

Comment on "A theoretical study of the dissociation energy of BH using quadratic configuration interaction"

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(Received 28 April 1989; accepted 31 May 1989)

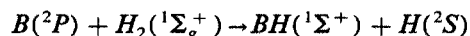
The dissociation energy of boron hydride has been the subject of some discussion recently. Huber and Herzberg¹ (HH) list a ground state D_0 of 78.9 kcal mol⁻¹. This value was based on the assumption, that the experimental predissociation limit² of 82.6 ± 0.4 kcal mol⁻¹ was the energy required to attain an outer repulsive maximum in the ¹Π potential curve, the height of which was estimated by Hurley³ as 0.16 eV. Several *ab initio* calculations^{4,5} appeared to corroborate the HH value: however, in both cases rather small basis sets were used.

Curtiss and Pople⁶ (CP) found a much larger value $D_e = 82.8$, $D_0 = 86.0$ kcal mol⁻¹ using their G1 theory,⁷ which is based on both basis set additivity and isogyric comparisons. As the general accuracy of this model is about 2 kcal mol⁻¹, this discrepancy is somewhat unexpected. In the paper on which the present work is a comment,⁸ they used their new quadratic configuration interaction [QCISD(T)]⁹ method, together with a large 6-311 + G(3df,3pd) basis set¹⁰ and an isogyric comparison,¹¹ to obtain a D_0 value of 84.9 kcal mol⁻¹, which they expected to be accurate to ± 1 kcal mol⁻¹. Combined with a precise calculation of the zero-point energy by Botschwina¹² of 3.36 kcal mol⁻¹, this amounts to a D_0 value of 8.15 kcal mol⁻¹, which certainly is not consistent with the value proposed by HH. As the value is quite close to the predissociation limit in Ref. 2, they suggested that the predissociation limit itself is perhaps quite close to the actual dissociation energy.

Recently, a new family of combined bond-polarization function basis sets has been developed in our laboratory,^{13,14} specially aimed at the cost-effective and accurate calculation of dissociation energies. Combined with an augmented coupled cluster method CCD + ST(CCD),¹⁵ which actually is quite comparable to the QCISD(T) method used by CP, mean absolute errors for the well-determined first-row hydride dissociation energies of 0.68 and 0.42 kcal mol⁻¹ were achieved¹⁶ for the 6-311 + G(*d,p*)B and 6-311 + G(2df,*p*)B basis sets,¹³ respectively. The corresponding value for the regular 6-311 + G(2df,*p*) basis set is 1.99 kcal mol⁻¹ (Ref. 16). Since the largest absolute errors were found in the polyatomic hydrides, expected errors for the diatomic hydrides are even less, perhaps on the order of

0.2 kcal mol⁻¹ at most. So the determination of the dissociation energy using this theoretical model should be of some value regarding the present issue.

Using the CCD + ST(CCD)/6-311 + G(2df,*p*)B basis set, which for BH and H₂ consists of the regular 6-311 + G(2df,*p*) basis set with a single *sp* shell (exponents 0.86 and 0.237, respectively) halfway each bond, we found a direct dissociation energy of 83.1 kcal mol⁻¹ at the HF/6-31G* geometry $R_e = 1.225$ Å. According to the isogyric reaction



which is also employed by CP, this leads to a D_e value of 85.8 kcal mol⁻¹, which corresponds to a D_0 of 82.5 kcal mol⁻¹, in perfect agreement with the predissociation limit. The same basis set without bond functions leads to values of 85.7 kcal mol⁻¹ D_e , and 82.3 kcal mol⁻¹ D_0 , again in good agreement with the predissociation limit. Finally, the 6-311 + G(*d,p*)B basis set comes up with values of 85.4 and 82.1 kcal mol⁻¹ for D_e and D_0 , respectively. This latter value, which again points to the predissociation limit, might be underestimated, as the same basis set exhibits this behavior for the relatively well-established dissociation energies of both LiH and CH. For OH and HF, overshooting is caused by elevated basis set superposition error for these species.¹⁷

In order to assess the effect of the geometry on this result, we have adopted the same cubic interpolation procedure, using the same reference geometries, as CP. The results are presented in Table I. For the BH molecule, cubic interpo-

TABLE I. CCD + ST(CCD)/6-311 + G(2df,*p*)B energies (hartree).

