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Cite as: AIP Conference Proceedings **2163**, 090003 (2019); <https://doi.org/10.1063/1.5130125>
Published Online: 22 October 2019

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Variational Calculations of the H_2^+ and HD^+ Rovibrational Energies

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Abstract. 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 H_2^+ and HD^+ . We perform calculations for the states of the total angular momentum $L=0-4$ with the complete set of vibrational numbers $v=0-10$.

I. INTRODUCTION

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

We use the following notation for the coordinate system of the three particles. Coordinates $\mathbf{R}, i=1,2,3$, are position vectors of the two proton and electron for the H_2^+ , and proton, deuteron and electron for HD^+ 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 proton (H_2^+), deuteron (HD^+), while \mathbf{r}_1 and \mathbf{r}_2 are the relative positions of the electron with respect to proton and proton (H_2^+), and proton and deuteron (HD^+). Atomic unites are used throughout: $m_e = \hbar = e = 1$.

II. VARIATIONAL WAVE FUNCTION

The variational bound-state wave functions were calculated by solving the three-body Schrödinger equation with Coulomb interaction:

$$\left[\frac{\mathbf{P}_1^2}{2M_1} + \frac{\mathbf{P}_2^2}{2M_2} + \frac{\mathbf{p}_e^2}{2m_e} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \frac{Z_1 Z_2}{R} \right] \psi_0 = E_0 \psi_0 \quad (1)$$

using the variational approach based on the exponential expansion with randomly chosen exponents. This approach has been discussed and developed in a variety of works [5-7]. Details and the particular strategy for choosing the variational nonlinear parameters and basis structure that have been adopted in the present work can be found in [8].

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:

$$\begin{aligned} \psi_{LM}^\pi(\mathbf{R}, \mathbf{r}_1) &= \sum_{l_1+l_2=L} Y_{LM}^{l_1 l_2}(\mathbf{R}, \mathbf{r}_1) G_{l_1 l_2}^{L\pi}(R, r_1, r_2), \\ G_{l_1 l_2}^{L\pi}(R, r_1, r_2) &= \sum_{n=1}^N \left\{ C_n \operatorname{Re}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}] + D_n \operatorname{Im}[e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}] \right\}, \end{aligned} \quad (2)$$

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].

In numerical calculations, the CODATA14 recommended values [10] have been used for the masses of a proton and deuteron, namely, $m_p = 1836.15267389$ and $m_d = 36703.48296785$.

III. RESULTS

Numerical results of calculations are shown in TABLE 1 and TABLE 2. 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 prediction for transition frequencies in rovibrational spectroscopy of the H_2^+ and HD^+ molecular ions. Our results show that the accuracy of these calculations exceeds the accuracy of previous works [11], this allows us to approve that subsequent calculations, in which, will be taken into account our results, will give more accurate theoretical data.

TABLE 1. Nonrelativistic energies (in a.u.) of rovibrational states for the orbital angular momentum $L=0-4$ (in a.u.) for H_2^+ . N is the number of basis function.

