Ab initio molecular orbital study of the catalytic exchange reaction between hydrogen and sodium amide

J. Pineda, O. Novaro,[a] J. P. Daudey,[b] and E. Blaisten-Barojas

Instituto de Física, Universidad Nacional Autónoma de México Apdo. Post. 20-364, México 20, D.F. Mexico

(Received 10 November 1978; accepted 4 September 1979)

An *ab initio* MO–SCF study of the reaction pathway of the catalytic exchange between $NaNH_2$ and HD is presented. The results compare quite well with previous studies of the kinetics of the ammonia–deuterium exchange reaction with homogeneous alkali amide catalysts, which is a process used for the production of heavy water. The capacity of the amide to effectively lower the activation barrier for the HD scission is evidenced from this study. A parallel study of the same reaction using the nonempirical pseudopotential method is also carried out in order to show the value and deficiencies of this alternative approach vis-à-vis the all-electron results.

I. INTRODUCTION

In the study of catalytic systems several *ab initio* results on adsorption and catalysis have begun to accumulate in the last few years.[1–5] It is only recently, however, that an *ab initio* MO–SCF catalytic reaction coordinate has been obtained.[1] On the other hand, nonempirical pseudopotential techniques have been proposed in order to save computing time in studies on the structure of organometallic complexes[6–7] and also on chemisorption by surfaces.[4] To our knowledge no study of a complete catalytic reaction using pseudopotential calculations has yet appeared in the literature.

In this work we present results using both the *ab initio* MO–SCF and the pseudopotential SCF techniques. In the latter case we have used the pseudopotential method in the version of Barthelat *et al.*[8]

The problem analyzed here is the reaction:

$$NaNH_2 + HD \rightarrow NH_2D + NaH . \qquad (1)$$

It has been chosen not only because it is relevant for the catalytic production of heavy water, as shall be discussed in the following section, but also because it is small enough to permit a full all-electron SCF study of the system composed by the catalyst and reactant molecules. By carrying out both all-electron and pseudopotential calculations in the same reaction we obtain a test for the latter method, which may become of great value for studies of catalysis that usually involve systems too large for a systematic analysis at the all-electron level.

The plan of this work is as follows: In Sec. II we give a brief review on experimental work related to the mechanism of Reaction (1). In Sec. III we describe the methods involved in the present calculations. Section IV contains the *ab initio* results of the reaction, emphasizing three main aspects, the features of the potential energy surface which make for a selective entrance of the HD molecule to the catalytic site, the formation of an intermediate complex through partial bonding of the reactant, and, finally, the deuterium exchange reaction coordinate proper. In Sec. V the pseudopotential results are analyzed and compared with the all-electron ones showing good qualitative agreement plus some discrepancies whose cause is sought specially in view of the desirability of the use of the pseudopotential method for catalytic reactions involving heavier metal atoms than Na. Finally, in Sec. VI we present a discussion of the results of this study.

II. ALKALI AMIDES AS CATALYSTS FOR THE CHEMICAL EXCHANGE REACTION

Before presenting the details of the calculations we shall make a brief review of some of the experimental work aimed at the determination of the reaction mechanism that has appeared in the literature. The homogeneous catalytic exchange between deuterium and ammonia is known since the early work of Wilmarth and Dayton,[9] who showed that alkali amides augmented the reaction rate substantially. This led to the ideal of producing heavy water making use of the high separation factor of deuterium with ammonia.[10] At the time several attempts to establish the reaction mechanism appeared.[11,12] Later the industrial interest has extended to other processes, for instance, those involving NH_2Me, NH_2Et, etc., instead of ammonia.[13] The mechanism of exchange is essentially the same for all these cases[11] and therefore the present analysis of the $NaNH_2$–HD exchange can be considered as a model study for this family of processes. The fact that sodium, instead of the industrially more efficient potassium amide, was chosen for our calculations was due to considerations on the time consumption of the all-electron calculations. In any case sodium amide efficiently catalizes the chemical exchange, although with a slower reaction rate as compared with potassium. This has been ascribed to its lower solubility in ammonia and its smaller degree of dissociation.[11]

In brief, the main conclusions of the mechanistic studies of Refs. 11 and 12 are the following: The HD (or D_2) molecule approaches the catalyst molecule and adheres to it forming an intermediate complex. In this transition state the catalyst, in the form of an ion pair

---

[a] Consultant of Instituto Mexicano del Petrôleo.

[b] Permanent address: Laboratoire de Physique Quantique, Université P. Sabatier, 118 Route de Narbonne, Toulouse, France.

0021-9606/79/245124-10$01.00

or an amide ion forms a partial bond with the deuterium molecule (or hydride) through its lone pair of electrons, consequently weakening the D–D (or H–D) bond. The transition state is stabilized when the catalyst abstracts one deuterium atom, the other going to form a new bond with another hydrogen coming from a solvent molecule.[11] Kinetic studies were also aimed at establishing whether the catalytic species is the alkali amide molecule, the free ion NH_2^-, or the ionic pair $[Na^+]$ $[NH_2^-]$.[12] Apparently all of them play a role.[11]

This all too brief presentation of the reaction mechanism as derived from experimental data will be valuable for the rationalization of the quantum mechanical results given in the following sections. A word of caution is needed, however. All the theoretical results reported here refer to the electronic states of the reactant–catalyst system. Therefore the isotopic effect is beyond the scope of the present work where only the bond breaking and bond formations are reported. Any theoretical study that would pretend to include the isotopic exchange effects, however, would need a reasonable knowledge of the potential energy surface for the process, and the main purpose of this paper is to show that such knowledge can be achieved.

III. DISCUSSION OF THE METHODS AND SELECTION OF THE BASES

The electronic structure of the amide and HD molecules and their interaction through the reaction was obtained using PSIBMOL.[8] This program has the option of performing *ab initio* LCAO–MO–SCF all-electron[14] or alternatively, pseudopotential SCF calculations.

Two all-electron Gaussian type basis sets were used to study the molecules of Eq. (1). A minimal set (which will henceforth be referred to as set I) N(7*s*, 4*p*),[16] Na(10*s*, 4*p*),[16] and *H*(3*s*)[1] and a double-zeta set including 3*p*-type polarization functions in Na (set II): N(9*s*, 5*p*)[17] contracted [5211/32], Na(12*s*, 8*p*)[18] contracted [531111/422], and H(4*s*)[19] contracted [31]. The Na 3*p* exponents of set II are identical to those of set IIIa discussed below.