$R(\text{Å})$	Energy	$R(\text{Å})$	Energy
	H		B
	-0.499 810		-24.596 562
	H ₂		BH
0.730	-1.169 763	1.214	-25.228 681
0.735	-1.169 857	1.224	-25.228 791
0.740	-1.169 917	1.234	-25.228 826
0.745	-1.169 942	1.244	-25.228 792
0.750	-1.169 935

lation leads to an optimum bond distance of 1.234 Å, and a total energy of $-25.228\ 826\ 3$ hartree. For the hydrogen molecule, involved in the isogyric comparison, the corresponding values are 0.746 Å and $-1.169\ 943\ 2$ hartree, respectively. The net result on the direct dissociation energy ($83.1\ \text{kcal mol}^{-1}$) is negligible; however, in the isogyric comparison a D_e lowering of about $0.1\ \text{kcal mol}^{-1}$ is observed, leading to $106.9\ \text{kcal mol}^{-1}$ for H_2 and a D_e value for BH of $85.7\ \text{kcal mol}^{-1}$. Since the small errors observed for the diatomic hydrides with this theoretical model from the UHF/6-31G* geometry were always positive rather than negative, this value should be even more accurate than the previous one. All taken into account, we here propose a theoretical dissociation energy for BH of $82.4 \pm 0.2\ \text{kcal mol}^{-1}$, which is in perfect agreement with the observed predissociation limit. This result confirms the conclusion of CP that the "outer repulsive hump" of the predissociation state should be investigated more fully, and that the observed predissociation limit is quite close to the actual dissociation energy.

At the time of writing this comment, no program capable of quadratic configuration interaction was available to the authors. We feel however quite confident that the use of QCI would lead to essentially the same results, and have therefore included in the text all data necessary to rerun our calculations using this theoretical model.

Note: The study in Ref. 16 has recently been repeated using CID/6-31G* instead of HF/6-31G* geometries. It was found that at the CCD + ST(CCD)/6-311 + G(2df,p)B level, a mean absolute error of 0.12 kcal-

mol^{-1} per bond could be achieved [Chem. Phys. Lett. (submitted)]. The dissociation energy of BH using these geometries is identical to two decimal places with the result in this paper. This supports our claims concerning the accuracy of the calculation.

¹K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

²J. C. W. Johns, F. A. Grimm, and R. F. Porter, *J. Mol. Spectrosc.* **22**, 435 (1967).

³A. C. Hurley, *Proc. R. Soc. London, A* **261**, 237 (1961).

⁴M. W. Schmidt, M. B. T. Lam, S. T. Elbert, and K. Ruedenberg, *Theor. Chim. Acta* **68**, 69 (1985).

⁵E. A. Carter and W. A. Goddard III, *J. Chem. Phys.* **88**, 3132 (1988).

⁶L. A. Curtiss and J. A. Pople, *J. Chem. Phys.* **89**, 614 (1988).

⁷L. A. Curtiss and J. A. Pople, *J. Chem. Phys.* **88**, 7405 (1988); J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).

⁸L. A. Curtiss and J. A. Pople, *J. Chem. Phys.* **90**, 2522 (1989).

⁹J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).

¹⁰M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984).

¹¹J. A. Pople, M. J. Frisch, B. T. Luke, and J. S. Binkley, *Int. J. Quantum Chem. Symp.* **17**, 307 (1983); *J. Phys. Chem.* **89**, 2198 (1985).

¹²P. Botschwina, *J. Mol. Spectrosc.* **118**, 76 (1986).

¹³J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* **10**, 152 (1989).

¹⁴J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

¹⁵K. Raghavachari, *J. Chem. Phys.* **82**, 4607 (1985).

¹⁶J. M. L. Martin, J. P. François, and R. Gijbels, *Chem. Phys. Lett.* **157**, 217 (1989).

¹⁷J. M. L. Martin, J. P. François, and R. Gijbels, *Theor. Chim. Acta* (in press).

ERRATA

Erratum: Vibrational excitation and quenching of N_2^+ in collision with He at relative energies below 1 eV [*J. Chem. Phys.* **88**, 213 (1988)]

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In the paper reporting the vibrational excitation and quenching of N_2^+ by He in the near thermal, 300 K–0.60 eV KE_{cm} energy range¹ there was an error in converting from the applied E/N scale in the flow drift tube to the average center of mass KE_{cm} scale. The correct expression is

$\text{KE}_{\text{cm}} = 1/2 Mv_d^2 + 3/2kT$, where M is the helium buffer gas mass and v_d is the ion drift velocity in the helium buffer gas given by $v_d = \mu E$, where μ is the ion mobility in He and E is the electric field strength. This leads to the following slightly corrected scale for Fig. 6:

$E/N(\text{Td})$	0	20	40	60	80	100	120	140	160
$\text{KE}_{\text{cm}}(\text{eV})$	0.045	0.064	0.13	0.20	0.29	0.38	0.47	0.54	0.60