the remaining term:

$$H - H_{\text{electronic}} = \frac{(\mathbf{p}_1 - \mathbf{p}_2)^2}{4M} + \frac{Z^2 e^2}{4\pi\epsilon_0 r_{12}} \quad (5)$$

as a perturbation.

Different variants of the Born–Oppenheimer approximation exist, where a small part (of the order of m/M) of the kinetic term in $H_{\text{electronic}}$ is incorporated in the perturbation [4, 5]. However, all these methods are basically perturbative methods where the small parameter is

[†] For heteronuclear molecular ions like HD^+ , a similar reduction is still possible, at the expense of an additional term in the final Hamiltonian, which slightly increases the number of non-zero matrix elements in the matrix to diagonalize. This, however, does not affect the sparse character of the matrix and the energy levels can be computed with the same accuracy as for homonuclear molecules.

m/M . Consequently, the error made in the energy levels will be of the order of m/M , i.e. several tens of cm^{-1} , at zeroth order. At first order, the usual adiabatic approximation where only the diagonal term of the perturbation is taken into account, the calculation is relatively easy, the error being of the order of $(m/M)^2$, i.e. about $0.01\text{--}0.1 \text{ cm}^{-1}$ [6]. At second order, the calculation becomes extremely difficult and complicated as it involves an infinite sum over all excited electronic states, including the dissociative ones. The best available results reach an accuracy of the order of 0.001 cm^{-1} , which is nevertheless insufficient for our metrological purpose.

We used the numerical calculations developed in recent years to obtain accurate *ab initio* energy level calculations for double excited states of the helium atom [7, 8] and transposed it to the H_2^+ molecular ion, a comparable three-body Coulomb problem, where only the particle charges and masses are changed. The general idea is to expand the eigenstates of the full exact Hamiltonian, equation (3), onto a suitable basis set such that: (i) the members of the basis set are reasonably close to the eigenstates; (ii) the matrix elements of the Hamiltonian have strong selection rules so that only a small fraction of them are non-zero; (iii) the remaining matrix elements are easy to calculate, preferably with simple analytic expressions. The existence of such a basis set is far from obvious. It can be constructed by a careful analysis of the dynamical symmetries of the Coulomb interaction [9] which goes beyond the scope of this paper.

The first step in building such a basis is to analyse the exact symmetry properties which make the calculation of energy levels simpler. The first one is the translational invariance already used above. The second one is the rotational invariance, the associated conserved quantity being the total angular momentum L (it is a purely orbital angular momentum as we do not include spin in this discussion) and the third one is the total parity. If two of the particles are identical, a further simplification is possible: states can be divided into ‘singlet’ and ‘triplet’ states. Here we use these traditional terms to distinguish between symmetric and antisymmetric (with respect to the exchange of the two particles) states. The ground state of the H_2^+ molecular ion (and also of the helium atom) is an $L = 0$, even-parity, singlet state, i.e. a $^1S^e$ state in the standard atomic notation.

For H_2^+ , in the Born–Oppenheimer approximation, additional approximate constants of motion exist: the projection of the angular momentum on the internuclear axis—associated with the Λ good quantum number—the two quantum numbers labelling the electronic state and the vibrational quantum number v . For the sake of simplicity, here we will only consider $L = 0$ states ($J = 0$ in the standard molecular notation)† belonging to the ground electronic state usually denoted as $X^2\Sigma_g^+$ in the molecular notation. There are 20 such bound states ranging from $v = 0$ to 19 in H_2^+ and 28 bound states from $v = 0$ to 27 in D_2^+ .

For all such states, the angular dependence can be exactly (i.e. not only in the Born–Oppenheimer approximation) factored out. The wavefunction depends only on the three mutual distances $\psi = \psi(r_1, r_2, r_{12})$. To solve the Schrödinger equation, it is convenient to use the so-called perimetric coordinates [10]:

$$x = r_1 + r_2 - r_{12} \quad y = r_1 - r_2 + r_{12} \quad z = -r_1 + r_2 + r_{12}. \quad (6)$$

When written in perimetric coordinates, the Schrödinger equation can be reduced to polynomial combinations of the $x, y, z, \partial/\partial x, \partial/\partial y$ and $\partial/\partial z$ operators. The expressions are too complicated to be given here (see [9]). Moreover, using the dynamical group structure $SO(2, 1)$ successfully developed for the Coulomb interaction [11], we can express the full Schrödinger equation as combinations of the generators of three different $SO(2, 1)$

