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# Complete basis set extrapolation limit for electronic structure calculations: Energetic and nonenergetic properties of HeBr and HeBr<sub>2</sub> van der Waals dimers

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The lowest  $^2\Sigma^+$  and  $^2\Pi$  electronic states of the HeBr molecule have been calculated by the *ab initio* coupled cluster approach in conjunction with a series of increasing size augmented correlation-consistent basis sets of double through quintuple zeta quality. Different extrapolation formulas to the complete basis set limit have been tested by comparing estimated and actual quintuple zeta quality counterpoise corrected interaction energies. Frozen-core approach is checked by performing calculations in which all electrons are correlated. The potential energy surfaces of the HeBr<sub>2</sub> van der Waals complex have been obtained from the HeBr potentials by means of the diatomic-in-molecule approach. Finally, transport, scattering, and spectroscopic properties of HeBr and HeBr<sub>2</sub>(*B*) systems derived from *ab initio* data for different basis sets are examined. It is shown that their convergence closely follows the convergence of corresponding potential energy surfaces.

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## I. INTRODUCTION

For years the general demand of molecular physics and physical chemistry on electronic structure theory—to provide reliable potential energy surfaces (PES's) suitable for nuclear dynamics calculations—remains virtually unchanged. What has undergone very rapid changes are the criteria for reliability and suitability. The requirements for accuracy and global definition of the PES become harder and harder to be satisfied solely by an increase in the computational resources available for *ab initio* quantum chemistry. Instead, advanced *ab initio* technologies are invented, many of them in line with Pople's concept of a “model chemistry.”<sup>1</sup>

One of the important steps in these developments was the discovery of practical routes to complete basis set (CBS) and complete correlation energy limits (see, e.g., Refs. 2–7). Recently, however, it has become apparent that “rather than correlation, basis set limitations are the greatest present weakness in *ab initio* electronic structure theory.”<sup>8</sup> In fact, current use of accurate methods such as the multireference configuration interaction treatment (MRCI)<sup>9–11</sup> and the coupled-cluster approach with single and double excitations (CCSD) often augmented with by a perturbative treatment of triple excitations [CCSD(T)],<sup>12,13</sup> have provided an accuracy quite close to full-configuration-interaction (FCI) limit for a given one-electron basis set. In particular, coupled-cluster

(CC) theory provides rapid convergence to the basis set (i.e., FCI) limit.<sup>12</sup> For this reason there is a renewed interest in the complementary problem of the convergence of the one-electron basis sets.<sup>14</sup> In order to minimize the error resulting from the use of finite one-particle expansions, the most popular and straightforward approach is based on implementation of correlation consistent basis sets cc-pVnZ type by Dunning and co-workers<sup>15–18</sup> followed by extrapolation to the CBS limit with  $n = \infty$ . Extensive evidence accumulated so far demonstrates the high accuracy of the extrapolation method for electronic energies, and these results have been used to establish quantitative relations between different *ab initio* methods,<sup>7</sup> databases of benchmark results,<sup>14,19</sup> and improve the knowledge of the electronic structure of many particular systems (see, e.g., Refs. 20 and 21).

However, despite significant experience with CBS extrapolations, many issues still deserve further inspection. Which analytical formula better describes the convergence to CBS? Should extrapolation be applied to the total electronic energy or to its Hartree–Fock and correlation counterparts? What are the scaling properties of the basis set superposition error? Does core electron correlation energy affect the CBS convergence, etc.?

As far as the potential for implementing CBS extrapolation to quantities other than total energy, it remains widely open. To our knowledge, only such quantities as dissociation energies, equilibrium structure parameters, vibrational frequencies, anharmonicities, electron affinities, and polarizabilities have been analyzed in prior studies.<sup>5,22,23</sup> It was only concluded that “energetic quantities tend to converge expo-

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entially, but such a behavior decreases as the quantities become less related to the energy.”<sup>22</sup> Since that time it has become clear that exponential extrapolation is only a crude approximation and much more accurate extrapolation formulas have been suggested and tested.<sup>5,6,19,23–25</sup> It has been proven that extrapolation is valid for some energy differences and structural parameters. However, the question can be put in more general terms, i.e., how far can one go from the “energy” while not losing the scaling properties of the correlation consistent basis sets? Do the results of spectroscopic and dynamical calculations on a series of cc-*VnZ* PES’s retain a memory of such a scaling?

It is not possible to answer the above questions with full generality, but it is worthwhile to undertake stringent tests. For this purpose we have chosen to study the HeBr molecule. Although we have had some practical interest in calculating the *ab initio* potential for it, this choice is quite reasonable for the present purpose. First, the He–Br interaction should be very weak and its description requires special care in its *ab initio* treatment. Despite the existence of some less artificial ways to saturate the basis sets for weak interaction calculations, such as the use of bond functions,<sup>26</sup> it is interesting to explore CBS extrapolations of the PES’s of weakly bound systems,<sup>20,21,27</sup> and to establish benchmarks. Second, HeBr is an open-shell molecule which has two close-lying <sup>2</sup>Σ<sup>+</sup> and <sup>2</sup>Π electronic states. Aside from the fact that accurate *ab initio* calculations of such systems are still regarded as state-of-the-art studies,<sup>28,29</sup> it is important to analyze the convergence behavior of the cc-*pVnZ* bases for distinct electronic states, or for the sum and difference of their potentials. This point is crucial since almost all observable dynamical quantities should be determined by the combinations of the PES’s.<sup>30</sup> Third, the *ab initio* potentials for small systems may not only be for direct use, but also for parametrizing semi-empirical models for treating larger systems. In our case this situation is represented by the HeBr<sub>2</sub> van der Waals complex whose PES’s can be obtained from those for HeBr by means of the diatomics-in-molecule (DIM) approach<sup>31</sup> and tested against available experimental data.<sup>32–34</sup>

This paper is organized as follows: The following section describes the *ab initio* and CBS extrapolation techniques. In Sec. III the results of the HeBr potential calculations are discussed. Sections IV and V are devoted to an analysis of transport, scattering, and spectroscopic properties of the HeBr system and to the PES’s and vibrational predissociation dynamics of the HeBr<sub>2</sub>(*B*) complex, respectively. Finally, conclusions follow.

## II. METHODOLOGY

All calculations have been performed with the GAUSSIAN 98 package of programs.<sup>35</sup> *Ab initio* potential energy curves were determined for the two electronic states X <sup>2</sup>Σ<sup>+</sup> and <sup>2</sup>Π using the spin unrestricted coupled-cluster method with all singles and doubles and a perturbative estimate of the triple excitations [UCCSD(T)]<sup>36,37</sup> starting from a spin-unrestricted Hartree–Fock (HF) reference wave function. We used the augmented correlation consistent polarized valence aug-cc-pVXZ (X=D,T,Q,5) basis sets of Dunning and co-workers.<sup>15,16,38,39</sup> The main reason for choosing this par-

ticular basis is that its systematic construction scheme makes it possible to carry out the basis set extrapolation to the CBS limit.<sup>40,41</sup> Moreover, this basis includes diffuse functions that are known to be essential for an accurate description of weak atomic interactions.

