

Ab-Initio-Based Global Double Many-Body Expansion Potential Energy Surface for the Electronic Ground State of the Ammonia Molecule

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We report a single-sheeted global double many-body expansion potential energy surface for the ground electronic state of NH_3 that has been calibrated from newly calculated ab initio energies. It employs realistic double many-body expansion functions previously reported from accurate ab initio data for the triatomic fragments plus four-body energy terms that have been calibrated from multireference configuration calculations carried out in the present work for the title system using the full valence complete active space wave function as reference and a triple- ζ basis set of the correlation consistent type. It provides therefore a reliable description of both short-range and long-range forces while dissociating correctly at all asymptotic limits. The major attributes of the NH_3 double many-body expansion potential energy surface have been characterized and found to be in good agreement both with the calculated ones from the raw ab initio energies and theoretical results available in the literature. It can then be recommended both as a reliable functional form on which dynamics calculations can be performed and as a model for improvement that is open to refinement through further accurate ab initio calculations, vibrational calculations, or both.

1. Introduction

The availability of a potential energy surface (PES) for small molecules plays a key role in reaction dynamics and kinetics studies. Among the tetratomic systems, the PES of NH_3 ^{1–10} assumes special relevance because this species is a major constituent of some planetary atmospheres whose Boltzmann temperatures require for their determination an accurate knowledge of the rovibrational transition energies and hence of its PES. Moreover, NH_3 is an important intermediate in atmospheric chemistry and combustion processes and a prototype pyramidal molecule that provides a benchmark system for theoretical spectroscopic models. In particular, its low-frequency large amplitude inversion motion makes it a challenge to understanding.

It is therefore not surprising that ammonia has been so extensively studied,¹ with related topics being MASER action,¹¹ microwave and infrared spectroscopy,^{12–16} chirality,¹⁷ and time-dependent multidimensional quantum wave packet dynamics under coherent laser excitation.¹⁸ Moreover, ammonia and its isotopomers also provide interesting prototypical systems for studying photodissociation dynamics^{8,9,19–21} and the role of atomic insertion versus molecular abstraction reactions.^{22,23} Having a relatively small number of electrons, NH_3 further allows calculations of its electronic structure with accurate ab initio methods and large basis sets, although being still too large to permit a dense exploration of its entire PES.

Much experimental and theoretical work has been reported recently for the ammonia molecule.^{1–4,18,24–29} Theoretically, representations of the PES have mostly utilized high-order Taylor expansions in the neighborhood of the equilibrium molecular structure, although some^{1,27} can describe large amplitude vibrations. Therefore, adiabatic representations of the PES reported thus far from ab initio calculations are either accurate but local or global but not sufficiently accurate to describe the complete set of experimental data. In particular, such adiabatic PESs often fail to show the correct behavior at

all dissociation channels related to the global PES. An alternative to adiabatic representations is to have diabatic representations.^{28,29} Although these offer generally smoother features and hence may be easier to model than adiabatic ones, especially when aiming at multisheeted forms, there are also cons associated with difficulties in defining proper dissociation limits (ref 30 and references therein). This situation prompted us to carry out electronic structure calculations extensively enough to cover the major features of the full six-dimensional (6D) configuration space of the ammonia molecule and to model globally the PES using double many-body expansion (DMBE) theory.^{31–33} This approach has been successfully applied to a wealth of triatomic systems (including all ground-state triatomic fragments arising from dissociation of ammonia, namely, NH_2 ,^{34,35} and H_3 ³⁶ as well as tetratomic (O_4 ,³⁷ HO_3 ,³⁸ HSO_2 ,³⁹ and N_2H_2 ⁴⁰), and even larger polyatomic (HO_4 ⁴¹ and HO_5 ⁴²) systems and can provide a physically motivated form to model accurate ab initio calculations at both the valence and long-range interaction regions. Because single-valued DMBE PESs have been reported for NH_2 and H_3 , such a work has paved the way for obtaining a similar form for the larger NH_3 molecule by providing the involved two- and three-body terms that arise in the cluster expansion of the molecular potential energy. In turn, $\text{NH}_3(1^1\text{A}_1)$ jointly with N_2H_2 ,⁴⁰ can serve as four-atom building-blocks for PESs of larger N_xH_y species like the ones of relevance in the synthesis of ammonia, and hence the current study may help to construct global DMBE forms for such polyatomic systems.

A final remark to note that proper dissociation at all asymptotes is warranted by employing a generalization of the Varandas-Poveda³⁴ switching function approach originally reported for triatomic species. (For a related approach developed almost concomitantly for N_2H_2 , see ref 40.) As calibration data, 476 ab initio energies calculated at the multireference configuration interaction with the popular quasi-degenerate Davidson correction (MRCI(Q)^{43,44}) level have been utilized. Such calculations employed the full valence complete active space (FVCAS) wave function as reference, and the aug-cc-pVTZ

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(AVTZ) basis set of Dunning.^{45,46} We emphasize that a major aim of this study has been to develop an adiabatic PES that displays the correct behavior at all dissociation channels while providing a realistic representation at all interatomic separations. The small number of required ab initio points is clearly an asset of DMBE theory (obviously of any cluster expansion⁴⁷) by allowing the use of work previously done for the molecular fragments. Naturally, electronic structure calculations of higher accuracy are nowadays feasible for the title molecule,²⁷ with the PES here reported then serving as a first global model toward more ambitious and expensive modeling endeavors. Of course, if combined with vibrational calculations (and/or ab initio data points), it may also serve as a 6D functional form that may afford sufficiently flexibility to fit available spectroscopic data, much on line with what has been done in the past with triatomic potentials.^{48–53}

The article is organized as follows. Section 2 describes the new ab initio calculations carried out for NH₃, whereas the DMBE methodology is discussed and applied in Section 3 by focusing on the title system. The characterization of the novel DMBE PES is then presented in Section 4. Section 5 gathers the major conclusions.

2. Ab Initio Electronic Structure Calculations

All ab initio calculations have been carried out at the MRCI(Q)^{43,44} level of theory using the FVCAS⁴³ wave function as reference. The AVTZ atomic basis set of Dunning^{45,46} has been employed, and the calculations have been carried out using the Molpro⁵⁴ package. The most important regions of the PES for spectroscopic studies are the two symmetry equivalent global minima (*C*_{3v}) and the region around the saddle point (*D*_{3h}) for the umbrella motion. However, because the aim is to obtain a fully 6D PES, there is the need to consider also the description of the PES away from such regions. A total of 476 ab initio points has been calculated, of which 205 are concentrated in the region of the two equivalent *C*_{3v} minima and *D*_{3h} saddle point for the umbrella motion that connects them. The remainder 271 ab initio points have been necessary to remove an unphysical minimum that occurs in the absence of the four-body energy correction and to refine the entrance barrier associated with the H + NH₂ channel. Because one seeks a reliable description of the inversion barrier, the above 205 raw ab initio energies there located have been carried out using state averaging of the two lowest states of the same symmetry. All others that have been employed to model the *V*_S and *V*_L contributions that will be discussed later (Section 3.4) have been generated at the cheaper single-state level. Note that the dissociation limit of H + NH₂ has been calculated by keeping NH₂ frozen at the geometry reported in ref 34 while moving away the hydrogen atom. Similarly, the dissociation energy of N + H₃ has been calculated by keeping H₃ frozen at its optimum FVCAS/AVTZ collinear geometry (the well-established saddle point in 3D) while moving away the nitrogen atom. (See Table 5.) For simplicity, the 1s electrons of nitrogen were kept frozen, with no attempt having therefore been made to include core-correlation effects. This will be hopefully compensated in part and empirically by employing diatomic curves that have been modeled from more accurate theoretical work, as described later.

3. Single-Sheeted DMBE Potential Energy Surface

Within the framework of DMBE theory, as applied to four-atom systems,^{38,39} a single-sheeted PES for ground-state NH₃ (labeled ABCD in the following) is written as

$$V_{\text{NH}_3}(\mathbf{R}) = \sum_{i=1}^4 V^{(i)}(\mathbf{R}) \quad (1)$$

where $\mathbf{R}$ is the vector of the six internuclear coordinates [*R_j* (*j* = 1,..., 6)], $V^{(1)} = V_{\text{N}(^2\text{D})}^{(4)} f^{(4)}(\mathbf{R})$ is a (pseudo-) one-body term, and $V_{\text{N}(^2\text{D})}^{(4)}$ represents the energy difference between the ²D and ⁴S states of atomic nitrogen: $V_{\text{N}(^2\text{D})}^{(1b)} = 0.091225E_h$, with *b* distinguishing the value here calculated at the AVTZ from the one in ref 34 for NH₂ at a higher basis set level, denoted by *a*. In turn, $f^{(4)}(\mathbf{R})$ is a 6D switching function, and $V^{(2)}$, $V^{(3)}$, and $V^{(4)}$ are two-, three-, and four-body terms in the cluster expansion of the molecular potential energy. The details of the analytical forms employed to represent the various *n*-body energy terms that are involved will be given in the following subsections.

