REDUCED DOUBLE-MINIMUM POTENTIAL CURVES FOR XY₃ PYRAMIDAL MOLECULES

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The reduced potential curve (RPC) method used by Jenč and Pliva for studying the diatomic potentials is adapted for three-parameter studies of the inversional double-minimum potential functions of XY₃ pyramidal molecules. Reduced double-minimum potential curves (RDMPC's) of the first, second and third row hydrides (CH_3^-, NH_3, OH_3^+; SiH_3^-, PH_3, SH_3^+; GeH_3^-, AsH_3, SeH_3^+) are constructed using CNDO/2 and *ab initio* MBPT(2) theoretical potentials. The theoretical RDMPC's corresponding to a group of isoelectronic hydrides coincide to a high degree of approximation, so that they can be represented by a single curve. Furthermore, there is a nearly perfect coincidence between the theoretical RDMPC's of the first row hydrides and the ammonia experimental RDMPC (the only curve known experimentally). To illustrate a practical use of the proposed RPC approach, several approximants to the genuine phosphine potential are constructed (over a wide range of values for the inversion motion coordinate) by combining the available experimental data and the calculated RDMPC's. The resulting potentials exhibit a very close coincidence.

One of the goals in molecular physics is the determination of potential functions of molecules. At the present time, there are two different ways in which the problem is being solved. Namely, either by solving an inverse eigenvalue problem (IEP) for the molecular rotation-vibration Hamiltonian or, alternatively, by calculating the desired function directly by using an *ab initio* method[1]. Unfortunately, the application of either of these approaches is, to some extent, limited. The *ab initio* methods can always be used to calculate a potential function in an optional range of internuclear distances but in practice, with the possible exception of some diatomics[2], the results currently available are not as accurate as those which can be deduced from experimental data. On the other hand, the solution of the IEP can usually provide a reliable potential function only in a relatively narrow neighbourhood of the molecular equilibrium configuration, and — in addition — due to its nonlinearity the solution of the IEP may be nonunique[3].

In this situation it seems to be worth-while to investigate suitable empirical functions which would be representing the behavior of the actual potential functions in suffficiently wide intervals for vibrational coordinates, and which would be involving a small number of adjustable parameters. To arrive at such a function in the case of a diatomic molecule the so-called reduced potential curve (RPC) method (as proposed by Frost and Musulin[4] and developed by Jenč[5])

may be used. The principle of the RPC method consists in the fact that experimental potential curves of a set of diatomic molecules involving the same type of chemical bonding can be reduced, within a single scheme, to a set of nearly coinciding curves (experimental RPC's). It was found[5] that an experimental RPC may be represented quite adequately by an *ab initio* RPC even if the corresponding *ab initio* potential curve represents only a poor approximation to the genuine experimental curve.

The aim of this paper is to demonstrate that the RPC approach may be successfully applied to polyatomic molecules, and to demonstrate that a relatively poor (but cheap) semiempirical CNDO/2 quantum mechanical method may be adequate. The actual procedure is carried out for the double-minimum inversion potential function in XY_3 pyramidal molecules.

THEORETICAL

One-Dimensional Effective Rotation-Vibration Hamiltonian
with a Double-Minimum Potential Function

A great variety of problems in molecular dynamics can be described, in a first approximation, by a one-dimensional Schrödinger equation with a double-minimum potential function (*e.g.*, the inversion of molecules and molecular parts[6], the Berry-pseudorotation of trigonal bipyramidal molecules and the alternative "turnstile" rotation[7], the motions of protons in hydrogen bonds in molecular systems[8], the ring-puckering motions in ring molecules[9]). One-dimensional problems are of interest not only as simple models allowing to display a certain number of properties which one encounters again in more complex situations but also because in a number of problems one is led, after some appropriate manipulations, to equations of the same type as the one-dimensional equation.

