About the ground state of the H$_3^+$ hydrogen molecular ion

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Abstract

Three simple 7−, (7 + 3)−, 10−parametric trial functions for the H$_3^+$ molecular ion are presented. Each of them subsequently provides the most accurate approximation for the Born–Oppenheimer ground state energy among several-parametric trial functions. These trial functions are chosen following a criterion of physical adequacy; they include the electronic correlation in the exponential form ∼ exp(γ r$_{12}$), where γ is a variational parameter. The Born–Oppenheimer energy is found to be $E = -1.34034$, $-1.34073$, and $-1.34159$ au, respectively, for the optimal equilateral triangular configuration of protons with the equilibrium interproton distance $R = 1.65$ au. The variational energy agrees to three significant digits with the most accurate results available at present as well as for major expectation values.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The two-electron hydrogenic molecular ion H$_3^+$ is one of the most abundant chemical compounds in the Universe. Its existence is of fundamental importance in chemistry and physics, in particular, because of its stability towards dissociation to H$_2$ + p; the H$_3^+$ ion is also a major proton donor in chemical reactions in interstellar space. The H$_3^+$ was discovered experimentally by Thomson in 1912 [1]. The system was very difficult for theoretical studies. Many theoretical methods were developed to study low-lying quantum states of this system. In particular, it became clear very quickly that interelectron correlation is of great importance and it should be included in the variational trial function explicitly which assures a faster convergence. This conclusion was similar to the one drawn by James and Coolidge for the H$_2$ molecule. Usually, the interelectron correlation was written in the form $r_{12}$ (Hylleraas [2] – James–Coolidge [3] form) or exp($-αr_{12}^2$) (Gaussian form, see e.g. [4]).

Recently, Korobov [5] showed in an explicit way that for the case of the helium atom the use of the exponential form exp($γ r_{12}$) dramatically improves convergence and leads, in fact, to the most accurate results for the ground state energy for the helium atom at present. Later on, it was shown that the similar use of the exponential correlation exp($γ r_{12}$) for the H$_3$ molecule allows us to construct the most accurate trial function among the few-parametric trial functions [6]. A hint of why this $r_{12}$-dependence leads to the fast convergent results was given in [6]. In 2006, a discussion meeting took place in London, UK, where different properties of the H$_3^+$ ion and, in particular, various theoretical approaches to study the H$_3^+$ ion were presented (see [7]).

The goal of this paper is to propose a simple, compact, easy-to-handle trial function depending exponentially on $r_{12}$ with few nonlinear parameters which leads to a highly accurate Born–Oppenheimer ground state energy and major expectation values. We are not aware of previous studies of the H$_3^+$ ion with trial functions involving $r_{12}$ in an exponential form with a single exception [8] where H$_3^+$ in a linear configuration was explored.

In this paper, atomic units ($h = e = m_e = 1$) are used throughout.