3.1. Two-Body Energy Terms. The potential energy curves for the two-body fragments are based on the extended Hartree–Fock approximate correlation energy method for diatomic molecules including the united atom limit⁵⁵ (EHFACE2U), which show the correct behavior at both asymptotic limits $R \rightarrow 0$ and $R \rightarrow \infty$. For the *j*th diatomic, it assumes the form

$$V^{(2)}(R_j) = V_{\text{EHF}}^{(2)}(R_j) + V_{\text{dc}}^{(2)}(R_j) \quad (2)$$

where $V_{\text{EHF}}^{(2)}$ and $V_{\text{dc}}^{(2)}$ are two-body terms of the extended Hartree–Fock and dynamical correlation types, respectively; eq 2 applies to all six diatomic fragments. The two-body extended Hartree–Fock energy term $V_{\text{EHF}}^{(2)}$ is written as

$$V_{\text{EHF}}^{(2)}(R) = -\frac{D}{R} \left(1 + \sum_{i=1}^n a_i r^i \right) \exp(-\gamma r) + \chi_{\text{exc}}(R) V_{\text{exc}}^{\text{asym}}(R) \quad (3)$$

where

$$\gamma = \gamma_0 [1 + \gamma_1 \tanh(\gamma_2 r)] \quad (4)$$

and

$$V_{\text{exc}}^{\text{asym}}(R) = -\tilde{A} R^{\tilde{\alpha}} (1 + \tilde{a}_1 R + \tilde{a}_2 R^2) \exp(-\tilde{\gamma} R) \quad (5)$$

is the asymptotic exchange energy and $\chi_{\text{exc}}(R)$ is a convenient damping function that accounts for charge overlap effects, *r* denotes the displacement coordinate relative to equilibrium geometry of the diatomic, $r = R - R_e$. In turn, the two-body dynamical correlation energy term, $V_{\text{dc}}^{(2)}$, is written as

$$V_{\text{dc}}^{(2)}(R) = - \sum_{n=6,8,10} C_n \chi_n(R) R^{-n} \quad (6)$$

where

$$\chi_n(R) = \left[1 - \exp\left(-A_n \frac{R}{\rho} - B_n \frac{R^2}{\rho^2}\right) \right]^n \quad (7)$$

is a charge-overlap dispersion damping function. Moreover, $A_n = \alpha_0 n^{-\alpha_1}$ and $B_n = \beta_0 \exp(-\beta_1 n)$ are auxiliary functions^{31,56} $\alpha_0 = 16.36606$, $\alpha_1 = 0.70172$, $\beta_0 = 17.19338$, and $\beta_1 = 0.09574$. For a given pair of atoms (say, AB), $\rho = 5.5 + 1.25(\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2})$ is a

scaling parameter. Finally, the coefficients that appear in eqs 2–7 are chosen such as to reproduce available theoretical (and experimental, although this will not be done here) data in diatomic, as described elsewhere.^{31,55} In this work, we employ the accurate EHFACE2U potential energy curve of ground-state, $\text{H}_2(\text{X}^1\Sigma_g^+)$, reported in ref 48 and the curve of ground-state imidogen, $\text{NH}(\text{X}^3\Sigma^-)$, reported in ref 57. As shown in Figure 2 of ref 34, both potential curves accurately mimic the calculated ab initio energies.

3.2. Three-Body Energy Terms. The three-body energy is written as

$$V^{(3)}(\mathbf{R}^3) = \sum_{i=1}^4 [V_{\text{EHF}}^{(3)}(\mathbf{R}^3) + V_{\text{dc}}^{(3)}(\mathbf{R}^3)] \quad (8)$$

where $V_{\text{EHF}}^{(3)}$ and $V_{\text{dc}}^{(3)}$ are the three-body terms of the extended Hartree–Fock and dynamical correlation types, respectively; $\mathbf{R}^3$ specifies the set of the three interatomic distances referring to each triatomic fragment.

The three-body energy terms employed in eq 8 have been taken from refs 34 and 36 for NH_2 and H_3 , respectively. In turn, the three-body dynamical correlation of NH_2 is modeled by the form⁴⁸

$$V_{\text{dc}}^{(3)}(\mathbf{R}^3; \text{NH}_2) = - \sum_i \sum_n f_i(\mathbf{R}^3) C_n^{(i)}(R_i, \theta_i) \chi_n(r_i) r_i^{-n} \quad (9)$$

where r_i , θ_i , and R_i are the Jacobi coordinates corresponding to a specific geometry of the triatomic and $f_i = 1/2\{1 - \tanh[\xi(\eta R_i - R_j - R_k)]\}$ is a convenient switching function. Following recent work on NH_2 ,³⁴ we have fixed $\eta = 6$, $\xi = 1.0a_0^{-1}$, and $\rho = 16.125a_0$. Regarding the damping function $\chi_n(r_i)$, we still adopt eq 7 but replace R in eq 7 by the center-of-mass separation for the relevant atom–diatom channel of NH_2 . In turn, the atom–diatom dispersion coefficients in eq 9 assume their usual form

$$C_n^{(i)}(R_i) = \sum_L C_n^L(R_i) P_L(\cos \theta_i) \quad (10)$$

where $P_L(\cos \theta_i)$ denotes the L th Legendre polynomial. The expansion in eq 9 has been truncated by considering only the coefficients C_6^0 , C_6^2 , C_8^0 , C_8^2 , C_8^4 , and C_{10}^0 . As noted elsewhere,⁴⁸ eq 9 causes an overestimation of the dynamical correlation energy at the atom–diatom dissociation channels. To correct such a behavior, we have multiplied the two-body dynamical correlation for the i th pair by $\prod_{j \neq i} (1 - f_j)$. This ensures^{34,48,52} that the only two-body contribution at the i th channel belongs to the JK atom pair. (In an obvious notation, IJK is any triatomic formed from atoms A to D.)

The three-body extended Hartree–Fock energy for the NH_2 fragments has been modeled via a three-body distributed-polynomial^{34,58} form

$$V_{\text{EHF}}^{(3)}(\mathbf{R}^3; \text{NH}_2) = \sum_{j=1}^5 \{P^{(j)}(Q_1, Q_2, Q_3) \times \prod_{i=1}^3 \{1 - \tanh[\gamma_i^{(j)}(R_i - R_i^{\text{ref}})]\}\} \quad (11)$$

where all polynomials $P^{(j)}(Q_1, Q_2, Q_3)$ are written in terms of symmetry coordinates, $\gamma_i^{(j)}$ is a nonlinear range-determining parameter, and R_i^{ref} is a reference geometry.

Following previous work,³⁶ the three-body dynamical correlation of H_3 assumes the form

$$V_{\text{dc}}^{(3)}(\mathbf{R}^3; \text{H}_3) = \sum_{i=1}^3 \sum_{n=6,8,10} C_n \left\{ 1 - \frac{1}{2} [g_n(R_{i+1(\text{mod } 3)}) h_n(R_{i+2(\text{mod } 3)}) + g_n(R_{i+2(\text{mod } 3)}) h_n(R_{i+1(\text{mod } 3)})] R_i^{-n} \right\} \quad (12)$$

where

$$g_n(R) = 1 + k_n \exp[-k'_n(R - R_m)] \quad (13)$$

and

$$h_n(R) = [\tanh(k'_n R)]^{\eta'} \quad (14)$$

The constants k'_n and η' control the rate of decay of the g_n and h_n functions, and these constants and the k_n are determined, for a given η' , by the requirement that the model reproduces the H– H_2 dispersion coefficients⁵⁹ $C_n^{\text{H-H}_2}$ at r_e for $n = 6, 8$, and 10.

Note that the eqs 9 and 12 represent dynamical correlation terms for different three-body interaction fragments. Specifically, eq 9 accounts for N– H_2 and H–NH long-range energies, whereas eq 12 describes the H– H_2 dissociation channels. As noted in ref 39, because of an overestimation of the dynamical correlation energy, each $V_{\text{dc}}^{(2)}(R_i)$ term in the DMBE PES of NH_2 has been multiplied by a switching function $\prod_{j \neq i} (1 - f_j)$ for the i th pair,³⁴ which transforms such contributions into three-body-like ones. Therefore, an extra three-body energy term should be added to eq 8. Taking into account the properties of the switching function, $\prod_{j \neq i} (1 - f_j)$, such an additional term should be written as follows

$$V_{\text{add}}^{(3)} = \sum_{i=1}^6 V_{\text{dc}}^{(2)}(R_i) \sum_{k=1}^2 \left\{ \prod_{j \neq i} [1 - f_j(\mathbf{R}_k^3)] - 1 \right\} \quad (15)$$

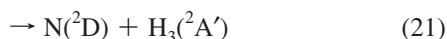
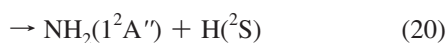
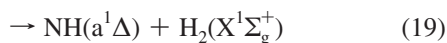
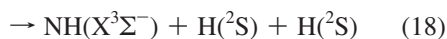
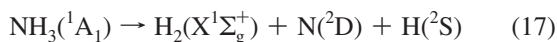
which, when taken into account, reproduces all of the asymptotic limits of the tetratomic PES (i.e., if one of the atoms is placed far away from the remaining triatomic, then the resulting PES matches exactly that of the triatomic fragment; $\mathbf{R}_k^3$ denotes the set of three interatomic distances referring to the k -th triatomic fragment. As shown later in Figure 14, the resulting PES matches exactly that of the NH_2 DMBE PES when one of the H atoms is placed far away from the remaining NH_2). We should also note that the diatomic potential (H_2) originally employed in the H_3 DMBE PES has been constructed using a previous formalism somewhat simpler than that used for NH_2 DMBE PES. For consistency, we have replaced it by a corresponding updated diatomic curve,^{34,48} which has been used for NH_2 DMBE PES. As shown in Table 5, the dissociation energy at the $\text{N}(^2\text{D}) + \text{H}_3(^2\text{A}')$ limit is $-0.0680E_h$. If one then removes from this amount the energy difference between the ^2D and ^4S states of atomic nitrogen, then we predict the energy of $\text{H}_3(^2\text{A}')$ at the reference geometry to be $-0.1592E_h$, which is in good agreement with the one of $-0.1591E_h$ that we have calculated using the original form. Therefore, the present update does not significantly affect the attributes of the H_3 PES in comparison with its original form.

In turn, the three-body extended Hartree–Fock energy of H_3 assumes the form³⁶

$$V_{\text{EHF}}^{(3)}(\mathbf{R}^3; \text{H}_3) = s^2(1 + s^3 \cos(3\phi))(b_{61} + b_{62}q) \times \exp[-b_{63}^2(q - q_0)^2] \quad (16)$$

where q , s , and ϕ are defined by eqs 4, 40, and 41 of ref 36, respectively. Finally, the parameters appearing in eqs 8–16 have been taken from refs 34 and 36 for NH_2 and H_3 , respectively; for clarity, the notation of such equations has been kept unchanged, with the reader being referred to the original papers for the numerical values of the coefficients.

