# Nonrelativistic energy of the hydrogen negative ion in the $2p^2\ ^3P^e$ bound state

Mirosław Bylicki* and Eugeniusz Bednarz
*Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziądzka 5, 87-100 Toruń, Poland*
(Received 15 November 2002; published 24 February 2003)

By using a Hylleraas configuration-interaction explicitly correlated expansion we compute an upper bound to the energy of the $2p^2\ ^3P^e$ bound state of $H^-$. The result is converged on eleven significant digits. It improves the previous best upper bound on the sixth significant figure.

DOI: 10.1103/PhysRevA.67.022503 PACS number(s): 31.25.Jf, 31.15.Ar, 31.15.Pf, 31.25.−v

## I. INTRODUCTION

There is still strong interest in reaching the limits of numerical exactness by computing energies of small atoms with increasing accuracy. The leading cases are the helium atom and heliumlike ions. This includes the hydrogen negative ion, which is the most challenging because negative ions are much more demanding as the electron correlation is considered.

The $H^-$ ion has only two bound states: the ground $1s^2\ ^1S$ state and the doubly excited $2p^2\ ^3P$ state. The former has been investigated both theoretically and experimentally. For references see recent papers of Drake, Cassar, and Nistor [1] and Sims and Hagstrom [2] where the ground-state energy has been computed with an extremely high precision. The other bound state of $H^-$, $2p^2\ ^3P$, has not been observed till date. It was predicted computationally [3] nearly 40 years ago. Its energy was computed repeatedly [4–8] and there is no doubt about its existence. The problem of its experimental nonappearance is due to the lack of an initial state from which it could be reached.

For such a small system an extremely high accuracy can be obtained by using expansions that depend explicitly on the interelectronic distance $r_{12}$. Recent computations for the $H^-$ ground state performed by Drake, Cassar, and Nistor [1] converged up to eighteen significant digits. Surprisingly, the results one can find in the literature for the $2p^2\ ^3P^e$ state are far from such a precision. The best one was obtained by Jauregui and Bunge [7] 24 years ago. They used a configuration-interaction (CI)-expansion of only 108 configurations and obtained the energy $-0.125\,354\,716\,6$ a.u. They analyzed the convergence pattern of their computations and extrapolated them obtaining $-0.125\,355\,08(10)$ a.u. On the other hand, the largest Hylleraas-type computation for this state, done by Drake [4] and then repeated by Banyard, Keeble, and Drake [8] gave only $-0.125\,353\,6$ a.u. though they used about 50 thousand linear terms containing powers of $r_{12}$ up to the 82nd one.

This implies that computing accurately the energy of the $2p^2\ ^3P$ state is a much more demanding and challenging problem than for the ground state.[1] In this work we try to meet this challenge by applying a Hylleraas CI method. The result we obtained as an upper bound to the energy of the $2p^2\ ^3P$ state is far below the extrapolated value of Jauregui and Bunge [7]. This led us to perform an extrapolation based on more elaborated CI computations than those of Ref. [7]. The extrapolated result is below but close to the upper bound we obtained within the $r_{12}$-correlated expansion.

## II. HYLLERAAS CI COMPUTATION

We applied an explicitly correlated trial function of the Hylleraas CI type:

$$\Psi(\vec{r}_1,\vec{r}_2)=\sum_{l=1}^{l_{max}} Y_{ll}^{L=1}(\Omega_1,\Omega_2)\sum_{i,j,\nu} c_{i,j,\nu}^{l}[\phi_i^l(r_1)\phi_j^l(r_2) + (1\leftrightarrow 2)]r_{12}^{\nu}. \quad (1)$$

This expansion differs from the Hylleraas-type one used in Refs. [4,8]. Several angular $ll$ terms are included explicitly and not only the $pp$ one. Apart from the configuration terms with $\nu=0$, low powers of $r_{12}$ are used as correlation factors, the first one being most important. The radial functions $\phi(r)$ are Slater-type orbitals with various exponent parameters, which may be optimized. This kind of approach to the explicitly correlated expansion problem was introduced by Sims and Hagstrom [9] under the name Hylleraas CI, and independently by Woźnicki [10] who named it superposition of correlated configurations.