† Exact *ab initio* calculations are also possible at least for $L = 1$ states as shown in [8], at the cost of diagonalizing slightly larger matrices.

groups. This leads to the idea of expanding the eigenstate on a basis associated with known irreducible representations of the $SO(2, 1)$ group. This ‘perimetric’ basis is of the type $|n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle$ with the following basis functions:

$$\langle u|n\rangle = \phi_n(u) = \sqrt{\alpha_u} L_n(\alpha_u u) e^{-\alpha_u u/2} \quad \text{for } u = x, y, z \quad (7)$$

where L_n is the Laguerre polynomial, n a non-negative integer and α_u a free positive scaling parameter.

This expression resembles the Hylleraas-type variational calculation [12, 13], but it has the enormous advantage that, due to the underlying group structure, all the operators in the Schrödinger equation have simple selection rules in the perimetric basis:

$$\begin{aligned} |\Delta n_x| &\leq 2 & |\Delta n_y| &\leq 2 & |\Delta n_z| &\leq 2 \\ |\Delta n_x| + |\Delta n_y| + |\Delta n_z| &\leq 3. \end{aligned} \quad (8)$$

Hence, when written in the perimetric basis, the Schrödinger equation takes the following form:

$$(\mathcal{A} - E_i \mathcal{B})|\psi_i\rangle = 0 \quad (9)$$

where $|\psi_i\rangle$ is the eigenvector associated with the eigenenergy E_i , and \mathcal{A} and \mathcal{B} are two sparse banded real-symmetric matrices. All matrix elements of \mathcal{A} and \mathcal{B} have simple algebraic expressions, polynomials of n_x , n_y and n_z .

If the full basis set, equation (7), is used, the energy levels are, of course, independent of the scaling parameters α_x , α_y and α_z . In a practical numerical calculation, the basis set has to be truncated. We choose to include in the basis all the states with $n_x + n_y + n_z \leq N_{\max}$. The scaling parameters are taken such that $\alpha = \alpha_x = 2\alpha_y = 2\alpha_z$. The resulting matrices have a size of approximately $N_{\max}^3/12$ and (half-)bandwidth $N_{\max}^2/4$. For a typical value, $N_{\max} = 70$, the size is 31 746 and the (half-)bandwidth is 1333. Even within the band of the matrix, many matrix elements are zero because of the selection rules, equation (8). The sparsity of the matrix (proportion of non-zero elements) is typically less than 1%. The generalized eigenvalue problem is solved by using the shifted Lanczos algorithm [14], allowing calculations of the few eigenvalues of interest in a reasonable CPU time. Results presented hereafter can be obtained on a normal workstation, in less than 10 min of CPU time.

In figure 1, we plot the numerically computed energy of the ground state $v = 0$ as a function of the scaling parameter α . For all the calculations reported in this paper, we use atomic units ($\hbar = 4\pi\epsilon_0 = e^2 = m = 1$) where m is the mass of the electron (not the reduced mass). We used $N_{\max} = 70$. The ratio M/m is taken equal to 1836.152 701, in order to compare with the published value in [12], one of the most accurate results available. The agreement is excellent (a difference at the level of 1×10^{-8} au). However, our result is more precise because, as shown in figure 1, the result of our calculation presents a minimum as a function of the scaling parameter α . From the variational principle, the exact result is slightly smaller than the value at the minimum. Variations in the vicinity of the optimum value of α , where the minimum is reached, allow us to roughly estimate the accuracy of the calculation. In figure 1, the energy is constant to within few 10^{-13} when the scaling parameter is changed. From complementary calculations (with a smaller basis size), we estimate the uncertainty of our result to be smaller than 1×10^{-12} au, i.e.

$$E\left(v = 0, J = 0, \frac{M}{m} = 1836.152\,701\right) = -0.597\,139\,063\,123 \pm 1 \times 10^{-12}. \quad (10)$$

This is, as far as we know, the most accurate calculation ever published for the non-relativistic H_2^+ molecular ion.