3.3. Switching Function. The use of a switching function to approximate the multivalued nature of a PES (i.e., to replace a crossing by an avoided crossing and hence allow proper dissociation with a single-sheeted form) was first proposed by Murrell and Carter,⁶⁰ who applied the formalism in the construction of an approximate PES for the ground state of H_2O . However, as noted in their paper, their switching function cannot reach a unique value at the three-atom limit. To solve this inconsistency and get a smooth three-body energy term, Varandas and Poveda³⁴ proposed an improved switching-function formalism and applied it successfully to ground-state NH_2 . A similar situation holds for the title system, where the following dissociation scheme applies



Because $\text{NH}(\text{X}^3\Sigma^-)$ dissociates to ground-state atoms, it will be necessary to introduce a switching function that removes $\text{N}(^2\text{D})$ from the dissociation channel as $\text{NH}(\text{X}^3\Sigma^-)$ dissociates to nitrogen and hydrogen atoms in their ground electronic states, respectively, $\text{N}(^4\text{S})$ and $\text{H}(^2\text{S})$. By comparing the PES that is obtained by using only two- and three-body terms with the ab initio calculations here carried out, we have established the major changes to warrant the proper dissociation limits. This was followed by modeling a convenient switching function that could also ensure the proper atom-permutational symmetry. Although not unique (for a similar extension that has been found convenient for the N_2H_2 molecule, see ref 40), of course, a form that satisfies such criteria is

$$f^{(4)}(\mathbf{R}) = \sum_{\alpha\beta\gamma} h(R_{\alpha\beta})g(R_{A-\alpha\beta})k(R_{A\gamma}) \quad (22)$$

where

$$h(R_{\alpha\beta}) = \frac{1}{4} \sum_{i=1}^2 \{1 - \tanh[\alpha_i(R_{\alpha\beta} - R_{\alpha\beta}^0) + \beta_i(R_{\alpha\beta} - R_{\alpha\beta}^1)^3]\} \quad (23)$$

$$g(R_{A-\alpha\beta}) = \frac{1}{2} \{1 + \tanh[\alpha_0(R_{A-\alpha\beta} - R_{A-\alpha\beta}^0)]\} \quad (24)$$

$$k(R_{A\gamma}) = \gamma_0 + \frac{(1 - \gamma_0)}{2} \{1 + \tanh[\gamma_1(R_{A\gamma} - R_{A\gamma}^0)]\} \quad (25)$$

with $R_{\alpha\beta}$ representing the H–H distance, $R_{A-\alpha\beta}$ representing the distance of the N atom to the center of mass of reference H_2 , $R_{A\gamma}$ representing the distance of the N atom to another H atom, and A and $(\alpha\beta\gamma)$ standing for the nitrogen and hydrogen atoms. Therefore, $h(R_{\alpha\beta})$ in eq 23 will allow the $\text{N}(^2\text{D})$ state to appear in the $\text{H}_2(\text{X}^1\Sigma_g^+) + \text{N}(^2\text{D}) + \text{H}(^2\text{S})$ channel while being absent in the $\text{NH}(\text{X}^3\Sigma^-) + \text{H}(^2\text{S}) + \text{H}(^2\text{S})$ channel. (See Figure 1a). Note that α_i and β_i ($i = 1, 2$) are parameters to be obtained as described elsewhere,³⁴ whereas the values of the $R_{\alpha\beta}^0$ and $R_{\alpha\beta}^1$ are chosen from the requirement that the PES has the correct energy dissociation limit at $\text{N}(^2\text{D}) + \text{H}_3(^2A')$ asymptote. Similarly, the value of the γ_0 in eq 25 is chosen from the requirement that the PES displays the correct energy dissociation limit at the $\text{NH}(\text{a}^1\Delta) + \text{H}_2(\text{X}^1\Sigma_g^+)$ asymptote. (See Figure 1b). To make the PES conform with the four- and three-atom cases, we represent the one-body term $V^{(1)}(\mathbf{R})$ by the following generalized form

$$V^{(1)}(\mathbf{R}) = V_{\text{N}(^2\text{D})}^{(1b)} f^{(4)}(\mathbf{R})[1 - f(\mathbf{R})] + V_{\text{N}(^2\text{D})}^{(1a)} f^{(3)}(\mathbf{R})f(\mathbf{R}) \quad (26)$$

where $V_{\text{N}(^2\text{D})}^{(1a)} f^{(3)}(\mathbf{R})$ is the one-body term utilized for $\text{NH}_2(^2A'')$ and $f(\mathbf{R})$ is a function of the internuclear coordinates that varies smoothly between 0 and 1 in such a way that $V_{\text{N}(^2\text{D})}^{(1b)} f^{(4)}(\mathbf{R})$ and $V_{\text{N}(^2\text{D})}^{(1a)} f^{(3)}(\mathbf{R})$ are switched on/off in different regions of the configuration space. An appropriate function that mimics the desired behavior is

$$f(\mathbf{R}) = \prod_{i=1,2,4} \frac{1}{2} \{1 - \tanh[\alpha(R_i - R_0^f)]\} \times \prod_{j=3,5,6} \frac{1}{2} \{1 + \tanh[\alpha(R_j - R_0^f)]\} \quad (27)$$

where $\alpha = 1.0$ and $R_0^f = 12a_0$. Note that the summations in eqs 22, 26, and 27 run over the three contributions referring to the ABCD, ACDB, and ADCB species, such as to keep the correct permutational symmetry on the H atoms. Finally, a smooth four-body energy term is obtained by choosing the coefficients α_0 and $R_{A-\alpha\beta}^0$ in eq 24 and γ_1 and $R_{A\gamma}^0$ in eq 25 via a trial-and-error procedure. The numerical values of all parameters in eq 22 are collected in Table 3. As a check to the switching function, we have compared the calculated energy dissociation limits obtained from a truncated DMBE (obtained as the sum of $V^{(1)}$, $V^{(2)}$, and $V^{(3)}$, hereafter referred to as DMBE₁₊₂₊₃ PES) with our own ab initio calculations. As seen from Table 5, the switching function imposes the correct behavior at every dissociation channel while providing a realistic representation at all interatomic distances.

3.4. Four-Body Energy Term. As a first step toward the four-body energy term $V^{(4)}$, we have examined in detail all features

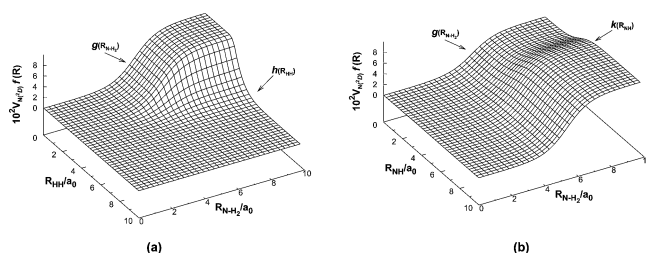


Figure 1. Switching function used to model the single-sheeted NH_3 DMBE PES: (a) $R_{\text{NH}} = 20a_0$; (b) $R_{\text{NH}} = 1.401a_0$.

TABLE 1: Comparison of Stationary Points (in angstroms and degrees) and Harmonic Frequencies (in inverse centimeters) Computed Using Different Methods with Available Experimental Results^a

symmetry	method	R_{NH}	θ_{HNH}	ω_1	ω_2	ω_3	ω_4
C_{3v}	DMBE PES ^b	1.0155	105.85	3482	1039	3569	1500
	dense grid ^b	1.0160	105.95	3747	1025	3892	1821
	B97-1/TZ2P ⁶²	1.0138	106.49	3485	1066	3606	1677
	CCSD(T)/cc-VTZP ⁶	1.0141	105.64	3471.9	1109.2	3597.5	1687.9
	CCSD(T)/cc-VQZP ⁶	1.0124	106.18	3480.5	1084.1	3608.8	1679.6
	QCISD(T)/5s4p2d1f,3s2p+core ⁶	1.0132	106.6	3486	1075	3616	1684
	MP4/6-31G** ⁶⁷	1.035	105.9	3546.2	1140.8	3687.3	1733.19
	CISDTQ/DZP ⁶⁸	1.0173	106.3	3528	1121	3676	1706
	Hoy et al. ⁶⁹	1.025	107	3503	1030	3591.6	1689.9
	Duncan and Mills ⁷⁰	1.0116	106.7	3504	1022	3577	1691
	Coy and Lehmann ⁷¹			3485(11)		3624(12)	1678(6)
	Lehmann and Coy ⁷²			3478(12)		3597(8)	1684(8)
D_{3h}	DMBE PES ^b	0.9983	120.0	3704	870i	3845	1572
	dense grid ^b	0.9983	120.0	3636	868i	3779	1561
	B97-1/TZ2P ⁶²	0.9971	120.0	3637	822i	3835	1577
	MC-QDPT ⁶⁴	0.998	120.0	3252	903i	3523	1596
	CCSD(T)/cc-pVDZ ¹⁰	1.0051	120.0				
	CCSD(T)/aug-cc-pVDZ ¹⁰	1.0054	120.0				
	CEPA-1/9s6p4d2f/5s3p ⁷³	0.9940	120.0				

^a Uncertainties are given in parentheses where applicable. ^b This work.