Let us consider a multidimensional molecular system with the Hamiltonian $\mathsf{H}(\varrho, \Omega)$:

$$\mathsf{H}(\varrho, \Omega) = -\frac{h^2}{2\mu} \frac{\mathrm{d}^2}{\mathrm{d}\varrho^2} + V(\varrho, \Omega) , \qquad (1)$$

where $\mu[\mu = \mu(\varrho, \Omega)]$ is the appropriate reduced mass function. Here we have divided the coordinates into a "reference" coordinate set ϱ (*e.g.*, inversion motion coordinate), and a collection of "angular" and "internal motion" coordinates Ω (*e.g.*, Euler angles and normal vibrational coordinates) which will be treated separately. Without loss of generality we can assume that a complete, orthonormal basis set $\Theta_m(\Omega)$ exists such that the wave function for the system, $\psi(\varrho, \Omega)$, can be written as[10]

$$\psi(\varrho, \Omega) = \sum_{m=1} \Phi_m(\varrho)\, \Theta_m(\Omega) . \qquad (2)$$

The Schrödinger equation $H\psi = E\psi$ now reduces to an infinite system of coupled ordinary differential equations. They may be written in matrix form as

$$\left[I \frac{d^2}{d\varrho^2} + E(\varrho) - U(\varrho) \right] \Phi(\varrho) = 0 , \tag{3}$$

where I is the infinite unit matrix and Φ is the infinite-dimensional vector with components $\Phi_m(\varrho)$,

$$[E(\varrho)]_{mn} = \frac{2}{h^2} E \int \Theta_m^+(\Omega)\, \mu(\varrho, \Omega)\, \Theta_n(\Omega)\, d\Omega , \tag{4}$$

and

$$[U(\varrho)]_{mn} = \frac{2}{h^2} \int \Theta_m^+(\Omega)\, \mu(\varrho, \Omega)\, V(\varrho, \Omega)\, \Theta_n(\Omega)\, d\Omega . \tag{5}$$

Let us now assume that the "reference" coordinate varies only slightly from the "reaction coordinate" under study, *i.e.*, the classical path of the reference molecular configuration (measured by ϱ) is nearly identical with the curve of steepest descent from one potential minimum to another one. Then to treat the system (3) perturbation theory method can be used and the originally infinite system (3) will be, to a certain level of approximation, decoupled into an infinite set of one-dimensional effective Schrödinger equations. For instance, when applying such a procedure for the study of the inversion motion phenomena in the XY_3 pyramidal molecules the following system of second-order effective vibration-rotation-inversion Schrödinger equations was obtained (see Eq. (27) of ref.[11])

$$\left[\frac{d^2}{d\varrho^2} + \frac{2}{h^2} I_{\varrho\varrho}^{eff} (V; J, K; \varrho) \{ E_{V;J,K} - V_0(\varrho) - U^{eff} (V; J, K; \varrho) \} \right] \psi_{V;J,K}(\varrho) = 0 . \tag{6}$$

In (6) the dynamic variable ϱ is the angle subtended by the $X-Y$ bond of the (nonrigid) reference configuration and the C_3 molecular axis; $I_{\varrho\varrho}^{eff}$ is the inversional component of the Hougen, Bunker and Johns inertia tensor[12]; $V_0(\varrho)$ is the "true" inversional double-minimum potential energy function; and, the function U^{eff} is the "state" dependent pseudopotential contribution to the total effective potential function of the system. The explicit forms of the dependences of the functions $I_{\varrho\varrho}^{eff}$ and U^{eff} on the vibrational ($V = [v_1, v_3, l_3, v_4, l_4]$) and rotational (J, K) quantum numbers are given in Appendix B of ref.[11].

The theoretical model (as described by Eq. (6)) was related to the experimental and *ab initio* data of the first row hydrides (refs[11,13-15]) and was found to be quite adequate to explain most features of the corresponding inversion-rotation spectra

of all low-lying vibrational states (with exception, of course, of "local resonances" effects).

The very same approximate approach can obviously be used in studies of all the above quoted problems, and it seems to be quite reasonable to expect that the accuracy of the resulting models will be comparable with that which was achieved in the case of the first row hydrides inversion motion problem. In other words, there are no principal limitations precluding the determination of the corresponding (and physically correct) potential function $V_0(\varrho)$. However, there are rather serious practical limitations due to the fact the necessary experimental data are rarely available for more than the first few vibrational states. In addition, the limitations might be strongly amplified by the fact that the general form of the potential function is not known and as yet cannot be derived from theory. For instance, when using the theoretical model of (Eq. (6)) to study the inversion motion phenomena in phosphine[16] the authors were unable to determine neither the inversion barrier nor the proper asymptotic behavior of $V_0(\varrho)$ for $|\varrho| \gg \varrho_{eq}$.

In the following sections of the paper a possible way for suppressing these limitations for the case of XY_3 pyramidal molecules is described.