The geometrical parameters involved in the present calculations were chosen as follows: for the isolated catalyst, an ammonialike pyramidal structure was considered with bond lengths and internal angles taken from experimental values,[15] except for the d_{NNa} length which was obtained from the all-electron calculations. The geometrical parameters used for the amide are: $\widehat{HNH}=\widehat{HNNa}=107°$, $d_{NH}=1.91a_0$ and $d_{NNa}=4.12a_0$.

For the hydrogen molecule, as well as for the reaction products ammonia and NaH, the experimental geometries[15] were taken.

TABLE I. Results from the minimal and double- zeta Gaussian bases, sets I and II, in the all-electron calculation for the reactants and products of Eq. (1), given in atomic units (a.u.).

	Set I	Set I	Set II
		Amide	
Total energy		−216.9755	−217.3773
atomic charges	N	−0.83	−0.91
	Na	0.58	0.52
bond orders	N–Na	0.20	0.53
	N–H	0.73	0.62
		HD molecule	
Total energy		−1.1167	−1.1266
bond order	H–D	0.79	0.81
		Ammonia	
Total energy		−56.0165	−56.1608
atomic charges	N	−0.72	−0.81
	H	0.24	0.27
bond order	N–H	0.73	0.81
		Sodium hydride	
Total energy		−162.0795	−162.3711
atomic charge	Na	0.09	0.27
	H	−0.09	−0.27
bond order	H–Na	0.47	0.66

The results for the reactant and product molecules using sets I and II are reported in Table I; total energies, bond orders, and charges are given. Both sets give a reasonable description of the reactants but the total energy obtained with the minimal basis set is obviously rather poor. Furthermore, for the molecules of the product valley, set I fails not only as concerns the total energy predictions, but also gives a very poor representation of the polarity of the NaH molecule. Hence, we conclude that a trustworthy prediction of the complete reaction pathway can not be obtained from the minimal basis set I results.

Before discussing the pseudopotential basis sets used, we shall briefly review the nature of the pseudopotential method.[20] This technique is very appealing in a molecular orbital type of approach, because it gives simplified nonempirical results at lower computational costs. The basic assumption in using pseudopotential is that the core electrons do not play an important role in the binding and polarization of molecules and they may be replaced by an effective potential capable of representing adequately the interactions of the core with the valence electrons. The complete Hamiltonian of an *N*-electron system with *n* nuclei

$$H=\sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2}+\sum_{\alpha=1}^{n}\frac{Z_\alpha}{r_{\alpha i}}\right)+\sum_{i>j}^{N}\frac{1}{r_{ij}} \qquad (2)$$

is therefore replaced by

$$H^{PS}=\sum_{i=1}^{N_v}\left[-\frac{\nabla_i^2}{2}+\sum_{\alpha=1}^{n}\left(\frac{Z_\alpha^{PS}}{r_{\alpha i}}+W_\alpha^{PS}\right)\right]+\sum_{i>j}^{N_v}\frac{1}{r_{ij}}, \qquad (3)$$

where N_v is the number of valence electrons, Z_α^{PS} is the net charge of the bare αth nucleus plus its core electrons. The function W_α^{PS} is the pseudopotential operator associated to the αth atom in the system. This atomic operator is obtained in the following way.[8] Let us project the αth pseudopotential on to the subspace of spherical harmonics *l* centered on the atom α

TABLE II. Extended Gaussian bases, sets III and IIIa, used in the pseudopotential calculations. These sets differ only in the representation of the $3p$ orbital for Na.

Na				N				H			
Orbital	Exp.	Coef.	Contraction	Orbital	Exp.	Coef.	Contraction	Orbital	Exp.	Coef.	Contraction
$3s$	2.587783	−0.012656	[3, 1]	$2s$	86.59344	−0.007435	[3, 1]	$1s$	19.2406	0.032828	[3, 1]
	0.437518	−0.137369			11.020	−0.048083			2.89915	0.231208	
	0.059323	0.620613			0.649914	0.545771			0.65341	0.817238	
	0.023595	0.471608			0.209477	0.520802			0.17758	1.00000	
$3p^a$	1.497104	−0.012169	[2, 1]		11.78189	0.043663	[3, 1]				
	0.100367	0.472890			2.742543	0.228844					
	0.038788	0.593081			0.766414	0.507691					
					0.213824	0.449304					
$3p^b$	0.093784	0.514926	[2]								
	0.036973	0.548028									

[a] Polarization function of set III.

[b] Polarization function of set IIIa and of set II (see text).

$$W_\alpha^{\mathrm{PS}} = \sum_{l=0}^{l_{\max}} W_l^{(\alpha)} P_l \,, \tag{4}$$

where P_l is a projection operator and $W_l^{(\alpha)}$ the pseudopotential components defined as

$$W_l^{(\alpha)} = \sum_{i=1}^{n_l} C_i r^{n_i} \exp(-\alpha_i r^2) \,. \tag{5}$$

The parameters C_i and α_i were optimized to reproduce the energy and functional shape of the atomic valence orbitals. The optimized parameters for atoms up to the third row of the periodic table have been given by Barthelat *et al.*[8]; we have used these values.

An extended basis set used for the pseudopotential calculations was obtained through the optimization of Gaussian exponents[21] of sets N($4s$, $4p$) and Na($4s$), and these exponents as well as the coefficients are given in Table II. For hydrogen the ($4s$) functions given in Table II are the same ones used for the all-electron calculations (Ref. 20). For sodium, $3p$ polarization functions were added, obtained by expanding a $3p$ Slater function[23] with exponent $\zeta_c = 0.8357$, into three Gaussians contracted [21] (set III). A smaller set, identical to set III except that it includes only two contracted p Gaussians (which are also reported in Table II) will be referred to as set IIIa. The results obtained from these sets will be analyzed in some detail in Sec. V.

For the search of the reaction pathway, crude calculations were done using the pseudopotential method with a minimal Gaussian basis set obtained by expanding each single-zeta STO[22] into three Gaussians (set IV). This set was used mainly as a "probe" for determining the general features of the potential surface and guiding us to establish how the hydrogen molecule approaches the catalyst site.

The results obtained with these different basis sets as well as their relevance for the understanding of Reaction (1), are reported in the following section.