2. The H$_3^+$ ion in the Born–Oppenheimer approximation

The Hamiltonian which describes the ion H$_3^+$ under the assumption that the protons are infinitely massive (the Born–Oppenheimer approximation of zero order) and located at the...
The variational procedure is used as a method to explore the problem. The recipe for choosing the trial function is based on arguments of physical relevance, e.g. the trial function should support the symmetries of the system, and has to reproduce the Coulomb singularities and the asymptotic behaviour at large distances adequately (see e.g. [12–14]). In practice, the use of such trial functions implies the convergence of a special form of the perturbation theory where the variational energy is the sum of the first two terms of the perturbation series. Let us recall the essentials of this perturbation theory (for details, see [12–14]). Let us assume that the original Hamiltonian has a form \( \mathcal{H} = -\Delta + V \), where \( \Delta \) is the Laplacian. As a first step we choose a trial function \( \psi^{(\text{trial})} \) (normalized to one) and find a potential for which such a trial function \( \psi^{(\text{trial})} \) is an exact eigenfunction, i.e. \( V_{\text{trial}} = \Delta \psi^{(\text{trial})}/\psi^{(\text{trial})} \), with energy \( E_{\text{trial}} = 0 \). In a pure formal way we can construct a Hamiltonian \( \mathcal{H}_{\text{trial}} = -\Delta + V_{\text{trial}} \) such that \( \mathcal{H}_{\text{trial}} \psi^{(\text{trial})} = 0 \). It can easily be shown that the variational energy \( E_{\text{var}} = \langle \psi^{(\text{trial})} | \mathcal{H}_0 | \psi^{(\text{trial})} \rangle \) is nothing but the first two terms in the perturbation theory where the unperturbed problem is given by \( \mathcal{H}_{\text{trial}} \) and the perturbation is the deviation of the original potential \( V \) from the trial potential \( V_{\text{trial}} \), namely \( V_{\text{perturbation}} = V - V_{\text{trial}} \). Eventually, we arrive at the formula

\[
E_{\text{var}} = E_{\text{trial}} + E_1(V_{\text{perturbation}}),
\]

Here, \( E_1(V_{\text{perturbation}}) = \langle \psi^{(\text{trial})} | V_{\text{perturbation}} | \psi^{(\text{trial})} \rangle \) is the first energy correction in the perturbation theory, where the unperturbed potential is \( V_{\text{trial}} \). It is worth noting that if the trial function is the Hartree–Fock function, the resulting perturbation theory is nothing but the Moeller–Plesset perturbation theory (see e.g. [16], section 15.18)³.

One of the criteria of convergence of the perturbation theory in \( V_{\text{perturbation}} = V - V_{\text{trial}} \) is a requirement that the ratio \( |V_{\text{perturbation}}/V| \) should not grow when \( r \) tends to infinity in any direction. If this ratio is bounded by a constant it should be less than 1. In fact, it is a condition that the perturbation potential is subordinate with respect to the unperturbed potential. The value of this constant controls the rate of convergence—a smaller value of this constant leads to faster convergence [13]. Hence, the above condition underlines the importance of the large-range behaviour of the trial functions. In the physics language the above requirement means that the phenomenon of Dyson’s instability should not occur (for a discussion see [12])².

4. Correlated trial function

Among the different forms to include explicit electronic correlation in the trial wavefunction for two-electron problems, we mention three major approaches (see e.g. [18]): the linear in \( r_{12} \) Gaussian \( \exp(\gamma r_{12}^2) \) and exponential \( \exp(\gamma r_{12}) \) terms. Among them, the only factor \( \exp(\gamma r_{12}) \) fulfills the adequate requirements for a trial function described above. Thus, following the guidelines of section 3 and the convergence requirement of the perturbation theory, we choose the trial function for the ground state in the following form:

\[
\psi_0 = (1 + P_{12}) \times \sum_{\text{perm}(A,B,C)} e^{-a_1 r_{1A} - a_2 r_{1B} - a_3 r_{1C} - a_4 r_{2A} - a_5 r_{2B} - a_6 r_{2C} + \gamma r_{12}^2},
\]

where the sum runs over the permutations of the identical protons \( A, B, C \) (\( S_3 \) symmetry), and \( P_{12} \) is the operator which interchanges electrons (\( 1 \leftrightarrow 2 \)). The variational parameters

³ It is worth noting that the question about convergence of the Moeller–Plesset perturbation theory is not settled yet [17].

² It is worth noting that this procedure for a selection of the trial function was applied successfully to a study of one-two-electron molecular systems in a magnetic field leading to highly accurate results. Many of these results are the most accurate at the moment (see [14] and [15]).
Table 1: A selection of the calculations for the Born–Oppenheimer ground state energy at equilibrium distance of \( \text{H}_3^+ \). Record calculations of [10] (2009) and [11] (1995). CI denotes configuration interaction, STO—Slater-type orbitals, GTO—Gaussian-type orbitals, GG—correlated Gaussians (Gaussian geminals), R12—the CI calculation augmented by terms linear in \( r_{12} \), ECSG—explicitly correlated spherical Gaussian functions. 