v	N	$E(L=0)$			N	$E(L=1)$		
0	10000	-0.597139	063 081 376 670963	12000	-0.596873	738 786 879 54923		
1	10000	-0.587155	679 101 444 713781	10000	-0.586904	320 924 614380		
2	10000	-0.577751	904 423 216 7853	10000	-0.577514	034 065 733 6467		
3	10000	-0.568908	498 741 500 3994	10000	-0.568683	708 270 965639		
4	16000	-0.560609	220 862 442689	16000	-0.560397	171 413 192 4453		
5	16000	-0.552840	749 911 11841	16000	-0.552641	171 564 8436		
6	20000	-0.545592	651 009 840162	20000	-0.545405	343 973 17974		
7	24000	-0.538857	386 984 525910	24000	-0.538682	224 258 07562		
8	24000	-0.532630	379 374 145566	24000	-0.532467	311 215 51050		
9	24000	-0.526910	124 034 590286	24000	-0.526759	184 677 6329		
10	24000	-0.521698	369 032 55114	24000	-0.521559	686 371 79901		
	N	$E(L=2)$			N	$E(L=3)$		
0	10000	-0.596345	205 491 918999	10000	-0.595557	638 983 371 69218		
1	10000	-0.586403	631 534 449060	10000	-0.585657	611 883 906690		
2	10000	-0.577040	237 171 615740	10000	-0.576334	350 228 669387		
3	10000	-0.568235	992 982 634681	10000	-0.567569	034 844 973164		
4	16000	-0.559974	864 833 213010	16000	-0.559345	838 241 807626		
5	16000	-0.552243	738 633 085362	16000	-0.551651	852 949 522041		
6	20000	-0.545032	389 922 32136	20000	-0.544477	065 066 36723		
7	24000	-0.538333	500 078 76060	24000	-0.537814	375 049 1274		
8	24000	-0.532142	722 751 55271	24000	-0.531659	669 699 48405		
9	24000	-0.526458	806 300162	24000	-0.526011	951 642 7957		
10	24000	-0.521283	780 692 0813	24000	-0.520873	535 563 8968		
	N	$E(L=4)$						
0	10000	-0.594517	169 242 725 6300					
1	10000	-0.58467	213 423 580 2976					
2	10000	-0.575402	003 308 47469					
3	10000	-0.566688	236 641 71939					
4	16000	-0.558515	281 639 920927					
5	16000	-0.550870	506 098 78926					
6	20000	-0.543744	177 116 6975					
7	24000	-0.537129	488 129 3674					
8	24000	-0.531022	638 509 38890					
9	24000	-0.525422	972 765 8310					
10	24000	-0.520333	189 780 5849					

TABLE 2. Nonrelativistic energies (in a.u.) of rovibrational states for the orbital angular momentum $L=0-4$ (in a.u.) for HD^+ . N is the number of basis function.

v	N	$E(L=0)$			N	$E(L=1)$		
0	10000	-0.597897	968 610 75746	12000	-0.597698	128 194 07502		
1	10000	-0.589181	829 561 598 31911	10000	-0.588991	111 996 806790		
2	10000	-0.580903	700 225 622 2635	10000	-0.580721	828 128 30538		
3	10000	-0.573050	546 561 443788	10000	-0.572877	277 103 90243		
4	12000	-0.565611	042 088 431 7035	16000	-0.565446	166 289 299394		
5	18000	-0.558575	520 838 957147	16000	-0.558418	863 272 3593		
6	20000	-0.551935	948 971 72246	20000	-0.551787	367 923 5169		
7	20000	-0.545685	915 309 083405	24000	-0.545545	303 425 6591		
8	24000	-0.539820	641 562 965801	24000	-0.539687	927 061 3431		
9	24000	-0.534337	013 579 132556	24000	-0.534212	162 118581		
10	24000	-0.529233	635 584 43106	24000	-0.529116	652 944043		
	N	$E(L=2)$			N	$E(L=3)$		
0	10000	-0.597299	643 353 92085	10000	-0.596704	882 764 44281		
1	10000	-0.588610	829 394 812 3556	10000	-0.588043	264 168 244666		
2	10000	-0.580359	195 207 49483	10000	-0.579818	002 035 836003		
3	10000	-0.572531	810 335 88176	10000	-0.572016	269 242 75329		
4	16000	-0.565117	449 775 665937	16000	-0.564626	942 074 290959		
5	16000	-0.558106	548 187 500297	16000	-0.557640	555 706 619105		
6	20000	-0.551491	172 855 16618	20000	-0.551049	278 520 73217		
7	24000	-0.545265	015 705 94894	24000	-0.544846	905 622 25467		
8	24000	-0.539423	405 228 383457	24000	-0.539028	8724 751 5705		
9	24000	-0.533963	339 712 74348	24000	-0.533592	290 174 06478		
10	24000	-0.528883	543 933 51798	24000	-0.528536	004 615 0233		
	N	$E(L=4)$						
0	10000	-0.595917	342 215 897764					
1	10000	-0.587291	784 380 128168					
2	10000	-0.579101	495 573 924028					
3	10000	-0.571333	786 056 66977					
4	16000	-0.563977	666 880 251251					
5	16000	-0.557023	807 071 968768					
6	20000	-0.550464	509 773 7052					
7	24000	-0.544293	707 787 20762					
8	24000	-0.538506	979 534 50243					
9	24000	-0.533101	587 096 5524					
10	24000	-0.528076	538 787 34155					

ACKNOWLEDGMENTS

The work was supported by the Ministry of Education and Science Republic of Kazakhstan under Grant No. IRN AP05132978.

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