IV. THEORETICAL STUDY OF THE CHEMICAL PROCESS

The SCF results for the catalytic exchange reaction described in Eq. (1) shall now be presented. Over one hundred SCF calculations were carried out for different geometrical arrangements of the amide–HD system[23] using the different sets discussed in the previous section. For the discussion of these results we shall divide this section into three subsections where we depict the following chemically distinct aspects of the HD–$NaNH_2$ interactions: (a) the closed-shell–closed-shell repulsion that appears in the movement of the HD molecule towards the Na–N bond, showing that in this particular approach the catalyst is not effectively weakening the H–D bond, (b) the formation of an intermediate complex which confirms previous assumptions in mechanistic studies of the process[11–13] and which is here identified as an attraction between HD and $NaNH_2$, which occurs only for a very well defined path of approach of the former towards the nitrogen, and (c) the reaction coordinate proper, where emphasis shall be given to the role played by the catalyst in substantially diminishing the high barrier for the HD scission.

A. HD approach towards the Na–N bond

To describe the interaction between the reactant and catalyst molecules, it is convenient to define a reference frame as depicted in Fig. 1. This selection puts the N atom at the origin with Na on the z axis (at a distance of $4.12a_0$ from N, see Sec. III) and with the yz plane bisecting the angle between the two N–H bonds. Thus the

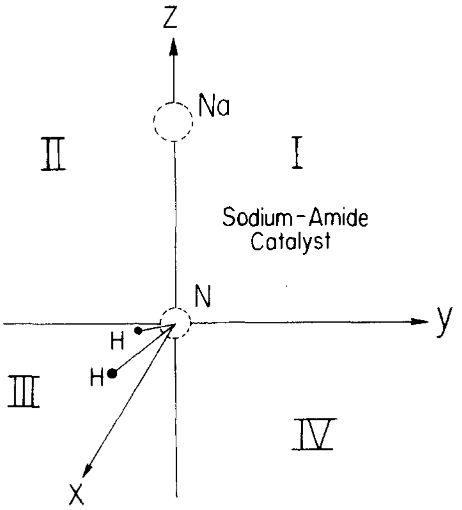

FIG. 1. Initial location of the amide in the selected framework.

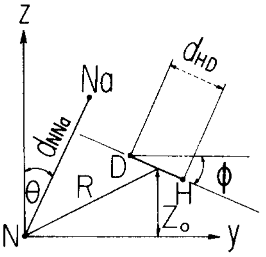

FIG. 2. Parameters used for the description of the reacting system.

N-bonded hydrogens have equal y and z coordinates and they lie above and below the yz plane.

The movement of the HD molecule towards the catalyst was studied mainly in the first and fourth quadrants (I, IV) of Fig. 1. Preliminary calculations in the second quadrant (II) and also with the HD axis perpendicular to the yz plane proved quite unfavorable and these alternatives were immediately abandoned. No attempts to allow an approach from the third quadrant were done, considering that the very unfavorable position of the amide hydrogens would necessarily hinder such an HD movement (see Fig. 1).

To describe the relative positions of the HD and the catalyst molecules we introduce six geometrical parameters as depicted in Fig. 2. R gives the magnitude of the radius vector to the midpoint of the H–D bond and z_0 its projection on the z axis; ϕ is the angle of orientation of HD, with $\phi = 0°$ when it is parallel to the y axis, d_{HD} is the HD interatomic distance; d_{NNa} is the distance between N and Na atoms in the amide; and finally θ is the angle between N–Na bond and the z axis.

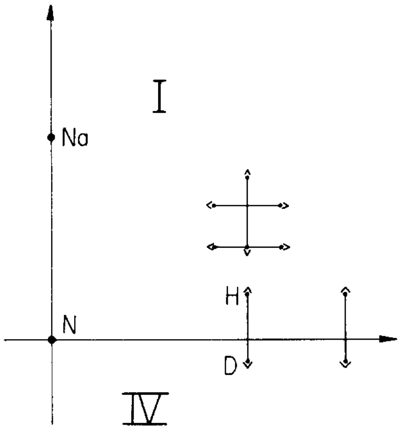

FIG. 3. Relevant configurations of the HD approach towards the N–Na bond reported in Table III.

Some HD movement within the first quadrant, approaching the N–Na bond while relaxing the H–D bond distance is depicted in Fig. 3. In Table III the corresponding interaction energies are reported.

The results of Table III come from calculations using the four sets (I to IV) mentioned in Sec. III; they all show a repulsive interaction that appears as soon as the HD approaches the amide. Furthermore all attempts to relax the H–D bond distance give essentially the same prohibitive barrier whether HD is infinitely separated or quite near to the catalytic site. Thus, the catalyst is not facilitating the H–D bond breaking at all.

These results are essentially basis set independent and apparently depend only on the HD internal energy, that is to say, its approach to the origin produces a

TABLE III. Interaction energy (a.u.) for the catalyst and the HD molecules when the latter moves in the first quadrant region (see Fig. 1). Distances in a_0 units, angles in degrees.

	Configurations						Relative energies			
	R	z_0	ϕ	d_{HD}	d_{NNa}	θ	set I	set II	set III	set IV
1	∞	⋯	⋯	1.4	4.12	0	0.0	0.0	0.0	0.0
2	∞	⋯	⋯	1.6	4.12	0	0.0136	0.0078	0.0078	0.0136
3	∞	⋯	⋯	1.8	4.12	0	0.0378	⋯	⋯	0.0378
4	∞	⋯	⋯	2.0	4.12	0	0.0676	⋯	⋯	0.0676
5	∞	⋯	⋯	2.4	4.12	0	0.1341	⋯	⋯	0.1341
6	10.0	0.22	90	1.4	4.12	0	0.0001	⋯	⋯	0.0001
7	8.0	0.22	90	1.4	4.12	0	0.0003	⋯	⋯	0.0003
8	6.0	0.22	90	1.4	4.12	0	0.0013	⋯	0.0019	0.0013
9	6.0	0.22	90	1.5	4.12	0	⋯	⋯	⋯	0.0064
10	6.0	0.22	90	1.6	4.12	0	0.0150	⋯	0.0099	0.0150
11	4.01	0.22	90	1.4	4.12	0	0.0235	⋯	0.0240	0.0157
12	4.01	0.22	90	1.44	4.12	0	⋯	⋯	⋯	0.0172
13	4.01	0.22	90	1.50	4.12	0	⋯	⋯	⋯	0.0208
14	4.01	0.22	90	1.60	4.12	0	0.0377	⋯	0.0320	⋯
15	4.01	0.22	90	1.4	4.12	10	⋯	⋯	⋯	0.0187
16	4.01	0.22	90	1.4	4.32	0	⋯	⋯	⋯	0.0148
17	4.01	0.32	90	1.6	4.32	0	⋯	⋯	⋯	0.0286
18	4.78	2.61	90	1.4	4.12	0	⋯	⋯	⋯	0.0172
19	4.83	2.71	90	1.6	4.12	0	⋯	⋯	⋯	0.0307
20	4.78	2.61	90	1.4	4.32	0	⋯	⋯	⋯	0.0162
21	4.83	2.71	90	1.6	4.32	0	⋯	⋯	⋯	0.0298
22	4.87	2.77	0	1.4	4.12	0	⋯	⋯	⋯	0.0267
23	4.43	1.91	0	1.4	4.12	0	⋯	⋯	⋯	0.0168

TABLE IV. Interaction energy (a. u.) for the catalyst and the HD moving in the fourth quadrant. The region of the intermediate complex is included.