### A. Basis set extrapolation

Several formulas have been proposed for extrapolating finite basis set results to the complete basis set limit. One is the empirically based exponential by Dunning–Feller<sup>15,42,43</sup>

$$f(n) = f_{\text{CBS}} + \alpha \exp^{-\beta n}, \quad (1)$$

where  $n$  is the cardinal number of the basis set:  $n=2$  for DZ, 3 for TZ, etc.,  $f(n)$  is the property of interest and  $f_{\text{CBS}}$  is the asymptotic value, which is taken to approximate the CBS limit. This formula was shown to be effective in estimating CBS limit energies at the HF level,<sup>6</sup> although studies employing larger sizes of correlation-consistent basis sets<sup>25,44</sup> combined with the results from other high accuracy methodologies<sup>45–47</sup> have shown that the actual convergence rate with  $n$  is much slower than the exponential decay as the asymptotic limit is approached.<sup>48</sup> This is due to the problem associated with obtaining a correct description of the Coulomb cusp with one-electron basis sets. The Coulomb cusp is a direct consequence of the singularity of the Coulomb interaction  $r_{12}^{-1}$  at  $r_{12}=0$ . Since in any wave-function approach which does not explicitly include  $r_{12}$ , this cusp condition is not satisfied, there is a poor rate of convergence. [To address this problem, an alternative is to explicitly include the  $r_{12}$  factors in the wave function, for example, the linear  $r_{12}$  methods (see, e.g., Refs. 45–47), where the interelectronic coordinate enter the wave function linearly. However, even these methods suffer from basis set limitations,<sup>8</sup> since the multielectronic integrals that appears in such an approach requires the use of closure relationships to obviate the calculation of those complete integrals. This closure relationship assumes the basis is complete. In this way, it is expected that these methods provide accurate results if very larger basis sets are used.] In this respect, Schwartz, in 1962,<sup>2,49</sup> investigated the convergence of the second-order energy of two-electron atoms and showed that the energy increments obtained by adding a saturated shell of atomic orbital (AO) basis functions of angular momentum  $l$  to the AO basis set are

$$\Delta E_l = A/(l+1/2)^4 + B/(l+1/2)^6 + \mathcal{O}(l^{-8}).$$

A similar formula was found empirically by Carroll *et al.*<sup>50</sup> for configuration interaction calculations on the helium atom. Later it was analyzed by Hill<sup>51</sup> for general variational calculations and extended by Kutzelnigg and Morgan<sup>52</sup> for second-order perturbation (MP2) energies of many electron atoms, where similar expressions were obtained with odd term contributions as well.<sup>51,52</sup>

From the increments  $\Delta E_l$  the total basis set truncation error due to the omission of all basis functions of  $l > L$  can be estimated. In the limit, where  $L$  approaches infinity, such an error can be expressed as

$$E = E_\infty + A(L+1)^{-3} + B(L+1)^{-5} + \dots \quad (2)$$

For atoms this extrapolation formula is commonly used. For molecules, however, such a formula can only be approximately implemented for two reasons. First, the angular momentum is not a good quantum number. Second, the basis sets are not constructed in such a way that function space of a given angular momentum is saturated before the next function space is added.<sup>53,54</sup> In spite of these objections and motivated by the fact that expression (2) has a theoretical foundation it has also been applied to molecules and has been shown to be very successful (see, e.g., Refs. 25, 44, 55, and 56). When the cc-pVXZ basis sets<sup>15,16,38</sup> are used,<sup>53</sup>  $L = X - 1$  for H and He and  $L = X$  for higher row atoms. As a compromise, Martin<sup>55,56</sup> suggested replacing  $L$  by  $X - 1/2$  and to use the extrapolation formulas of the form

$$f(n) = f_{\text{CBS}} + \frac{B}{(n + \frac{1}{2})^4}, \quad (3)$$

$$f(n) = f_{\text{CBS}} + \frac{B}{(n + \frac{1}{2})^4} + \frac{C}{(n + \frac{1}{2})^6}, \quad (4)$$

$$f(n) = f_{\text{CBS}} + \frac{B}{(n + \frac{1}{2})^\alpha}. \quad (5)$$

In this study we tested and compared the performance of the formulas (3) and (4).

Due to the different rate of convergence of the HF and correlation levels, it has been argued that the HF and correlation energy have to be treated separately for an accurate prediction of the total energy at the CBS limit.<sup>4,56-58</sup> Taking this point into consideration, Truhlar *et al.*<sup>6</sup> proposed a two-point extrapolation formula, where HF and correlation energies are extrapolated to CBS limits using the power laws  $n^{-\alpha}$  and  $n^{-\beta}$ , respectively, where  $\alpha$  and  $\beta$  are empirical parameters to be optimized separately for HF and correlation energies. Halkier *et al.*,<sup>57</sup> on the other hand, suggested a different scheme where HF energies are fitted to the Dunning-Feller exponential formula while correlation energies ( $E^{\text{cor}}$ ) are extrapolated using the two-parametric expression

$$E^{\text{cor}} = E_\infty^{\text{cor}} + An^{-3} \quad (6)$$

that is obtained after identifying  $L$  with  $X - 1$  and retaining only the first term in the partial-wave expansion formula (2). We believe that extrapolating total energies is preferable for several reasons. First, the extrapolation is shorter and it is hoped that some of the basis set errors will cancel. Second, the correlation-consistent basis sets are optimized for the correlated energies. Third, if one is interested in calculating the energies of excited states the HF approach is not advised. Finally, since the correlation-consistent basis sets are not constructed by saturating each angular-momentum space functions separately but by systematically adding basis functions of different angular momentum that provide similar decreases in energy lowerings, it may not be appropriate<sup>44,48</sup> to apply the wave expansion results directly to the correlation energy for these particular basis sets. Anyway, we explored the usefulness of the expression (6) when applied to total energies.

Finally, as an alternative approach, we have also tested an empirical mixed exponential/Gaussian function that has been shown<sup>19,23</sup> to provide better results than the simpler exponential functional form

$$f(n) = f_{\text{CBS}} + B \exp^{-(n-1)} + C \exp^{-(n-1)^2}. \quad (7)$$

## B. Core correlation

We have carried out two sets of calculations. In the first set the core orbitals were kept frozen in the calculation of the correlation energies, which is sometimes called the frozen-core (FC) approximation, while in the second set the core orbitals were included. Core correlation effects have been shown to be insignificant for the evaluation of dissociation energies.<sup>59</sup> In fact, the majority of *ab initio* electronic structure calculations today include only the correlation energy of the valence electrons. We wanted to investigate how large the core correlation energy is in the present case, where we have a heavy atom bond.

In order to estimate the core contribution at the correlated level, it should be more appropriate to use the core-valence aug-cc-CpVXZ basis sets rather than the valence aug-cc-pVXZ basis sets of Dunning and co-workers. However, such basis sets are not yet available.

## C. Basis set superposition error

One problem in the computation of potential energy surfaces of weakly bonded systems such as HeBr is due to the basis set superposition error (BSSE). This error arises because in the calculation of the energy of the complex, each constituent can lower its energy artificially by taking advantage of basis functions of the other constituent. With the goal of correcting for BSSE we have used the full-counterpoise (FCP) scheme of Boys and Bernardi.<sup>60,61</sup> Within the FCP scheme the interaction energy  $V(R)$  of each electronic state of HeBr at each geometry is calculated as

$$V(R) = E_{\text{HeBr}}(R) - E_{\text{He}}^{\{\text{HeBr}\}}(R) - E_{\text{Br}}^{\{\text{HeBr}\}}(R), \quad (8)$$

where the quantities  $E_{\text{HeBr}}$ ,  $E_{\text{He}}^{\{\text{HeBr}\}}$ , and  $E_{\text{Br}}^{\{\text{HeBr}\}}$  are the electronic energies of HeBr, He, and Br, respectively, calculated in the complete HeBr basis set.

Despite the fact that the FCP scheme has been the most successful procedure to correct for BSSE, it is still viewed with skepticism.<sup>62</sup> The main argument against the FCP procedure invokes the Pauli exclusion principle, because of which, the basis set that is actually available to a monomer it is not the complete basis set of its partner but only the space of the unoccupied orbitals (see, for example, Ref. 62). For this reason, Daudey *et al.*<sup>63</sup> proposed to modify slightly the scheme using only the self-consistent-field (SCF)-virtual orbitals of the other fragment, which is referred to as VCP procedure. However, studies that compare both approaches (see, e.g., Ref. 64) provide numerical evidence in support of the FCP scheme, which continues to be the most commonly used.

