# ASSESSMENT OF ATOMS-IN-MOLECULES APPROACHES TO THE DIATOMIC INPUT DATA GENERATION FOR THE DIATOMICS-IN-MOLECULES METHOD

Rudolf Polák and Jan Vojtík

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
*Czechoslovak Academy of Sciences, 182 23 Prague 8*

Received December 14th, 1987
Accepted January 3rd, 1988

*Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.*

Various versions of the atoms-in-molecules method as a source for diatomic input data, and various approaches of the diatomics-in-molecules method are applied to calculate three lowest valence states of the $NH_2$ radical. By comparing the results among themselves and with other presently available accurate data, conclusions are drawn concerning the reliability of individual solutions. Also, possible causes for inadequacy of diatomics-in-molecules models are discussed.

The coincidence of Rudolf Zahradník's 60th birthday with the 25th anniversary of Ellison's Diatomics-in-Molecules (DIM) method[1] suggests that we begin this paper with a short review of the latter.

The DIM method is a quantum chemical procedure for calculating potential energy surfaces (PES's) of a polyatomic molecule by partitioning the total energy into atomic and diatomic fragment contributions. Since 1963, more than hundred and fifty papers involving the DIM method have appeared, the majority of them being quoted in several review articles[2-5]. The basic features of the DIM theory[1,6-16], specific approximations inherent in the DIM approach[12,17,18], possible extensions for including spin-orbit and nonadiabasic interactions[19], and calculation of general types of molecular properties[20] within the DIM method have been outlined and discussed in a number of papers. Table I should give a notion which kind of molecular systems were treated within the DIM scheme. We notice that the overwhelming majority of DIM applications has concerned three-atomic systems, and that calculations on four- and more-centre systems, involving atomic states of other than spherical symmetry, are exceptional, although in principle feasible. In addition to systems displayed in Table I, DIM models were deduced for the description of $\pi$-electron systems[21], adsorption processes[22] and rare gas clusters[23].

Interestingly, in the first decade (1963 - 1972) less than two dozen papers related to DIM were published. The growing interest in the DIM method during the next years was mainly motivated by dynamical studies of molecular systems including the interpretation of simple chemical reactions[2-5], molecular beam scattering cross sections[2-5], chemisorption[24] and chemiionization[25] processes. This tendency can be illustrated by an example: the DIM model for the $H_4^+$ system[26] developed more than ten years ago is providing a useful framework for an up-to-date study of the state-to-state dynamics of the $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction[27].

This situation reflects the fact that the DIM method is well suited for the construction of PES's appearing in dynamical calculation schemes. Relatively low computer time consumption, correct asymptotic behaviour upon separation to atomic and diatomic fragments, capability to provide both ground and excited state properties on the same footing and adaptability to eventually match the true surfaces are the essential points counting to the positive features of the DIM method.

The validity, and therefore also the usefulness, of a DIM model depend on two factors: on the selection of atomic states which combine to form polyatomic valence bond structures and on the numerical representation assigned to the potential energy curves and mixing-coefficient functions (cf. next section) entering the model as input. Concerning the first item, the problem is to find the smallest DIM basis with inclusion of the essential VB structures, enabling an ådequate description of the required electronic states of a given polyatomic species in the full range of nuclear configurations. This step ensures the physical soundness of the model, providing at least a qualitatively correct description of the states. The next step, the appropriate estimation of diatomic input data (obtained eventually by a fitting procedure in the sense of refs[28,29]) is assumed to lead finally to quantitatively correct representations of the corresponding PES's.

In a previous paper[30], a DIM model was developed for describing three low-lying valence states of the $NH_2$ radical, using diatomic-input data generated by means of the symmetrically orthogonalized (SOM) version[31] of the atoms-in-molecules (AIM) method[32,33]. Because the character of both the AIM and DIM approaches allows to formulate various versions of these methods, depending on the kind of assumptions and approximations applied, we show in this paper how the outcome

TABLE I

DIM bibliography — number of papers devoted to the various systems (classification according to type of system and frequency of treatment)

| Type of system[a] | Number of atoms in the system | | |
|---|---|---|---|
| | 3 | 4 | 5 |
| $A_1A_2 \ldots A_n$ | 35 | 12 | 8 |
| $[A_1A_2 \ldots A_n]^+$ | 25 | 6 | 1 |
| $XH_{n-1}$ | 25 | 1 | 1 |
| $[XH_{n-1}]^+$ | 14 | — | — |
| $[XH_{n-1}]^-$ | 1 | — | — |
| $XYH_{n-2}$ | 9 | — | — |
| $[XYH_{n-2}]^+$ | 2 | — | — |
| $(NeHe_2)^+$, $NO_2$, $HeLi_2$, $Ne_2F$, $Ar_2F$, $Kr_2F$, $Kr_2Cl$ | 6 | — | — |
| $X_n$ | 2 | — | — |

[a] $A_i$ denotes either of H, D, Li, Na; X(Y) denotes an atom different from H, D, Li.

of DIM calculations is sensitive with respect to changes in the numerical representation of the diatomic input, and the DIM versions used. Comparison of the results among themselves, and with available accurate energy data on $NH_2$, brings evidence on the reliability of various versions of the AIM and DIM methods.