	Configurations						Relative energies			
	R	z_0	ϕ	d_{HD}	d_{NNa}	θ	set I	set II	set III	set IV
1	4.04	−0.56	0	1.4	4.12	0	⋯	⋯	⋯	−0.0050
2	3.94	−0.56	0	1.6	4.12	0	⋯	⋯	⋯	0.0031
3	4.24	−0.56	0	1.4	4.12	0	⋯	⋯	⋯	−0.0058
4	4.24	−0.56	0	1.4	4.12	10	⋯	⋯	⋯	−0.0053
5	4.53	−0.56	0	1.4	4.12	0	⋯	⋯	⋯	−0.0041
6	3.54	−0.56	0	1.4	4.12	0	⋯	⋯	⋯	0.0002
7	4.01	−0.21	30	1.4	4.12	0	⋯	⋯	⋯	−0.0013
8	4.10	−0.91	−30	1.4	4.12	0	⋯	⋯	⋯	−0.0040
9	4.22	−0.36	0	1.4	4.12	0	⋯	⋯	⋯	−0.0043
10	4.27	−0.76	0	1.4	4.12	0	⋯	⋯	⋯	−0.0060
11	3.5	−0.91	−15	1.4	4.12	0	⋯	⋯	⋯	0.0005
12	3.5	−1.14	−19	1.4	4.12	0	⋯	⋯	⋯	−0.0002
13	3.5	−1.02	−17	1.4	4.12	0	⋯	⋯	⋯	0.0001
14	3.7	−1.08	−17	1.4	4.12	0	⋯	⋯	⋯	−0.0040
15	4.2	−1.22	−17	1.4	4.12	0	⋯	⋯	⋯	−0.0069
16	4.7	−1.38	−17	1.4	4.12	0	⋯	⋯	⋯	−0.0053
17	3.6	−1.17	−19	1.6	4.12	0	⋯	⋯	⋯	0.0028
18	3.7	−1.20	−19	1.8	4.12	0	⋯	⋯	⋯	0.0161
19	3.8	−1.23	−19	2.0	4.12	0	⋯	⋯	⋯	0.0357
20	3.6	−1.17	−19	2.0	4.12	0	⋯	⋯	⋯	0.0303
21	3.4	−1.10	−19	2.4	4.12	0	⋯	⋯	⋯	0.0440
22	4.0	−2.07	−31.12	1.4	4.12	0	⋯	⋯	⋯	−0.0075
23	4.2	−2.17	−31.12	1.4	4.16	18.35	⋯	⋯	⋯	−0.0071
24	4.2	−2.17	−31.12	1.4	4.12	0	0.0001	−0.0017	0.0016	−0.0076
25	4.4	−2.27	−31.12	1.4	4.12	0	⋯	−0.0030	⋯	−0.0071

mere closed-shell–closed-shell repulsion and no weakening of the H–D bond is evidenced.

This very unfavorable interaction as HD approaches the polar N–Na bond lies in marked contrast with results for other processes of catalytic heavy water production, for which the capacity of organometallic complexes to heterolitically break the H–D bond has been experimentally well established.[24,25] Moreover, for such processes, molecular orbital calculations of a semiempirical nature have shown that the highly polar organometallic bonds in the catalyst, typically $(RuCl_6)^{3-}$, can indeed polarize and break the H–D bond.[26] The present process is quite different because this bond is not weakened and no polarity is induced in it by the polar N–Na bond. Charges on the H and D atoms, in fact are never more than a few hundredths of an electron for any of the configurations of Table III. Therefore a completely different mechanism must be assumed.

B. Formation of the intermediate complex

Table IV shows that a much more favorable situation is found when HD moves in the fourth quadrant (see Fig. 4) for instance when $\phi = 0°$ and $z_0 = -0.56a_0$ the interaction energy for the system is already attractive by more than 3 kcal/mole. Furthermore, if the H–D bond distance is relaxed by $0.2a_0$ the barrier is now approximately 40% lower than for the isolated HD molecule. The energy cost for rotating the sodium $\theta = 10°$ towards the HD molecule is now much smaller than in the first quadrant. Notice, however, that the cost of a complete HD scission is still prohibitively high. The actual *value* of this energy cannot, of course be precise at a Hartree–Fock level.

The last four configurations (with $\phi = -31.12°$) were proposed based on extrapolations from the other numbers on Table IV and also noticing that apparently the optimal entrance of the D atom would lead it, in a natural fashion, to a site corresponding to an ammonialike structure. The corresponding interaction energies ($\Delta E = -2$ kcal/mole) show that these configurations are quite stable. This is supported by other data, especially concerning the last configuration, which shall henceforth be referred to as the intermediate complex (IC). In

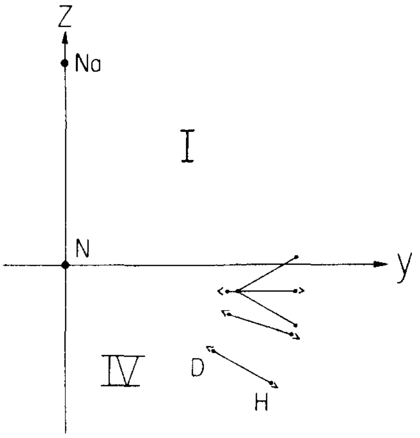

FIG. 4. Positions of HD depicting its movement towards the intermediate complex configuration.

TABLE V. Molecular orbital coefficients and energies (a.u.) associated with the 1σ state of the HD molecule, showing the effects of the formation of an intermediate complex IC.