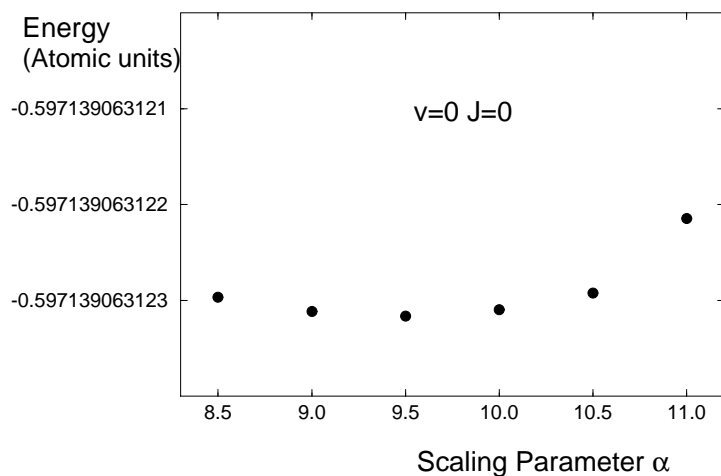


Figure 1. The energy of the ground state ($v = 0$, $J = 0$) of the H_2^+ molecular ion, computed using numerical diagonalization of the ‘exact’ non-relativistic Hamiltonian (beyond the Born–Oppenheimer approximation), equation (3), in a perimetric basis, versus the scaling parameter $\alpha = \alpha_x = 2\alpha_y = 2\alpha_z$, see equation (7). $N_{\max} = 70$ has been used, corresponding to a basis size equal to 31 746; the ratio M/m of the proton mass to the electron mass is taken to be equal to 1836.152 701. The energy is given in atomic units where the electron mass is 1. The plot shows that the energy is well converged with an accuracy of better than 1×10^{-12} au.

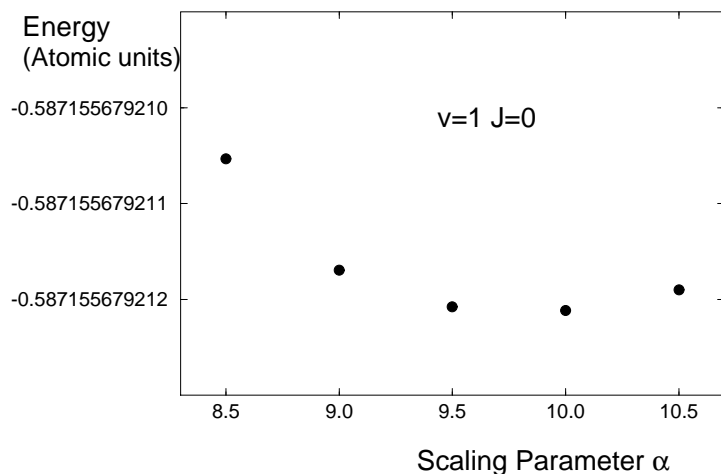


Figure 2. Same as figure 1, but for the ($v = 1$, $J = 0$) excited state. $N_{\max} = 74$ has been used. Again, the energy level is determined with an accuracy of around 1×10^{-12} au.

A similar accuracy can be reached for excited states, although with a slightly larger basis. For example, figure 2 shows the change of the energy of the first excited state $v = 1$ as a function of the scaling parameter α . We used $N_{\max} = 74$ and the same value of M/m .

The result is converged at the level of 1×10^{-12} au:

$$E\left(v = 1, J = 0, \frac{M}{m} = 1836.152701\right) = -0.587155679212 \pm 1 \times 10^{-12}. \quad (11)$$

For a larger basis size, the calculations will have to be accomplished on a supercomputer and we believe that our method is able to compute the energies of the excited states, at least up to $v = 10$, with an accuracy of the order of 1×10^{-12} au, i.e. 2×10^{-7} cm $^{-1}$ or 6 kHz. For the lowest vibrational states, 1×10^{-15} could probably be reached, only limited by the rounding errors in the computer. We have also checked our calculations against the published ones [4–6, 12, 13] for different values of m/M . In general, we have found good agreement, our calculations being the most accurate ones.