Reduced Double-Minimum Potential Curves for the Pyramidal Hydrides

After following the arguments of Jenč[5] (concerning the potential functions of diatomic molecules) we can conclude that the potential function of XY_3 molecules should depend (in the adiabatic approximation) just on three parameters, Z_X, Z_Y and N, where Z_X and Z_Y are the nuclear charges and N is the number of electrons in the molecule. Hence, despite of considerable differences in absolute characteristics of potential functions of different molecules, a universal three-parameter potential function should exist which would describe the potential energy of all XY_3 molecules equally well (supposing, of course, that the breakdown of the Born–Oppenheimer approximation plays only a negligible role). This assertion seems to be justified, to some extent, by the experience collected in the "pure" one-dimensional studies of the inversion motion problem in ammonia (see refs[17-19]). However, not one of the empirical potential functions used (more or less successfully) in these studies was found to be adequate in analogous studies of the phosphine molecules[16,20].

The very same situation is encountered when dealing with diatomic molecules. There is a series of the three-parameter empirical potential functions which can be directly fitted to experiment with reasonable accuracy, however, the accuracy of the fit afforded by the individual functions is significantly different for different molecules[21]. A less direct, but much more universal, scheme allowing a three-parameter systematic study of diatomic potentials — the so-called reduced potential curve (RPC) method — was proposed by Frost and Musulin[4], modified by Jenč and Plíva[21], and probed in detail by Jenč (ref.[5]). Let us briefly review this approach.

The simplest Frost and Musulin (FM) definition of the reduced potential energy, u, and the reduced internuclear distance, r, is given as

$$u = U(R)/D_e \,, \tag{7}$$

$$r = R/R_e \,, \tag{8}$$

where U is the potential function, R is the internuclear distance, D_e is the depth of the minimum of the potential energy curve, and R_e is the equilibrium internuclear distance. With this definition a very good coincidence of the reduced potential curves of H_2^+ and H_2 was observed. However, the definition was found to be unsatisfactory for other molecules, so that the authors (FM) proposed a more flexible definition of the reduced internuclear distance, r:

$$r = (R - R_{ij})/(R_e - R_{ij}) \,. \tag{9}$$

In (9), the molecular constant R_{ij} was interpreted to be due to the repulsion effect of inner-shell electrons. To rationalize this constant a universal (dimensionless) force constant, $\varkappa$, defined as

$$\varkappa = \left(\frac{d^2 u}{dr^2}\right)_{r=1} \tag{10}$$

was introduced and the authors found that

$$R_{ij} = R_e - [\varkappa D_e/K_e]^{1/2} \,, \tag{11}$$

where

$$K_e = \left(\frac{d^2 U}{dR^2}\right)_{R=R_e} \,. \tag{12}$$

To evaluate $\varkappa$ the authors assumed that for H_2^+ and H_2 $R_{ij} = 0$. The result was $\varkappa_{H_2^+} = 3.96$ and $\varkappa_{H_2} = 4.14$. With the use of a rounded average value, $\varkappa = 4.0$, the values of the cubic and quartic force constants of the reduced potential functions for a series of diatomic molecules were calculated and compared. Although the agreement in values of these constants was not too satisfactory the results supported the hope that the idea of the reduced potential curve might be fruitful.

The hope was fully justified by Jenč and Plíva (JP) (see ref.[21]). These authors found that the definition of the reduced internuclear distance as given by Eq. (9) is physically "incorrect"* and proposed for it the following definition

$$r = [R - (1 - \exp\{-R/\varrho_{ij}\})\,\varrho_{ij}]/[R_e - (1 - \exp\{-R/\varrho_{ij}\}\,\varrho_{ij}] \,, \tag{13}$$

where

$$\varrho_{ij} = (R_e - [\varkappa D_e/K_e]^{1/2})/(1 - \exp\{-R_e/\varrho_{ij}\}) \,, \tag{14}$$

and

$$\varkappa = 3.96 \,. \tag{15}$$

With the use of this "physically legal" definition the RPC's of a number of diatomics were studied[5] and a series of interesting regularities was observed. In our opinion, the following two

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*   A closer inspection of Eq. (9) shows that this definition is not satisfactory since, for $R = 0$, the value of r assumes different values for different molecules.

are the most important. *1*) The RPC's of molecules (adjacent molecules) coincide to a high degree of accuracy. *2*) There is a really good coincidence between the reduced potential curves constructed from the *ab initio* CI-MO(SCF-LCAO) potential and from the corresponding experimental RKRV potentials.