TABLE 2: Inversion Energy Barrier of Ammonia (in inverse centimeters)

method	ΔE_{inv} (cm ⁻¹)	E_{min} (E_{h})	E_{TS} (E_{h})
theoretical			
DMBE PES ^a	2033.5	-0.4660	-0.4567
dense grid ^a	2029.4	-0.4660	-0.4567
DFT ⁶⁵	2013.5		
B97-1/TZ2P ⁶²	1820		
focal-point scheme ³	2021		
CCSD(T)/aug-cc-pVDZ ¹⁰	2033.4		
CCSD(T)/aug-cc-pVTZ ¹⁰	1936.5		
CCSD(T)/aug-cc-pVQZ ¹⁰	1866.9		
CCSD(T)/cc-pVDZ ¹⁰	3104.5		
CCSD(T)/cc-pVTZ ¹⁰	2237.9		
CCSD(T)/cc-pVQZ ¹⁰	2025.6		
experimental			
Swalen and Ibers ⁶⁶	2018		
Špirko and Kraemer ¹³	1885		
Špirko ¹²	1834		

^a This work.

TABLE 3: Parameters (in atomic units) in Switching Function of Equation 22

parameter	numerical value
α_1	0.718244
α_2	0.719351
β_1	0.493967
β_2	0.066742
$R_{\alpha\beta}^{10}$	3.17557
$R_{\alpha\beta}^{11}$	5.11353
$R_{\alpha\beta}^{20}$	4.19386
$R_{\alpha\beta}^{21}$	6.27869
α_0	0.75
$R_{\alpha-\alpha\beta}^0$	5.35
γ_0	0.6478
γ_1	0.8
$R_{\text{A}\gamma}^0$	3.6

predicted by the PES when truncated at the $V^{(1)} + V^{(2)} + V^{(3)}$ level. As already noted in the previous section, the DMBE₁₊₂₊₃ PES so obtained shows the correct behavior while providing a fair representation at all interatomic separations. Therefore, it has been found to qualitatively describe the NH₃ PES. By comparing DMBE₁₊₂₊₃ with our own ab initio calculations, we have estab-

lished the major differences that ought to be corrected by adding four-body energy terms. We have found convenient the following correction

$$V^{(4)} = \sum_{i=1}^4 V_{\text{Si}}^{(4)} + \sum_{l=1}^3 V_l^{(4)} + P^{(4)}T^{(4)} \quad (28)$$

where $V_{\text{Si}}^{(4)}$ is a Gaussian-type function

$$V_{\text{Si}}^{(4)} = \sum_{\alpha\beta\gamma} \{d_i[1 + a_{i1}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^0) + a_{i2}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^0)^2 + a_{i3}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^0)^3] \exp[-b_{i1}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^0)] \exp[-b_{i2}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^0)^2]\} T_{\alpha\beta\gamma}^{(i)} \quad (29)$$

and $T_{\alpha\beta\gamma}^{(i)}$ in eq 29 is a range function defined by

$$T_{\alpha\beta\gamma}^{(1)} = \exp[-\gamma_{11}(2R_{\text{A}\alpha} - R_{\text{A}\beta} - R_{\text{A}\gamma})^2] \times \exp\{-\gamma_{12}[(R_{\alpha\beta} - R_{\alpha\beta}^0)^2 + (R_{\alpha\gamma} - R_{\alpha\gamma}^0)^2 + (R_{\beta\gamma} - R_{\beta\gamma}^0)^2]\} \quad (30)$$

$$T_{\alpha\beta\gamma}^{(2)} = \exp[-\gamma_{21}(R_{\text{A}\beta} - R_{\text{A}\gamma})^2] \times \exp\{-\gamma_{22}[(R_{\alpha\beta} - R_{\alpha\beta}^0)^2 + (R_{\alpha\gamma} - R_{\alpha\gamma}^0)^2 + (R_{\beta\gamma} - R_{\beta\gamma}^0)^2]\} \quad (31)$$

$$T_{\alpha\beta\gamma}^{(3)} = \exp[-\gamma_{31}(R_{\text{A}\beta}^2 - R_{\text{A}\alpha}^2 - R_{\beta\gamma}^2 + R_{\text{A}\alpha}R_{\beta\gamma})^2] \times \exp[-\gamma_{32}[(R_{\text{A}\beta} - R_{\text{A}\alpha}^0)^2 + (R_{\alpha\gamma} - R_{\alpha\gamma}^0)^2 + (R_{\beta\gamma} - R_{\beta\gamma}^0)^2]] \quad (32)$$

$$T_{\alpha\beta\gamma}^{(4)} = \exp[-2(R_{\alpha\beta} - R_{\alpha\gamma})^2 - 2(R_{\text{A}\beta} - R_{\text{A}\gamma})^2] \times \exp[-\gamma_{41}(R_{\beta\gamma} - R_{\beta\gamma}^0)^2] \times \exp\{-\gamma_{42}[(R_{\text{A}\beta} - R_{\text{A}\alpha}^0)^2 - (R_{\text{A}\gamma} - R_{\text{A}\alpha}^0)^2]\} \quad (33)$$

In turn, $V_{\text{S1}}^{(4)}$, $V_{\text{S2}}^{(4)}$, and $V_{\text{S3}}^{(4)}$ have been chosen to correct the energy at the N + H₃ channel, with the parameters in $V_{\text{S1}}^{(4)}$, $V_{\text{S2}}^{(4)}$, and $V_{\text{S3}}^{(4)}$

TABLE 4: Geometries (in a_0 and degrees) and Harmonic Frequencies (in inverse centimeters) for $\text{NH}\cdots\text{H}_2$ Transition State (TS) As Obtained from the DMBE PES^a

species	R_{NH_a}	R_{NH_b}	R_{NH_c}	$R_{\text{H}_a\text{H}_c}$	$R_{\text{H}_a\text{H}_b}$	$R_{\text{H}_b\text{H}_c}$	ΔE	harmonic frequencies
$\text{NH}\cdots\text{H}_2$ (TS)	1.983	4.860	4.860	1.405	5.361	5.361	13.1	657i, 3219, 330, 222, 4257, 914
$\text{NH} + \text{H}_2$	1.9565			1.401			0.0	

^a ΔE (in kilocalories per mole) denotes the energy difference relative to the $\text{NH} + \text{H}_2$ asymptote.

TABLE 5: Energy Dissociation Limits (in E_h) of NH_3 PES

fragments ^a	R_1/a_0	R_2/a_0	R_3/a_0	R_4/a_0	R_5/a_0	R_6/a_0	DMBE ₁₊₂₊₃	DMBE	ab initio ^b	error ^c
$\text{N}(^4\text{S}) + 3\text{H}(^2\text{S})$	19.0000	19.0000	19.0000	32.9090	32.9090	32.9090	-0.000001	-0.000001	0.000000	0.000001
$\text{H}_2(\text{X}^1\Sigma_g^+) + \text{N}(^2\text{D}) + \text{H}(^2\text{S})$	10.0000	10.0245	10.0245	20.0123	20.0123	1.4010	-0.083330	-0.083330	-0.083311	0.000019
$\text{NH}(\text{X}^3\Sigma^-) + 2\text{H}(^2\text{S})$	1.9650	10.0245	10.0245	10.3491	10.3491	20.0000	-0.130233	-0.130233	-0.128466	0.001767
$\text{NH}(\text{a}^1\Delta) + \text{H}_2(\text{X}^1\Sigma_g^+)$	1.9565	15.0163	15.0163	16.9710	16.9710	1.4010	-0.243414	-0.243414	-0.243997	0.000583
$\text{NH}_2(1^2\text{A}') + \text{H}(^2\text{S})$	15.0000	1.9405	1.9405	16.2839	16.2839	3.0289	-0.285765	-0.285765	-0.282517	0.003248
$\text{N}(^2\text{D}) + \text{H}_3(^2\text{A}')$	20.0000	20.0773	20.0773	1.7605	1.7605	3.5210	-0.067950	-0.067950	-0.067262	0.000688

^a H_3 is taken here at the collinear saddle point geometry ($D_{\infty h}$), although it is a well-known van der Waals species. ^b Energy calculated using FVCAS/MRCI(Q)/AVTZ. ^c Taken as the difference between the calculated ab initio energy and the DMBE PES energy.

TABLE 6: Coefficients^a of the Four-Body Energy Terms $V_{\text{SI}}^{(4)}$ and $V_{\text{I}}^{(4)}$ in Equations 28–39

V_{S1}	V_{S2}	V_{S3}	V_{S4}	V_1	V_2	V_3
$d_1 = -0.108983$	$d_2 = 0.0198257$	$d_3 = 0.0022601$	$d_4 = -0.023724$	$C_1 = 0.035$	$C_2 = 0.025$	$C_3 = -0.050$
$a_{11} = 2.24483$	$a_{21} = 1.2956$	$a_{31} = 2.37549$	$a_{41} = 0.423244$	$R_1^0 = 3.5$	$R_2^0 = 3.7$	$\alpha'_1 = 0.6$
$a_{12} = 0.678106$	$a_{22} = 0.909194$	$a_{32} = 1.23576$	$a_{42} = 0.737368$	$R_2^0 = 1.9405$	$R_2^0 = 1.9405$	$R'_1 = 4.4$
$a_{13} = 0.582107$	$a_{23} = 0.622791$	$a_{33} = 0.181617$	$a_{43} = 0.273109$	$R_3^0 = 1.9405$	$R_3^0 = 1.9405$	$\alpha'_2 = 2.0$
$b_{11} = 2.12763$	$b_{21} = 1.04963$	$b_{31} = 1.56864$	$b_{41} = 1.40199$	$R_4^0 = 2.742728$	$R_4^0 = 5.141385$	$R'_2 = 3.2$
$b_{12} = 0.0$	$b_{22} = 0.919367$	$a_{32} = 0.0$	$a_{42} = 0.639717$	$R_5^0 = 2.742728$	$R_5^0 = 5.141385$	$\alpha'_3 = 2.0$
$\gamma_{11} = 9.1$	$\gamma_{21} = 0.1$	$\gamma_{31} = 0.1$	$\gamma_{41} = 1.0$	$R_6^0 = 3.028850$	$R_6^0 = 3.028850$	$R'_3 = 2.5$
$\gamma_{12} = 100$	$\gamma_{22} = 100$	$\gamma_{32} = 100$	$\gamma_{42} = 0.5$	$\gamma_{51} = 0.75$	$\gamma_{61} = 1.05$	$\gamma_{71} = 5.0$
$R_{\text{A}\alpha}^{10} = 2.9072$	$R_{\text{A}\alpha}^{20} = 4.4$	$R_{\text{A}\alpha}^{30} = 4.58303$	$R_{\text{A}\alpha}^{40} = 3.69261$		$\gamma_{62} = 10$	$R_{\text{A}\alpha}^{50} = 1.965$
$R_{\alpha\beta}^0 = 1.7605$	$R_{\alpha\beta}^0 = 1.7605$	$R_{\alpha\beta}^0 = 1.7605$	$R_{\alpha\beta}^0 = 3.080698$			
$R_{\alpha\gamma}^0 = 1.7605$	$R_{\alpha\gamma}^0 = 1.7605$	$R_{\alpha\gamma}^0 = 1.7605$	$R_{\alpha\gamma}^0 = 3.080698$			
$R_{\beta\gamma}^0 = 3.5210$	$R_{\beta\gamma}^0 = 3.5210$	$R_{\beta\gamma}^0 = 3.5210$	$R_{\beta\gamma}^0 = 1.401$			

