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Variational calculations of the HT^+ rovibrational energies

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In this Brief Report, we use the exponential explicitly correlated variational basis set of the type $\exp(-\alpha_n R-\beta_n r_1-\gamma_n r_2)$ to calculate systematically the nonrelativistic bound-state energies for the hydrogen molecular ion HT^+. We perform calculations for the states of the total orbital angular momentum $L=0$ and 1 with the complete set of vibrational quantum numbers $v=0$–23, as well as for the states of $L=2$–5 and $v=0$–5. The $E1$ dipole transition moments, which are of importance for the planning of spectroscopic laser experiments, have been obtained as well.

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I. INTRODUCTION

In recent years, the precision theoretical study of H_2^+ and HD^+ hydrogen molecular ions has been performed [1] with the aim of improved determination of m_e/m_p, the proton-to-electron mass ratio [2,3] via rovibrational spectroscopy. The latest experimental results [4] demonstrate the feasibility of this project.

In our paper, we want to address another problem, which is also related to the precision spectroscopy of hydrogen molecular ions, namely, to study properties of the triton, the heaviest hydrogen isotope, which is known with lower accuracy than other hydrogen isotopes [5]. Thus, the atomic mass of triton has a relative uncertainty of 8.3×10^{-10}, while the atomic masses of other nuclei are typically known with accuracy one order of magnitude higher.

The HT^+ molecular ion has been studied numerically since the 1970s [6,7]. The most recent work is the numerical nonrelativistic calculation of all the vibrational states with the total orbital momentum $L=0$ [8]. The major aim of our paper is to extend these calculations to a wide range of states and with a numerical fractional accuracy of less than 10^{-14}. To this end, we will use a very accurate variational approximation based on Slater wave functions with nonlinear parameters in exponentials generated in a quasirandom way [9].

For the design of experiments, it is also important to know the dipole transition matrix elements. They may be used to evaluate the strengths of one- and two-photon transitions. We calculate the dipole moments for all the transitions between the states within the range $L=0$–5 and $v=0$–5.

II. VARIATIONAL WAVE FUNCTION

We adopt the following notation for the coordinate system of the three particles. Coordinates $\mathbf{R}_i$, $i=1,2,3$, are position vectors of the triton, proton, and electron, respectively, in the center-of-mass frame. The vector $\mathbf{R}=\mathbf{R}_2-\mathbf{R}_1$ is a relative position of the proton with respect to the triton, while $\mathbf{r}_1$ and $\mathbf{r}_2$ are the relative positions of the electron with respect to triton and proton. Atomic units are used throughout: $m_e=\hbar=e=1$.

The variational bound-state wave functions were calculated by solving the three-body Schrödinger equation with Coulomb interaction using the variational approach based on the exponential expansion with randomly chosen exponents. This approach has been discussed in a variety of works [10–12]. Details and particular strategy of choice of the variational nonlinear parameters and basis structure that have been used in the this Brief Report can be found in [9].

Briefly, the wave function for a state with a total orbital angular momentum L and of a total spatial parity $\pi=(-1)^L$ is expanded as follows:

$$\begin{aligned}\Psi^{\pi}_{LM}(\mathbf{R},\mathbf{r}_1)&=\sum_{l_1+l_2=L}\mathcal{Y}^{l_1l_2}_{LM}(\hat{\mathbf{R}},\hat{\mathbf{r}}_1)G^{L\pi}_{l_1l_2}(R,r_1,r_2),\\ G^{L\pi}_{l_1l_2}(R,r_1,r_2)&=\sum_{n=1}^{N}\{C_n\,\mathrm{Re}[e^{-\alpha_nR-\beta_nr_1-\gamma_nr_2}]\\ &\quad+D_n\,\mathrm{Im}[e^{-\alpha_nR-\beta_nr_1-\gamma_nr_2}]\},\end{aligned}\tag{1}$$

where the complex exponents α,β,γ are generated in a pseudorandom way. When exponents α_n, β_n, and γ_n are real, the method reveals slow convergence for molecular-type Coulomb systems. Thus, the use of complex exponents allows us to reproduce the oscillatory behavior of the vibrational part of the wave function and to improve convergence [9,12].

