IMPROVED GROUND STATE DISSOCIATION ENERGY FOR THE HYDROGEN MOLECULE*

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A wavefunction depending explicitly on the interelectronic distance r_{12}^n ($n \leqslant 3$), and containing 4 nonlinear and 130 linear parameters has been used to calculate the Born-Oppenheimer ground state energy of the hydrogen molecule for the equilibrium internuclear distance. The improvement over the previous best value amounts to 0.14 cm^{-1} and removes part of the small discrepancy between the theoretical and experimental dissociation energies.

1. Introduction

Recently, on the occasion of the 50th anniversary of the Schrödinger equation, one of the present authors [1] has discussed the accuracy of theoretical determination of the energy of the hydrogen molecule in its ground state and in some excited states. The comparison of the theoretical and experimental results has indicated that there are discrepancies which seem to be larger than the experimental error limits for the electronic ground state [2–4], and are certainly larger than the error limits for the lowest stable triplet state of the molecule [5]. The discrepancies have been pointed out recently by LeRoy and Barwell [4] who narrowed the experimental error limits for the ground state of D_2, and by Jost et al. [5] who determined very accurately the energy of D_2 in the $a^3\Sigma_g^+$ state.

Dabrowski and Herzberg [6] have analysed the vibrational energies in the electronic ground state of H_2, HD and D_2, and their results also indicate that the mass-independent part of the theoretical energy is too high by about 0.2 cm^{-1}.

In the present paper we shall consider the discrepancy between the theoretical and experimental values of the ground state dissociation energy of the hydrogen molecule. Since the discrepancy is mass-independent only the Born-Oppenheimer potential energy curve or the relativistic and radiative corrections can be responsible for it. Both the relativistic and radiative corrections [7, 8], however, are fairly small and are not likely to be in error by a few tenths of a reciprocal centimeter. Hence the Born-Oppenheimer potential seems to be the most likely offender.

For the electronic ground state a perfect agreement between theory and experiment would be obtained [1] if the clamped nuclei potential energy were lowered by at least 0.3 cm^{-1} in the vicinity of the equilibrium internuclear distance. The calculations reported below were undertaken to test whether an electronic wavefunction more flexible than the previous ones [7, 9, 10] might yield this effect.

2. Results and discussion

In the most accurate previous calculations for the ground state of H_2 in the vicinity of the equilibrium internuclear separation a 100-term wavefunction with one non-linear parameter was employed [10]. In the present work we used a wavefunction with 4 non-linear parameters, identical with that used previously by Wolniewicz and one of the present authors for excited states (see, e.g., [11]). The program has been generalized, however, to include also the third powers of the interelectronic distance, r_{12}, in the wavefunction, similarly as in the work with the one-exponent wavefunction [7, 10].

Thus the wavefunction employed was of the form

$$\Psi = \sum_{i=1}^{N} c_i [\Phi_i(1, 2) + \Phi_i(2, 1)]$$

$$\Phi_i(1, 2) = (1/4\pi) \exp(-\alpha\xi_1 - \bar{\alpha}\xi_2) [\exp(\beta\eta_1 + \bar{\beta}\eta_2)$$

$$+ (-1)^{s_i + \bar{s}_i} \exp(-\beta\eta_1 - \bar{\beta}\eta_2)] \xi_1^{r_i} \xi_2^{\bar{r}_i} \eta_1^{s_i} \eta_2^{\bar{s}_i} \varrho^{\mu_i},$$

where ξ and η are the elliptic coordinates; $\varrho = 2r_{12}/R$; r_{12} and R denote the interelectronic and internuclear distance, respectively; $c_i, \alpha, \bar{\alpha}, \beta$ and $\bar{\beta}$ are variational parameters. The maximum powers of $\xi_1 \xi_2, \eta_1$ and η_2 were related to those of ϱ by the inequality $t_i + \mu_i \leqslant 5$ where $t_i = r_i, \bar{r}_i, s_i, \bar{s}_i$ and $\mu_i \leqslant 3$.

All four exponents were optimized in a 40-term expansion for $R = 1.4$ a.u. and the same values were used in longer expansions. Numerous test runs have been made to select the most important terms for the final wavefunction which was composed of 130 terms. For short expansions the introduction of four non-linear parameters to the wavefunction, rather than of one, improves the convergence of the energy. In Table I we give two sets of results obtained using wavefunctions with various numbers of terms denoted by N.