^a Distances and energies are in atomic units.

calibrated by fitting ab initio points that cover the regions that describe the dissociation process $\text{NH}_3 \rightarrow \text{N} + \text{H}_3$. In turn, $V_{\text{S4}}^{(4)}$ is rather localized and hence chosen to remove a small unphysical minimum that occurred in the $\text{H} + \text{N} + \text{H}_2$ channel, whereas the parameters in $V_{\text{S4}}^{(4)}$ were fitted to ab initio points in the vicinity of the corresponding geometry.

In turn, the terms $V_{\text{I}}^{(4)}$ that appear in eq 28 are local Gaussian functions defined by

$$V_1^{(4)} = \sum_{\alpha\beta\gamma} \sum_{j=1}^6 C_1 \exp[-\gamma_{51}(R_j - R_j^0)^2] \quad (34)$$

$$V_2^{(4)} = \sum_{\alpha\beta\gamma} \sum_{j=1}^6 C_2 \exp[-\gamma_{61}(R_j - R_j^0)^2] \exp[-\gamma_{62}(|\cos \phi| - 1)] \quad (35)$$

$$V_3^{(4)} = \sum_{\alpha\beta\gamma} \{G_1 G_2 G_3 C_2 \exp[-2(R_{\alpha\beta} - R_{\alpha\gamma})^2 - 2(R_{\alpha\beta} - R_{\alpha\gamma})^2] \exp[-\gamma_{71}(R_{\text{A}\alpha} - R_{\text{A}\alpha}^{50})]\} \quad (36)$$

where

$$G_1 = \frac{1}{2} \left\{ 1 + \tanh \left[\alpha'_1 \left[\frac{1}{4}(R_{\text{A}\beta} + R_{\text{A}\gamma})^2 - \left(\frac{1}{4}R_{\beta\gamma} \right)^2 - R'_1 \right] \right] \right\} \quad (37)$$

$$G_2 = \frac{1}{2} \{ 1 - \tanh[\alpha'_2(R_{\beta\gamma} - R'_2)] \} \quad (38)$$

$$G_3 = \frac{1}{2} \{ 1 + \tanh[\alpha'_3(R_{\beta\gamma} - R'_3)] \} \quad (39)$$

Moreover, $V_1^{(4)}$ and $V_2^{(4)}$ have been chosen to refine the entrance barrier of $\text{H} + \text{NH}_2$ channel, $V_3^{(4)}$ is a rather localized and chosen to remove an unphysical minimum in the $\text{NH} + \text{H} + \text{H}$ channel, and the parameters of $V_{\text{I}}^{(4)}$ were chosen from a fit to the ab initio points in the vicinity of the corresponding geometry. In summary, the addition of such local terms $V_{\text{I}}^{(4)}$ have been found necessary particularly to eliminate spurious unphysical minima during the fitting procedure. Table 6 gathers the parameter values in eqs 28–39. Recall that A and $(\alpha\beta\gamma)$ stand for the nitrogen and hydrogen atoms, and note that the summation in $V_{\text{SI}}^{(4)}$ and $V_{\text{I}}^{(4)}$ run over the three equivalent terms (ABCD, ACDB, and ADBC) such as to keep the correct permutational symmetry on the H atoms. Note further that $T^{(4)}$ in eq 23 is a range-determining factor chosen to be of the Gaussian type³⁹

$$T^{(4)} = \sum_{\alpha} \exp\{-[g_{\text{NH}}(R_{\text{A}\alpha} - R_{\text{NH}}^{\text{ref}})^2 + g_{\text{HH}}(R_{\alpha\beta} - R_{\text{HH}}^{\text{ref}})^2]\} \quad (40)$$

where $P^{(4)}$ is a fourth-order polynomial written as⁶¹

$$P^{(4)} = \sum_{i,j,k_p} a_{i,j,k_p} S_1^i S_4^j \prod_{p=1}^8 t_p^{k_p} \quad (41)$$

with S_1 , S_4 , and

$$t_p = \{S_2^2 + S_3^2 + S_5^2 + S_6^2, S_2S_5 + S_3S_6, S_3^3 - 3S_3S_2^2, S_6^3 - 3S_6S_5^2, S_6(S_3^2 - S_2^2) - 2S_2S_3S_5, S_3(S_2^2 - S_5^2) - 2S_2S_5S_6, (S_3 + S_6)^3 - 3(S_3 + S_6)(S_2 + S_5)^2\} \quad (42)$$

being 10 totally symmetric integrity functions,^{38,61} which are invariant under permutation operation of any two equivalent H atoms of NH₃. Consequently, the NH₃ PES is totally symmetric under permutation of any two H atoms of NH₃. Note that S_i are the D_{3h} symmetric coordinates defined as eq 43 of ref 38 but using a different set of reference geometries ($R_{\text{NH}}^{\text{ref}}$ and $R_{\text{HH}}^{\text{ref}}$). In turn, the coefficients $R_{\text{NH}}^{\text{ref}}$, $R_{\text{HH}}^{\text{ref}}$, g_{NH} , and g_{HH} in eq 40 have been calculated using a trial-and-error procedure, whose numerical values are reported in Table 7. The linear coefficients appearing in eq 41 have been calibrated from a least-squares fitting procedure to our own 205 ab initio points. Table 7 gathers the values of the 54 linear coefficients a_{i,j,k_p} appearing in eq 41. The fitted surface shows a root-mean-square deviation (rmsd) of 0.065 kcal mol⁻¹ with a maximum error of 0.420 kcal mol⁻¹. The stratified rmsd of the final PES with respect to all fitted ab initio energies is reported in Table 8. The DMBE form is seen to fit the ab initio data with chemical accuracy, with a stratified rmsd $\ll 1\%$ of the reference energy.

4. Features of the NH₃ Potential Energy Surface

The reaction path with C_{3v} symmetry connects in the title system the D_{3h} transition state with the C_{3v} minimum.⁶² Table 1 shows the results of the ab initio calculations and DMBE PES for the D_{3h} structure. As shown, the D_{3h} transition state structure on the DMBE PES shows the characteristic bond length in very good agreement with the one predicted ab initio. In turn, Table 1 reports the properties of the DMBE PES at the C_{3v} equilibrium structure. Besides our own results,

TABLE 7: Coefficients,^a a_{i,j,k_p} in Equations 40 and 41

$R_{\text{NH}}^{\text{ref}}$	1.89	$R_{\text{HH}}^{\text{ref}}$	3.273411
g_{NH}	5.0	g_{HH}	2.0
$a_{0,0,0}$	-0.0149239509	$a_{2,0,1}$	-0.0000047329
$a_{1,0,0}$	0.0393566682	$a_{2,0,2}$	-0.0000249623
$a_{0,1,0}$	-0.0207103175	$a_{2,0,3}$	0.0000004764
$a_{2,0,0}$	-0.1460667641	$a_{1,1,1}$	-0.0000134270
$a_{1,1,0}$	0.0802288866	$a_{1,1,2}$	-0.0000655363
$a_{0,2,0}$	-0.0453661202	$a_{1,1,3}$	0.0000071649
$a_{0,0,1}$	-0.0956785052	$a_{1,3,0}$	-0.0221918415
$a_{0,0,2}$	-0.0399175663	$a_{1,0,4}$	0.0000145569
$a_{0,0,3}$	-0.0210753673	$a_{1,0,5}$	0.0000308448
$a_{3,0,0}$	0.0112004510	$a_{1,0,6}$	-0.0000055180
$a_{2,1,0}$	-0.0414751468	$a_{1,0,7}$	0.0000056313
$a_{1,2,0}$	-0.0186598337	$a_{1,0,8}$	0.0000457415
$a_{1,0,1}$	0.0003457716	$a_{0,4,0}$	-0.0717617678
$a_{1,0,2}$	0.0022309626	$a_{0,2,1}$	-0.0000314825
$a_{1,0,3}$	-0.0003883413	$a_{0,2,2}$	-0.0000927060
$a_{0,3,0}$	-0.0619437295	$a_{0,2,3}$	-0.0000167492
$a_{0,1,1}$	0.0008785003	$a_{0,1,4}$	0.0000332154
$a_{0,1,2}$	0.0017967763	$a_{0,1,5}$	0.0000834940
$a_{0,1,3}$	0.0009600578	$a_{0,1,6}$	-0.0000174075
$a_{0,0,4}$	-0.0004633714	$a_{0,1,7}$	-0.0000144196
$a_{0,0,5}$	-0.0056973880	$a_{0,1,8}$	0.0000212283
$a_{0,0,6}$	0.0004316154	$a_{0,0,2,1}$	-0.0000302394
$a_{0,0,7}$	0.0014237697	$a_{0,0,2,2}$	-0.0000088146
$a_{0,0,8}$	-0.0005946042	$a_{0,0,2,3}$	0.0000026353
$a_{4,0,0}$	0.0006812888	$a_{0,0,2,2}$	-0.0000500316
$a_{3,1,0}$	-0.0037633238	$a_{0,0,2,3}$	-0.0000417883
$a_{2,2,0}$	0.0153576383	$a_{0,0,2,3}$	0.0000005487

^a Distances and energies are in atomic units.