## THEORETICAL

### *Characterization of the* DIM *Approach*

In the DIM theory, the polyatomic wavefunction is expanded in terms of polyatomic basis functions $\psi_i$, each of which is constructed in the form of an antisymmetrized product

$$\psi_i = \boldsymbol{A}\psi^A_{\alpha i}\psi^B_{\beta i} \ldots, \qquad (1)$$

where $\psi^A_{\alpha i}$, $\psi^B_{\beta i}$, ... are considered to be atomic eigenfunctions associated with states $\alpha_i$, $\beta_i$, ... of separate atoms A, B, ... Formally, basis functions $\psi_i$ call up a polyatomic eigenvalue equation which we write in the form

$$\boldsymbol{H} = \boldsymbol{SCEC}^{-1} = \boldsymbol{SB}, \qquad (2)$$

where $\boldsymbol{H}$ is the Born–Oppenheimer Hamiltonian matrix and $\boldsymbol{S}$ the metric matrix related to the given basis. The essence of the DIM method consists in that it furnishes matrix elements of $\boldsymbol{B}$ in an approximative way by using external information on atomic and diatomic fragments. The matrix $\boldsymbol{B}$, having the same eigenvalues as $\boldsymbol{H}$ and being generally non-Hermitian, is in practical applications the source for DIM energy values.

The construction of $\boldsymbol{B}$ is based on the partitioning of the polyatomic Hamiltonian into appropriate atomic and diatomic Hamiltonians, enabling to express $\boldsymbol{B}$ in terms of independent contributions from diatomic $\boldsymbol{B}^{AB}$ and monatomic $\boldsymbol{B}^A$ fragment matrices. While the monatomic contributions are simply related to atomic states energies, the diatomic fragment matrices have to be interpreted in a more complicated way. The link to external data are diatomic equations of the type

$$\boldsymbol{h}^{AB}_{\lambda i} = \boldsymbol{s}^{AB}_{\lambda i}\boldsymbol{c}^{AB}_{\lambda i}\boldsymbol{e}^{AB}_{\lambda i}(\boldsymbol{c}^{AB}_{\lambda i})^{-1} = \boldsymbol{s}^{AB}_{\lambda i}\boldsymbol{b}^{AB}_{\lambda i} \qquad (3)$$

related to diatomic bases $\{\varphi^{AB}_{\lambda i}\}$ which are implied by the set of atomic functions furnished by atoms A and B. In Eq. (*3*), the subscript $\lambda_i$ labels the spin and space symmetry of the diatomic state and the matrix $\boldsymbol{b}^{AB}$ is a diatomic analog to the matrix $\boldsymbol{B}$ in Eq. (*2*), usually, however, of a smaller dimension. The relationship between the diatomic matrices represented in the polyatomic and diatomic bases is best viewed in the form of a mapping[16], $Q(\mathbf{R})$, which depends on the geometrical arrangement of atomic nuclei:

$$\mathbf{B}^{AB} \xleftarrow{Q(\mathbf{R})} \{\mathbf{b}_{\lambda i}^{AB}, \text{all } \lambda_i\}\,. \tag{4}$$

The matrices $\mathbf{b}$ (for all possible pairs of atoms and for all $\lambda_i$) constitute the input for constructing $\mathbf{B}$.

In general, the matrices $\mathbf{b}$ (omitting the sub- and superscripts)

$$\mathbf{b} = \mathbf{cec}^{-1} \tag{5}$$

are not Hermitian and, therefore, lead to a non-Hermitian matrix $\mathbf{B}$. We define now three modifications of the DIM method which are applied in the next section to the $NH_2$ system.

*a*) Non-Hermitian formulation (labelled NH) which consists in diagonalizing $\mathbf{B}$ itself.

*b*) Hermitian formulation (labelled H) applies diagonalization to the symmetrized form

$$\mathbf{B}_{\text{sym}} = \tfrac{1}{2}(\mathbf{B} + \mathbf{B}^{+})\,. \tag{6}$$

*c*) Formulation using a symmetrized basis of diatomic basis function (labelled S). In this formulation, the mixing coefficient matrices $\mathbf{c}'$ are associated with diatomic basis functions obtained by the Löwdin symmetric orthogonalization of the original VB(AIM) basis. Hence, $\mathbf{c}$ in Eq. (5) is replaced by $\mathbf{c}' = \mathbf{s}^{1/2}\mathbf{c}$, leading to Hermitian $\mathbf{b}$, and therefore also to Hermitian $\mathbf{B}$ matrices.

## DIM *Models of* $NH_2$

The DIM treatments of $NH_2$ presented in this paper are using the model structure corresponding to basis *d* in Table 1 of ref.[30]. This DIM model structure derives from atomic states $N(^4S_u, {}^2D_u, {}^2P_u, {}^4P_g)$, $N^-(^3P_g)$, $H(^2S_g)$ and $H^+$. Interestingly, in our earlier analysis[30] we found that an appropriate DIM description of low-lying electronic states of $NH_2$ is achieved only when the VB structures involving the excited $^4P_g\ (2s)^1\ (2p)^4$ term of nitrogen are included.

Concerning the numerical representation of the model, we use two orthogonalized versions of the AIM method for the calculation of mixed state energies[5,8] and mixing parameters: the (Schmidt)-orthogonalized[33] (OM) and the symmetrically orthogonalized[34] (SOM) ones, because they have appeared superior[35] to the other AIM modifications in a number of respects. Details of the AIM calculations on the NH and $NH^-$ fragments[31] and information on accurate potential energy curves[30] (PEC's) as well as are given elsewhere.