The regularities observed suggest the following applications of the RPC method as most important: *1*) Estimation of the values of spectroscopic constants. *2*) Detection of anomalies and non-adiabatic perturbations which are not disclosed by the usual criteria. *3*) Construction of sufficiently accurate three-parameter potential curves for molecules from the RKRV curves of adjacent molecules or from the respective *ab initio* theoretical curves.

Summarizing we can conclude that the RPC method appears to be a very convenient tool for studying the diatomic potentials. Thus, taking into account the problems we had to face in the case of phosphine, we thought it worth-while to consider the possibility of a reduced double--minimum inversion potential function in XY_3 pyramidal molecules.

In the above discussion we have assumed the existence of a three-parameter universal double-minimum potential function. Let us denote it as $V(\mathcal{A})$, where $\mathcal{A}$ is an inversion motion coordinate. There is no unique recipe for defining $\mathcal{A}$, however, we found as most convenient to use

$$\mathcal{A} = 3r_{XY}^0 \cos \varrho , \qquad (16)$$

where r_{XY}^0 is the reference $X-Y$ bond length[11].

To describe $V(\mathcal{A})$ we have put $V(\mathcal{A} = 0) \equiv 0$ and the following molecular constants have been chosen:

1) $\mathcal{A}_e(\mathcal{A}_e > 0)$ — the "equilibrium" value of the inversion motion coordinate, *i.e.*, the absolute value of $\mathcal{A}$ for which $V(\mathcal{A})$ acquires minima.

2) B — the "barrier height", defined as

$$B = -V(\mathcal{A}_e) . \qquad (17)$$

3) $f_{\varrho\varrho}$ — the "harmonic force constant", defined as

$$f_{\varrho\varrho} = \left(\frac{\mathrm{d}^2 V}{\mathrm{d}\mathcal{A}^2}\right)_{\mathcal{A} = \mathcal{A}_e} . \qquad (18)$$

The assumed existence of a three-parameter $(\mathcal{A}_e, B, f_{\varrho\varrho})$ universal double minimum potential function implies the existence of a single reduced counterpart to it. But nothing else. As yet there is no constructive method allowing us to find such a function. Nevertheless, our trial calculations (see below) have revealed that a very simple semiempirical CNDO/2 method[22] might be adequate for these purposes.

One of the most important discoveries of Jenč is that the RPC's resulting from the calculations which account for correlation energy give a very satisfactory fit to the corresponding experimental RPC's even if the potentials yield a poor approxi-

mation to the genuine experimental potential curves. On the other hand, however, the complete failure of the SCF-MO approach was demonstrated[23].

Taking these heuristic facts into account we searched the literature for the theoretical functions $V(\mathcal{A})$ of the selected molecules. With exception for the case of the first row hydrides NH_3 and OH_3^+ (see refs[13,14,24,25]) we were unable to find any other function which satisfies our requirements (*i.e.*, the function which is determined over an enough wide range of values for $\mathcal{A}$ and with respecting the correlation energy effects). Therefore we performed the required calculations ourselves. The simplest method which accounts for correlation energy (in a semiempirical manner) is the standard version of the CNDO/2 method[22]. In addition, the CNDO/2 method is extremely "cheap" and thus applicable even to very complex molecular systems. Because of these features this method was employed in our case. In addition, to allow for a more detailed calibration of the CNDO/2 theory, rather accurate MBPT(2) inversional potential functions have been calculated for the second row hydrides (SiH_3^-, PH_3, SH_3^+) (beyond-Hartree–Fock studies on the inversion barriers in PH_3 (refs[26−28]), SiH_3^- (ref.[29]) and SH_3^+ (ref.[30]) have already been performed but different basis sets and post-Hatree–Fock methods used preclude any systematic calibration of the CNDO results).