	D atom		H atom		Nitrogen		Molecular orbital energy
	$1s$	$1s'$	$1s$	$1s'$	$2p_y$	$2p_z$	
1σ state for the isolated HD molecule	0.31	0.28	0.31	0.28	...	...	−0.59
1σ state HD in the intermediate complex	0.29	0.22	0.30	0.32	0.14	−0.03	−0.50

fact, the Mulliken population analysis of the all-electron basis set (set II) calculation gives the following bond orders: 0.45 for N–Na, 0.65 for H–D, and 0.18 for N–D. The first two values show a weakening of the corresponding bonds for the amide and HD molecules, which in Table I are 0.53 and 0.81, respectively. The gradual formation of a new N–D bond is evidenced by the fact that its bond order in the intermediate complex is already a large fraction of that for the N–Na bond. The atomic charges for the IC structure are also meaningful; they are −0.89 for N, 0.57 for Na, 0.13 for D and −0.22 for the H atom. We note that the HD presents a significative polarization which in fact is more notable for the farthest atom H. The Na atom is slightly more positive (see Table I). On the contrary, N loses some electronic charge which can be considered as its tendency to replace a new covalent bond with D for the purely ionic N–Na bond. Another relevant aspect of the IC configuration is depicted in Table V, where the structure of the molecular orbital corresponding to the 1σ state of HD is given for the isolated molecule and for the IC. In the latter case the molecular orbital energy is somewhat higher (in keeping with the weaker HD bond). Moreover, a significant admixture of p states from nitrogen appears. This may be considered as a reasonable confirmation of the Bar-Eli and Klein hypothesis[11] of a formation of a partial bond between HD and N through the latter's "lone pair electrons"; the p_y and p_z atomic orbital coefficients in Table V, indeed represent a directed orbital towards D.

C. Reaction coordinate

Taking the stable intermediate complex described in the previous section as a starting point and looking for the evolution of Process (1) towards the valley of the products, calculations using sets I to IV were done in order to find a reaction pathway. The corresponding numbers are given in Table VI. We remember that, while probing other regions of the potential energy surface, all the basis sets used gave grossly the same results. In Table VI, on the contrary, important differences appear. Therefore, for the reliable determination of the exchange reaction coordinate, the use of the basis set that gives a higher sensitivity is necessary. Consequently all the results discussed below are those of the all-electron extended basis set II. The predictions from the minimal and pseudopotential sets shall be critically discussed in Sec. V.

TABLE VI. Relative energies (a.u.) of the system going from the IC region to the product valley through different configurations.

	Configurations						Relative energies			
	R	Z_0	ϕ	d_{HD}	d_{NNa}	θ	Set I	set II	set IIIa	set IV
1	4.4	−2.27	−31.12	1.4	4.12	0	...	−0.0030	−0.007	−0.0071
2	4.4	−2.27	−31.12	1.47	4.12	0.0	...	−0.0029	...	...
3	4.2	−2.17	−31.12	1.4	4.12	0.0	0.0001	−0.0017	...	−0.0076
4	3.84	−1.87	−21.20	1.5	4.16	18.35	...	...	...	−0.0050
5	3.84	−1.87	−21.20	1.5	4.27	36.30	...	...	...	−0.0014
6	3.84	−1.87	−21.20	1.5	4.14	14.07	0.0082	0.0004	0.0038	−0.0051
7	3.49	−1.58	−12.75	1.64	4.27	36.30	...	...	...	0.0005
8	3.49	−1.58	−12.75	1.64	4.16	18.35	...	...	...	0.0026
9	3.49	−1.58	−12.75	1.64	4.12	0.0	...	...	...	0.0074
10	3.49	−1.58	−12.75	1.64	4.21	27.95	0.0259	0.0050	0.0105	0.0012
11	3.15	−1.28	−5.74	1.81	4.27	36.30	...	...	...	−0.0011
12	3.15	−1.28	−5.74	1.81	4.16	18.35	...	...	...	0.0107
13	3.15	−1.28	−5.74	1.81	4.32	41.51	0.0336	−0.0013	0.0080	−0.0042
14	3.07	−1.13	−2.47	2.10	4.51	49.87	...	−0.0181	−0.0070	...
15	3.00	−0.99	0.0	2.4	4.79	57.4	...	−0.0249	−0.0133	...
16	2.72	−0.99	0.0	1.8	4.12	45.0	...	...	...	0.0083
17	2.72	−0.99	0.0	1.8	4.27	36.30	...	...	...	−0.0011
18	2.91	−0.99	0.0	1.8	4.29	53.0	...	...	...	−0.0065
19	2.81	−0.99	0.0	2.0	4.29	53.0	...	...	...	−0.0073
20	2.91	−0.99	0.0	2.2	4.62	56.0	...	...	...	−0.0163
21	2.81	−0.99	0.0	2.0	4.46	54.63	0.0362	−0.0039	0.0088	−0.0064

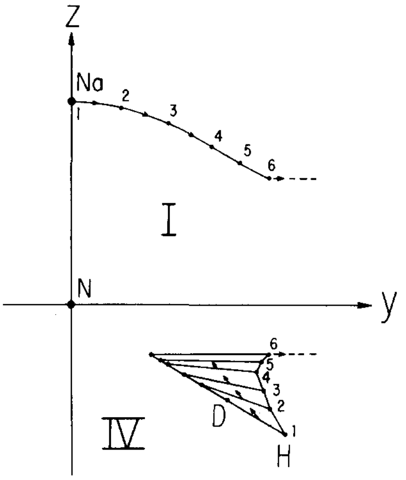

FIG. 5. Sequence of positions for HD and Na through the reaction pathway.

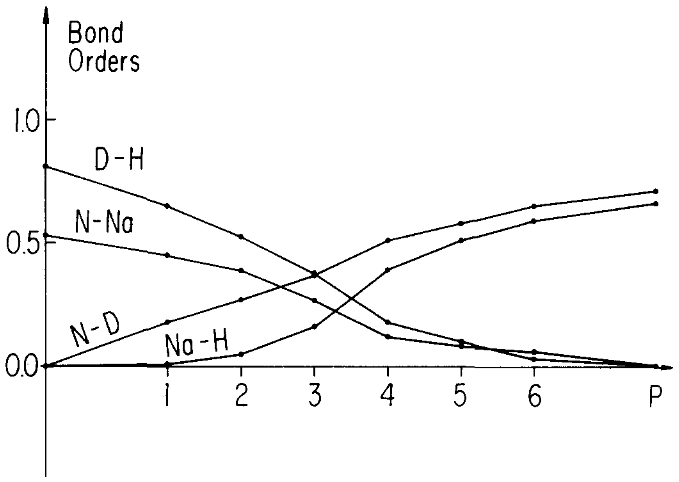

FIG. 7. Changes in the relevant bond orders along the reaction coordinate.