In our earlier study[30], we represented all diatomic energies [*e*-parameters in Eq. (5)] by means of the most accurate available PEC's with the exception of those states for which correct dissociation limit has to be ensured by using the AIM energies calculated within the DIM restricted diatomic basis. The reason for using this numerical representation (labelled A) was that it produced the best overall description of the three lowest valence states with regard to accurate *ab initio* calculations[36].

On the other hand, however, projection analysis[37] applied to the AIM wave functions[30] indicated that, from the total manifold of NH($NH^-$) states implied by the DIM model, only the $^3\Sigma^-(1)$ and $^3\Pi(1)$ states of the NH species satisfy conditions for being treated as "pure" states. According to Kuntz and Schreiber[37] only "pure" states can be replaced by accurate curves. Thus, we consider for comparative purposes an alternative numerical representation, labelled B, where accurate PEC's are assigned to all $H_2$ and $H_2^+$ interactions, and to the NH $^3\Sigma^-(1)$, $^3\Pi(1)$ states. All other *e*-parameters are considered to be mixed state energies.

The definition of the coordinate system, including the labelling of electronic states by symmetry species, is given in ref.[30].

## RESULTS AND DISCUSSION

Throughout the paper, distances are expressed as relative quantities $R = X/X_0$, with $X_0 = 0{\cdot}052917$ nm, and referred to as atomic units (a.u.).

Figs 1*a* and 1*b* show $NH_2$ energies, calculated by the symmetrized ($S$) version of the DIM method using numerical representations of type $A$ and $B$, respectively, as a function of the HNH angle with bond lengths fixed at the experimental ground state equilibrium value 1·935 a.u. We plot here, in addition to the $^2B_2(1)$, $^2A_1(1)$ and $^2B_1(1)$ states, being pure valence in character at all internuclear distances[38], the $^2B_2(2)$ state which is the second lowest excited doublet electronic state at $D_{\infty h}$ nuclear configuration[36] for the given N—H separation. Comparison with *ab initio* MO CI calculations[36] reveals that the agreement in the overall pattern of these states for the one-dimensional cut through the PES's is good, particularly with regard to the behaviour of the Renner–Teller pair of surfaces emanating from the $^2\Pi_u$ state. Leaving a deeper assessment of both types of numerical representations to a later moment, we first want to clear up the question how sensitive the results presented in Fig. 1 are to the choice of the AIM and DIM versions.

Restricting ourselves to the A type numerical representation (at this moment, this seems to be the more perspective one), we end up with six different numerical realizations of the DIM model: each of the three DIM versions (NH, H, S) can be supplied with either SOM or OM AIM diatomic input. Because of the topographical similarity of the corresponding PEC's produced by various calculations, the discrepancies of the individual solutions are easier to understand and categorize, if we consider changes in energy with respect to a reference system rather than the absolute values of energy. Taking the SOM (S) solution, presented in Fig. 1*a*, as the frame of reference, we obtain energy-difference functions for the four investigated states as displaced in Fig. 2.

Primarily, it is pleasant to observe that, for all three pure valence states, the SOM (NH) version deviates from the SOM(S) version by less than 0·5 eV in the whole variable interval considered. This fact corroborates the correctness of the S version of the DIM method, the advantages of which have been well recognized[11,31,37,39,40]. Since both the OM(S) and OM(NH) DIM versions yield results lying in the 0·5 eV discrepancy interval as well, we take this fact as not contradicting our former conclusion[31,41], expressible in the form of a mild preference of the SOM(S) version over the OM(S) one for given applications. The most discrepant behaviour of the results based on both H versions of the DIM method is again in accord with previous results[8,34] which found the artificial Hermitization step (*6*) unsuitable. On grounds of all this evidence we use only the SOM(S) version of the DIM method in all remaining applications.

For the three states, we present in Figs 3 and 4 contour diagrams of the PES's in $C_{2v}$ geometries, as calculated by using the numerical representations of type A and B, respectively. Table II serves then the purpose to assess the quality of DIM models

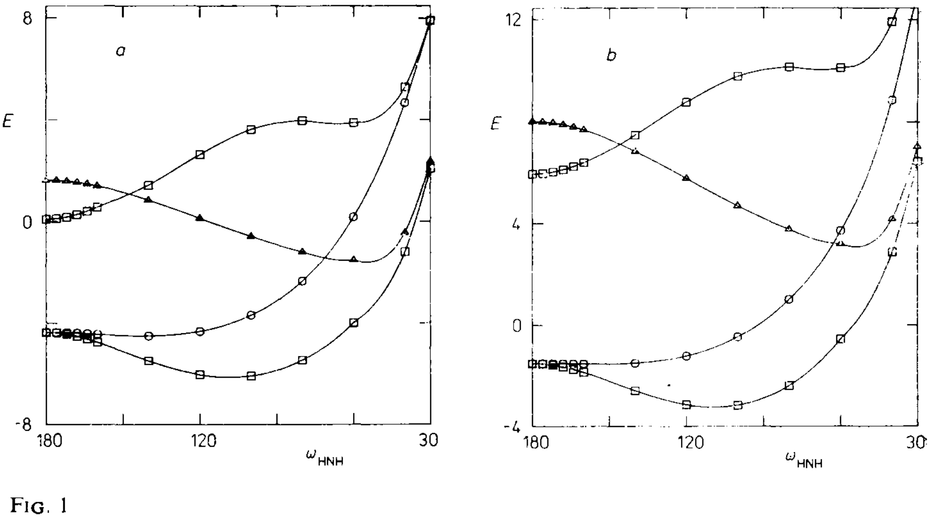

FIG. 1

Potential energy curves for $NH_2$ in ground and three excited states for fixed bond length ($R_{NH}$ = = 1·935 a.u.) as function of bond angle (in degrees). Calculation performed using the DIM model SOM(S). State labelling: □ $^2B_2$; ○ $^2A_1$; △ $^2B_1$. Energy ($E$) relative to separated atoms 2 H($^2S_g$) + N($^4S_u$) is in eV. Numerical representations applied are of type A(*a*) and B(*b*) by comparing selected points on these surfaces with available accurate theoretical and experimental data on geometry and energy characteristics.