MBPT *and* CNDO *Calculations*

We have used Huzinaga's $(12s9p)$ primitive sets[31] for Si, P and S in the $[6s5p]$ contraction[32]. For the calculations of SiH_3^- we added to the $[6s5p]$ set a diffuse p-type function with the exponent of 0·027 as recommended by Dunning and Hay[33] for treatments of negative species. The hydrogen basis set used was Huzinaga's $(5s)$ primitive set[34] in Dunning's scaled $[3s]$ contraction[35]. On each atom polarization functions were added: two sets of d-type functions on Si, P and S and a single set of p-type functions on H. Their exponents were selected according to the paper by Ahlrichs and coworkers[36]: 0·69 and 0·23 for Si, 0·8 and 0·26 for P, 0·95 and 0·32 for S, and 0·55 for H. In all cases the SCF runs were followed by the second-order Møller–Plesset (MP 2) calculations. The program used was HONDO MP 2 (ref.[37]). The KL cores were kept frozen and also the excitations to the four highest virtual molecular orbitals (counterparts of inner shells) were disregarded. This approximation has been found[38] to have little effect on the potential surface of PH_3.

Points on the energy hypersurface were chosen in order to sample a wide range of values for the inversion coordinate and partially to probe the effects of the symmetric stretching vibration. The geometry parameters and the corresponding energies are given in Table I.

Any use of the CNDO/2 method requires the knowledge of a set of semiempirical parameters, the so-called β bonding parameters, which characterize atoms of a given

TABLE I

Total energies[a] of the PH_3, SiH_3^- and SH_3^+ molecules in different geometrical configurations

ρ/deg	PH₃			SiH₃⁻			SH₃⁺		
	$r/Å^b$	SCF	SCF + MP2	$r/Å^b$	SCF	SCF + MP2	$r/Å^b$	SCF	SCF + MP2
90	1·25	−342·395211	−342·544712	1·39	−290·588776	−290·721978	1·29	−398·929207	−399·090318
90	1·30	−342·413553	−342·563458	1·42	−290·593435	−290·726740	1·32	−398·931477	−399·093197
90	1·33	−342·419295	−342·569498	1·45	−290·595578	−290·729025	1·35	−398·930771	−399·093129
90	1·35	−342·421247	−342·571671	1·48	−290·595507	−290·729138	1·38	−398·927526	−399·090555
90	1·37	−342·421855	−342·572518	1·50	−290·594364	−290·728141	1·40	−398·924140	−399·087636
90	1·39	−342·421240	−342·572161	1·53	−290·591182	−290·725215	1·43	−398·917477	−399·081705
90	1·41	−342·419515	−342·570711	1·56	−290·586443	−290·720776	1·46	−398·909175	−399·074175
90	1·45	−342·413140	−342·564944	1·60	−290·578041	−290·712846	1·50	−398·896001	−398·062099
90	1·37377	−342·421829	−342·572539	1·4665	−290·595795	−290·729338	1·3341	−398·931488	−399·093504
95	1·37377	−342·425720	−342·575708	1·4665	−290·598550	−290·731787	1·3341	−398·935037	−399·096544
105	1·37377	−342·449614	−342·596244	1·4665	−290·615312	−290·747016	1·3341	−398·957057	−399·116123
115	1·37377	−342·472531	−342·617686	1·4665	−290·630119	−290·761256	1·3341	−398·978486	−399·136746
120	1·37377	−342·476840	−342·622576	1·4665	−290·631264	−290·763027	1·3341	−398·982415	−399·141555
122·5	1·37377	−342·476497	−342·622910	1·4665	−290·629633	−290·762012	1·3341	−398·981941	−399·141907
125	1·37377	−342·474318	−342·621688	1·4665	−290·626372	−290·759604	1·3341	−398·979647	−399·140717
130	1·37377	−342·464061	−342·614271	1·4665	−290·614609	−290·750372	1·3341	−398·969109	−399·133276
135	1·37377	−342·445392	−342·599922	1·4665	−290·595447	−290·735190	1·3341	−398·949958	−399·118504
140	1·37377	−342·417752	−342·578343	1·4665	−290·568597	−290·714393	1·3341	−398·921589	−399·095740
150	1·37377	−342·332323	−342·507588	1·4665	−290·491157	−290·653233	1·3341	−398·832086	−399·018533

[a] In atomic units: 1 a.u. = 2 625·46 kJ mol⁻¹. [b] 1 Å = 10⁻¹⁰ m.