The reaction coordinate proposed here leads from the valley of the reactants to that of the products of reaction of Eq. (1) and its evolution is represented by six steps based on the results of Table VI. These steps are depicted in Fig. 5, where the first position of HD corresponds to the intermediate complex from which it gradually moves towards the origin relaxing its internal distance while the Na breaks away from N to eventually form NaH. This coordinate was obtained by only a partial optimization considering the many degrees of freedom in the potential energy surface; consequently, we cannot rule out that a more complete optimization could yield a better pathway. The main interest of the present study, however, is not to obtain absolute numerical predictions (e.g., a precise value of the activation energy) but general trends which clearly show the role of the catalyst in the process. The proposed pathway of Fig. 5, represents a sequence of steps where HD (later only the D atom) gradually approaches the N atom, while the H atom breaks away from D. The Na movement, as mentioned in the previous subsections, is energetically inexpensive and therefore, any energy cost at the earlier stages will basically arise from the HD scission. At the last stages of the reaction, this movement of the Na atom permits an important lowering of the energy as the two new N–D and Na–H bonds are formed, as will be discussed below. The energy changes during the reaction are reported in Fig. 6, where it is seen that after a minimum corresponding to the intermediate complex, a small barrier has to be surmounted. This barrier of about 3 kcal/mole is reached at step 3 (which corresponds to a transition stadium where the N–Na and H–D bonds are breaking and the new Na–H and N–D bonds are forming as will be shown below). The most impressive result shown in Fig. 6, is the fact that the almost prohibitive barrier for the HD scission is drastically lowered in the intermediate complex. This low activation energy, as is evident from the results of the previous subsections, can only be achieved through a very particular approach to the catalyst site. This can be related to the high entropy of activation for the process[11] and the fact that the chemical exchange can take place at an exceptionally low temperature among all heavy water production processes.[13]

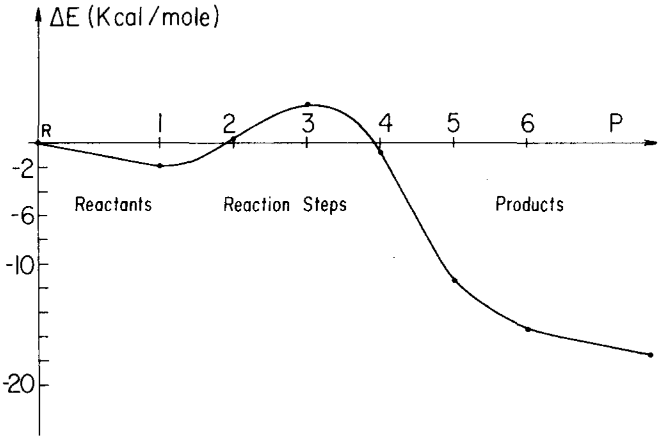

FIG. 6. Changes in the interaction energy of the system along the reaction coordinate, obtained from the all-electron calculations with set II.

In Fig. 7, the changes in the bond orders through the reaction coordinate are depicted. The bond breaking (of N–Na and H–D bonds) and bond formation (of N–D and Na–H bonds) take place gradually through the coordinate. Figure 7 depicts at step 3 (i.e., the one that corresponds to the emergence of the barrier in Fig. 6), a characteristic transition stadium where a multiple crossing of the original and newly formed bonds is evident. The notable breaking of the H–D bond is the basis of our previous statement, that the activation barrier is to be related to the HD scission. The energy lowering of the latter stages of Fig. 6, comes from the stabilization of the strong new N–D bond and the sodium hydride bond.

Figure 8 shows the evolution of the charges on the H, Na, D, and N atoms through the reaction coordinate. One aspect of interest is the induction of a polarity on HD through its interaction with the catalyst. This polarity, as was discussed in the previous subsection,

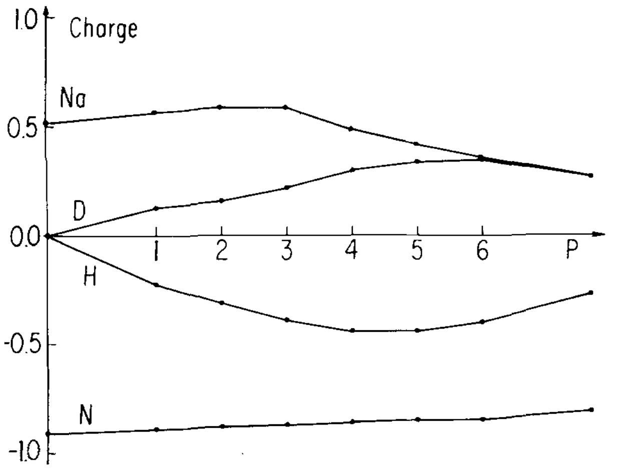

FIG. 8. Atomic charge distribution along the reaction coordinate.

plays a role in the capacity of the catalyst to attract HD for the intermediate complex stabilization. We may conclude that the HD scission is enhanced through its polarization by the amide catalyst. Consequently, the polarity of the alkali amide is related to its catalytic capacity. The remarkable difference between the rate for the chemical exchange of HD and ammonia with and without a catalyst can then be adscribed to the role played by the potassium or sodium ions to induce a polarity on the NH_2^- moiety, which by itself can[12] also catalyze the exchange. Also the superiority of the former alkali atom over the latter, probably stems from the greater polarity of potassium amides.

Going back to the mechanism derived from the kinetic data we must remember that the presence of an extra solvent (ammonia) molecule is proposed[11,12] to describe the reaction as:

$$NaNH_2 + HD \rightarrow NH_2D + Na^+H^- \xrightarrow{+NH_3} H_2 + NaNH_2 + NH_2D\,, \tag{6}$$

where the last step of the process implies the liberation, by the solvent molecule, of a hydrogen that reacts with the H liberated by hydrogen scission and forms H_2.

In a study of the type of the present one, the introduction of another large molecule at an intermediate stage of the process, would lead to several complications (difficulties for reliable comparisons, excessive computing time, enormous growth of degrees of freedom for the description of the interaction between all molecules, etc.). But this is not really necessary at all, because we can consider the formation of the sodium hydride as a metastable structure which may then interact with an ammonia molecule of the solvent:

$$Na^+H^- + NH_3 \rightarrow NaNH_2 + H_2 \tag{7}$$

This allows the reformation of the $NaNH_2$ catalyst, liberating an H_2 molecule. This means that the above-discussed reaction coordinate is also the coordinate for process described in Eq. (7) for which evolution of the energy, bond orders, and atomic charges can be read from right to left in Figs. 6 to 8. If a solvent molecule is present from the beginning, of course, the Na^+H^- molecule would not necessarily acquire any real existence during the process.