In figure 3, we plot the energy difference between the $v = 0$ and 1 states, as a function of the mass ratio M/m . As expected from the Born–Oppenheimer approximation and assuming a harmonic approximation of the molecular potential around the equilibrium distance, it is roughly proportional to $\sqrt{m/M}$. In fact, anharmonicity is responsible for small deviations from this simple law, and a straight line with slope 0.47 (instead of 0.5) is observed in a double-logarithmic plot. The plotted energy difference, or a similar one between different (v, J) ro-vibrational states, is a quantity which could be accurately measured in a two-photon experiment (see the discussion at the beginning of this paper). The present results

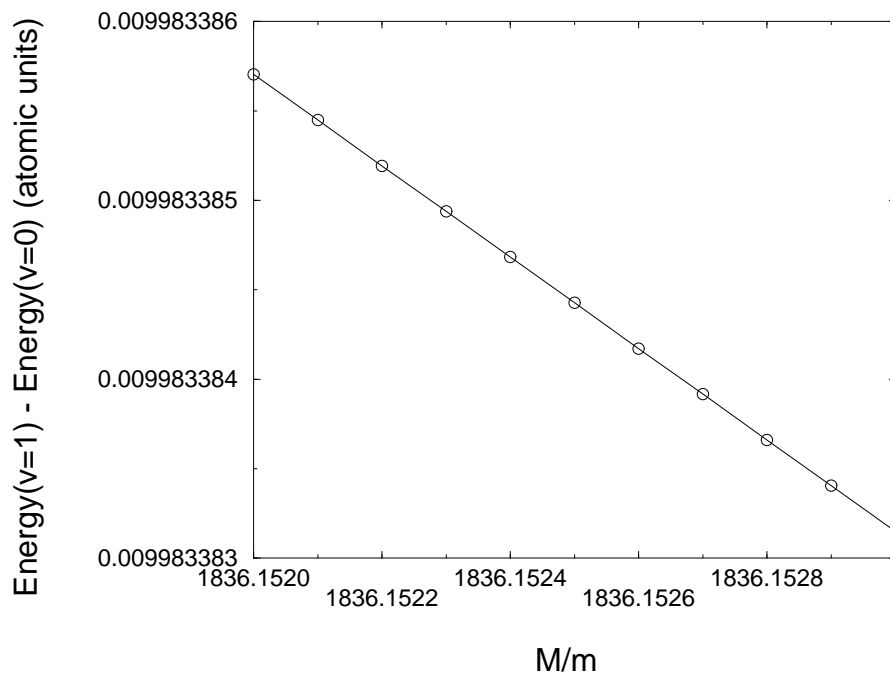


Figure 3. The energy difference between the $(v = 0, J = 0)$ and $(v = 1, J = 0)$ states plotted as a function of the ratio M/m . As expected from a harmonic approximation in the well of the molecular potential (in the Born–Oppenheimer approximation), the energy difference is approximately proportional to the classical vibration frequency, scaling like $\sqrt{m/M}$. For these exact results, one finds a slope -0.47 in a double-logarithmic plot, instead of the predicted -0.5 slope. The difference comes from the anharmonic character of the molecular potential. In any case, measuring such an energy difference in a spectroscopic experiment would allow us to determine m/M .

show that it can be computed, in the non-relativistic approximation, with a *relative* accuracy of better than 1×10^{-10} , allowing the determination of m/M with an accuracy 10 times better than the present measurement [2].

The wavefunctions, calculated from the eigenvectors of equation (9), are also interesting and make possible accurate tests of the Born–Oppenheimer approximation. For example, in figure 4, we have plotted the numerically computed electronic wavefunction at a fixed value of the internuclear distance. Because of the invariance around the internuclear axis (exactly valid for $J = L = 0$ states), it has to be plotted only in a plane containing the internuclear axis. In figures 4(a) and (b), it is represented for the $v = 0$ and 1 states at the internuclear distance $r_{12} = 2$ au, close to the equilibrium distance. As expected from the Born–Oppenheimer approximation, both states show almost exactly the same electronic density, the differences being indistinguishable in the figure. However, at the Born–Oppenheimer approximation, the $v = 1$ wavefunction should vanish exactly at $r_{12} = 2.0863$ au, where the vibrational function has its node. Thus, a plot of the exact electronic density at this value is a *direct* test of the breakdown of the Born–Oppenheimer approximation. This is done in figure 4(c): as expected, the electronic wavefunction has a completely different shape resulting from small admixtures of excited electronic states—with the same exact quantum numbers, i.e. $L = 0$, even-parity ‘singlet’ states—in the zero-order Born–Oppenheimer wavefunction. As can be seen in figure 4(c), the electronic density is almost zero at the nucleus—in sharp contrast with the maximum observed in figure 4(b), and roughly displays nodal lines perpendicular to the internuclear axis. This can be interpreted as the dominant admixture coming from the $2p, m = 0$ atomic orbital. Also, the maximum value of the electronic density at $r_{12} = 2.0863$ au is about 10^{-6} of the total maximum of the electronic density (reached around $r_{12} = 1.75$ au), i.e. of the order of $(m/M)^2$. This confirms that the admixture of other electronic states in the wavefunction is of the order of m/M , as expected from a perturbative approach [15].