(i) Trial function (5) with the parameters of \( \psi_0 \) kept fixed and equal to ones found for (3). 
(ii) Trial function (5) with all ten parameters optimized.

| \( E \) (au) | \( R \) (au) | Method | Reference |
|-----------|---------|--------|-----------|
| \(-1.339 \) 7 | 1.66 | CI-GTO, \( > 120 \) configurations | [25] (1970) |
| \(-1.306 \) 29 | 1.65 | GG, 3 terms, 5 nonlinear parameters | [20] (1973) |
| \(-1.327 \) 25 | 1.65 | GG, 6 terms, 7 nonlinear parameters | |
| \(-1.351 \) 47 | 1.65 | GG, 10 terms, 9 nonlinear parameters | |
| \(-1.332 \) 29 | 1.65 | GG, 15 terms, 11 nonlinear parameters | |
| \(-1.334 \) 382 | 1.65 | R12, 10s basis set | [21] (1993) |
| \(-1.343 \) 632 | 1.65 | R12, 30s basis set | |
| \(-1.340 \) 7 | 1.65 | 7-parametric trial function (3) | Present |
| \(-1.340 \) 5 | 1.6405 | CI-GTO, 48 configurations | [23] (1971) |
| \(-1.340 \) 5 | 1.65 | CI-STO, 100 configurations | [24] (1971) |
| \(-1.340 \) 7 | 1.65 | \((7+3)\)-parametric trial function (5) | Present |
| \(-1.341 \) 6 | 1.650 \pm 0.008 | 10-parametric trial function (5) | Present |
| \(-1.342 \) 72 | 1.65041 | CI-GTO, 108 terms | [27] (1985) |
| \(-1.342 \) 784 | 1.6504 | CI-GTO, 8s3p1d/[6s3p1d] basis set | [28] (1978) |
| \(-1.343 \) 40 | 1.6504 | CI-GTO, 10s4p2d basis set (104 terms) | [29] (1986) |
| \(-1.343 \) 822 | 1.65 | CI-GTO, 700 terms | [30] (1990) |
| \(-1.342 \) 03 | 1.6504 | CI with r12, 36 configurations | [31] (1982) |
| \(-1.343 \) 422 | 1.6504 | CI with r12, 192 configurations | [32] (1984) |
| \(-1.343 \) 500 | 1.6504 | CI with r12, 13s3p/[10s2p] basis set | [33] (1988) |
| \(-1.343 \) 828 | 1.65 | CI with r12, 13s5p3d basis set | [34] (1990) |
| \(-1.343 \) 835 | 1.65 | R12, 30s20p12d9f basis set | [21] (1993) |
| \(-1.343 \) 35 | 1.65 | GG, 15 terms, 135 nonlinear parameters | [20] (1973) |
| \(-1.343 \) 835 624 | 1.65 | GG, 600 terms | [11] (1995) |
| \(-1.343 \) 835 625 02 | 1.65 | ECSG, 1000 terms | [10] (2009) |

The trial function (3), with the parameters of \( \psi_0 \) kept fixed and equal to ones found for (5), is a symmetrized product of 1s Slater-type orbitals multiplied by the exponential correlation factor \( e^{-\gamma r_{12}} \). The function (3) is a \((7+3)\)-parametric trial function. With optimal values of parameters, it took about 20 min (wall clock time) to compute a variational energy with relative accuracy 10^-7.