In the present work, several such expansions were used differing in the number of angular terms explicitly included, $l_{max}$, and in the maximum power of the $r_{12}$ distance, $\nu_{max}$. The nonlinear parameters were partially optimized. The results are collected in Table I. The best upper bound energy we obtained is $-0.125\,355\,451\,24$ a.u. This result is confirmed by our computations using various particular trial expansions (Table I). So we believe that the decimal digits given above are converged. Our result is far below the previous upper bound as well as below the extrapolated result, both obtained over 20 years ago by Jauregui and Bunge [7].

## III. EXTRAPOLATED CI COMPUTATION

Hence, it seemed to us to be necessary to perform an extrapolation similar to that of Jauregui and Bunge [7] but

*Email address: mirekb@phys.uni.torun.pl

[1]The details of electron correlations were discussed by Banyard, Keeble, and Drake [8] in terms of the Coulomb-hole and partial-Coulomb-hole description. They compare the $2p^2\ ^3P$ excited state with the ground state.

 

TABLE I. Explicitly correlated computations of the $2p^2\ ^3P$ state energy, $E$. The expansions used are characterized by $l_{max}$ and $\nu_{max}$ parameters regarding Eq. (1). The total number of linear terms is $N_{total}$. The basis sets are contracted after the Löwdin canonical orthogonalization, due to very restrictive constraints preventing quasilinear dependence.

| $l_{max}$ | $\nu_{max}$ | $N_{total}$ | $N_{reduced}$ | $E$ (in a.u.) |
|---|---|---|---|---|
| 1 | 1 | 342 | 276 | −0.12534552291344 |
| 1 | 2 | 198 | 187 | −0.12535532145467 |
| 1 | 2 | 273 | 241 | −0.12535541251296 |
| 1 | 2 | 360 | 292 | −0.12535543420024 |
| 1 | 2 | 408 | 326 | −0.12535543763169 |
| 1 | 2 | 459 | 351 | −0.12535544026560 |
| 2 | 1 | 684 | 481 | −0.12535544966128 |
| 3 | 1 | 468 | 381 | −0.12535544736695 |
| 3 | 1 | 1026 | 542 | −0.12535545116416 |
| 3 | 1 | 1800 | 712 | −0.12535545123940 |
| 3 | 2 | 702 | 488 | −0.12535545098811 |
| 3 | 2 | 1539 | 745 | −0.12535545123037 |
| 4 | 1 | 468 | 468 | −0.12535545120759 |
| 4 | 1 | 876 | 859 | −0.12535545124225 |
| 4 | 1 | 1566 | 1197 | −0.12535545124281 |
| 4 | 1 | 2456 | 1350 | −0.12535545124284 |
| 4 | 2 | 702 | 680 | −0.12535545123956 |
| 4 | 2 | 1314 | 1118 | −0.12535545124278 |
| 4 | 2 | 2349 | 1442 | −0.12535545124280 |

based on more extensive computations. We carried out a series of CI computations in which the trial space was systematically enlarged by adding consecutively angular terms $ll$ and extending the number of radials.

In Table II the contributions of $ll$ terms are presented for different levels of radial expansion (a row corresponds to a given level of radial expansion), including those extrapolated (as given in Table III) for infinite radial expansion. For each series of a given level of radial suturation they were fitted to the formula $\delta E_l = a(l+b)^c$. Jauregui and Bunge [7] used the same formula with the $b$ and $c$ parameters frozen: $b=\frac{1}{2}$ and $c=-7$. In the present investigation all three parameters were optimized to obtain the best fit. In all the series $b$ turned out to be close to $-0.5$ and the exponent $c\approx -5.6$. Thus the convergence of the angular contributions is much slower than was found by Jauregui and Bunge [7]. The summarized contribution of $l\geqslant 8$ terms is about $16.4\times 10^{-8}$ a.u. which is 50% more than the value estimated by Jauregui and Bunge. This is because in our *ab initio* calculations the higher angular parts are much better represented by considerably longer radial expansions than those used in Ref. [7]. The $l_{max}\to\infty$ extrapolated results are given in the last column of Table II. The last-row last-column result, $\Delta E^{\infty}(\infty)=355\,453\,060\times 10^{-12}$ a.u., was extrapolated first with respect to the radial and then with respect to the angular expansion.