Employing the aug-cc-pVXZ basis to get extrapolated CBS limits, Dunning *et al.*<sup>62</sup> and Paizs *et al.*<sup>65</sup> have shown that the convergence properties of molecular properties such

TABLE I. Equilibrium properties derived from the nonrelativistic FCP-corrected HeBr interaction energies. Percentage accuracy given in parentheses for V5Ze values is with respect to V5Z value. Results corresponding to the calculations without frozen-core approximation are given between brackets in the second line for each basis set.

Basis set	$V_{\Sigma}$		$V_{\Pi}$		$T_e, \text{cm}^{-1}$
	$R_e, \text{\AA}$	$D_e, \text{cm}^{-1}$	$R_e, \text{\AA}$	$D_e, \text{cm}^{-1}$	
VDZ	3.779	14.083	4.289	7.749	17.57
	[3.779]	[14.061]	[4.299]	[7.974]	[17.58]
VTZ	3.641	20.372	4.066	12.098	20.72
	[3.652]	[20.761]	[4.076]	[12.159]	[19.76]
VQZ	3.549	25.156	4.020	14.182	29.44
	[3.558]	[25.101]	[4.025]	[14.183]	[28.63]
V5Z	3.535	26.991	4.002	14.979	30.30
V5Ze/mix	3.525 (0.2)	27.291 (1.1)	4.002 (0.0)	14.979 (0.0)	32.47 (7)
	[3.526]	[28.058]	[3.995]	[15.419]	[32.44]
/exp	3.514 (0.6)	28.457 (5.2)	4.013 (0.3)	14.934 (0.3)	35.37 (17)
$/n^{-3}$	3.557 (0.6)	25.169 (6.7)	4.023 (0.5)	14.186 (5.2)	28.58 (6)
$/(n+1/2)^{-4}$	3.535 (0.0)	26.882 (0.4)	4.002 (0.0)	14.880 (0.7)	30.96 (2)
$/(n+1/2)^{-4,-6}$	3.525 (0.2)	27.361 (1.4)	4.002 (0.0)	14.986 (0.0)	32.55 (7)
CBS <sup>a</sup> /mix	3.514	28.573	3.992	15.451	33.90
	[3.526]	[28.059]	[3.995]	[15.419]	[32.44]
CBS <sup>b</sup> /mix	3.514	28.080	3.970	15.206	32.45
CBS <sup>b</sup> $/(n+1/2)^{-4}$	3.514	28.524	3.992	15.459	33.71
DIM-inverted	3.74	26.6	3.99	14.0	15.64

<sup>a</sup>Using the basis sets  $D \sim Q$  in the extrapolation procedure.

<sup>b</sup>Using the basis sets  $T \sim 5$  in the extrapolation procedure.

as intermolecular bond lengths<sup>65</sup> for weakly bounded systems, are improved if the results are corrected for BSSE with the FCP scheme.

### III. RESULTS AND DISCUSSION FOR HeBr POTENTIALS

As mentioned above, in order to calculate the potential energy curves of HeBr we used a spin-unrestricted reference wave function. The spin contamination was small ( $2\bar{S}+1 = 2.0063$  for the aug-cc-pVDZ basis set and  $2\bar{S}+1 = 2.0024$  for higher quality basis sets) and kept constant over the whole range of interatomic distances. The value of  $2\bar{S}+1$  was also the same for Br and HeBr.

Bond lengths  $R_e$ , well depths  $D_e$ , and vertical excitation energies  $T_e$ , extracted from counterpoise-corrected potential energy curves by spline interpolation for ground,  $X^2\Sigma^+$  and excited  $^2\Pi$  electronic states are presented for each basis set in Table I. Valence aug-cc-pVXZ ( $X = D, T, Q, 5$ ) basis sets are referred to as VDZ, VTZ, VQZ, and V5Z, respectively. The values extrapolated to the V5Z level through  $X = D-Q$  data (V5Ze) are also given along with their percentage accuracy with respect to the V5Z values. In order to distinguish complete basis set estimates for CBS and quintuple zeta basis set estimates V5Ze obtained from the five formulas (1), (3), (4), (6), and (7), we use the notation /exp,  $/(n+1/2)^{-4}$ ,  $/(n+1/2)^{-4,-6}$ ,  $/n^{-3}$ , and /mix, respectively. For each set, the first line referred to is the FC calculation, while the second line, in which the values are between brackets, corresponds to the calculation in which all electrons were correlated. It will be referred to as an all-electron (AE) calculation.

#### A. Basis set extrapolation

From the comparison of the percentage accuracy of the estimated V5Z values for the five extrapolation formulas used in this work, we can see that the performance of the extrapolation with expressions (3), (4), and (7) is very similar. In all cases the results are very encouraging. The percentage accuracy of the estimated V5Z values for the equilibrium properties of both the  $V_{\Sigma}$  and  $V_{\Pi}$  potentials is within 1.5%. On the other hand, the exponential formula (1) and the  $n^{-3}$  formula (6) are clearly worse with a percentage error that goes up to 5.5% and 6.7%, respectively. These results are not surprising, of course. As we mentioned above, it is well known that the exponential form works well for the HF energy, where the convergence is fast. On the contrary it has been found, theoretically, that the correlation energy does not converge exponentially but as the inverse power in the highest angular-momentum function presented in the basis set.<sup>2,50-52</sup> Thus an exponential convergence is not expected for the total correlated energy which is the sum of the HF and the correlation energy. This explains why by using the exponential extrapolation procedure, one gets an extrapolated value of the dissociation energy for the  $\Sigma$  state that is too large, while the equilibrium distance is too short. On the other hand, because the  $n^{-3}$  formula (6) was suggested to get the extrapolated value of the correlation energy alone, it is expected that such a trend will be reversed when the  $n^{-3}$  form is used. From Table I we can see that the extrapolated values of the dissociation energy of both the  $\Sigma$  and  $\Pi$  states are too small while those corresponding to the equilibrium distance are too large. However, when using the exponential formula for the  $\Pi$  state the convergence is too slow, contrary to what it is expected. This unsuspected behavior may be due

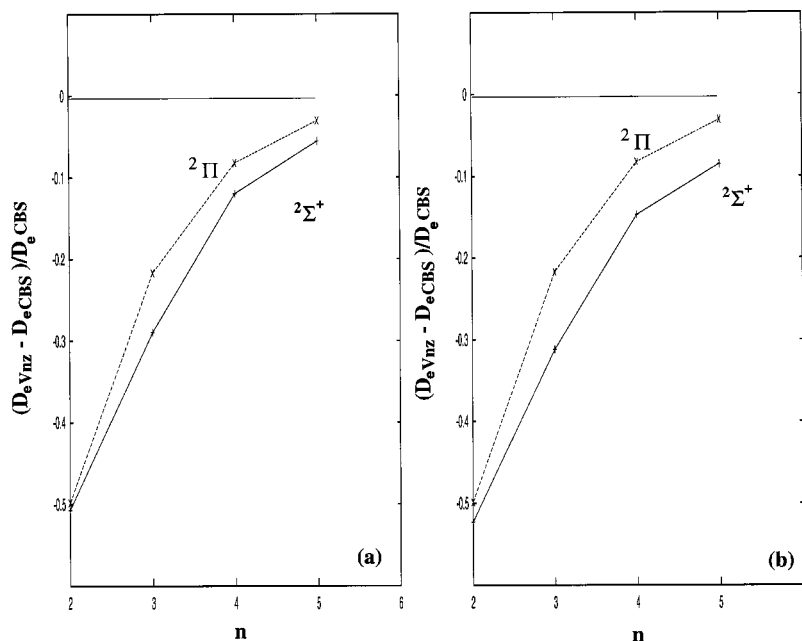


FIG. 1. Convergence rate for dissociation energies. The results in (a) correspond to extrapolation formula (3), and in (b) to extrapolation formula (7).

