Properties of the ground state of the hydrogen molecular ion

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The ground-state energies of the ions H_2^+ and D_2^+ have been calculated without making use of the Born-Oppenheimer approximation. Instead, the ions are treated as three-body systems whose ground states are spherically symmetric. The wave function of the ground state is taken to be a generalized Hylleraas form, but it is necessary to use high powers of the internuclear coordinate to simulate the localized motion of the nuclei. We obtain good values of the ground-state energies and compare them with those obtained from earlier calculations. Expectation values are calculated for various operators, the Fermi contact parameter, and the permanent quadrupole moment. The cusp condition is also calculated. The results are compared with the results of other calculations, where available. [S1050-2947(98)05410-9]

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I. INTRODUCTION

Recent experiments [1] on high Rydberg states of H_2 have prompted us to calculate the H_2^+ ground-state energy using Hylleraas-type wave functions, which have been used successfully for the two-electron systems. These functions, when used in a conventional manner, do not give an accurate value of the ground-state energy or expectation values of various operators even when a large number of terms are used in the wave function. The reason is that these functions do not localize motion of the nuclei, which can be done very easily in the Born-Oppenheimer approximation by using a product of electronic and nuclear wave functions. This approximation further assumes that there is no coupling between the electronic and nuclear motions. Since the relative motion of nuclei is fairly localized near an equilibrium point and looks like a Gaussian, we modified recently [2] the Hylleraas wave function so that the nuclear motion is localized, i.e., is Gaussian. This has helped the convergence of the energy value considerably in H_2^+, but not to the same extent in D_2^+. Using the wave functions obtained in minimizing the energy using the Rayleigh-Ritz variational principle, we calculate expectation values for various operators, the Fermi contact parameter, the permanent quadrupole moment, and the cusp condition. The results are compared with other calculations, where available.

II. FORMULATION AND RESULTS

The unperturbed Hamiltonian of the H_2^+ system in the center-of-mass system is [2]

$$H=-\nabla_{r_1}^2-\nabla_{r_2}^2-2\mu\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{r_2}+\frac{2}{r_{12}}-\frac{2}{r_1}-\frac{2}{r_2}, \qquad (1)$$

where the reduced mass $\mu=M/(M+1)$, M is the nuclear mass, energies are in reduced rydbergs, $R\mu=\mu$ Ry, and $\vec{r}_1$ and $\vec{r}_2$ are the relative distances of the electron from the nuclei in units of reduced Bohr radius. The proton and deuteron masses are 1836.152 70 and 3670.483 02, respectively, when the electron mass is 1.0. The ground state is described by *S*-wave Hylleraas trial functions

$$\Psi_0=e^{-a(r_1+r_2)}e^{-br_{12}}\sum_{l,m,n=0}^{\Omega_0}C_{lmn}r_1^l r_2^m r_{12}^n+[1\leftrightarrow 2], \qquad (2)$$

where $\vec{r}_{12}=\vec{r}_1-\vec{r}_2$. The eigenvalues are calculated by the Rayleigh-Ritz variational principle

$$E=\frac{\langle\Psi_0|H|\Psi_0\rangle}{\langle\Psi_0\Psi_0\rangle}, \qquad (3)$$

which requires minimizing E with respect to variation of the nonlinear parameters. For 615 terms in the expansion, Eq. (2), we obtain $E=-1.192\,92$ Ry for H_2^+, which is far from the accurate value, $-1.194\,278\,131$ Ry of Ref. [3]. This is unlike the two-electron systems where accurate results can be obtained by using fairly short expansions in Eq. (2). As explained in Ref. [2], the exponentials and powers appearing in Eq. (2) are capable of describing the correlations between the nuclei and the electrons but not the internuclear motion, which we know from the Born-Oppenheimer approximation is described by a Gaussian-like function centered around the equilibrium positions of the nuclei. This Gaussian-like function can be well approximated by the form $r_{12}^N e^{-br_{12}}$ provided N is large and $b\approx N/2$ (cf. Fig. 1 in Ref. [2]). This leads to a simple modification of multiplying Eq. (2) by r_{12}^N. For the ground state the nonlinear parameters are chosen to minimize the energy, keeping Ω_0+N constant as we increase Ω_0. The convergence of the ground-state energy for H_2^+ with respect to Ω_0 is shown in Table I. For $\Omega_0=13$, i.e., 308 terms in the expansion, taking $N=10$, we obtain $E=-1.194\,277\,909$ Ry, differing by only about 2.2×10^{-7} Ry

TABLE I. Convergence of the ground-state energy E for H_2^+ with respect to Ω_0 Units are Ry.

Ω_0	N	E (Ry)
10	13	−1.194 275 130
11	12	−1.194 277 094
12	11	−1.194 277 168
13	10	−1.194 277 909

TABLE II. Ground-state energy E and expectation values of various parameters for H_2^+ and D_2^+. Units are Ry and a_0.