TABLE 8: Accumulated (acc.) and Stratum (strat.) Root-Mean-Square Deviations (in kilocalories per mole) of DMBE PES^a

energy		N^b		max dev. ^c		rmsd		$N_{>\text{rmsd}}^d$	
acc.	strat.	acc.	strat.	acc.	strat.	acc.	strat.	acc.	strat.
10	0–10	211	211	0.420	0.420	0.066	0.066	8	8
20	10–20	212	1	1.215	1.215	0.106	1.215	8	0
30	20–30	214	2	6.538	6.538	0.463	4.661	3	1
40	30–40	215	1	6.538	4.734	0.563	4.734	4	0
50	40–50	217	2	6.538	1.617	0.572	1.161	5	1
60	50–60	219	2	6.538	2.915	0.615	2.425	7	1
70	60–70	221	2	6.538	2.587	0.641	2.017	9	1
80	70–80	223	2	6.538	1.983	0.654	1.525	11	1
90	80–90	224	1	6.538	0.698	0.655	0.698	12	0
100	90–100	227	3	6.538	1.679	0.662	1.072	13	1
120	100–120	305	78	6.538	4.322	1.170	2.019	69	23
140	120–140	320	15	7.230	7.230	1.247	2.309	75	2
160	140–160	325	5	7.230	4.331	1.261	1.963	76	1
180	160–180	335	10	7.230	5.371	1.287	1.948	78	2
200	180–200	351	16	7.230	3.806	1.310	1.729	87	3
300	200–300	465	114	10.444	10.444	1.663	2.449	98	20
500	300–500	472	7	10.444	7.081	1.738	4.465	97	2
930	500–930	476	4	10.444	3.810	1.741	2.086	96	1

^a Defined here by $\text{rmsd} = [\sum_{i=1}^N [V(\mathbf{R}_i) - E(\mathbf{R}_i)]^2 / N]^{1/2}$, where $V(\mathbf{R}_i)$ and $E(\mathbf{R}_i)$ are the DMBE and calculated ab initio energies.

^b Number of calculated MRCI/AVTZ points up to the indicated energy range. ^c Maximum deviation up to the indicated energy range. ^d Number of calculated MRCI/AVTZ points with an energy deviation larger than the root-mean-square deviation.

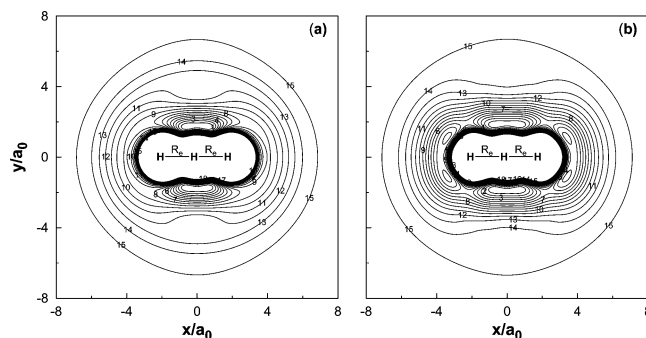


Figure 2. Contour plot for N moving coplanarly around an H₃ species whose geometry has been fixed at the $D_{\infty h}$ saddle point geometry (common bond distance, $R_e = 1.7605a_0$). Contours in panels a and b start at $-0.21E_h$, being equally spaced by $0.01E_h$. (a) DMBE₁₊₂₊₃ surface. (b) Full DMBE PES.

we give for comparison the results from other theoretical and experimental work. Here too, the DMBE PES predicts bond lengths in good agreement with other results. Furthermore, the predicted bond angle from DMBE agrees with other predictions within 2°. These two facts suggest that the harmonic frequencies should also be in good agreement with one another, as is indeed observed from Table 1.

Figures 2–15 illustrate the major topographical features of the NH₃(¹A₁) DMBE PES. As seen, it shows a smooth and correct behavior over the whole configuration space. Also visible are its global minimum and the D_{3h} transition state. Specifically, Figure 2 shows energy contours for N moving coplanarly around a partially relaxed H₃ (this is frozen at its optimum FVCAS/AVTZ geometry) with the central H atom fixed at the origin. Note that H₃ is not a stable species, with the chosen structure corresponding to a well-established saddle point of $D_{\infty h}$ symmetry for the hydrogen-atom exchange reaction.^{36,63} From Figure 2a,b we can see that both the DMBE₁₊₂₊₃ and DMBE PES predictions for the dissociation limit at the N + H₃ dissociation limit are in good agreement with our ab initio results. (See also the fifth entry

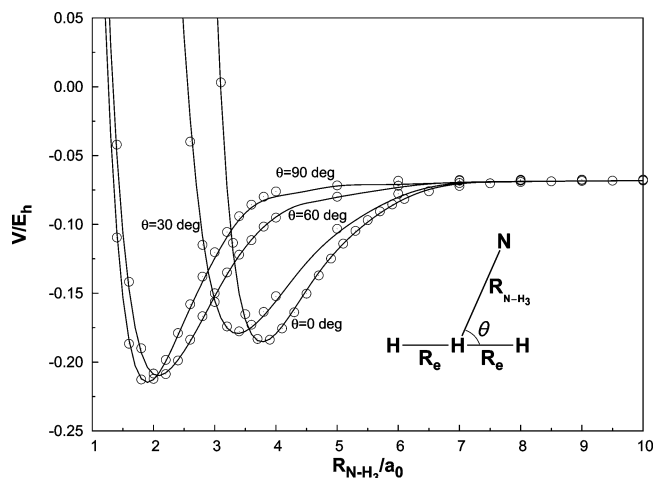


Figure 3. Comparison of the DMBE PES with the MRCI(Q)/AVTZ energies for N moving coplanarly around H_3 (common bond distance fixed at $R_e = 1.7605a_0$). R_{N-H_3} is the distance between N and the mass center of H_3 , and θ the indicated NHH bond angle.

of Table 5.) However, inclusion of the four-body energy term makes the full DMBE PES improve significantly the accuracy by improving the description at other regions in the $N + H_3$ channel.

Figure 3 compares the DMBE PES with the ab initio energies at MRCI(Q)/AVTZ for N moving in a coplanar manner around a partially relaxed H_3 molecule. The curves obtained from the DMBE PES are seen to be in good agreement with the calculated values. A diagram showing contour plots for H moving in a coplanar manner around a partially relaxed NH_2 molecule (by keeping NH_2 frozen at the geometry reported in ref 34) is shown in Figure 4. Figure 4a shows that the $DMBE_{1+2+3}$ PES cannot attain a unique value at the $H + NH_2$ limit. Fortunately, as illustrated in Figure 4b, this inconsistency is overcome through the inclusion of the four-body energy term (i.e., in the full DMBE PES). Similarly, the accuracy in describing the C_{2v} insertion of H atom into NH_2 molecular is significantly enhanced by the full DMBE PES. Figure 5 compares the DMBE PES with the MRCI(Q)/AVTZ energies for H moving in coplanarly around a partially relaxed NH_2 molecule. As shown by this plot, the curves obtained from the DMBE PES are in good agreement with the calculated energies. The above referred discrepancies for the coplanar geometries are mainly caused by a sudden change in the MRCI(Q) energy with the R_{H-NH_2} distance. At those geometries, there are strong configuration-mixing effects^{1,64} due to a change in the lowest electronic configuration from 1A_1 to A_2' as one approaches the strong-interaction regions. Therefore, the lowest adiabatic PES exhibits complicated topographical features. As a result, a multivalued approach may be required to obtain a more realistic potential model.

Figure 6 shows a 2D cut of the DMBE PES of NH_3 including the two minima and the saddle point for the umbrella inversion. The optimized DMBE potential curve is shown in the inset of Figure 6 and compared with other reported inversion potential curves.^{62,65} A notable feature from such a plot is the fairly good agreement between our optimized DMBE inversion potential curve and the one by Aquino et al.,⁶⁵ particularly for small values of the inversion coordinate where the optimized DMBE inversion potential curve is almost indistinguishable from their curve. Table 2 gives the results of calculations for the inversion barrier computed using different methods and available experimental results. The predicted DMBE inversion barrier of 2033.5 cm^{-1} is clearly in very good agreement with the result of 2029.4 cm^{-1}

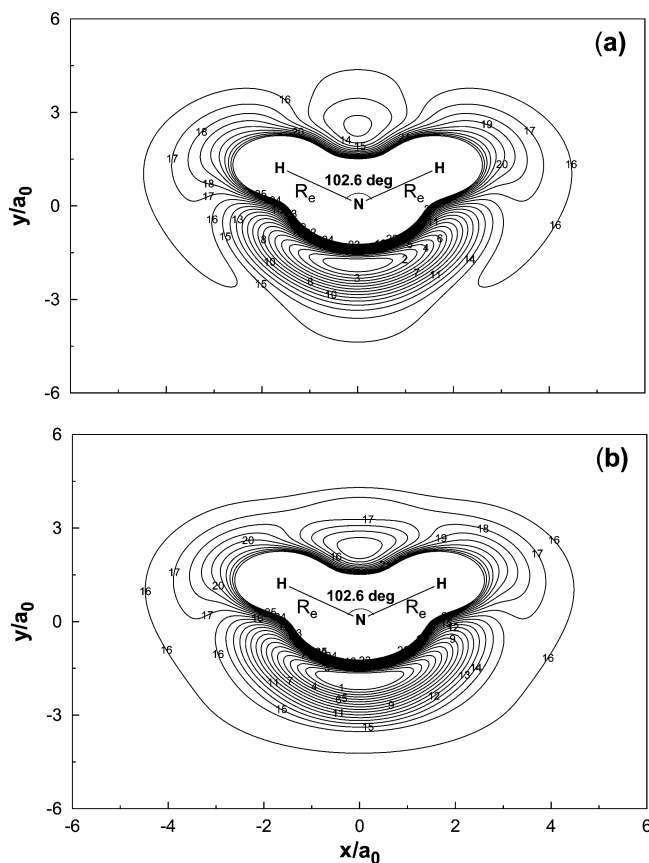


Figure 4. Contour plot for H moving coplanarly around a NH_2 molecule with $R_e = 1.9405a_0$ and included angle 102.6° . Contours in panels a and b start at $-0.458E_h$, being equally spaced by $0.01E_h$: (a) $DMBE_{1+2+3}$ surface; (b) full DMBE PES.