At the level of accuracy reached by our calculations, the relativistic and QED corrections [16] have to be calculated carefully. The most important ones, like the p^4 term in the kinetic energy, can be included in the Hamiltonian at a negligible cost, as only a few non-zero matrix elements would have to be added. The other corrections will have to be calculated perturbatively. Fortunately, most of the corrections are due to the motion of the electron, the protons being much slower. Hence, the situation is more favourable than in the helium atom. The relativistic and QED corrections are mainly one-electron contributions, similar in principle to those calculated in the hydrogen atom.

The starting point of the perturbative analysis is, of course, the non-relativistic wavefunction. Again, the Born–Oppenheimer wavefunctions (accurate only at first order in m/M) will be sufficient to determine the first corrections, let us say at the level 5×10^{-9} au $\simeq 0.001$ cm $^{-1}$ as done, for example, in [6]. At the 10^{-12} au accuracy level, an ‘exact’ non-relativistic wavefunction is necessary. Our calculations are able to provide them. This is illustrated in figure 5 which shows the calculated electronic density (square of the wavefunction) on one of the nuclei as a function of the scaling parameter α for the internuclear distance $r_{12} = 2$ au. This density is an essential ingredient for the calculation of, for example, the Lamb shift correction. As shown in figure 5, for the ground state $v = 0$ of the H_2^+ molecular ion, it can be determined with 10^{-6} accuracy, three orders of magnitude better than the first-order Born–Oppenheimer approximation. This should be sufficient for calculating relativistic and QED corrections at the 10^{-12} au level. Moreover, it is likely that most corrections will be very similar for the different bound ro-vibrational levels, because they have essentially the same electronic state. Hence, most of the corrections should cancel out in the energy difference between states, the quantity to be measured experimentally. It