To be more confident about the extrapolated result, another extrapolation was performed in the reversed order. Table III presents the extrapolation with respect to the radial expansion. The formula $\delta E(n)=[p/(n+q)]^r$ was used to fit the $\delta E_{l_{max}}(n)$ contributions at a given $l_{max}$ level. The last row contains the results extrapolated in Table II for $l_{max}\to\infty$. So, $\Delta E_{\infty}(\infty)=355\,453\,062\times 10^{-12}$ a.u. is a result of extrapolating first with respect to angular expansion and then for $n\to\infty$. This number is essentially the same as $\Delta E^{\infty}(\infty)$ obtained in Table II.

Thus we conclude that the extrapolated energy value for the $2p^2\ ^3P$ $H^-$ state is $-0.125\,355\,453\,06$ a.u. This is $0.37\times 10^{-6}$ a.u. below the extrapolated value of Jauregui and

TABLE II. Extrapolation of CI calculations to the infinite angular-wave expansion. The radial expansion is characterized by $n$ related to the number of orbitals used; the number of orbitals of angular momentum $l$ is $n-l+1$. $\Delta E^n(l\leqslant 2)$ is the electron affinity (with respect to the H $2p$ state) obtained by using the expansion built of $n$ orbitals of $p$-type and $n-1$ $d$ orbitals. The contributions $\delta E^n(l)$ coming from the $ll$ angular waves were obtained from the actual CI computations. $R^n_{l\geqslant 9}$ is a sum of contributions from $l\geqslant 9$. It was obtained by using the formula $\delta E(l)=a/(l+b)^c$ fitted to the $\delta E^n(l)$ values for $l=4,\ldots,8$. Finally, $\Delta E^n(\infty)$ is the extrapolated electron affinity value obtained as a sum of all the $ll$ contributions at a given level $n$ of radial expansion (along a given row of the table). The last row values were obtained by extrapolating with respect to increasing radial expansions as given in Table III. The value $\Delta E^{\infty}(\infty)$ is extrapolated with respect to both radial ($n$) and angular ($l$) expansions. (All the energy contributions are given in $10^{-12}$ a.u.).

| | | $\delta E^n(l)$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $\Delta E^n(l\leqslant 2)$ | $l=3$ | $l=4$ | $l=5$ | $l=6$ | $l=7$ | $l=8$ | $R^n_{l\geqslant 9}$ | $\Delta E^n(\infty)$ |
| 13 | 309772659 | 38158479 | 5433495 | 1318993 | 428029 | 167235 | 74272 | 87928 | 355441090 |
| 14 | 309775727 | 38158523 | 5433608 | 1319166 | 428177 | 167420 | 74477 | 88376 | 355445474 |
| 15 | 309778423 | 38158310 | 5433678 | 1319264 | 428343 | 167602 | 74722 | 88912 | 355449254 |
| 16 | 309779487 | 38158304 | 5433734 | 1319319 | 428408 | 167683 | 74819 | 89127 | 355450881 |
| 17 | 309780116 | 38158272 | 5433761 | 1319358 | 428452 | 167732 | 74876 | 89252 | 355451819 |
| 18 | 309780410 | 38158282 | 5433778 | 1319372 | 428473 | 167755 | 74906 | 89319 | 355452295 |
| 19 | 309780629 | 38158274 | 5433788 | 1319390 | 428490 | 167776 | 74927 | 89365 | 355452639 |
| ∞ | 309780878 | 38158270 | 5433803 | 1319411 | 428512 | 167803 | 74955 | 89428 | 355453060 |