For comparison the previous results [7, 10] are listed in the last column. The results given in columns (a) and (b) were obtained with wavefunctions which differed in the order of terms. In the case (a) the first 114 terms did not contain r_{12}^3, whereas in the case (b) the first 66 terms were the same as in (a) but the remaining ones were intermixed to speed up the convergence. The best previous binding energy for $R = 1.4$ was $D = 38292.783$ cm^{-1}

TABLE I

Binding energies (in cm^{-1}) of the hydrogen molecule at $R = 1.4$ a.u. obtained using various numbers of terms in the wavefunction (1 atomic unit of energy = 219474.62 cm^{-1})

N	D		
	a	b	[7, 10]
40	38291.106	38291.106	38290.8
50	38292.081	38292.081	38291.4
66	38292.458	38292.458	
80	38292.493	38292.814	38292.7
100	38292.557	38292.881	38292.783
114	38292.620	38292.907	
120	38292.880	38292.915	
130	38292.922	38292.922	

[10]. Hence the total improvement obtained in the present calculation by introducing 3 additional non-linear and 30 linear parameters amounts to 0.14 cm^{-1}. In our opinion the improvement which can be obtained by using a still more flexible wavefunction in the calculation of the Born-Oppenheimer potential energy curve amounts at the most to a few hundredths of cm^{-1}.

The diagonal nuclear motion corrections have also been recalculated using a more accurate wavefunction than in previous calculations [7, 10]. The resulting improvement was however completely negligible.

To make our results reproducible we give the values of all the parameters which determine the basis functions: $\alpha = 1.062$, $\bar{\alpha} = 1.021$, $\beta = 0.442$, $\bar{\beta} = 0.233$, and the values of μ_i, r_i, s_i, $\bar{r}_i$ and $\bar{s}_i$ for the case (b) are listed in Table II.

In Table III the final theoretical dissociation energies for H_2 and D_2 are compared with the experimental values. The present correction to the Born-Oppenheimer potential energy curve calculated for the equilibrium internuclear distance, 0.14 cm^{-1}, is likely to have approximately the same value over the whole region of zero-point vibrations and therefore it has been treated as an additive correction to D_0. Two sets of theoretical dissociation energies are given in Table III. They differ in the employed values of the non-adiabatic correction. In the first case the values resulting from van Vleck's formula [12] obtained in an approximate second-order perturbation theory were used [13, 9]. In the second case the recent values derived by Dabrowski and Herzberg [6] from experimental data were utilized. The small residual discrepancy between the theoretical and experimental dissociation energies seems to be meaningful. The only component of the theoretical