While the DIM model based on the numerical representation of type A yields a reasonable overall description of all three pure valence states, numerical representation of type B fails badly in two points: in giving an adequate estimation of the ground state stability with respect to dissociation and in reproducing a real minimum on the $^2B_1$ surface representing a small-angle structure. Both of these deficiencies are very likely to be in great part due to the fact that the strongly bound NH $^1\Delta$ and $^1\Sigma^+$ states (with binding energies[30] of about 3·9 eV and 4·5 eV, respectively) occurring in numerical representation of type A are substituted in the numerical representation

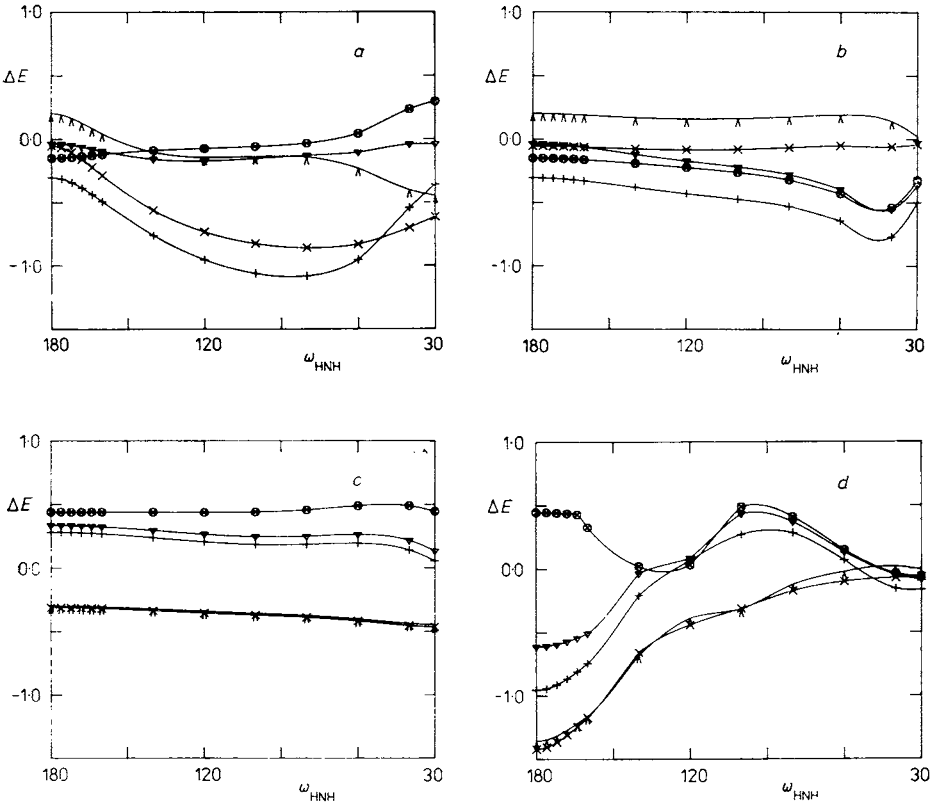

FIG. 2

Energy differences $\Delta E = E_V - E_{SOM(S)}$ for fixed bond length ($R_{NH} = 1{\cdot}935$ a.u.) versus bond angle as calculated by various DIM models (V) corresponding to numerical representation of type A. For units cf. caption for Fig. 1. Labelling of DIM models: ⊗ OM(S); ∧ SOM(NH); ▽ OM(NH); × SOM(H); + OM(H). States: *a* $^2B_2(1)$ *b* $^2A_1$ *c* $^2B_1$ *d* $^2B_2(2)$