. molecule[22]. The quantum chemistry literature recommends certain values of β's for particular atoms $(e.g.,\quad \beta_H = -9, \quad \beta_N = -25, \quad \beta_P = -15; \quad [\beta] = eV, \ 1 eV = = 96\cdot4868 \ kJ \ mol^{-1})$. However, the arguments which are supporting this so-called standard parametrization are, in our opinion, rather vague. For this reason we have performed our calculations for β's varying within rather wide intervals $(e.g., \ \beta_H \in \in \langle -6, -12\rangle, \ \beta_N \in \langle -21, -32\rangle, \ \beta_X \in \langle -10, -32\rangle)$. In addition, the X—H bond lengths $(X = N, C, P, ...)$ were fixed at various values $(e.g., \ r_{NH} \in \langle 0\cdot95, 1\cdot2\rangle, \ r_{PH} \in \in \langle 1\cdot35, 1\cdot55\rangle; \ [r_{XN}] = Å, \ 1 \ Å = 10^{-10} \ m)$. The results of the calculations are available on the request.

The calculations have revealed that the CNDO/2 potentials strongly depend on β_X and r_{XH}, but only a small dependence on β_H was observed (some illustrative results are collected in Table II), i.e., the CNDO/2 potentials are approximately only two-parameter functions. This obviously indicates that the CNDO/2 potentials might be reduced to a set of nearly identical functions within a two-parameter reduction scheme. As a matter of fact, we have found that such reduced inversion potential functions (i.e., relations between a reduced inversion potential energy, u_ϱ, and a reduced inversion motion coordinate, r_ϱ) can be obtained by means of the following modification of the simplest FM scheme (see Eqs (7) and (8))

$$u_\varrho = V(\mathcal{A})/B,\qquad\qquad (19)$$

$$r_\varrho = \mathcal{A}/\mathcal{A}_e.\qquad\qquad (20)$$

From an inspection of Fig. 1 one can deduce that only slightly different CNDO reduced potential curves (CNDO-FM curves) correspond separately to the different row hydrides. The dispersion of the individual CNDO-FM curves corresponding to a given class of isoelectronic molecules is even smaller and, quite surprisingly, the CNDO curves coincide very closely with the corresponding MBPT reduced potential curves (Fig. 2). Nevertheless, the shape of the CNDO curves still exhibits "parametrization" dependence. It seems to be natural to expect that a better coincidence of the CNDO reduced potentials might be obtained by means of a three--parameter JP-like scheme (see Eqs (7, 13—15)). We have probed several schemes of this kind and the best results have been obtained for u_ϱ as given by Eq. (19) and for r_ϱ as follows

$$r_\varrho = \frac{\mathcal{A} - \mathrm{sign}\{\mathcal{A}\}\left[1 - \exp\{-\mathcal{A}^2/\varrho_{ij}\}\right]\varrho_{ij}/\mathcal{A}_e}{\mathcal{A}_e - \left[1 - \exp\{-\mathcal{A}^2/\varrho_{ij}\}\right]\varrho_{ij}/\mathcal{A}_e},\qquad\qquad (21)$$

where

$$\varrho_{ij} = \mathcal{A}_e\left[\mathcal{A}_e - \left(\varkappa_\varrho B/f_{\varrho\varrho}\right)^{1/2}\right]/\left[1 - \exp\{-\mathcal{A}_e^2/\varrho_{ij}\}\right],\qquad\qquad (22)$$

TABLE II

Characteristics of some *ab-initio* and CNDO/2 potentials of the NH_3, CH_3^-, OH_3^+, PH_3, SiH_3^-, SiH_3^+, AsH_3, GeH_3^- and SeH_3^+ compounds[a]