In numerical calculations, the CODATA06 recommended values [5] have been used for the masses of a proton and triton, namely, $m_p=1836.152\,672\,47\,m_e$ and $m_t=5496.921\,526\,9\,m_e$.

III. RESULTS

Numerical results of calculations are shown in Tables I and II. All the digits presented are converged. Thus, we claim that the accuracy of about 10^{-14}–10^{-15} a.u. is achieved. This precision is sufficient for making accurate theoretical predictions for transition frequencies in rovibrational spectroscopy of the HT^+ molecular ion. Higher-order contributions, such as leading-order relativistic and radiative corrections, are in progress. Analysis of the computed results shows that a good candidate transition for high-resolution spectroscopy is

$(v,L)_{\rm up}$	$(v',L')_{\rm int}$	$(v'',L'')_{\rm low}$	detuning (cm^{-1})	laser λ (μm)
(2,1)	(1,0)	(0,1)	−5.462 50	5.666 199 1 .

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TABLE I. Nonrelativistic energies (in a.u.) of rovibrational states for the total orbital angular momentum $L = 0$ and 1 (in a.u.). N is the number of basis functions used.

v	N	$E(L = 0)$	N	$E(L = 1)$
0	3000	−0.598 176 134 637 481	4000	−0.597 998 173 104 645
1	4000	−0.589 932 814 045 480	4000	−0.589 762 517 213 812
2	4000	−0.582 080 048 852 003	5000	−0.581 917 194 988 024
3	4000	−0.574 606 743 768 115	5000	−0.574 451 136 983 272
4	4000	−0.567 503 160 024 656	5000	−0.567 354 629 734 384
5	4000	−0.560 760 877 913 885	6000	−0.560 619 278 572 532
6	4000	−0.554 372 772 448 159	6000	−0.554 237 983 574 960
7	5000	−0.548 333 002 238 221	6500	−0.548 204 928 759 59
8	5000	−0.542 637 011 999 689	7000	−0.542 515 584 945 61
9	5000	−0.537 281 549 435 559	7500	−0.537 166 727 044 62
10	6000	−0.532 264 697 630 064	7500	−0.532 156 466 939 93
11	6000	−0.527 585 924 539 969	8000	−0.527 484 303 572 35
12	7000	−0.523 246 151 695 058	9000	−0.523 151 192 389 60
13	7000	−0.519 247 844 815 581	10000	−0.519 159 636 936 32
14	8000	−0.515 595 129 667 854	10000	−0.515 513 806 012 60
15	9000	−0.512 293 936 913 004	10000	−0.512 219 680 327 87
16	9000	−0.509 352 179 357 565	11000	−0.509 285 232 348 15
17	9000	−0.506 779 962 109 62	11000	−0.506 720 640 353 74
18	9000	−0.504 589 815 348 17	11000	−0.504 538 527 393 40
19	9000	−0.502 796 904 356 02	12000	−0.502 754 181 895 56
20	9000	−0.501 419 066 407 48	13000	−0.501 385 615 799 88
21	9000	−0.500 476 417 695 58	13000	−0.500 453 250 219 70
22	10000	−0.499 998 391 808 02	14000	−0.499 988 140 076 73
23	10000	−0.499 917 016 416 95	14000	−0.499 914 289 390 14

TABLE III. Comparison of $L = 0$ calculations with results of [8]. Here, we have chosen smaller basis sets than needed for 10-digit accuracy.