5. Results

In table 1, we present the results for the ground state energy at interproton equilibrium distance of the \( \text{H}_3^+ \) molecular ion obtained by different researchers using different methods. It can be seen that the Born–Oppenheimer ground state energy obtained using the trial function (3) is the most accurate (the lowest) energy obtained with a few parametric functions. In particular, the trial function (3) gives a lower energy than the energies obtained with the explicitly correlated functions based on both Gaussians in \( r_{12} \) and linear in \( r_{12} \), when a relatively small number of terms with nonlinear parameters is involved. The trial function (3) is more accurate than almost all(!) traditional CI calculations which were performed before 1971 (see [22]) even including the one with the largest set of 100 configurations [24]. In those CI calculations no explicit correlation was included. The variational energy obtained with (3) is even of comparable accuracy to the large CI calculations.
Table 2. The ground state energy of H$_i^+$ at $R_{eq} = 1.65$ au and the nonlinear variational parameters in (au)$^{-1}$ corresponding to the trial function (3), to the trial function (5) with parameters corresponding to $\psi_0$ fixed and to (5) with ten optimized parameters.

| $E$ (au) | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\alpha_5$ | $\alpha_6$ | $\gamma$ | $A$ | $\tilde{\alpha}$ | $\tilde{\gamma}$ |
|---------|-------------|-------------|-------------|-------------|-------------|-------------|---------|-----|----------------|----------------|
| $-1.340$ | $3$         | $-0.00353$  | $0.18548$   | $1.4245$    | $1.0471$    | $0.15082$   | $0.58912$ | $0.21632$ | $-$           | $-0.03000$     |
| $-1.340$ | $7$         | $-0.00294$  | $0.21022$   | $1.3849$    | $1.0199$    | $0.17103$   | $0.59084$ | $0.26044$ | $-0.51154$    | $0.59589$      |
| $-1.341$ | $6$         | $-0.00294$  | $0.21022$   | $1.3849$    | $1.0199$    | $0.17103$   | $0.59084$ | $0.26044$ | $-0.51154$    | $0.59589$      |

Table 3. Expectation values (in au) for the H$_i^+$ ion in its ground state obtained with the trial functions (3) and (5)$^{(i,ii)}$. Corresponding results obtained with other methods are displayed for comparison. The coordinates $x$, $y$, $z$ and $r$ are measured from the centre of the equilateral triangle formed by protons.

| Expectation value | Trial function (3)/ (5)$^{(i)}$ / (5)$^{(ii)}$ | Others |
|-------------------|---------------------------------------------|--------|
| $\langle r_{12} \rangle$ | $2.0032$ | $2.0013$ | $1.9931$ |
| $\langle 1/r_{12} \rangle$ | $0.6315$ | $0.6304$ | $0.6302$ |
| $\langle 1/r_{1A} \rangle$ | $0.8584$ | $0.8584$ | $0.8584$ |
| $\langle \langle x^2 \rangle = \langle y^2 \rangle \rangle$ | $0.7711$ | $0.7703$ | $0.7711$ |
| $\langle z^2 \rangle$ | $0.5399$ | $0.5402$ | $0.5451$ |
| $\langle r^2 \rangle$ | $2.0822$ | $2.0773$ | $2.0669$ |

$^a$ [23] CI-43; $^b$ CI wavefunction (I) in [24]; $^c$ correlated Gaussian (unrestricted) wavefunction with 15 terms in [20]; $^d$ CI wavefunction in [26]; $^e$ CISD-R12 wavefunction with the 10s8p6d4f basis set in [21].

[23, 24]$^4$. Table 2 shows the optimal values of the variational parameters in (3).