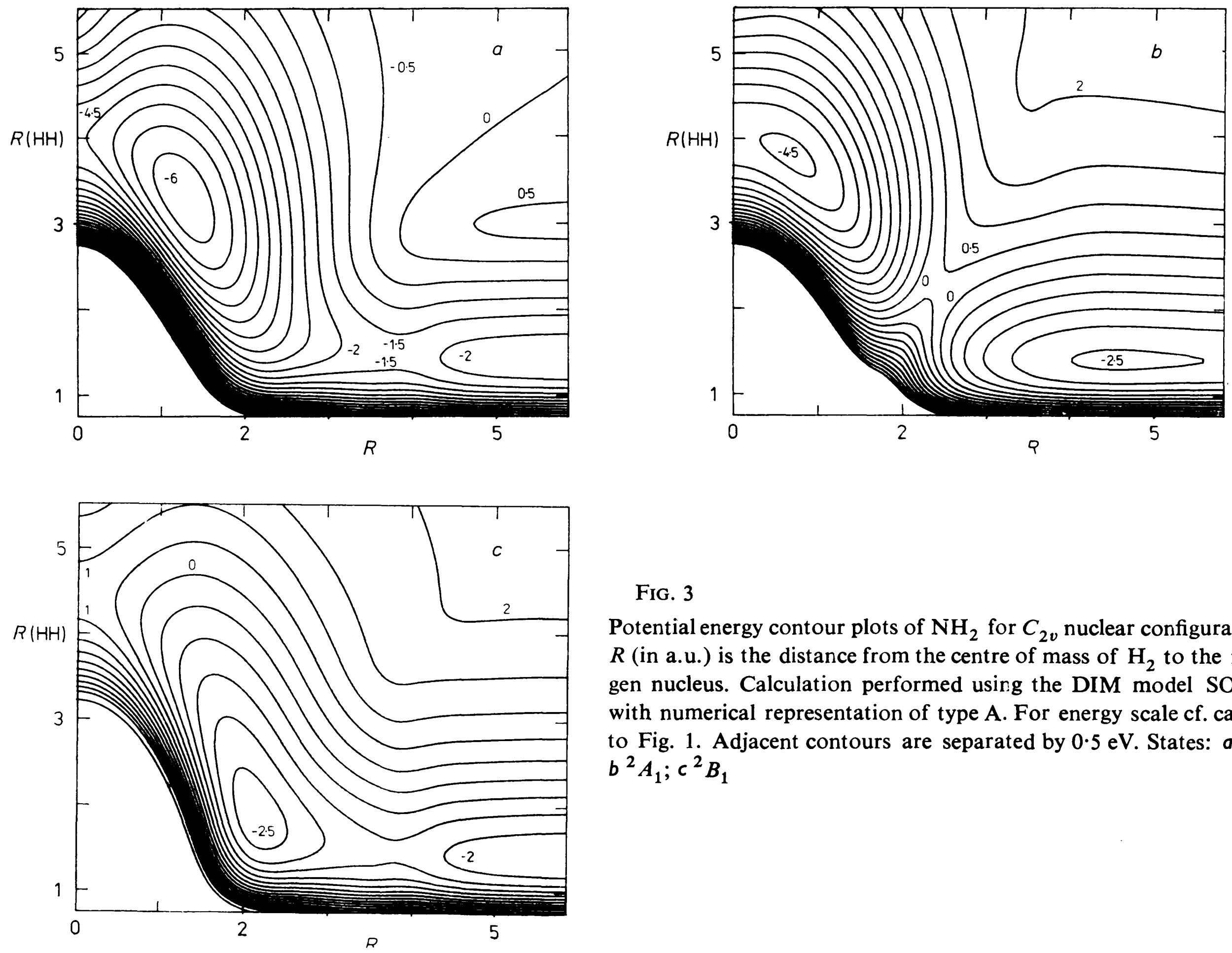

FIG. 3

Potential energy contour plots of $NH_2$ for $C_{2v}$ nuclear configurations. $R$ (in a.u.) is the distance from the centre of mass of $H_2$ to the nitrogen nucleus. Calculation performed using the DIM model SOM(S) with numerical representation of type A. For energy scale cf. caption to Fig. 1. Adjacent contours are separated by 0·5 eV. States: $a\ ^2B_2$; $b\ ^2A_1$; $c\ ^2B_1$