TABLE II

Parameters which define the basis set used in present work

i	$\mu_i\ r_i\ s_i\ \bar r_i\ \bar s_i$	i	$\mu_i\ r_i\ s_i\ \bar r_i\ \bar s_i$	i	$\mu_i\ r_i\ s_i\ \bar r_i\ \bar s_i$	i	$\mu_i\ r_i\ s_i\ \bar r_i\ \bar s_i$
1	0 0 0 0 0	34	2 0 1 0 1	67	3 0 0 0 0	100	3 2 0 1 0
2	0 0 0 1 0	35	0 1 0 4 0	68	3 0 0 1 0	101	2 0 1 1 3
3	1 0 0 0 0	36	0 1 0 0 4	69	3 1 0 1 0	102	1 1 0 4 0
4	0 0 0 2 0	37	0 0 1 1 3	70	3 0 1 0 1	103	3 1 2 0 2
5	0 0 0 0 2	38	0 0 1 3 1	71	3 0 1 1 1	104	3 1 1 2 1
6	0 1 0 1 0	39	0 2 0 3 0	72	3 1 1 1 1	105	0 1 3 1 1
7	0 0 1 0 1	40	0 0 2 3 0	73	3 1 1 0 1	106	0 0 3 2 1
8	1 0 0 1 0	41	0 0 2 1 2	74	3 0 2 0 2	107	0 2 1 0 3
9	2 0 0 0 0	42	1 1 0 0 0	75	3 2 0 2 0	108	1 2 2 1 0
10	0 0 0 3 0	43	1 0 0 3 0	76	2 0 2 0 2	109	2 2 0 1 0
11	0 0 0 1 2	44	0 2 1 0 1	77	2 2 0 3 0	110	1 0 0 3 2
12	0 1 0 2 0	45	2 1 0 2 0	78	1 1 0 1 2	111	1 1 1 1 1
13	0 1 0 0 2	46	2 0 1 1 1	79	2 0 1 2 1	112	0 0 1 0 5
14	0 0 1 1 1	47	2 1 1 1 1	80	1 0 2 2 0	113	0 0 5 0 1
15	1 0 0 2 0	48	0 2 0 0 0	81	0 0 1 2 3	114	0 0 0 5 0
16	1 0 0 0 2	49	0 2 0 1 0	82	0 2 3 0 1	115	0 3 2 0 0
17	1 1 0 1 0	50	0 0 0 4 0	83	2 2 0 2 0	116	1 3 1 1 1
18	1 0 1 0 1	51	0 4 0 0 0	84	0 5 0 0 0	117	1 0 4 1 0
19	2 0 0 1 0	52	2 2 0 0 0	85	0 1 3 0 1	118	2 3 0 1 0
20	0 0 0 2 2	53	0 3 0 1 0	86	0 0 3 0 1	119	1 3 1 0 1
21	0 0 0 0 4	54	1 1 1 0 1	87	1 1 2 0 0	120	2 2 2 0 0
22	0 1 0 3 0	55	2 1 0 0 0	88	0 1 2 2 0	121	2 3 1 1 1
23	0 1 0 1 2	56	0 1 1 2 1	89	1 1 0 3 0	122	2 2 1 1 1
24	0 0 1 2 1	57	0 0 0 4 2	90	1 0 2 0 2	123	0 1 0 5 0
25	0 2 0 2 0	58	1 1 2 1 0	91	1 0 1 2 1	124	1 2 0 3 0
26	0 2 0 0 2	59	1 3 0 1 0	92	0 0 0 3 2	125	1 1 2 3 0
27	0 0 2 0 2	60	0 4 2 0 0	93	0 1 0 2 2	126	0 1 0 0 0
28	0 1 1 1 1	61	1 2 0 0 2	94	1 0 0 1 2	127	0 1 1 0 1
29	1 1 0 2 0	62	1 0 1 3 1	95	2 1 0 0 2	128	1 1 1 2 1
30	1 1 0 0 2	63	0 2 2 2 0	96	2 2 0 0 2	129	3 0 2 1 2
31	1 0 1 1 1	64	0 0 1 0 3	97	3 0 0 2 0	130	3 1 2 0 0
32	2 0 0 2 0	65	0 1 0 3 2	98	2 0 0 0 2		
33	2 1 0 1 0	66	1 2 0 2 0	99	3 1 0 2 0		

energy whose value may be questioned is the nonadiabatic correction. However, since the discrepancy is mass independent it is not likely that it can be removed by improving the value of $\Delta D'_{\text{nonad}}$. Hence we are not able to indicate which theoretical quantity may be responsible for the discrepancy. In addition it may be pointed out that the analysis of the theoretical and experimental vibrational energies performed by Dabrowski and Herzberg [6] makes a further lowering of the adiabatic potential energy curve by more than 0.1 cm^{-1} very unlikely.

TABLE III

Comparison of the theoretical and experimental dissociation energies of the hydrogen molecule (in cm^{-1})

	Reference	H_2	D_2
D_0 exper.	[2–4]	36118.6 ± 0.5	36748.9 ± 0.3
D_0 theor. adiabatic	[9]	36117.33	36747.93
ΔD_{nonad}	[13, 9]	0.65	0.23
D_0 theor. nonadiabatic	[9]	36117.98	36748.16
Correction to B.O. energy	present work	0.14	0.14
D_0 theor. nonadiabatic	present work	36118.12	36748.30
Residual discrepancy		0.5 ± 0.5	0.6 ± 0.3
ΔD_{nonad} exper.	[6]	0.45	0.17
D_0 theor. (with ΔD_{nonad} exper.)	present work	36117.92	36748.24
Residual discrepancy		0.7 ± 0.5	0.7 ± 0.3

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