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CONFIRMATION OF THE DISCREPANCY BETWEEN THE THEORETICAL AND EXPERIMENTAL GROUND-STATE ENERGIES OF H_2†

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(Received 9 January 1968)

A double-precision calculation of the dissociation energy of the hydrogen molecule has been carried out and the results confirm the existing discrepancy with the experimental value, the discrepancy being one order of magnitude larger than the experimental error.

A discrepancy exists between the experimental dissociation energy of the hydrogen molecule, $D_0 = 36\,113.6 \pm 0.3$ cm^{-1}, measured by Herzberg and Monfils,[1] and the theoretical value, $D_0 = 36\,117.3$ cm^{-1}, obtained by the present authors.[2-3] The larger theoretical value of the dissociation energy means that the theoretical total energy of the molecule is <u>lower</u> than the experimental one. However, since the discrepancy is in the sixth significant figure of the total energy which was calculated with an accuracy of eight significant figures, it was conceivable that part, if not all, of the discrepancy was caused by rounding errors in the numerical computation. To clarify the situation, a double-precision calculation with a more flexible wave function was carried out. The nonrelativistic four-particle Hamiltonian was used and the calculation was performed in the adiabatic approximation[1,4] which gives an <u>upper bound</u> to the exact eigenvalue. The relativistic and radiative corrections calculated as a perturbation were added to the final energy.

In the present work the electronic wave function was represented by an 80-term expansion in elliptic coordinates, identical with that used in the single-precision calculation,[2] and also by a more flexible 100-term expansion. Since the wave function depends explicitly on the interelectronic distance, and many of the integrals must be computed by numerical integration (Simpson's rule), it was proper to test the accuracy of the integration. The results of the fixed-nucleus calculation are shown in Table I where the first row represents the previous single-precision result. The next three rows represent, for the same wave function, the present results of the double-precision calculation with a varying number of integration points N. The next two rows show how a change of N affects the results obtained with

Table I. The fixed-nucleus total energy, E, and binding energy, D, for the electronic ground state of the hydrogen molecule calculated in double precision and varying the number of terms, n, in the electronic wave function, the number of integration points, N, and the internuclear distance R. Conversion factor for the energy: 1 a.u. = 219 474.62 cm^{-1}.

n	N	R (a.u.)	E (a.u.)	D (cm^{-1})
80	110	1.4011	-1.1744746	38292.8
80	150	1.4011	-1.174474657624	38292.75903
80	250	1.4011	-1.174474657935	38292.75910
80	350	1.4011	-1.174474657970	38292.75911
100	350	1.4011	-1.174474982924	38292.830427
100	500	1.4011	-1.174474982931	38292.830428
100	500	1.401075	-1.17447498301568	38292.83044693
100	500	1.401076	-1.17447498301674	38292.83044717
100	500	1.401077	-1.17447498301743	38292.83044732
100	500	1.401078	-1.17447498301776	38292.83044739
100	500	1.401079	-1.17447498301771	38292.83044738
100	500	1.401080	-1.17447498301730	38292.83044729

a more flexible 100-term wave function. Finally, in the last six rows one can see the energies obtained by varying the internuclear distance, R, around the equilibrium value. The energy has also been computed for other values of R.

The above results show clearly that the previous single-precision energy for the equilibrium internuclear distance was accurate up to the eighth figure. They also strongly suggest, especially in connection with the previous results,[2] that a calculation with a still more flexible wave function would not lower the energy by more than a small fraction of a reciprocal centimeter.

The diagonal corrections for nuclear motion[2,4] computed previously with a 54-term wave function have now been recomputed in double precision and using a different algorithm. They fully agree with the single-precision results, and an extension of the expansion length to 66 terms (for $R = 1.4011$ and $R = 2.2$ a.u.) decreased the nuclear motion corrections by only 0.01 cm^{-1}.

Using for $1.0 \leq R \leq 3.2$ the energies calculated in double precision, and for $R < 1.0$ as well as for $R > 3.2$ the previously calculated values, and also the previously computed corrections for nuclear motion, the vibrational equation was solved and for the ground state the dissociation energy $D_0 = 36\,118.1\ \text{cm}^{-1}$ was obtained. The above value of D_0 can easily be corrected for the relativistic and radiative effects. Using[2,5] $\Delta D_{\text{rel}} = 0.5\ \text{cm}^{-1}$ and[6] $\Delta D_{\text{rad}} = -0.2\ \text{cm}^{-1}$ one gets the final ground-state dissociation energy $D_0 = 36\,117.4\ \text{cm}^{-1}$, and hence the final theoretical total energy of the molecule is 3.8 cm^{-1} lower than the experimental value. The discrepancy is one order of magnitude larger than the experimental error and any improvement of the adiabatic energy would increase the discrepancy.

Since all known effects of non-negligible magnitude have been included in the theoretical calculation, and since we see no reason to doubt the accuracy of the experimental value, the explanation of the discrepancy remains to be found.

The authors are indebted to Professor R. S. Mulliken and Professor C. C. J. Roothaan for their kind hospitality, and to Professor C. C. J. Roothaan for his continuous interest in the present work and for stimulating discussions.

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†This work was supported in part by the National Science Foundation under Grant No. NSF GP-7774, and in part by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham), under Contract No. DA-31-124-ARO-D-447, ARPA Order No. 368.

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COLLISIONS OF SINGLET EXCITONS IN MOLECULAR CRYSTALS

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(Received 25 August 1967)

The recent publication of an experimental study of singlet-singlet exciton annihilation in crystalline anthracene[1] has been followed by two communications[2,3] attempting to provide a theoretical analysis of these experimental data. This Letter presents a study of the metastable exciton states resulting from singlet-exciton collisions in molecular crystals. Any coherent theoretical analysis of the collision annihilation[1-10] of singlet excitons in crystalline anthracene has to be consistent with the following experimental facts.

(a) Kinetic data.—The rate constants for singlet-singlet annihilation γ_S, and for the production of charge carriers by exciton-exciton annihilation γ_i, can be expressed in terms of the exciton density n_E and the charge carrier density n_e:

$$\gamma_s = n_E^{-2}(-dn_E/dt); \quad \gamma_i = n_E^{-2}(dn_e/dt). \tag{1}$$