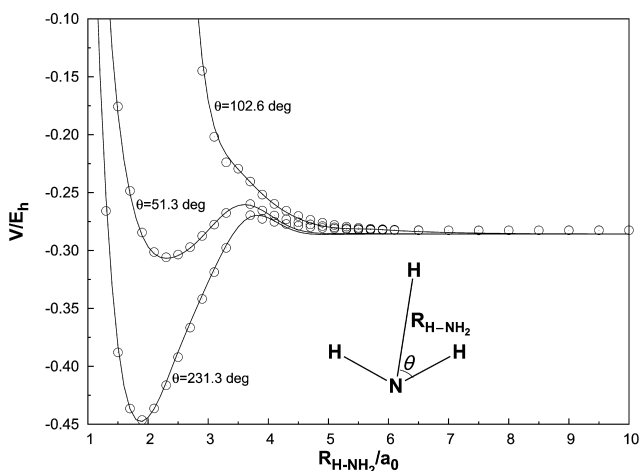


Figure 5

Figure 5. Comparison of the DMBE PES with the MRCI(Q)/AVTZ energies for H moving in a coplanar manner around a partially relaxed NH_2 molecule. R_{H-NH_2} refers to the distance between H and the N in the NH_2 molecule, and θ is the HNH angle.

obtained from the fit to the dense grid of ab initio points close to the equilibrium geometry and D_{3h} saddle point, being also in quite good agreement with the experimental value of 2018 cm^{-1} by Swalen and Ibers.⁶⁶

Figure 7 shows the global minimum, while illustrating that the DMBE PES is totally symmetric under permutation of any two H atoms of NH_3 . However, inclusion of the four-body energy term in the DMBE PES makes the global minimum be lowered to $-0.4660E_h$, in good agreement with the result of

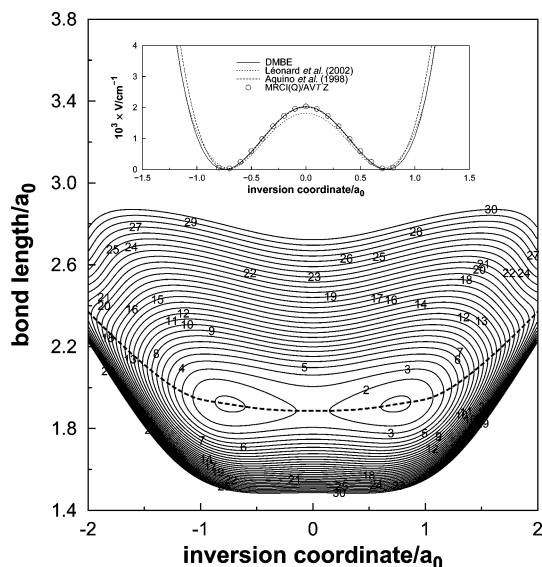


Figure 6. 2D section of the DMBE PES of NH_3 including the two minima and the saddle point of the 6D space considered in the present work. Contours start at $-0.4650E_h$, being equally spaced by $0.0075E_h$. Shown in the inset is the optimized inversion potential curve: dashed line, from ref 65; dotted line, from ref 62; solid line, DMBE (this work).

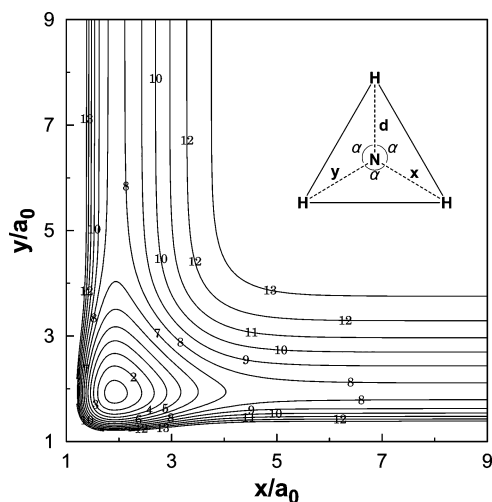


Figure 7. Contour plot of DMBE PES for bond stretching in NH_3 , with $d = 1.919a_0$ and keeping the included angle fixed at 105.85° . Contours start at $-0.455E_h$, being equally spaced by $0.025E_h$.

$-0.4660E_h$ from our ab initio prediction. To obtain further information on the global minimum, we also compare the DMBE PES with the ab initio energies at MRCI(Q)/AVTZ. This is illustrated in Figure 8, where cuts are shown of the DMBE PES along one bond length. Values for the remaining coordinates are: bond lengths fixed at $d = 1.919a_0$ and bond angles at $\alpha = 105.85^\circ$, respectively, the optimum equilibrium bond length and equilibrium bond angle of the DMBE PES. Clearly, the 1D cuts of the DMBE PES show good agreement with the calculated ab initio energies. Figure 9 shows a contour plot of the full DMBE PES for the channel $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH}_3 \rightleftharpoons \text{NH} + \text{H} + \text{H}$, with a 2D minimum being apparent from Figure 9, which corresponds to the D_{3h} transition-state structure of energy $-0.4567E_h$, in good agreement with the result of $-0.4567E_h$ from our ab initio prediction. Moreover, as Figures 10 a,b and 11a,b clearly show, both the DMBE₁₊₂₊₃ and DMBE PESs predict a barrier for the $\text{NH}_3 \rightleftharpoons \text{H}_2 + \text{NH}$ channel in agreement with the calculated ab initio result. By comparing

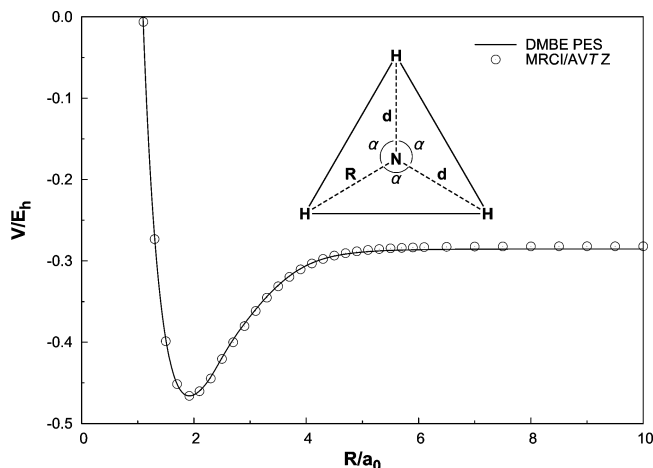


Figure 8. Cut of DMBE PES along one bond length, with remaining coordinates lengths fixed at their MRCI(Q)/AVTZ equilibrium values of $d = 1.919a_0$ and $\alpha = 105.85^\circ$.

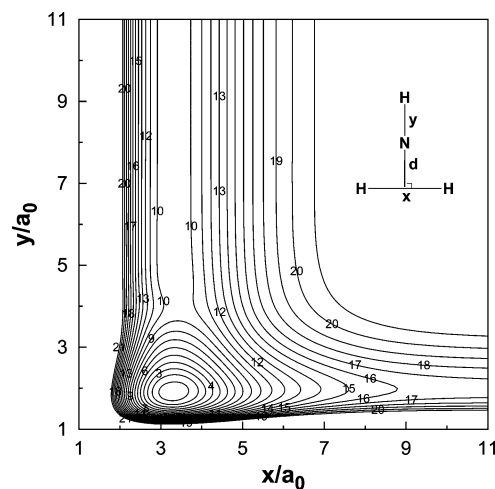


Figure 9. Contour plot of DMBE PES for the channel $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH}_3 \rightleftharpoons \text{NH} + \text{H} + \text{H}$, where $d = 0.95a_0$. Contours start at $-0.4435E_h$, being equally spaced by $0.02E_h$. The plot for the DMBE₁₊₂₊₃ PES is nearly indistinguishable and hence not shown.

Figures 10 a,b and 11a,b, we stress the significant improvement obtained by eliminating the unphysical minimum with the addition of a four-body energy term, as discussed above. Figures 12 and 13 show the contour plot of the full DMBE PES for the channel $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH} + \text{H}_2$, from which it is apparent that the DMBE PES also predicts the barrier on the $\text{H}_2 + \text{NH}$ channel. Such a barrier has been found to be $13.1 \text{ kcal mol}^{-1}$ higher than the $\text{NH} + \text{H}_2$ dissociation energy. Table 4 collects the geometries and harmonic frequencies for the $\text{NH} \cdots \text{H}_2$ transition state, calculated from the DMBE PES. As shown in Figure 12, there is no barrier for this dissociation to $\text{NH}_2 + \text{H}$ geometry. Along this direction, the H atom can more easily escape, as can also be seen from Figure 5. If an atom is placed far away from the remaining triatomic, the resulting PES matches exactly that of the triatomic fragment. Although not shown, a comparison of Figure 14 with the DMBE PES for NH_2 (Figure 7 of ref 34) also shows that the DMBE PES for NH_3 does yield upon dissociation a function indistinguishable from the one originally reported. Finally, Figure 15 shows a schematic diagram of the energetics of the title system according to the DMBE PES reported in the present work, whereas Table 5 summarizes the reference ab initio MRCI(Q)/AVTZ energy.