Quantity	H_2^+ [a]	H_2^+ [b]	D_2^+ [a]	D_2^+ [f]
E	−1.194 277 909	−1.194 278 126	−1.197 572 175	−1.197 577 413[g]
cusp(r_1)	−0.999 46	−0.999 451 778	−0.999 74	
$\langle\delta(r_1)\rangle$	0.206 74	0.206 736 364	0.207 73	
$\langle R^4\rangle$	19.542 88	19.542 349 39	18.419 80	
$\langle R^3\rangle$	9.125 80	9.125 657 555	8.774 09	
$\langle R^2\rangle$	4.310 97	4.313 285 944	4.216 29	4.2156
$\langle R\rangle$	2.063 92	2.063 913 868	2.044 16	2.0441
$\langle 1/R\rangle$	0.490 71	0.490 707 799	0.493 66	0.493 65
$\langle 1/R^2\rangle$	0.244 19	0.243 923 499	0.245 95	0.245 92
$\langle r_1^4\rangle$	24.035 14	24.034 835 140	23.236 48	
$\langle r_1^3\rangle$	8.709 95	8.709 881 574	8.505 20	
$\langle r_1^2\rangle$	3.558 81	3.558 797 930	3.507 84	3.5075
$\langle r_1\rangle$	1.692 97	1.692 966 208	1.682 40	1.6823
$\langle 1/r_1\rangle$	0.842 49	0.842 494 2962	0.845 62	0.845 62
$\langle r_1 r_2\rangle$	2.808 59	2.804 309 915[c]	2.777 41	
$\langle\cos\theta_{12}\rangle$	0.251 99	0.251 989 493	0.254 33	
$\langle r^2\rangle$	2.481 07	2.480 48[d]	2.453 76	2.4536
$\langle r_1^2 r_2^2/R^2\rangle$	3.158 65		3.156 26	
$\langle r_1^4/R^2\rangle$	5.502 14		5.462 16	
$\langle z^2\rangle$	1.171 74	1.171 74[d]	1.152 95	1.1528
Q	1.638 40	1.639 27[d]	1.605 61	
$\langle\nabla_1^2\rangle$	−5.228 501	−5.226 740 693[e]	−7.205 68	

[a]Present work.
[b]Reference [5].
[c]The value given in Ref. [5] appears to be off by a factor of 2.
[d]Reference [6].
[e]The value given in Ref. [5] should be negative.
[f]Reference [8].
[g]Reference [4].

from the accurate value [3]. A similar calculation was carried out for D_2^+. We obtain $E=-1.197\,572\,175$ Ry, $\Omega_0=13$, and $N=10$ for the ground-state energy, differing by 5.2×10^{-6} Ry from the accurate value [4]. To get a much better value of the ground-state energy nuclei must be localized by using N much higher than 10, which is not feasible numerically. An improvement could be made by using a combination of functions such as $r_{12}^N e^{-br_{12}}$.

Using the wave function obtained variationally, expectation values of various quantities are calculated. They are given for H_2^+ and D_2^+ in Table II. In the table, $\vec{r}$ represents the distance of the electron from the center of mass of the nuclei and z is the projection of $\vec{r}$ onto $\vec{r}_{12}$ and they are given by the expressions

$$r^2=\frac{r_1^2+r_2^2}{2}-\frac{r_{12}^2}{4}, \tag{4}$$

$$z=\frac{\vec{r}\cdot\vec{r}_{12}}{r_{12}}=\frac{r_1^2-r_2^2}{2r_{12}}, \tag{5}$$

and $Q=\langle r_{12}^2+r^2-3z^2\rangle/2$ is the permanent quadrupole moment. In the table $R\equiv r_{12}$, energies are in the units of Ry, and distances are in units of a_0. The cusp value with respect to r_{12} is equal to zero because of nonzero powers of r_{12}, while the cusp value with respect to r_1 is very close to $-\mu$ (0.999 455 679 for H_2^+ and 0.999 727 630 for D_2^+). The Dirac δ function $\delta(\vec{r}_1)$ required in the calculation of the Fermi contact term is also given in the table. We compare our results for H_2^+ with the recent results of Frolov [5], where 500 linear parameters and 1200 nonlinear paremeters were used, and also (when Ref. [5] does not have a particular one) with those of Babb and Shertzer [6] obtained by using the finite-element method. The agreement is very good considering only two nonlinear parameters were employed in the wave function. In spite of the fact that the individual expectation values of R^2, r^2, and z^2 agree very well with those of Ref. [5], the value of Q does not agree well with the accurate value 1.639 272 80 calculated by Moss [7]. Babb and Shertzer [6] compare their results with results of other calculations and we have not repeated those here (see Ref. [6]).

The expectation values of various operators for D_2^+ are compared, where available, with those given by Bishop and Cheung [8]. They carried out a nonadiabatic calculation in addition to the Born-Oppenheimer and adiabatic calculations, using a deuteron mass equal to 3670.479 07. This differs by 0.003 95 compared to the mass used in the present calculation. We give their nonadiabatic results in Table II. The agreement with their calculation is quite good.

III. CONCLUSION

In summary, we have shown that with a suitable modification of the Hylleraas wave function accurate ground-state energy and expectation values of various operators can be obtained that compare favorably with the results obtained using more elaborate wave function.

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