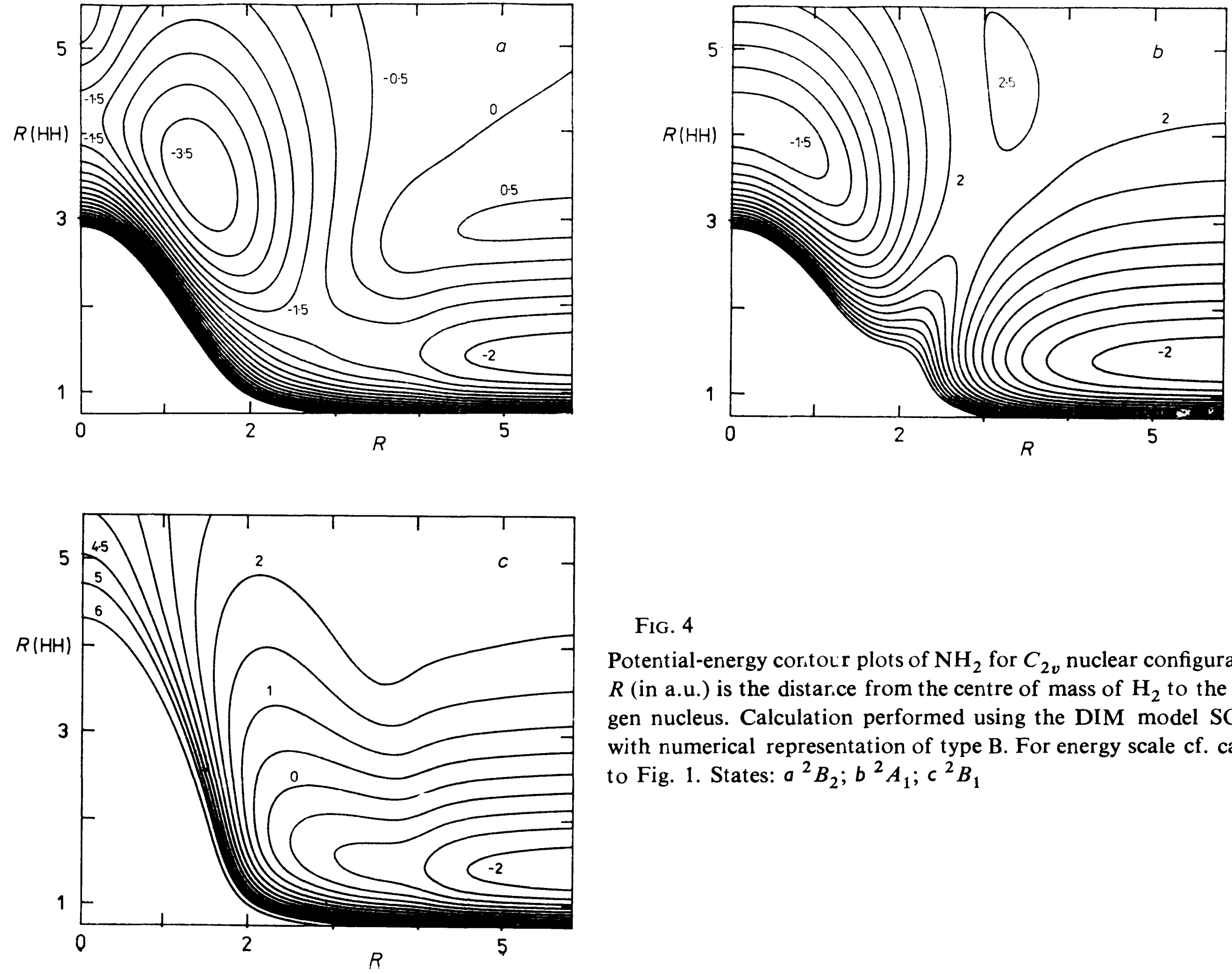

FIG. 4

Potential-energy contour plots of $NH_2$ for $C_{2v}$ nuclear configurations. $R$ (in a.u.) is the distance from the centre of mass of $H_2$ to the nitrogen nucleus. Calculation performed using the DIM model SOM(S) with numerical representation of type B. For energy scale cf. caption to Fig. 1. States: $a\ ^2B_2$; $b\ ^2A_1$; $c\ ^2B_1$

of type B by mixed states both bound by only about 0·9 eV. The importance of the $^1\Delta$ and $^1\Sigma^+$ states for the description of the two excited valence states can be anticipated on grounds of state correlations, $NH_2(^2A_1) \rightarrow NH(^1\Delta) + H$, and $NH_2(^2B_1) \rightarrow$ $\rightarrow NH(^1\Sigma^+) + H$, via asymmetric route (Fig. 8 of ref.[30]). This situation, together with the fact that the $^2B_1(1)$ state correlates in our calculations with the $^2\Pi_g(1)$ state at $D_{\infty h}$ configuration instead of with the $^2\Sigma_u^+$ state, as it is predicted by the MO CI calculation[36] and Walsh's qualitative theory (this point is extensively discussed in ref.[30]), indicates that the choice of the DIM atomic basis functions is still not quite sufficient to provide a complete description of all subtle features of the three pure valence states. However, on grounds of evidence collected in Table II on the existency and positions of the energy minima, together with the overall pattern of these surfaces agreeing with *ab initio* calculations[36,38,42], and considering that the $^2B_1(1)$ state

TABLE II

Energies (in eV) relative to equilibrium energy of the $^2B_2$ ground state and geometry characteristics (length in a.u., angle in degrees) of important points on the $C_{2v}$ PES's of three low-lying $NH_2$ valence states

| State | Quantity | Experiment | Calculation type | | | | |
|---|---|---|---|---|---|---|---|
| | | | DIM SOM(S) | | ref.[36] | ref.[42] | ref.[38] |
| | | | A | B | | | |
| $^2B_2$ | $E_{\text{min}}$ | 0 | 0 | 0 | 0[a] | 0 | 0 |
| | $R_{\text{NH}}$ | 1·935[b] | 2·07 | 2·22 | — | 1·944 | 1·987 |
| | $\omega_{\text{HNH}}$ | 103·3 | 105 | 103 | — | 103·1 | 101·1 |
| | $E_{\text{dis}}$[c] | 4·0[d] | 2·97[e] | 0·56[e] | — | — | 3·86 |
| $^2A_1$ | $E_{\text{min}}$ | — | 1·74 | 2·12 | 1·51[f] | 1·47 | — |
| | $R_{\text{NH}}$ | 1·897[b] | 2·02 | 2·08 | (1·935) | 1·889 | — |
| | $\omega_{\text{HNH}}$ | 144 ± 5 | 139 | 148 | 141·4 | 143·4 | — |
| | vert. TE[g] | | 2·26 | 2·89 | 2·16[a] | — | 2·26 |
| $^2\Pi_u$ | $E_{\text{min}}$[h] | | 1·91 | 2·16 | 1·65[f] | — | — |
| | $R_{\text{NH}}$ | | 2·00 | 2·08 | (1·935) | — | — |
| $^2B_1$ | $E_{\text{min}}$ | — | 3·54 | none | 4·60 | 4·79 | — |
| | $R_{\text{NH}}$ | — | 2·32 | | 2·135 | 2·196 | — |
| | $\omega_{\text{HNH}}$ | — | 47 | | 50·0 | 47·5 | — |
| | vert. TE[g] | | 5·25 | 6·60 | 6·64[a] | — | 6·50 |

[a] Calculated at experimental GS equilibrium; [b] quoted in ref.[42]; [c] dissociation energy to $H + NH(^3\Sigma^-)$; [d] quoted in ref.[38]; [e] by using the value 3·37 eV for the binding energy of the $NH(^3\Sigma^-)$ state (ref.[43]); [f] calculated at experimental NH bond length corresponding to GS equilibrium; [g] vertical transition energy; [h] within $D_{\infty h}$ geometries.

becomes a high excited surface embedded in a group of Rydberg states at $D_{\infty h}$ geometry[36], we accept the DIM model based on the numerical representation of type A as adequate for the DIM description of $NH_2$ valence states.