to the nonlinearity of the fitting parameter  $\alpha$  in the exponential formula, since multiple solutions may exist. This is one of the reasons for avoiding nonlinear fitting parameters in an extrapolation procedure. We will comment later on this aspect. On the other hand, despite both formulas  $/(n+1/2)^{-4}$  (3) and  $/n^{-3}$  (6) have the same physical basis and simple two-parameter form, the former improves a lot all of the estimated values with respect to the latter. Returning to the basis of both expressions, we see that since HeBr contains both first and higher row atoms, it makes more sense to identify  $L$  by  $X-1/2$  than by  $X-1$  in the partial-wave expression (2). On the other hand, by comparison of the performance of the formulas  $/(n+1/2)^{-4}$  (3) and  $/(n+1/2)^{-4,-6}$  (4) we see that the former works slightly better. Numerical experience<sup>57</sup> indicates that the inclusion of energies of lower cardinal numbers in extrapolation procedures that work with partial-wave expansion expressions may spoil the quality of the fits. To explore this fact we repeated the extrapolation with the formula  $/(n+1/2)^{-4}$  (3) by using the basis sets VDZ and VTZ, obtaining an error of 16% for  $D_e$  in the  $\Sigma$  state and 28% for  $T_e$ . These results are very conclusive and corroborate the previous ones.<sup>57</sup>

Another aspect that can be clearly noticed from Table I is that the error of the extrapolated vertical excitation energies,  $T_e$ , are larger than the error of the extrapolated  $D_e$  and  $R_e$  values regardless of the specific extrapolation formula used. The error of  $T_e$  accounts for the independence of the convergence rate on the nature of electronic state. Indeed, Figs. 1(a) and 1(b) demonstrates the convergence of the reduced dissociation energies  $(D_e^{VnZ} - D_e^{CBS})/D_e^{CBS}$  for the two electronic states. Convergence rates with respect to  $n$  are slightly different for the two states, in particular, at  $n=3$  and 4. This means that the energy splitting between  $^2\Pi$  and  $^2\Sigma^+$  states does not scale perfectly with  $n$ . However, when expression (3) is used, the errors in the  $\Sigma$  and  $\Pi$  potentials are most close to each other and, therefore, the error in the  $T_e$  is smallest.

The difference between interaction energies calculated and extrapolated at the V5Z level with expressions (3)  $[(n+1/2)^{-4}]$  and (7) (mix) at each internuclear distance exceeds  $1 \text{ cm}^{-1}$  only at short range, being quite similar for the  $^2\Sigma^+$  and  $^2\Pi$  states.

We will continue the discussion on the results with the two extrapolation formulas that provide better results, namely (3) and (7).

## B. Core correlation and basis set superposition error

We can see from Table I that the values of the three properties derived from FCP-corrected interaction energies calculated with and without FC approximation are very similar. In fact, the maximum difference in the value corresponding to the bond length  $R_e$  is  $0.009 \text{ \AA}$ , the one corresponding to the binding energy  $D_e$  is  $0.225 \text{ cm}^{-1}$ , which is 1.46% of the total HeBr interaction energy, and the one corresponding to the vertical excitation energy  $T_e$  is  $0.96 \text{ cm}^{-1}$ , which is 2.96% of the total HeBr excitation energy.

The extrapolation has been performed at each value of  $R$  in two ways: for the energies of dimer and monomers separately, i.e.,  $E_{\text{HeBr}}$ ,  $E_{\text{He}}^{\{\text{HeBr}\}}$ , and  $E_{\text{Br}}^{\{\text{HeBr}\}}$ , and for the counterpoise-corrected interaction energy, i.e.,  $V(R)$ . We notice that if we used linear fit parameters are used in the extrapolation, both procedures are equivalent. In fact, it can be easily shown that in such a case we have the matching property

$$E(a_\infty) - E(b_\infty) - E(c_\infty) \\ = E(a_1 - (b_1 + c_1), a_2 - (b_2 + c_2), a_3 - (b_3 + c_3)),$$

where  $E(x_\infty) = E(x_1, x_2, x_3)$ ,  $E$  is the energy,  $x_\infty$  represents the complete basis set, and  $x_i$  enumerates the different basis sets ( $i=1$  for VDZ,  $i=2$  for VTZ and so on). The notation  $x=a$ ,  $b$ , and  $c$  refers to the distinct species (i.e., HeBr, Br and He). This *size-consistency* property (in a sense of the correct separation into fragments) is another argument in fa-

TABLE II. Counterpoise correction to the calculated dissociation energy of the HeBr complex.

Basis set	$\Delta D_e^a(\text{cm}^{-1})$			
	$V_\Sigma$		$V_\Pi$	
	FC	AE	FC	AE
VDZ	28.42	37.78	15.28	20.61
VTZ	29.89	50.61	18.20	40.50
VQZ	25.49	40.29	14.04	24.15
V5Z	19.22		12.18	
V5Z <sub>e</sub> /mix	24.17	28.26	13.95	17.61
CBSe <sup>b</sup> /mix	23.15	23.20	13.90	14.95
CBSe <sup>c</sup> /mix	16.16		10.46	

<sup>a</sup>Difference in dissociation energy calculated with and without the counterpoise correction. A positive sign indicates that inclusion of the counterpoise correction lowers the dissociation energy.

<sup>b</sup>Using the basis sets  $D\sim Q$  in the extrapolation procedure.

<sup>c</sup>Using the basis sets  $T\sim 5$  in the extrapolation procedure.

vor of using the linear fit parameters. The numerical evidence is very convincing, when expression (1) was employed for the dimer and monomer energies separately, we obtained a purely repulsive interaction. It is the reason why van Mourik and Dunning<sup>66</sup> observed an irregular convergence behavior when extrapolating the energies of the complex and monomers separately for Ar–HF.

In Table II, the differences in dissociation energies,  $\Delta D_e$ , calculated from FCP corrected and uncorrected interaction energies, are tabulated for the different basis sets and CBS limits obtained with extrapolation formula (7). These values are estimations of the BSSE errors and provide us with an idea of the saturation of the atomic basis set at each level. We note that in our case the dissociation energies are of the same order of magnitude as the BSSE. Those errors are not particularly large for this system but the dissociation energies are extremely small and then correction for BSSE requires particular care. From Table II, we see also that the trend is that the larger the basis set the smaller the values of  $\Delta D_e$  for both the  $\Pi$  and  $\Sigma$  states. However, when one goes from the VDZ to VTZ levels, the direction is reversed. This result provides an indication that the VDZ basis set may be too small. Of course, BSSE should be zero at the true CBS limit. We see that at the extrapolated CBS limit, BSSE does not vanish. By using the VTZ, VQZ, and V5Z basis sets instead of the VDZ, VTZ, and VQZ ones, the BSSE becomes smaller at the CBS limit by a significant quantity. On the contrary, returning to Table I, we notice that the change in the values of equilibrium properties is very small. It is clear that BSSE is very sensitive to the quality of the extrapolation procedure. At this point, we have to take into account that the FCP scheme is only approximate and that regular convergence is more important than absolute values. It is interesting to note that the errors at AE and FC levels are significantly different for low cardinal numbers of the basis sets. The analysis of those differences gives an idea of the degree of saturation of low angular-momentum space functions. By using the VDZ, VTZ, and VQZ basis sets, the differences are of the same order of magnitude that the errors themselves. It indicates that, for those basis sets, there is a low degree of saturation of function space of low angular momentum. Once

the FCP recipe is applied, however, AE and FC results become very similar. This numerical result is a clear evidence in support of FCP scheme for correcting BSSE. As we mentioned above, the main criticism of the FCP invokes Pauli principle arguments, however, as it has been clearly shown,<sup>67</sup> Pauli principle affects only the dimer energy leading to the intermolecular exchange effects and such criticism is unjustified. On the other hand, at the estimated V5Z limit, both the AE and FC errors become much more similar indicating that the atomic functions of low angular momentum are nearly saturated at this level. At the estimated CBS limit both errors are nearly identical. However, they do not vanish because the saturation of the higher angular momentum space functions may not be complete.