	[8]		This work	
v	N	E	N	E
0	1500	−0.598 176 134 5	1500	−0.598 176 134 6
1	1500	−0.589 932 813 7	1500	−0.589 932 814 0
2	2000	−0.582 080 048 6	1500	−0.582 080 048 9
3	2000	−0.574 606 743 5	1500	−0.574 606 743 8
4	2500	−0.567 503 159 8	2000	−0.567 503 160 0
5	2500	−0.560 760 877 7	2000	−0.560 760 877 9
6	2500	−0.554 372 772 0	2000	−0.554 372 772 4
7	2500	−0.548 333 001 5	2500	−0.548 333 002 2
8	2500	−0.542 637 011 4	2500	−0.542 637 012 0
9	2500	−0.537 281 546 4	2500	−0.537 281 549 4
10	2500	−0.532 264 693 1	2500	−0.532 264 697 6
11	2500	−0.527 585 922 4	2500	−0.527 585 924 5
12	2500	−0.523 246 148 0	3000	−0.523 246 151 7
13	2500	−0.519 247 835 9	3000	−0.519 247 844 8
14	2500	−0.515 595 121 7	3000	−0.515 595 129 7
15	2500	−0.512 293 913 8	3500	−0.512 293 936 9
16	2500	−0.509 352 167 1	3500	−0.509 352 179 3
17	3000	−0.506 779 939 2	3500	−0.506 779 962 1
18	3000	−0.504 589 807 9	4000	−0.504 589 815 3
19	3000	−0.502 796 855 1	4000	−0.502 796 904 3
20	4000	−0.501 419 014 9	4000	−0.501 419 066 4
21	5000	−0.500 476 391 2	4500	−0.500 476 417 7
22	5000	−0.499 998 389 3	5000	−0.499 998 391 8
23	5000	−0.499 917 007 3	5000	−0.499 917 016 4

This transition starts from $(v'', L'') = (0,1)$, where a significant population fraction can be in thermal equilibrium at 300 K, or into where one can pump the molecules. The detuning is sufficiently small to allow a two-photon Doppler free excitation with sufficiently high excitation probability for available laser power, and the number of hyperfine lines in the spectrum will be modest as compared to transitions between states with larger L, leading to a relatively simple spectrum. Lasers at 5.66 μm are commercially available (quantum cascade lasers).

Table III compares our results with recent calculations performed in [8]. The difference in energies due to replacement of CODATA02 to CODATA06 values has been evaluated and our estimate is $\sim 10^{-11}$ a.u. In the rightmost columns, we present our calculations with 10 significant digits and the length of the corresponding basis set. As may be seen, with an increase of vibrational quantum number, a disagreement between two calculations is growing and is about 10^{-8} a.u. for last vibrational states. We attribute this to insufficient flexibility of the Gaussian variational wave functions used in [8], especially for the states with 22 to 23 nodes.

In Table IV, reduced matrix elements $d = \langle L'v' \| \mathbf{d} \| Lv \rangle$ of the dipole electric moment operator $\mathbf{d} = \sum_{i=1}^{3} Z_i \mathbf{R}_i$ are presented. The moments were calculated numerically using the variational wave functions with basis sets of $N = 1000$–2000. The data are in atomic units. To obtain the dipole moments in Debye, one may use the following expression:

$$\mu_{n'n} = C_{1\mu;LM}^{L'M+\mu} \frac{d}{\sqrt{2L+1}} (2.541\,77 \text{ Debye}). \tag{2}$$

This may be used in evaluation of the intensities of various transitions both for a one- and two-photon spectroscopy.

TABLE II. Nonrelativistic energies (in a.u.) of the rovibrational states for $L = 2$–5 (in a.u.). N is the number of basis functions used.

v	N	$E(L = 2)$	$E(L = 3)$	$E(L = 4)$	$E(L = 5)$
0	4000	−0.597 643 197 287 777	−0.597 113 085 250 637	−0.596 410 613 669 588	−0.595 539 411 144 737
1	5000	−0.589 422 838 278 589	−0.588 915 590 706 580	−0.588 243 455 384 297	−0.587 409 935 240 132
2	5000	−0.581 592 371 028 481	−0.581 107 328 963 789	−0.580 464 658 567 024	−0.579 667 743 318 555
3	5000	−0.574 140 777 725 399	−0.573 677 359 513 888	−0.573 063 385 513 164	−0.572 302 125 753 237
4	5000	−0.567 058 395 467 948	−0.566 616 095 191 358	−0.566 030 149 835 548	−0.565 303 721 808 818
5	6000	−0.560 336 879 635 856	−0.559 915 266 376 607	−0.559 356 781 783 664	−0.558 664 486 365 752

TABLE IV. Dipole moments $d = \langle v'L'\|\mathbf{d}\|vL\rangle$ of transitions between states in HT$^+$ (in a.u.).