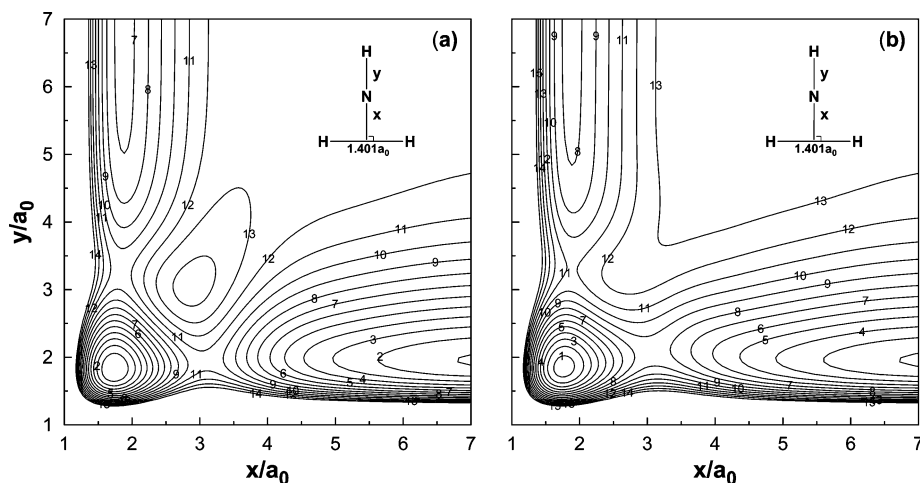


Figure 10. Contour plot for the channel $\text{H}_2 + \text{N} + \text{H} \rightleftharpoons \text{NH}_3 \rightleftharpoons \text{H}_2 + \text{NH}$. Contour in panels a and b start at $-0.252E_h$, being equally spaced by $0.0135E_h$: (a) DMBE_{1+2+3} surface; (b) full DMBE PES.

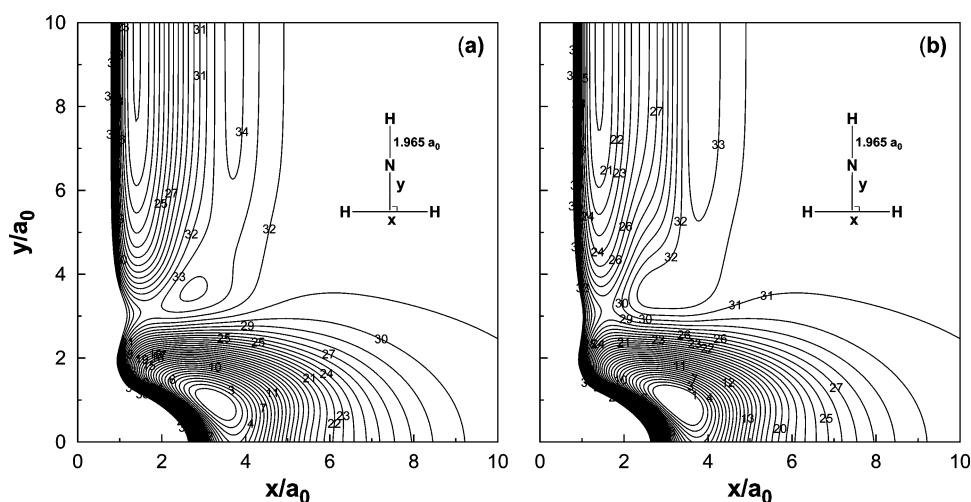


Figure 11. Contour plot for the channel $\text{NH} + \text{H}_2 \rightleftharpoons \text{NH}_3 \rightleftharpoons \text{NH} + \text{H} + \text{H}$. Contour in panels a and b start at $-0.432E_h$, being equally spaced by $0.01E_h$: (a) DMBE_{1+2+3} surface; (b) full DMBE PES.

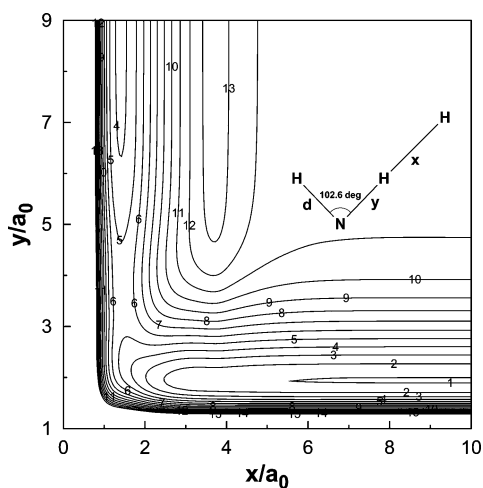


Figure 12. Contour plot of the DMBE PES for the channel $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH} + \text{H}_2$, where $d = 1.9405a_0$. Contour starts at $-0.285E_h$, being equally spaced by $0.015E_h$. The corresponding plot for the DMBE_{1+2+3} surface is nearly indistinguishable and hence not shown.

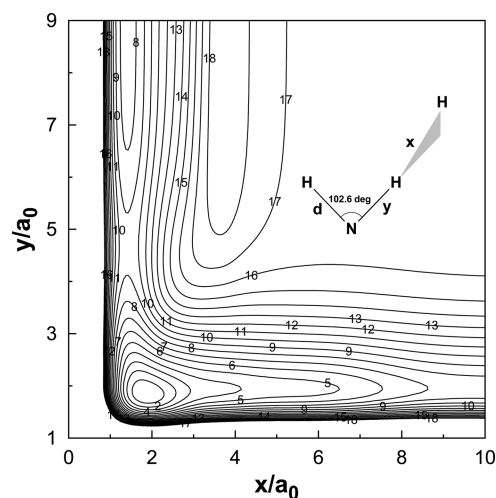


Figure 13. Contour plot of the DMBE PES for the channel $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH} + \text{H}_2$, with $d = 1.9405a_0$ and dihedral angle of 90° . Contours start at $-0.325E_h$, being equally spaced by $0.0125E_h$. The corresponding plot for the DMBE_{1+2+3} surface is nearly indistinguishable and hence not shown.

5. Conclusions

We have reported a single-sheeted DMBE PES for the ground electronic state of NH_3 , partially based on MRCI(Q)/AVTZ

calculations for the tetratomic also given in the present work and shown to be in fair agreement with previously reported ab initio results. The DMBE function warrants the proper atomic

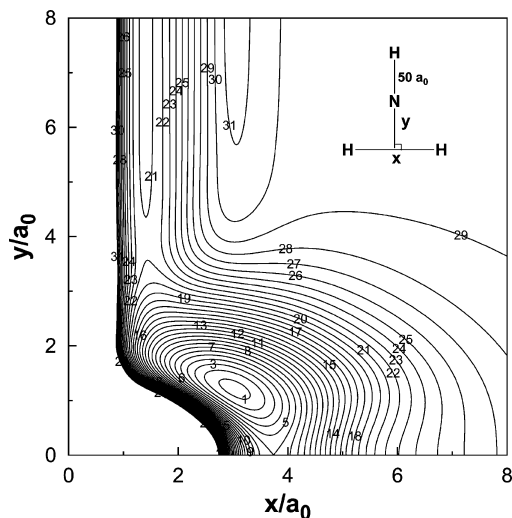


Figure 14. Contour plot of the NH_3 DMBE PES for the C_{2v} insertion of the N atom into H_2 , keeping the distance of the N to another H atom. Contours start at $-0.282E_h$, being equally spaced by $0.01E_h$. This plot is indistinguishable from the corresponding one for the NH_2 DMBE³⁴ PES alone.

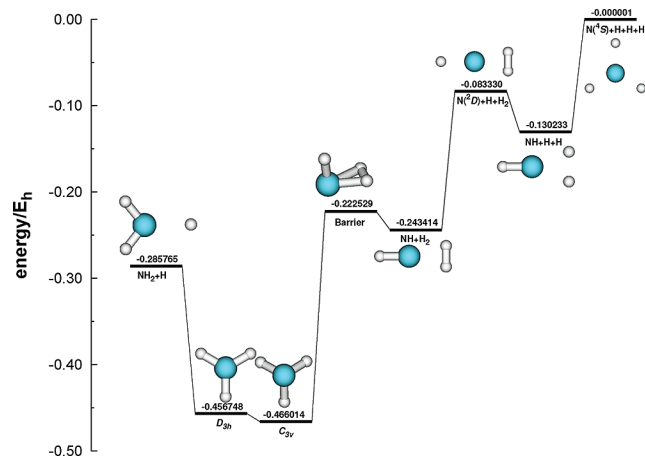


Figure 15. Energetics of full NH_3 DMBE PES reported in the present work.

permutational symmetry, while being based on a modest number of ab initio energies (when judged from the popular X^{3N-6} law, which shows that the number of required energy points grows exponentially with the number of atoms, with X being the number of points typically required per dimension) at an affordable (relatively low) level of theory. Therefore, it may pave the way for an ab-initio-based study aiming at a more sophisticated level of ab initio theory, or else for improvement via a direct fit to spectroscopic data (ref 52 and references therein). Despite the above, the attributes of the function here reported have been found to be generally in good agreement with those from the fitted raw ab initio energies and the results from previous theoretical calculations and experiment. To warrant that the PES dissociates to the correct asymptotes, a generalization of the switching function proposed elsewhere³⁴ (see ref 40 for a related development for the N_2H_2 species) has been extended to the present four-atom species. As usual in DMBE theory, the PES is expected to mimic the correct behavior at all dissociation channels while providing a realistic representation at all interatomic separations. It can therefore be recommended both for dynamics studies and as a building block for construction of DMBE forms for larger N_xH_y species. Such a work is currently in due course.

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