The estimated BSSE in the  $\Pi$  state is nearly half of that in the  $\Sigma$  state. This can be understood taking into account the different nature of the bonds in the two states. In the  $\Pi$  state, the He atom is aligned with the doubly occupied orbital of Br. On the other hand, in the  $\Sigma$  state the He atom is interacting with a single occupied orbital. In this way, BSSE is larger in the  $\Sigma$  where there is an additional unoccupied spin-orbital to describe atomic electron density of He.

In summary, the results that have been presented in this section indicate that the use of the extrapolation formulas (3) and (7) within the FC approximation are adequate to get estimated CBS total energies of the HeBr system. For definiteness, in what follows we will consider BSSE corrected *ab initio* data obtained within the FC approximation and implement the mixed extrapolation formula (7). Within this framework, we can proceed confidently to the next step, which is an investigation of the convergence behavior of transport, scattering, and spectroscopic properties of HeBr and HeBr<sub>2</sub>(B) systems. Before doing so, however, it is worthwhile to represent the *ab initio* potentials by an analytical form.

### C. Analytical HeBr potentials

*Ab initio* points (calculated or extrapolated) were fitted by the Morse-switching function–van der Waals (MSV) form

$$V_\Lambda(R) = \begin{cases} V_M^\Lambda(R), & R \leq R_\Lambda^*, \\ V_{\text{vdW}}^\Lambda(R) + [V_M^\Lambda(R) - V_{\text{vdW}}^\Lambda(R)]f_\Lambda(R), & R > R_\Lambda^*, \end{cases} \quad (9)$$

where

$$V_M^\Lambda(R) = D_\Lambda \{ \exp[-2\alpha_\Lambda(R - \bar{R}_\Lambda)] - \exp[-\alpha_\Lambda(R - \bar{R}_\Lambda)] \}, \quad (10)$$

$$V_{\text{vdW}}^\Lambda(R) = -\frac{C_{6\Lambda}}{R^6} - \frac{C_{8\Lambda}}{R^8}, \quad (11)$$

$$f_\Lambda(R) = \exp\{-4[(R - R_\Lambda^*)/\bar{R}_\Lambda]^2\}, \quad (12)$$

and

$$R_\Lambda^* = \bar{R}_\Lambda + \ln(2)/\alpha_\Lambda. \quad (13)$$

Here  $\bar{R}_\Lambda$  is the diatomic equilibrium distance in the  $V_M^\Lambda$  Morse potential and  $\Lambda = \Sigma, \Pi$ . The value of the long-range

TABLE III. Parameters of the MSV potentials.

Potential	$\bar{R}_\Lambda, \text{\AA}$	$D_\Lambda, \text{cm}^{-1}$	$\alpha_\Lambda, \text{\AA}$	$C_{6\Lambda}, \text{cm}^{-1} \text{\AA}^6$
		$V_\Sigma$		
VDZ	3.76	14.94	1.73	80 228
VTZ	3.64	21.53	1.70	82 219
VQZ	3.555	25.84	1.72	82 501
V5Z	3.53	28.09	1.72	82 560
V5Ze	3.52	27.84	1.74	82 598
CBSe	3.51	29.10	1.74	82 605
DIM-inverted	3.74	26.6	1.58	79 809
		$V_\Pi$		
VDZ	4.26	7.80	1.63	90 914
VTZ	4.07	13.16	1.63	93 022
VQZ	4.01	14.74	1.65	94 127
V5Z	3.98	15.35	1.66	94 220
V5Ze	3.99	15.50	1.65	94 270
CBSe	3.98	15.93	1.65	94 265
DIM-inverted	3.99	14.0	1.53	90 219

$C_{8\Lambda}$  parameter was kept fixed at  $C_{8\Lambda} = 278\,009 \text{ cm}^{-1} \text{\AA}^8$  as determined from the simple correlation rule (see, e.g., Ref. 68) for both the  $\Sigma$  and  $\Pi$  potentials.

These simple fits provide the relative accuracy of 3–9% in the well region.  $V_\Sigma$  potentials are reproduced slightly better than the  $V_\Pi$  ones, but the accuracy of the fits to the potentials of the same symmetry is similar for different *ab initio* calculations. Parameters of the fits are listed in Table III. All potentials are compared in Fig. 2.

The *ab initio* potentials can be compared with so-called DIM inverted potentials determined elsewhere<sup>31</sup> by adjusting the parameters of the first-order intermolecular DIM perturbation theory (IDIM PT1) analytical formula (see below) for the HeBr<sub>2</sub> *B*-state PES to experimental data on the spectra and vibrational predissociation dynamics. The DIM inverted potentials were represented in the same MSV form (9) and their long-range parameters were obtained by the same cor-

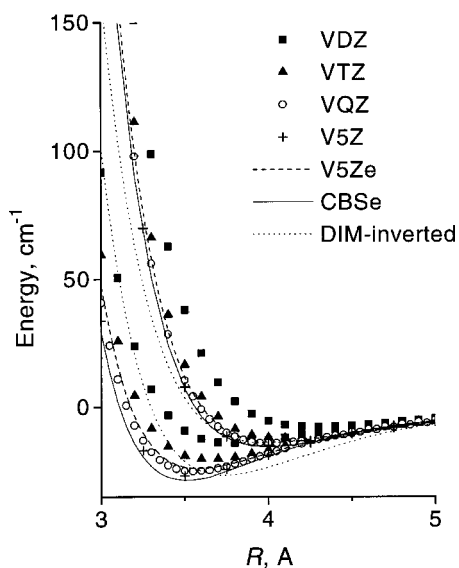


FIG. 2.  $V_\Sigma$  (lower curve) and  $V_\Pi$  (upper curve) nonrelativistic potentials of the HeBr molecule.

relation rules. The parameters of DIM inverted potentials are listed in Table III, while their equilibrium properties are presented in Table I. Evidently, they are in agreement with the best *ab initio* data, although it can be noticed that the exponential parameter  $\alpha$  for both states is underestimated, while the equilibrium distance for the  $^2\Sigma^+$  state is slightly underestimated. The long-range coefficients are also somewhat underestimated. Correlation rules suggested in Ref. 69 give a better agreement with *ab initio* data:  $C_{6\Sigma} = 82\,268 \text{ cm}^{-1} \text{\AA}^6$  and  $C_{6\Pi} = 91\,947 \text{ cm}^{-1} \text{\AA}^6$ .

#### IV. HeBr COLLISION AND TRANSPORT PROPERTIES

Reliable calculations on the He + Br collision dynamics must take into account strong spin-orbit (SO) interaction. It was included using the atoms-in-molecule model which expresses the relativistic electronic Hamiltonian matrix for the HeBr molecule through the nonrelativistic  $V_\Sigma$  and  $V_\Pi$  potentials and the SO splitting  $\Delta$  of the Br atom (see, e.g., Refs. 68, 70, and 71), assuming then that the SO interaction is mainly of atomic origin.

The adiabatic relativistic HeBr potentials for the Hund's case (c) three electronic states  $X1/2$ ,  $I3/2$ , and  $III1/2$  are

$$\begin{aligned} V_{X1/2} &= (V_\Pi + V_\Sigma + \Delta - \delta)/2, \\ V_{I3/2} &= V_\Pi, \\ V_{III1/2} &= (V_\Pi + V_\Sigma + \Delta + \delta)/2, \end{aligned} \quad (14)$$

where

$$\delta = [(V_\Pi - V_\Sigma)^2 - 2\Delta(V_\Pi - V_\Sigma) + \Delta^2]^{1/2},$$

and  $\Delta = 3685.2 \text{ cm}^{-1}$ . The  $V_{I3/2}$  potential depends only on the  $V_\Pi$  term, while all other potential are represented as an average between  $V_\Sigma$  and  $V_\Pi$  potentials with a minor correction depending on their difference.