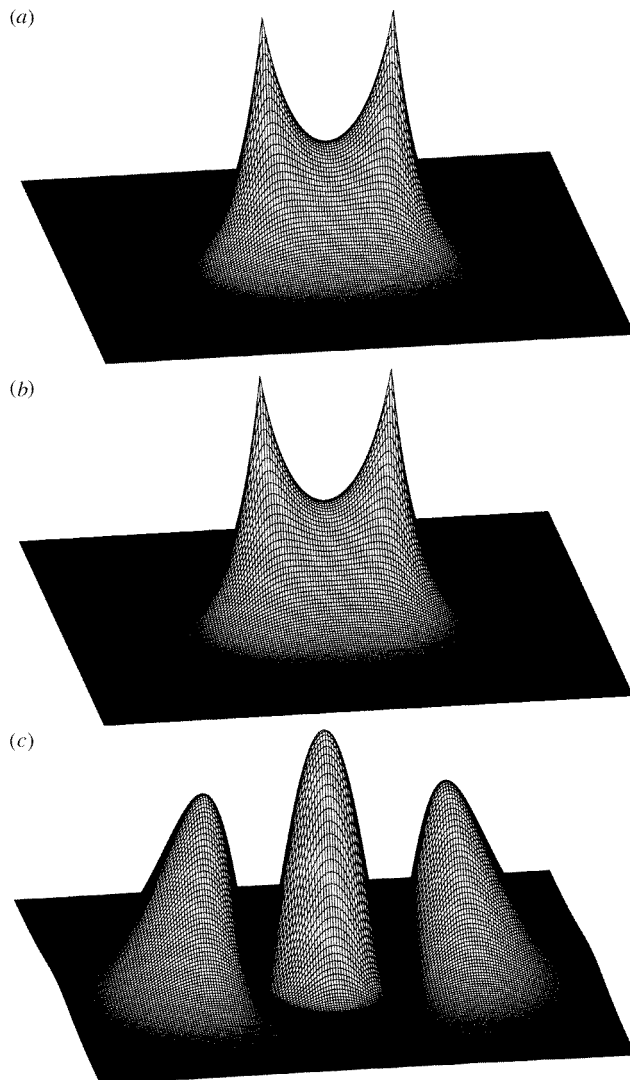


Figure 4. Electronic density probability of the numerically calculated eigenfunctions of the H_2^+ molecular ion, at fixed internuclear distance r_{12} , plotted in a plane containing the internuclear axis, with respect to the two electronic coordinates (X_e, Y_e) . The displayed part of the wavefunctions correspond to values of X_e and Y_e ranging from -4 to 4 au. (a) $(v = 0, J = 0)$ ground state, $r_{12} = 2$ au. The electronic density is peaked at the nuclei, as expected from the Born–Oppenheimer approximation. (b) $(v = 1, J = 0)$ excited state, $r_{12} = 2$ au. The electronic density is almost exactly identical to the one of the $v = 0$ state, as expected from the Born–Oppenheimer approximation. (c) $(v = 1, J = 0)$ excited state $r_{12} = 2.0863$ au. This value is the node of the vibrational wavefunction in the Born–Oppenheimer approximation. Hence, this plot is a direct measure of the breakdown of this approximation. It shows a minimum at the nuclei, and three maxima along the internuclear axis. This is due to the admixture in the exact wavefunction of excited electronic states, here mainly coming from the $2p, m = 0$ atomic orbital, as can be seen from the nodal line roughly perpendicular to the internuclear axis. As expected, this admixture is of the order of m/M in the wavefunction, i.e. $(m/M)^2$ in the electronic density.

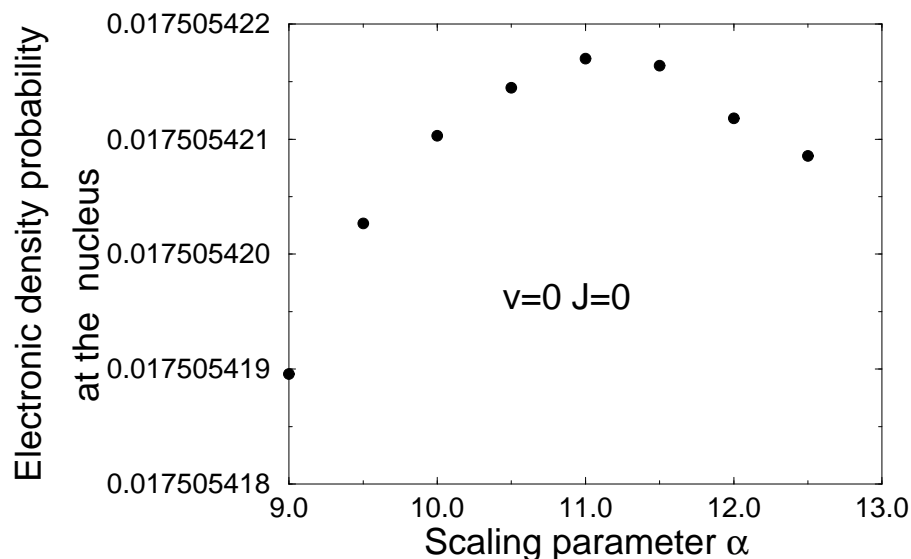


Figure 5. The probability of finding the electron on one nucleus ($r_1 = 0$) at the internuclear distance $r_{12} = r_2 = 2$ au versus the scaling parameter α . This shows that our numerically calculated wavefunction has an accuracy of better than 1×10^{-6} and thus provide a good starting point for accurate calculations of the relativistic and QED corrections.

could be that less accurate calculations of the relativistic and QED corrections will be sufficient.

In conclusion, we have presented a new numerical method which allows a highly accurate ‘exact’ calculation of the energy levels of the H_2^+ molecular ion, beyond the standard Born–Oppenheimer approximation. Our results agree with previously published results, and are the most accurate ever published, reaching an accuracy of 10^{-12} for the ($v = 0$, $J = 0$) and ($v = 1$, $J = 0$) states. They also provide a starting point for accurate calculations of relativistic and QED corrections.

Acknowledgments

We thank F Biraben and P Indelicato for useful discussions. CPU time on Cray C98 and J90 computers has been provided by IDRIS. Laboratoire Kastler Brossel is laboratoire de l’Université Pierre et Marie Curie et de l’Ecole Normale Supérieure, unité associée 18 du CNRS.

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