V. RESULTS AND PERSPECTIVES OF THE PSEUDOPOTENTIAL METHOD

The reaction coordinate for the sodium amide–hydrogen exchange reaction studied at the all-electron level was discussed in the previous section. Now we analyze exactly the same sequence of stages (represented in Fig. 5) but carrying the calculations with the nonempirical SCF pseudopotential method.[7-8] The corresponding energy curve is depicted in Fig. 9. Comparing these pseudopotential results with the all-electron energy of Fig. 6 we notice that they are quite alike in several respects. Among the similarities we remark the formation of a shallow intermediate complex at stage 2 and a barrier that is surmounted after stage 3. Thereafter an almost parallel descent towards the product valley is observed in both curves. All in all, it is apparent from Fig. 9 that the main conclusions derived in the preceding section are substantiated in the pseudopotential approach, especially considering that the main goal of the present study is to obtain trends to compare with the experimental behavior and *not* absolute values of the reaction parameters (e.g., activation energies, heats of reaction, etc.).

The latter do differ substantially in both methods. The intermediate complex is much more shallow in Fig. 9, with an energy of only $\frac{1}{2}$ kcal/mole against 2 in the all-electron case. The barrier is also different, ammounting to 6.5 kcal/mole in the pseudopotential case, or over twice the maximum in Fig. 6. Also the energy difference between the valleys of the products and of the reactants (i.e., the heat of reaction) is about 5 kcal/mole smaller in Fig. 9.

These differences can also be analyzed in Table VII where the results for the reactant and product molecules obtained with the pseudopotential sets III and IIIa (which differ only in their 3*p* polarization functions, see Table II) are compared with those of set II. Although the comparison of the energy *differences*, bond orders, and polarities in Table VII is much more satisfactory than that of Table I (which practically eliminated the use of

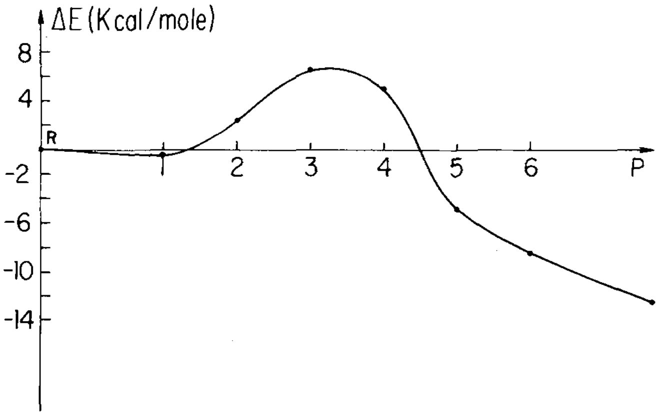

FIG. 9. Interaction energy along the reaction coordinate from the pseudopotential calculations using set IIIa.

TABLE VII. Comparison of the all-electron and pseudopotential results for the reactants and products of Eq. (1), given in atomic atomic units.

		Set II	Set III	Set IIIa
			Amide	
Total energy		−217.3773	−11.0281	−11.0268
atomic charge	N	−0.91	−1.0	−1.02
	Na	0.52	0.63	0.66
bond orders	N–Na	0.53	0.46	0.43
	N–H	0.62	0.63	0.62
			HD molecule	
Total energy		−1.1266	−1.1266	−1.1266
bond order	H–D	0.81	0.81	0.81
			Ammonia	
Total energy		−56.1608	−11.4655	−11.4655
atomic charge	N	−0.81	−0.79	−0.79
bond order	N–H	0.71	0.70	0.70
			Sodium hydride	
Total energy		−162.3711	−0.7082	−0.7077
net charge	Na	0.27	0.27	0.27
bond order	H–Na	0.66	0.69	0.69

the minimal all-electron set I) there are differences between the all-electron and pseudopotential values. The most notable discrepancy appears in the description of the amide. The pseudopotential sets predict too small a bond order between the sodium and nitrogen atoms while overestimating the polarity of the N–Na bond.

Thus, apparently the differences noted above between the energy curves for the process, Figs. 6 and 9, stem mostly from a poor description of the valley of the reactants that also affects the earlier stages of the reaction.

Even if the pseudopotential approach attempted here has not, by any means, been thoroughly optimized and we cannot rule out that a future development may reduce the above-mentioned discrepancies, it would seem interesting to attempt at this stage the determination of their origin. Two possible causes for the relatively poor description of the amide are apparent. One is the fact that in this molecule two directly bonded atoms are represented by pseudopotentials. These in turn have been optimized for each isolated atom, sodium and nitrogen, without any reference to the molecule to be studied. We believe that not enough tests on this type of situation exist but it could be suggested that an optimization of the Na and N pseudopotentials in the molecular fragment N–Na should be tried. This shall be attempted in the near future.[27] Another possible source of errors is the fact that sodium is an extreme case for the pseudopotential method. Evidently the complicated changes in the environment for the Na atom during the reaction could not be adequately represented by its valence shell alone, consisting of a single, very easily ionizable 3*s* electron. Evidently the polarization of the 2*s* and 2*p* core electrons might be far from negligible. Even more important perhaps, may be the inability of the pseudopotential model to properly describe the repulsion between the Na core and the N valence electrons. This limitation of pseudopotentials has already been pointed out by various authors.[28] It may well be the cause of the small pseudopotential value for the heat of reaction, already mentioned. In fact the $NaNH_2$ energy would be too low because of this underestimation of the Na–N repulsion.

Studies for the exchange reaction involving potassium amide as a catalyst are now in progress.[27] To overcome the above-stated difficulties a pseudopotential core for K consisting of the 1*s*, 2*s*–2*p* shells is being optimized in order to treat explicitly the 3*s*–3*p* and 4*s*–4*p* shells' wave functions.