It is of interest to check whether the CBS extrapolation works for relativistic potentials. They can be constructed using the sequence of VDZ, VTZ, VQZ, V5Z, V5Ze, and CBSe nonrelativistic potentials. On the contrary, the relativistic potentials obtained from the nonrelativistic ones at VDZ, VTZ, and VQZ levels can be extrapolated themselves to V5Z and CBS levels. We will designate the latter extrapolation as V5Zeq and CBSeq in order to distinguish the relativistic potentials calculated from the extrapolated nonrelativistic ones from the relativistic potentials extrapolated themselves. Table IV compares the equilibrium properties of the relativistic  $V_{X1/2}$  and  $V_{III1/2}$  potentials.

It is evident that extrapolation of the relativistic potentials themselves works quite well. Still, however, the relativistic potentials are not more than some combination of the nonrelativistic energies. A more thorough test of the validity of extrapolations is provided by transport and collision properties of the He + Br system.

First, the diffusion coefficient of Br atom in He can be calculated. For this purpose the adiabatic approximation was used, which consists of the calculations of collision integrals for each relativistic potential followed by averaging over thermal populations of Br( $^2P_{3/2}$ ) and Br( $^2P_{1/2}$ ) atomic states.<sup>72</sup> The results are presented in Table V along with the



TABLE IV. Equilibrium properties of the relativistic HeBr potentials. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

Potential	$V_{X1/2}$		$V_{II/2}$	
	$R_e$ , Å	$D_e$ , cm <sup>-1</sup>	$R_e$ , Å	$D_e$ , cm <sup>-1</sup>
VDZ	3.98	10.70	4.14	8.78
VTZ	3.83	16.65	3.97	14.35
VQZ	3.76	19.35	3.90	16.32
V5Z	3.73	20.92	3.87	17.35
V5Ze	3.73	20.56 (1.7)	3.88	17.22 (0.7)
V5Zeq	3.73	20.37 (2.6)	3.87	17.04 (1.8)
CBSe	3.72	21.38	3.87	17.79
CBSeq	3.72	20.97 (2.0)	3.86	17.49 (2.0)
DIM-inverted	3.82	21.75	3.90	17.55

data obtained with the DIM inverted potentials and measured value.<sup>73</sup> Extension of the basis set and extrapolation lead to results closer to experimental data. The diffusion coefficient is, however, not very sensitive to the details of the potentials. It varies only slightly and this may be a reason for the results of the V5Zeq and CBSeq extrapolations agree within the error bars.

As a second quantity we consider the absolute total cross sections of the He + Br collisions. Although they were not measured for HeBr so far, a number of such measurements were performed for analogous systems and they were proven to be quite accurate and sufficiently representative to allow empirical determination of interaction potentials, see e.g., Ref. 70. The velocity dependencies of the cross sections calculated within the adiabatic approximation are shown in Fig. 3. It follows from the figure that the *ab initio* results are fully converged and agree very well with the results for the DIM inverted potentials. In order to test the extrapolations in more detail the temperature averaged cross sections were evaluated. They are given in Table VI. Again the results indicate that the cross sections calculated on the sequence of *ab initio* potentials can be extrapolated with high accuracy.

The last quantity to be considered is the room-temperature rate constant for quenching of excited Br(<sup>2</sup>P<sub>1/2</sub>) atoms in collisions with He. They were calculated using a close-coupling approach as discussed in<sup>71</sup> and are presented in Table VII.

TABLE V. Diffusion coefficient of atomic bromine in helium at room temperature and pressure 1 atm cm<sup>2</sup>/s. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

Potential	Diffusion coefficient
VDZ	0.562
VTZ	0.580
VQZ	0.588
V5Z	0.593
V5Ze	0.591 (0.3)
V5Zeq	0.591 (0.1)
CBSe	0.592
CBSeq	0.593 (0.2)
DIM-inverted	0.611
Experiment	0.66 ± 0.11

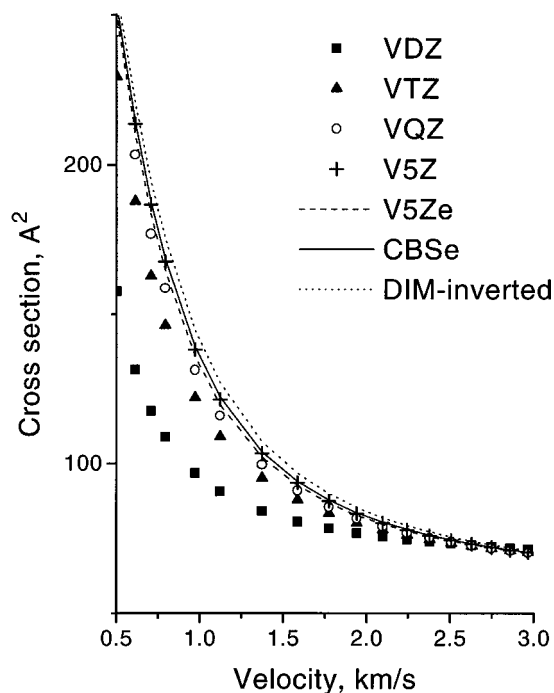


FIG. 3. Velocity dependence of the absolute total cross sections for the He + Br collisions calculated with different  $V_{\Sigma}$  and  $V_{II}$  potential energy curves.

The extrapolation of the calculated rate constant gives inaccurate results, but is still within 10% error. The failure of extrapolation in this case stems from the fact that the quenching rate constant is determined mainly by the difference between  $V_{\Sigma}$  and  $V_{II}$  potentials, a quantity which may not converge steeply if the convergence rates for the potentials of two states are different (see Fig. 1). At the same time, taking into account the high sensitivity of the quenching efficiency to the potential energy curves,<sup>71</sup> and in particular to the consistent description of the  $V_{\Sigma}$  and  $V_{II}$  potentials, the agreement between theoretical data is quite impressive, and especially between the V5Z and V5Ze values. The measured rate constant values are seven orders of magnitude higher. In fact, as was noted in Ref. 74, its value is just at the limit of experimental accuracy determined mainly by the purity of the rare gas. As such, it should be taken only as an upper bound for the actual quenching rate.

TABLE VI. Averaged total cross sections for He + Br collisions at the temperature 300 K, Å<sup>2</sup>. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

Potential	Cross section
VDZ	74.50
VTZ	84.28
VQZ	87.51
V5Z	89.88
V5Ze	89.10 (0.9)
V5Zeq	88.68 (1.3)
CBSe	90.17
CBSeq	89.36 (0.9)
DIM-inverted	92.06

TABLE VII. Rate constant for quenching of the Br ( $^2P_{1/2}$ ) atom in collisions with He at the temperature 300 K cm<sup>3</sup>/molec s. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

Potential	Rate constant
VDZ	$3.34 \times 10^{-21}$
VTZ	$4.04 \times 10^{-21}$
VQZ	$4.12 \times 10^{-21}$
V5Z	$4.13 \times 10^{-21}$
V5Ze	$4.09 \times 10^{-21}$ (1.0)
V5Zeq	$4.14 \times 10^{-21}$ (0.2)
CBSe	$3.85 \times 10^{-21}$
CBSeq	$4.15 \times 10^{-21}$ (8.0)
DIM-inverted	$1.36 \times 10^{-21}$
Experiment	$(1.6 \pm 0.3) \times 10^{-14}$

### V. HeBr<sub>2</sub>(B) VIBRATIONAL PREDISSOCIATION DYNAMICS

As has been already mentioned in Introduction, atom-atom potentials are frequently used as an input information for constructing the model PES of polyatomic systems, e.g., by means of DIM method. Here we exemplify such an application by considering HeBr<sub>2</sub> van der Waals molecule in the electronically excited  $B0_u^+$  state. In the frame of IDIM PT1 model,<sup>75</sup> its PES is expressed in terms of the nonrelativistic HeBr potentials by the following simple formula:

$$U_B = \frac{1}{4} \sum_{\alpha=a,b} \{3V_{\Pi}(R_{\alpha}) + V_{\Sigma}(R_{\alpha}) - [V_{\Pi}(R_{\alpha}) - V_{\Sigma}(R_{\alpha})] \cos^2(\beta_{\alpha})\}, \quad (15)$$

where  $\alpha=a,b$  refers to distinct Br nuclei,  $R_{\alpha}$  are the distances between the He and Br atoms, and  $\beta_{\alpha}$  are the angles between the  $R_{\alpha}$  vectors and the Br<sub>2</sub> axis  $r$ . The same form of the PES was used in Ref. 31 in order to parametrize the DIM inverted  $V_{\Sigma}$  and  $V_{\Pi}$  potentials.