The list of major expectation values obtained with the trial function (3) and its comparison with results of other calculations is given in table 3. A reasonable agreement for the expectation values is observed. In particular, for the expectation values (1/$r_{12}$), $\langle x^2 \rangle$, $\langle z^2 \rangle$ and $\langle r^2 \rangle$ agreement within $\sim$ 1% with ours and all other calculations is observed, including ones obtained in the large CISD-R12 calculations [21]. Also, for the expectation value of (1/$r_{12}$) we have agreement to the first significant digit (s.d.) with the other calculations, and we are also in close agreement to the value obtained with the correlated Gaussian (unrestricted) wavefunction with 15 terms [20]. For the expectation values (1/$r_{1A}$) and (z$^2$) we observe agreement with the other calculations to 3 and 2 s.d., respectively. These facts seem to indicate that the presented expectation values are very accurate, corroborating the quality of the trial function (3) which gives 2–3 s.d. correctly. It is worth noting that since there are no criteria about the accuracy of the obtained expectation values, we can only comment about the agreement of our result with those obtained by other approaches.

6. Conclusion

We presented a simple and compact 7-parametric variational trial function together with its possible natural generalization by addition of the Heitler–London (HL)-type function. This function already provides surprisingly accurate Born–Oppenheimer energy for the ground state of such a complicated molecular system as H$_i^+$. It is chosen following a criterion of physical adequacy which suggests taking the electronic correlation in the form $\sim \exp(\gamma r_{12})$, where $\gamma$ is a variational parameter. The minimum energy is found to be $E = -1.340$ 34 au at an equilibrium interproton distance $R = 1.65$ au. This result for the energy is the most accurate among the values obtained with several parametric trial functions. In particular, it is more accurate than the energies obtained with the explicitly correlated approaches of [21] (linear in $r_{12}$) and that of [20] (Gaussian in $r_{12}$), when a relatively small number of terms and nonlinear parameters are involved.

In the spirit of the approach presented in [6] (see also [5]), the trial function (3) can be modified by adding a similar function, in particular, one of Heitler–London type:

$$\psi_{HL} = e^{-\alpha(r_{1A}-r_{1B})-\alpha(r_{1B}-r_{2A})-\alpha(r_{2A}-r_{2B})} \psi_{12},$$

where $\tilde{\alpha}$, $\tilde{\gamma}$ are parameters. The function (4) alone gives a dominant contribution to small interproton distances. Taking a linear superposition with (3)

$$\Psi = \psi_0 + A \psi_{HL},$$

and minimizing with respect to the parameters $A$, $\tilde{\alpha}$ and $\tilde{\gamma}$ only (see table 2) gives an essential improvement in the energy (see table 1). In particular, this function, which contains $(7 + 3)$ variational parameters, allows us to obtain a more accurate result for the energy than the one obtained in [24] within CI-STO with 100 configurations. In figure 2, the potential curve $E$ versus $R$ is presented. It is worth noting that for larger $R$ the accuracy provided by a 10-parametric function increases. If at equilibrium ($R = 1.65$ au) the difference in energy is $\sim$2.4E-03 au versus that obtained in [29] while for $R = 2.700618$ au the difference is reduced to 1.7E-03 au.

Releasing all ten parameters in (5) (see table 2) we obtain a further improved result (see table 1), even though we are
still unable to reproduce the fourth significant figure in the energy. However, the obtained energy is among the 13 most accurate variational results ever calculated so far. It is slightly worse than the one obtained in [31] based on CI using the r12 method with 36 configurations. The expectation values in table 3 are gradually changed with the moves from one ansatz to another seemingly demonstrating a convergence. It seems evident that taking a linear superposition of two (or more) functions (3) instead of (5) will improve significantly the variational energies. This work is in progress and it will be published elsewhere. Without doubt, the trial functions (3), (5) can be used to study potential energy surfaces. It is worth emphasizing that the main virtue of functions (3), (5) is their compactness.

The function (3) can easily be modified for a study of spin-triplet states, as well as the low-lying states with non-vanishing magnetic quantum number. A generalization to more than two electron molecular systems also seems straightforward.

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Figure 2. Potential energy curve for the $H^+$ ion in triangular equilateral configuration as a function of the triangle size $R$ obtained with the (7+3) parameter ansatz (5). Results by Meyer et al obtained using CI 10s4p2d GTO basis [29] are shown for comparison.
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