	$L(0\to 1)$	$L(1\to 2)$	$L(2\to 3)$	$L(3\to 4)$	$L(4\to 5)$
$v(0\to 0)$	0.512 974	0.726 143	0.891 341	1.032 300	1.158 544
$v(0\to 1)$	0.049 489	0.066 889	0.078 170	0.086 003	0.091 471
$v(0\to 2)$	0.006 171	0.008 618	0.010 402	0.011 817	0.012 975
$v(0\to 3)$	0.001 346	0.001 906	0.002 333	0.002 687	0.002 992
$v(0\to 4)$	0.000 394	0.000 563	0.000 696	0.000 808	0.000 906
$v(0\to 5)$	0.000 140	0.000 201	0.000 249	0.000 292	0.000 330
$v(1\to 0)$	0.053 955	0.079 519	0.101 358	0.121 654	0.141 208
$v(1\to 1)$	0.540 312	0.765 038	0.938 861	1.087 144	1.219 825
$v(1\to 2)$	0.070 577	0.095 260	0.111 180	0.122 145	0.129 713
$v(1\to 3)$	0.010 678	0.014 892	0.017 952	0.020 371	0.022 340
$v(1\to 4)$	0.002 657	0.003 758	0.004 597	0.005 290	0.005 882
$v(1\to 5)$	0.000 860	0.001 228	0.001 514	0.001 756	0.001 969
$v(2\to 0)$	0.006 300	0.008 982	0.011 068	0.012 841	0.014 405
$v(2\to 1)$	0.077 123	0.113 771	0.145 164	0.174 397	0.202 607
$v(2\to 2)$	0.568 661	0.805 102	0.987 911	1.143 763	1.283 100
$v(2\to 3)$	0.087 184	0.117 517	0.136 973	0.150 270	0.159 336
$v(2\to 4)$	0.015 103	0.021 043	0.025 348	0.028 724	0.031 458
$v(2\to 5)$	0.004 156	0.005 874	0.007 170	0.008 238	0.009 144
$v(3\to 0)$	0.001 335	0.001 876	0.002 278	0.002 606	0.002 882
$v(3\to 1)$	0.010 922	0.015 587	0.019 229	0.022 334	0.025 081
$v(3\to 2)$	0.095 519	0.141 059	0.180 147	0.216 622	0.251 885
$v(3\to 3)$	0.597 974	0.846 570	1.038 690	1.202 381	1.348 618
$v(3\to 4)$	0.101 591	0.136 768	0.159 183	0.174 363	0.184 577
$v(3\to 5)$	0.019 534	0.027 177	0.032 690	0.037 005	0.040 484
$v(4\to 0)$	0.000 384	0.000 534	0.000 645	0.000 731	0.000 802
$v(4\to 1)$	0.002 642	0.003 713	0.004 517	0.005 173	0.005 728
$v(4\to 2)$	0.015 481	0.022 109	0.027 314	0.031 766	0.035 717
$v(4\to 3)$	0.111 551	0.164 925	0.210 858	0.253 805	0.295 394
$v(4\to 4)$	0.628 421	0.889 621	1.091 415	1.263 256	1.416 674
$v(4\to 5)$	0.114 672	0.154 157	0.179 160	0.195 933	0.207 057
$v(5\to 0)$	0.000 135	0.000 188	0.000 224	0.000 252	0.000 274
$v(5\to 1)$	0.000 840	0.001 171	0.001 414	0.001 605	0.001 762
$v(5\to 2)$	0.004 140	0.005 838	0.007 113	0.008 149	0.009 029
$v(5\to 3)$	0.020 082	0.028 717	0.035 505	0.041 330	0.046 520
$v(5\to 4)$	0.126 224	0.186 818	0.239 110	0.288 100	0.335 625
$v(5\to 5)$	0.660 155	0.934 476	1.146 351	1.326 703	1.487 622

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