On the one hand, the use of Eq.(15) parametrized by a sequence of *ab initio* HeBr potentials for calculations of the HeBr<sub>2</sub>(B) spectra and dynamics provides us with the suitable example for analyzing the CBS extrapolation procedure for the properties whose relation to HeBr energy is very complicated. On the other, the implementation of the most accurate *ab initio* parametrization allows us to test the accuracy of IDIM PT1 model by comparison between theoretical and experimental results.

The PES (15) possesses two minima, the ground state minimum in the T-shaped configuration of the complex and a very shallow long-range one in the linear geometry of the complex. The data on equilibrium distances  $\rho_e$  from He to the Br<sub>2</sub> center of mass and depths of these stationary points calculated by Eq. (15) with different HeBr potentials are summarized in Table VIII. The table also presents the values obtained by extrapolating the VDZ–VQZ-based PES's to V5Z (V5Zeq) and CBS (CBSeq) levels.

The best *ab initio*-based PES's are in very close agreement with the DIM inverted ones, pointing again to the accuracy of both *ab initio* calculations for HeBr and the IDIM PT1 formula (15). Extrapolation of  $\rho_e$  and  $D_e$  values themselves works very well. This is not surprising, because ac-

TABLE VIII. Equilibrium properties of the HeBr<sub>2</sub>(B) potentials at the equilibrium Br<sub>2</sub> distance  $r_e = 2.6776$  Å. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

HeBr potentials	T shaped		Linear	
	$\rho_e$ , Å	$D_e$ , cm <sup>-1</sup>	$\rho_e$ , Å	$D_e$ , cm <sup>-1</sup>
VDZ	3.94	17.13	5.40	10.34
VTZ	3.76	28.20	5.24	16.26
VQZ	3.69	32.00	5.17	18.62
V5Z	3.65	33.90	5.14	19.94
V5Ze	3.66	33.74 (0.5)	5.14	19.68 (1.3)
V5Zeq	3.66	33.38 (1.5)	5.14	19.50 (2.2)
CBSe	3.65	34.83	5.13	20.37
CBSeq	3.65	34.19 (2.0)	5.13	20.01 (2.0)
DIM-inverted	3.69	33.82	5.18	20.56

ording to Eq. (15) the HeBr<sub>2</sub> potential is determined mainly by an average of  $V_{\Sigma}$  and  $V_{\Pi}$  potentials, while the anisotropic term depending on their difference has little effect on the equilibrium properties.<sup>31</sup> This situation is very close to that with the relativistic HeBr potentials.

More interesting is the comparison of dynamical calculations carried out on the HeBr<sub>2</sub>(B) PES's parametrized by different HeBr potentials. Such calculations were performed for vibrational predissociation (VP) of this complex at  $v = 8, 10,$  and  $12$ . Dissociation energies  $D_0$ , VP half-widths  $\Gamma/2$  and lifetimes  $\tau$ , as well as the averaged rotational product state energies  $E_{\text{rot}}$  were calculated by means of the diabatic golden rule method, which was proven to be accurate for this case.<sup>76</sup> The calculations were performed on the PES's parametrized by *ab initio* VDZ–V5Z and extrapolated nonrelativistic HeBr potentials. All quantities were also extrapolated by themselves. These results are shown in Table IX along with experimental data taken from Ref. 34.

The performance of the best *ab initio*-based PES's with respect to experimental data is very good. Although they tend to underestimate the dissociation energy in comparison with the DIM inverted PES, the results for lifetimes presented graphically on Fig. 4 only slightly underestimate the experimental data. The latter are not accurate enough, as is clear from the somewhat nonsmooth dependence on  $v$ , which is impossible to reproduce with a reasonable estimate of the potential.<sup>31,34,76</sup> The DIM inverted potentials were adjusted in order to reproduce the lifetime at  $v = 10$  in addition to the lifetimes at higher  $v$ 's.<sup>31</sup>

Extrapolation of both dissociation energies and lifetimes works perfectly. However, it is not possible to obtain such good results for the averaged rotational energy of the products, which is ill-behaved function on the basis set size. The difference between VTZ and VQZ values is quite small, and thus the rotational product state distributions are almost converged at this level, see Fig. 5. However, the results of the lowest level VDZ calculations are significantly different, overemphasizing the second peak on the distribution. This second peak is determined by the interference effects related to anisotropy of the PES, which in turn depends strongly on the difference between the  $V_{\Sigma}$  and  $V_{\Pi}$  potentials, see Eq. (15). Therefore, the reason for the extrapolation failure for

TABLE IX. Results for vibrational predissociation of the HeBr<sub>2</sub> (*B*) complex. Percentage accuracies given in parentheses are with respect to V5Z values for V5Ze and V5Zeq entries and with respect to CBSe values for CBSeq entry.

Potential	$D_0$ , cm <sup>-1</sup>	$\Gamma/2$ , cm <sup>-1</sup>	$\tau$ , ps	$E_{rot}$ , cm <sup>-1</sup>
$v=8$				
VDZ	-4.0635	0.0035	758	1.83
VTZ	-9.6474	0.0109	244	1.72
VQZ	-11.6452	0.0153	173	1.74
V5Z	-12.6336	0.0180	148	1.74
V5Ze	-12.6312 (0.2)	0.0175 (2.8)	152	1.74
V5Zeq	-12.3768 (2.3)	0.0170 (5.6)	156	
CBSe	-13.2696	0.0188	141	1.74
CBSeq	-12.8025 (3.0)	0.0180 (4.0)	147	
DIM-inverted	-13.7869	0.0129	206	1.60
Expt.		0.018	150	
$v=10$				
VDZ	-4.0459	0.0051	520	1.75
VTZ	-9.6144	0.0158	168	1.66
VQZ	-11.6072	0.0222	120	1.67
V5Z	-12.6234	0.0259	102	1.67
V5Ze	-12.5908 (0.3)	0.0252 (2.7)	105	1.67
V5Zeq	-12.3370 (2.3)	0.0247 (4.6)	107	
CBSe	-13.2278	0.0271	98	1.67
CBSeq	-12.7617 (4.0)	0.0262 (3.0)	101	
DIM-inverted	-13.7511	0.0190	149	1.54
Expt.		0.019	140	
$v=12$				
VDZ	-4.0278	0.0073	364	1.66
VTZ	-9.5798	0.0227	117	1.58
VQZ	-11.6671	0.0317	84	1.59
V5Z	-12.5808	0.0370	72	1.60
V5Ze	-12.5480 (0.3)	0.0360 (2.7)	74	1.60
V5Zeq	-12.2949 (2.3)	0.0352 (4.6)	75	
CBSe	-13.1835	0.0387	69	1.60
CBSeq	-12.7184 (4.0)	0.0373 (4.0)	71	
DIM-inverted	-13.7131	0.0277	96	1.47
Expt.		0.031	86	

rotational distributions is the same as for the Br quenching rate constants and  $T_e$  of HeBr (see above).

## VI. CONCLUDING REMARKS

To our opinion, several interesting findings are worthy of mentioning. First, we formulate the main conclusions drawn from *ab initio* calculations, then summarize the experience with CBS extrapolation, and finally discuss the implications to the HeBr<sub>2</sub> complex.