VI. DISCUSSION

We have presented an *ab initio* SCF–MO analysis of the catalytic exchange reaction between hydrogen and ammonia. The main aspect studied concerns the interaction between the sodium amide catalyst and the HD molecule. It was shown that most approaches of the latter towards the catalytic site are not favorable at all. In particular one must exclude that an interaction between the N–Na bond of the amide and the H–D bond can bring about a polarization and weakening of the latter. This lies in marked contrast with the situation concerning other chemical exchange processes where the catalyst also contains polar organometallic bonds (e.g., ruthenium chloride catalysts) which do induce heterolytic breaking of HD.[24–26]

The present theoretical results imply a substantially different mechanism for the amide process, predicting a very directional approach of HD towards the catalyst moving on a line where the HD molecule is pointed toward the lone pair electrons of nitrogen. Furthermore it is found that this N–D line forms ammonialike angles (107°) with the original N–H bonds. By moving along this line the HD first reaches a position where an intermediate complex $NaNH_2$–HD is formed. This complex formation is clearly manifested in the quantum mechanical results by a lowering of the interaction energy, the formation of an N–D bond and the admixing of the 1σ state of HD with the nitrogen *p* orbitals giving rise to a molecular orbital that corresponds to this new bond. Going along the pathway that leads from this intermediate complex towards the reaction products of Eq. (1), a very small activation barrier (of about 3 kcal/mole) has to be surmounted. Considering the high energy necessary to break the H–D bond for the isolated molecule, the catalyst is obviously very effectively inducing the scission.

Everything in all these conclusions of the theoretical study merely confirm the assumptions of the experimentalists that made the mechanistic studies several years ago.[11,12] The description of the process, however, is presented here at a more fundamental level and their assumptions are given a quantitative justification. This is, in our opinion, the role that quantum mechanical studies of catalytic process should play at present, following and related experimental data and concentrating on the description of these metastable structures that the kinetical and mechanistic studies necessarily postulate as virtually unobservable entities.

Obviously the present study is limited in several aspects, not including, by its very nature, isotope effects, solvent effects, entropy, and temperature contributions, etc. However a good knowledge of the main features of the potential energy surface and the reaction coordinate is a starting point to derive theoretically all this information and consequently it should be interesting to extend and refine the present results, also studying potassium amide catalysts for comparison.[27]

ACKNOWLEDGMENTS

We would like to express our gratitude to Joaquim M. Ferreira, head of the Catalysis Division at the Mexican Petroleum Institute for his valuable comments. We also thank J. C. Barthelat and Ph. Durand, Université de Toulouse, France, for the use of their PSIBMOL program. Finally we acknowledge the effective help of the Computing Center (CSC) of UNAM.

[1] O. Novaro, E. Blaisten-Barojas, E. Clementi, G. Giunchi, and M. E. Ruiz, J. Chem. Phys. **68**, 2337 (1978).

[2] H. F. Schaefer, Acc. Chem. Res. **10**, 287 (1977).

[3] C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. **62**, 4815 (1975).

[4] W. A. Goddard, S. P. Walch, A. K. Rappe, T. H. Upton, and C. F. Melius, J. Vac. Sci. Technol. **14**, 416 (1977) and other presently unpublished papers.

[5] C. W. Bauschlicher, C. F. Bender, H. F. Schaefer, and P. Bagus, Chem. Phys. **15**, 227 (1976) and further work currently in progress.

[6] J. Demuynck, Chem. Phys. Lett. **45**, 74 (1977).

[7] A. Serafini, J. C. Barthelat, and Ph. Durand, Mol. Phys. **36**, 1341 (1978).

[8] C. Barthelat, Ph. Durand, and A. Serafini, Mol. Phys. **33**, 159 (1977).

[9] W. K. Wilmarth and J. K. Dayton, J. Amer. Chem. Soc. **75**, 4553 (1953).

[10] J. Bigeleisen, in *Proceedings of the International Symposium on Isotope Separation* (North Holland, Amsterdam, 1958), p. 121; J. Ravoire, P. Grandcallot, and G. Dirian, J. Chem. Phys. **60**, 130 (1963), S. Walter and U. Schindewolf, Chem. Ind. Tech. **37**, 1185 (1965).

[11] K. Bar-Eli and F. S. Klein, J. Chem. Soc. **1962**, 1378, 3083 (1962).

[12] G. Dirian, F. Botter, J. Ravoire, and P. Grandcollot, J. Chim. Phys. Phys. Chim. Biol. **60**, 139 (1960); R. Delmas, P. Courvoisier, and J. Ravoire, Adv. Chem. Ser. **89**, 25 (1969).

[13] A. R. Kenyon and D. Pepper, J. Appl. Chem. **14**, 399 (1964); H. K. Rae, "Chemical Exchange processes for heavy water," Atom. En. Canada Ltd. Report 2555, 1966; M. Bolan, G. Lang, and U. Schindewolf, Chem. Ind. Tech. **45**, 1136 (1973).

[14] E. Clementi and J. Mehl, IBM J. Res. Devel. 833 (1971).

[15] "Interatomic Distances in Molecules and Ions," Chem. Soc. Spec. Publ. No. 11 (1958).

[16] B. Roos and P. Siegbahn, Theor. Chim. Acta **17**, 209 (1970).

[17] S. Huzinaga, J. Chem. Phys. **42**, 1263 (1965).

[18] A. Veillard, Theor. Chim. Acta **12**, 405 (1968).

[19] A. Serafini (personal communication).

[20] Although we are here mainly concerned with the work developed by the Toulouse group (Refs. 7 and 8) several other valuable approaches to the pseudopotential method exist, see for instance: M. Horn and J. N. Murrell, J. Chem. Soc. Faraday Trans. 2 **70**, 769 (1974); C. S. Ewig and J. R. van Wazer, J. Chem. Phys. **63**, 4035 (1975); D. Mc Williams and S. Huzinaga, J. Chem. Phys. **63**, 4678 (1975); R. N. Dixon and J. M. V. Hugo, Mol. Phys. **29**, 953 (1975), etc.

[21] The optimization was obtained using J. C. Barthelat's modification of the "Atomic" program of B. Roos, C. Salez, A. Veillard, and E. Clementi, IBM J. Res. Devel. 518 (1968).

[22] E. Clementi, "Tables of Atomic Functions" Suppl. IBM J. Res. Devel. **9**, 2 (1965).

[23] For identification purposes and also for easier comparison with the experimental papers, we shall call one of the atoms in the hydrogen molecule the "D" atom although, of course, no isotope differentiation can be given within the present framework. The other atom in this molecule will be simply referred to as the "H" atom unless confusion can arise with the other two hydrogens bonded to nitrogen.

[24] J. Halpern and B. R. James, Can. J. Chem. **44**, 671 (1966).

[25] U. Schindewolf, J. Chim. Phys. **60**, 124 (1963).

[26] O. Novaro and J. Pineda, J. Molec. Cat. **3** (1978) and references therein.

[27] Work in progress.

[28] A. Pullman, N. Gresh, J. P. Daudey, and J. W. Moscowitz, Int. J. Quantum Chem. Symp. **11**, 501 (1977); A. Leš and I. Ortega-Blake, Int. J. Quantum Chem. Biol. Symp. (in press).