TABLE III. Extrapolation of CI computations to an infinite radial expansion. The angular $ll$-wave expansion is characterized by the maximum number of $l$: $l_{max}$. Each row corresponds to a given level of angular expansion. The last row contains the values extrapolated to the infinite angular expansion as given in Table II. The radial expansion increases along a row. $\Delta E_{l_{max}}(n=13)$ is the electron affinity obtained by using $14-l$ orbitals of $l$ type for $l=1,\ldots,l_{max}$. $\delta E_{l_{max}}(n)$ is a contribution due to the extension of radial expansion from $n-1$ to $n$. $R^{\infty}_{l_{max}}$ is the remaining contribution expected to come from the enlargement of expansion from $n=19$ to an infinite one. This residue is evaluated as a sum of extrapolated terms $\delta E(n)=[p/(n+q)]^r$ obtained by fitting the formula to the $\delta E_{l_{max}}(n)$ values of $n=14,\ldots,19$. $\Delta E_{l_{max}}(\infty)$ is the electron affinity value extrapolated to infinity with respect to the radial expansion. (All the energy contributions are given in $10^{-12}$ a.u.)

| | | $\delta E_{l_{max}}(n)$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $l_{max}$ | $\Delta E_{l_{max}}(n=13)$ | $n=14$ | $n=15$ | $n=16$ | $n=17$ | $n=18$ | $n=19$ | $R^{\infty}_{l_{max}}$ | $\Delta E_{l_{max}}(\infty)$ |
| 2 | 309772659 | 3068 | 2696 | 1064 | 629 | 294 | 219 | 249 | 309780878 |
| 3 | 347931138 | 3112 | 2483 | 1058 | 597 | 304 | 211 | 245 | 347939148 |
| 4 | 353364633 | 3225 | 2553 | 1114 | 624 | 321 | 221 | 260 | 353372951 |
| 5 | 354683626 | 3398 | 2651 | 1169 | 663 | 335 | 239 | 281 | 354692362 |
| 6 | 355111655 | 3546 | 2817 | 1234 | 707 | 356 | 256 | 303 | 355120874 |
| 7 | 355278890 | 3731 | 2999 | 1315 | 756 | 379 | 277 | 330 | 355288677 |
| 8 | 355353162 | 3936 | 3244 | 1412 | 813 | 409 | 298 | 358 | 355363632 |
| $\infty$ | 355441090 | 4384 | 3780 | 1627 | 938 | 476 | 344 | 423 | 355453062 |

Bunge [7] and $1.8\times10^{-10}$ a.u. below our upper bound energy value. The latter difference is just 2% of the gain due to the extrapolation. So the agreement between the energy upper bound and the extrapolated energy value we obtained is very good. Obviously, the extrapolated value is just an estimation and the only reliable result is the energy upper bound.

## IV. SUMMARY

The Hylleraas CI method was used to compute an upper bound to the energy of the $2p^2\ ^3P$. The result is $-0.125\,355\,45\,124$ a.u. It is much lower than the previously published ones and below the CI-extrapolated value obtained by Jauregui and Bunge [7]. It agrees within the eight significant digits with the CI-extrapolated value obtained also in this work. Because of the mutual confirmation of results obtained by using different basis sets we believe that 11 significant figures are converged. The result can be improved for further figures by using a higher precision numerics (the double precision computer arithmetics was used in this work) and enlarged Hylleraas CI trial functions.

## ACKNOWLEDGMENT

This research was partially supported by a grant from the Polish Committee for Scientific Research (KBN Grant No. 2 P03B 125 18).

[1] G.W.F. Drake, M.M. Cassar, and R.A. Nistor, Phys. Rev. A **65**, 054501 (2002).
[2] J.S. Sims and S.A. Hagstrom, Int. J. Quantum Chem. **90**, 1600 (2002).
[3] For references see Ref. [7].
[4] G.W.F. Drake (unpublished), as quoted in Ref. [8].
[5] G.W.F. Drake, Phys. Rev. Lett. **24**, 126 (1970).
[6] A.K. Bhatia, Phys. Rev. A **2**, 1667 (1970).
[7] R. Jauregui and C.F. Bunge, J. Chem. Phys. **71**, 4611 (1979).
[8] K.E. Banyard, D.R.T. Keeble, and G.W.F. Drake, J. Phys. B **25**, 3405 (1992).
[9] J.S. Sims and S.A. Hagstrom, Phys. Rev. A **4**, 908 (1971).
[10] W. Woźnicki, in *Theory of Electronic Shells in Atoms and Molecules*, edited by A. Jucys (Mintis, Vilnius, 1971), p. 103.