For weakly bonded systems, it is imperative to use some correction scheme for BSSE that, in this case, is of the same order of magnitude that the interaction energy itself. Through comparison between uncorrected FC and AE approaches, numerical evidence has been shown in favor of FCP scheme for correcting BSSE. Uncorrected AE interaction energies are less accurate than uncorrected FC interaction energies because in the development of the basis sets, only the valence electrons were correlated.<sup>39</sup> At the estimated CBS limit, the nonzero value of BSSE indicates that the saturation of the higher angular momentum space functions has not been reached. To reach completeness, it would be needed to add very high cardinal number basis sets with  $l \geq 5$  (past *h*) what

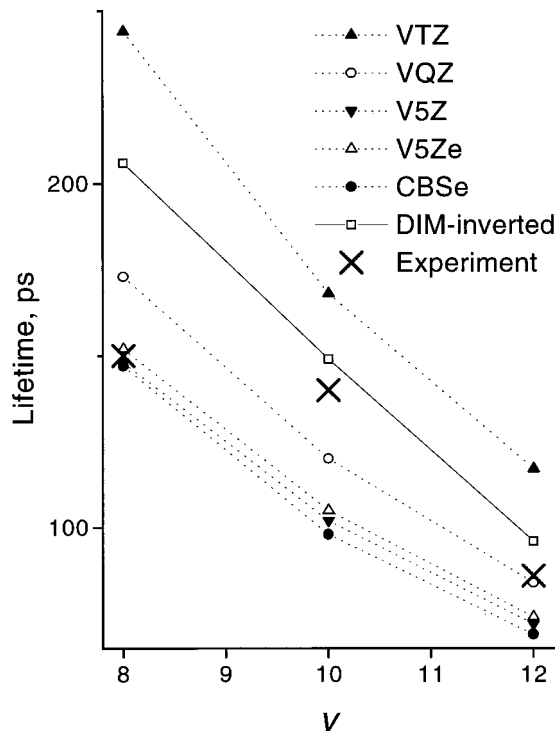


FIG. 4. Dependence of the predissociation lifetime of the HeBr<sub>2</sub>(*B*) complex on  $v$  quantum number calculated using IDIM PT1 PES parameterized by different  $V_{\Sigma}$  and  $V_{\Pi}$  HeBr potential energy curves.

it is not practical. Fortunately, the FCP scheme has been shown to be safe to correct for the BSSE due to this basis set incompleteness. The good convergence properties of the FCP-corrected interaction energies indicate that the estimated complete basis set limits are reliable.

Accuracy of various CBS extrapolation formulas was estimated by applying them to the total electronic energies. The most accurate results were obtained with the  $(n + 1/2)^{-4}$  (3) and (7) mixed exponential-Gaussian expressions. The latter (7) arises from the observation of the convergence behavior of total energies towards a CBS limit when correlation consistent basis sets are used<sup>40,41</sup> while the former (3) is a two parametric function derived from the partial-wave expansion expression.<sup>57</sup> Combination of extrapolation and FCP correction procedure requires additional care. The formulas with linear adjustable parameters [like (3) and (7)] provide the size-consistent results, equivalent if the extrapolation is employed for the dimer and monomer energies separately or to the FCP corrected energy. The formulas containing nonlinear parameters give wrong results being implemented for the dimer and monomer properties separately.

CBS extrapolation works unexpectedly well for the non-energetic properties. Not only quantities expressed as the linear combinations of electronic energies [like nonrelativistic HeBr potentials or HeBr<sub>2</sub>(*B*) IDIM PT1 PES], but also the quantities sensitive to global behavior of the PES [like those characterizing He + Br transport and collisions or HeBr<sub>2</sub>(*B*) vibrational predissociation dynamics] retain the scaling properties of underlying *ab initio* data. This indicates that the *ab initio* calculations with low-order aug-cc-pVXZ ( $X > D$ ) basis sets already reproduce reasonably the global features of

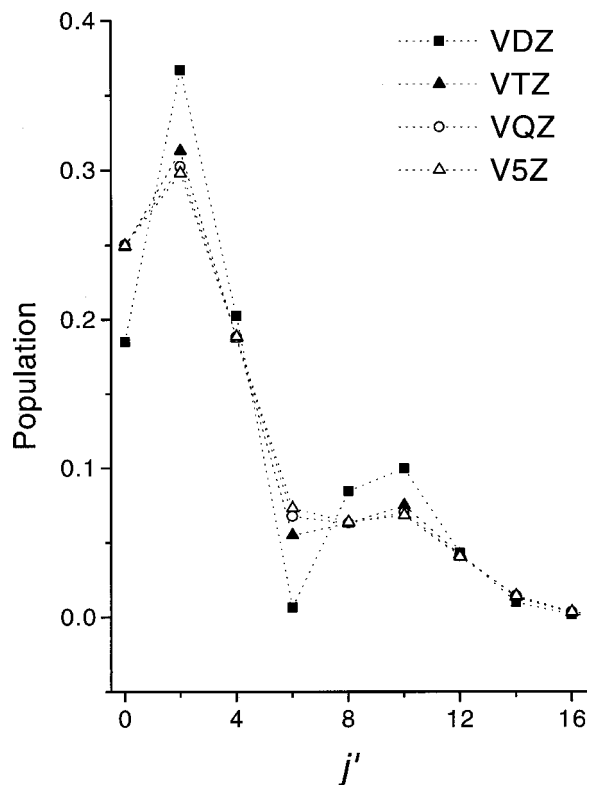


FIG. 5. Rotational distributions of the  $\text{Br}_2$  ( $v'=7$ ) products of the  $\text{HeBr}_2$  ( $B, v=8, J=0$ ) predissociation calculated using IDIM PT1 PES parametrized by different  $V_\Sigma$  and  $V_\Pi$  HeBr potential energy curves.

the PES, while their extensions provide regular improvement over a wide region of configuration space.

As we found here, the main problem which affects the scaling of the nonenergetic properties derived from the sequence of *ab initio* PES's is the different convergence rates for different electronic states. It does not affect significantly those properties of open-shell systems which are mainly determined by a single PES or by some average PES, but significantly worsen the CBS extrapolation of quantities sensitive to the PES differences. To address this problem, perhaps the simplest way would be to use the equation of motion (EOM-CC) method<sup>77</sup> that is also within coupled-cluster framework. As the wave function of excited electronic state is created from the ground coupled-cluster wave function simply by an excitation operator, a common set of molecular orbitals is being used for both ground and excited states. In this way, it is expected that the convergence rates for the two states become closer and the convergence of properties that depend mainly on PESs differences become smoother. The exploration of this possibility is addressed in ongoing work.

The use of *ab initio* HeBr potentials in the IDIM PT1 model for the  $\text{HeBr}_2(B)$  PES gives very encouraging results. Spectra and vibrational predissociation dynamics of this complex exhibit a wealth of interesting phenomena sensitive to the PES<sup>31-34,76,78,79</sup> and it is of interest to analyze them using new PES's in more detail. Another perspective is to undertake high-level *ab initio* calculations on the  $\text{HeBr}_2$  system itself. Experience with the HeBr molecule greatly facilitates such work.

*Note added to proof.* Very recently, Partridge *et al.* presented the HeBr potentials calculated using the same CCSD(T) method and aug-cc-pVQZ basis augmented by the (33211) set of the bond functions.<sup>80</sup> Their results  $R_e=3.52 \text{ \AA}$ ,  $D_e=28.31 \text{ cm}^{-1}$  for  $\Sigma$  and  $R_e=3.99 \text{ \AA}$  and  $D_e=15.30 \text{ cm}^{-1}$  for the  $\Pi$  state are very close to our estimated CBS values (see Table I) indicating once again the efficiency of bond functions for saturating the basis set for calculations of weakly bonded systems.

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