It is of interest to mention the large role of the ionic functions at the nuclear configurations corresponding to the minima on all three valence PES's: the percentage of ionic contribution ranges there between 45% and 56%. The $^2A_1(1)$ wave function at the minimum has also a large contribution from the state-group involving the $^4P_g$ state of nitrogen (27%). Because of the large role of the ionic functions with the singly charged ion $N^-$, one can expect on grounds of analogy with the $H_2O$ molecule[16,28,29] that ionic structures with $N^{2-}$ would further favourably affect the stability of the ground state.

Having described the rather successful results on the development of DIM models for $NH_2$, we shall conclude this paper by adding a few words of caution, realizing fully that there exist several possible causes for an erroneous application of the DIM method. Some of them can be traced even within our treatment of $NH_2$.

The validity of the DIM model can be seriously hampered, if structures important for the description of given states are missing. Thus, we witnessed that polyatomic basis functions involving the $^4P_g$ term of nitrogen are indispensable for an appropriate DIM description of $NH_2$. Further, care must be exercised in specifying diatomic input data, since these decide about the extent of quantitative correctness of the model. In this connection it is pleasant to mention that diatomic input information obtained by SOM and OM AIM methods appears to be consistent with that obtained from large scale *ab initio* calculations by means of projection[41].

Because common errors emerging from the two above points were scrutinized recently,[44-47] we rather touch the question what happens, if atomic eigenfunctions

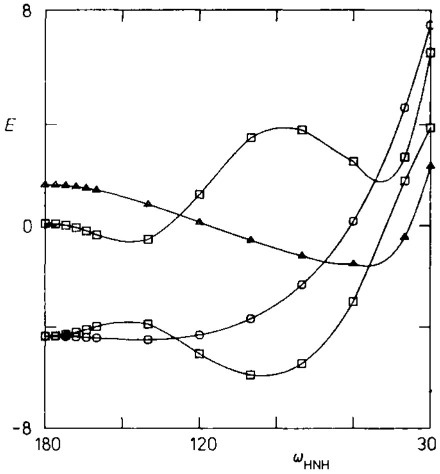

FIG. 5

Recalculation of Fig. 1a by using the phase-inconsistent numerical representation of the DIM model SOM(S) of type A as defined in the text appearing both in DIM diatomic and polyatomic basis functions are not fully consistent in phase definition. Such an error can occur very easily when use is made of a quantum chemical calculation with unsufficient knowledge of atomic function phases and/or axis orientation. As an example, we quote some of our own calculations on the $NH_2$ radical.[30]

In ref.[30] our aim was to develop the DIM model for the low-lying valence states of $NH_2$. In the course of this study it appeared that $D_{\infty h}$ collinear configurations (lying in $z$ axis) are critical for indicating the important atomic states entering the DIM polyatomic basis set. In this symmetry arrangement, of course, the problem of phases in the DIM method disappears, for no rotation of the atomic functions is needed to achieve the coordinate frame used for the calculation on separated diatomic fragments. Deviation from collinearity, however, makes inconsistency in phases generally perceivable. Suppose we make use of diatomic mixing coefficients obtained by a VB AIM calculations employing $^2D_u$ term functions with phases which do not follow the definition of basis vectors implying a standard angular momentum representation[48]. Particularly, we choose the basis vector of the $N(^2D_u, M = 0)$ state, appearing in the $NH(^3\Sigma^-)$ manifold, with an opposite phase than it would correspond to the convention based on the application of step-down operators. Because the transformation properties of this set of $N(^2D_u)$ atomic functions are different from those supposed by the DIM scheme,[15] operation (*4*) leads to an erroneous matrix **B**. In Fig. 5 we show the outcome of the DIM calculation for the same nuclear arrangements as in Fig. 1, using the above described phase non-adapted numerical representation. Because of symmetry reasons, only states of $A''(A_2, B_2)$ symmetry are affected by the phase inconsistency. Interestingly, we notice that the agreement of the solutions shown in Figs 1 and 5 is very good in important points of the surfaces: at $D_{\infty h}$ configuration the coincidence is total, and the ground state minimum is shifted by 0·14 eV. This makes the phase inconsistency intricately hidden. It is clearly manifested, however, by the anomalous behaviour of the splitting of the Renner–Teller pair of surfaces.

## REFERENCES

1. Ellison F. O.: J. Am. Chem. Soc. *85*, 3540 (1963).
2. Tully J. C. in the book: *Modern Theoretical Chemistry* Vol. 7A. *Semiempirical Methods of Electronic Structure Calculation* (G. A. Segal, Ed.), Chap. 6. Plenum Press, New York 1977.
3. Kuntz P. J. in the book: *Atom–Molecule Collision Theory. A Guide for the Experimentalist* (R. B. Bernstein, Ed.), Chap. 3. Plenum Press, New York 1979.
4. Tully J. C.: Adv. Chem. Phys. *42*, 63 (1980).
5. Kuntz P. J.: Ber. Bunsenges. Phys. Chem. *86*, 367 (1982).
6. Kuntz P. J., Roach A. C.: J. Chem. Soc., Faraday Trans. 2, *68*, 259 (1972).
7. Tully J. C.: J. Chem. Phys. *58*, 1396 (1973).
8. Steiner E., Certain P. R., Kuntz P. J.: J. Chem. Phys. *59*, 47 (1973).
9. Pickup B. T.: Proc. R. Soc. London, A *333*, 69 (1973).

10. Tully J. C., Truesdale C. M.: J. Chem. Phys. *65*, 1002 (1976).
11. Eaker C. W.: J. Chem. Phys. *69*, 1453 (1978).
12. Faist M. B., Muckerman J. T.: J. Chem. Phys. *71*, 225, 233 (1979).
13. Wu A. A.: Mol. Phys. *38*, 843 (1979).
14. Ellison F. O.: J. Chem. Phys. *78*, 5024 (1983).
15. Vojtík J.: Int. J. Quantum Chem. *28*, 593, 943 (1985).
16. Polák R., Paidarová I., Kuntz P. J.: J. Chem. Phys. *82*, 2352 (1985).
17. Last I.: Chem. Phys. *55*, 237 (1981).
18. Polák R.: Chem. Phys. *103*, 277 (1986).
19. Tully J. C.: J. Chem. Phys. *59*, 5122 (1973).
20. Tully J. C.: J. Chem. Phys. *64*, 3182 (1976).
21. Roach A. C., Gimzewski E.: J. Chem. Phys. *73*, 1294 (1980).
22. Kuntz P. J.: Chem. Phys. *94*, 371 (1985); Int. J. Quantum Chem. *29*, 1105 (1986).
23. Kuntz P. J.: Z. Phys. D — Atoms, Molecules and Clusters *2*, 251 (1986).
24. Vojtík J., Šavrda J., Fišer J.: Chem. Phys. Lett. *97*, 397 (1983); Collect. Czech. Chem. Commun. *50*, 2028 (1985).
25. Vojtík J., Paidarová I.: Chem. Phys. Lett. *91*, 280 (1982).
26. Polák R.: Chem. Phys. *16*, 353 (1976).
27. Eaker C. W., Schatz G. C.: J. Phys. Chem. *89*, 2612 (1985).
Eaker C. W., Muzyka J. L.: Chem. Phys. Lett. *119*, 169 (1985).
Eaker C. W., Schatz G. C.: Chem. Phys. Lett. *127*, 343 (1986).
Schatz G. C., Badenhoop J. K., Eaker C. W.: Int. J. Quantum Chem. *31*, 57 (1987).
28. Kuntz P. J., Polák R.: Chem. Phys. *99*, 405 (1985).
29. Polák, Paidarová I., Kuntz P. J.: J. Chem. Phys. *87*, 2863 (1987).
30. Polák R., Vojtík J.: Chem. Phys. *114*, 43 (1987).
31. Polák R., Vojtík J.: Chem. Phys. *87*, 273 (1984).
32. Moffitt W.: Proc. R. Soc., A *210*, 245 (1951).
33. Balint-Kurti G. G., Karplus M. in the book: *Orbital Theories of Molecules and Solids* (N. H. March, Ed.), p. 250. Clarendon Press, Oxford 1974.
34. Polák R.: Chem. Phys. *60*, 287 (1981).
35. Polák R., Vojtík J., Schneider F.: Chem. Phys. Lett. *85*, 107 (1982).
Polák R., Vojtík J.: Chem. Phys. *78*, 107 (1983); Collect. Czech. Chem. Commun. *48*, 1799 (1983).
36. Peyerimhoff S. D., Buenker R. J.: Can. J. Chem. *57*, 3182 (1979).
37. Kuntz P. J., Schreiber J. L.: J. Chem. Phys. *76*, 4120 (1982).
38. Saxon R. P., Lengsfield III B. H., Liu B.: J. Chem. Phys. *78*, 312 (1983).
39. Kendrick J., Kuntz P. J.: J. Chem. Phys. *70*, 736 (1979).
40. Schneider F., Zülicke L., Polák R., Vojtík J.: Chem. Phys. *84*, 217 (1984).
Schneider F., Polák R., Vojtík J.: Chem. Phys. *99*, 265 (1985).
41. Polák R., Kuntz P. J.: Mol. Phys. *63*, 865 (1988).
42. Bell S., Schaefer III H. F.: J. Chem. Phys. *67*, 5173 (1977).
43. Meyer W., Rosmus P.: J. Chem. Phys. *63*, 2356 (1975).
44. Roach A. C., Kuntz P. J.: J. Chem. Phys. *74*, 3435 (1981).
45. Kuntz P. J., Chang C. C.: J. Phys. Chem. *86*, 1212 (1982).
46. Schreiber J. L., Kuntz P. J.: J. Chem. Phys. *76*, 1872 (1982).
47. Roach A. C., Kuntz P. J.: J. Chem. Phys. *84*, 822 (1986).
48. Messiah A.: *Quantum Mechanics*, Vol. II. North-Holland, Amsterdam 1965.

Translated by the author (R.P.)