Source	Calc. No	r_{X-H} Å	$\varrho_e - \pi/2$ deg	B cm^{-1}	$f_{\varrho\varrho}$ cm^{-1}Å^{-2}	ϱ_{ij} Å^2	β_H eV	β_X eV
				NH_3				
Experiment[b]	1	0·99893	21·912	1 833	11 182	0·2330		
ab-initio[c]	2	0·95252	19·17	1 090	9 850	0·1797		
CNDO	3	1·0116	18·174	2 124	16 755	0·1380	— 8	— 30·5
CNDO	4	1·0058	22·195	4 569	22 744	0·1501	—9	—24·0
CNDO	5	0·9529	13·0	560	10 276	0·0756	—9	— 32·0
CNDO	6	0·9529	14·90	956	13 168	0·0944	—9	— 30·0
CNDO	7	0·9529	16·70	1 491	16 053	0·1103	—9	— 28·0
CNDO	8	1·1558	22·50	4 922	18·077	0·2046	—9	— 32·0
				CH_3^-				
ab-initio[d]	9	1·081	17·208	566	4 916	0·1899		
CNDO	10	1·0	10·5	263	6 779	0·0560	—9	— 30·0
CNDO	11	1·0	14·6	986	12 680	0·0972	—9	— 26·0
				OH_3^+				
ab-initio[e]	12	0·97186	16·905	687	7 650	0·1475		
CNDO	13	1·0	18·161	1 258	10 400	0·1432	—9	- 28·0
CNDO	14	1·0	15·90	791	8 691	0·1194	—9	— 31·0
				PH_3				
Experiment[f]	15	1·41159	32·504	12 500	13 207	0·6417		
ab-initio MO-SCF[e]	16	1·41159	32·231	13 107	13 325	0·5106		
ab-initio	17	1·37377	31·795	11 071	14 533	0·8340		
CNDO	18	1·35	25·091	8 479	17 351	0·4904	—9	— 32·0
CNDO	19	1·35	27·035	10 863	17 594	0·4246	—9	—26·0
CNDO	20	1·45	27·30	11 567	15 759	0·4703	—9	— 29·0
				SiH_3^-				
ab-initio	21	1·4665	29·352	7 405	10 081	0·8667	—9	— 25·0
CNDO	22	1·45	25·565	8 711	13 830	0·4708	—9	—25·0
CNDO	23	1·35	22·371	5 100	13 895	0·4650	— 9	— 30·0

TABLE II

(*Continued*)

Source	Calc. No	r_{X-H} Å	$\varrho_e - \pi/2$ deg	B cm^{-1}	$f_{\varrho\varrho}$ cm^{-1}Å^{-2}	ϱ_{ij} Å^2	β_{II} eV	β_X eV
				SH$_3^+$				
ab-initio	24	1·3341	31·833	10 638	15 226	0·8444		
CNDO	25	1·35	23·296	6 689	24 266	0·8924	−9	−32·0
CNDO	26	1·45	26·469	7 963	12 492	0·5876	−9	−32·0
				AsH$_3$				
CNDO	27	1·5	28·845	14 381	14 901	0·6502	−9	−23·0
CNDO	28	1·6	29·686	15 873	13 429	0·7273	−9	−23·0
				GeH$_3^-$				
CNDO	29	1·5	29·260	15 528	13·792	0·3913	−9	−17·0
CNDO	30	1·5	27·753	12 719	14 213	0·6148	−9	−22·0
				SeH$_3^+$				
CNDO	31	1·7	29·507	12 237	9 653	0·9223	−9	−25·0
CNDO	32	1·6	29·926	11 814	13 700	1·5341	−9	−25·0

[a] 1 Å $= 10^{-10}$ m, 1 eV $\cong 96.4868$ kJ mol^{-1}, 1 cm^{-1} $\cong 1.196256 . 10^{-2}$ kJ mol^{-1}; [b] ref.[11]; [c] ref.[14]; [d] ref.[39]; [e] ref.[13]; [f] ref.[16].

and where

$$x_\varrho = \left(\frac{d^2 u_\varrho}{dr_\varrho^2}\right)_{r_\rho = \pm 1} \tag{23}$$

is the inversional reduced force constant.

Any use of the JP-like scheme requires the knowledge of x_ϱ. There is, again, no recipe for obtaining this constant. Nevertheless, the numerical experiments performed within this scheme revealed that the dispersion in the coincidence of the CNDO/2 reduced potential curves (CNDO-JP curves) significantly depends on x_ϱ. In the case of the first row hydrides we found that the best coincidence is achieved for $x_\varrho \approx 5\cdot06$. Moreover, the coincidence between the CNDO-JP curves, the MBPT--JP curves and the ammonia experimental reduced curve calculated with $x_\varrho = 5\cdot06$ is remarkably good (Figs 3 and 4).

With the use of $\varkappa_\varrho = 5\cdot06$ the CNDO-JP curves were calculated also for the second row hydrides. While we had no problems with the reduction of all the calculated potentials for the first row hydrides, in this case we arrived at some troubles. Namely, not all the second row potentials provide real solutions of Eq. (22) with respect to ϱ_{ij}. As a matter of fact, this concerns the potentials which were obtained for β_X's $(X = Si, P, S)$ fixed at their standard and higher than standard values. In addition, the CNDO-JP curves resulting from the reducible potentials do not coincide so well as in the case of the first row hydrides. For some time we thought that this is because we were using the (s, p) basis set only. However, when the d orbitals were involved the troubles with the solution of Eq. (22) were even more serious*. On the
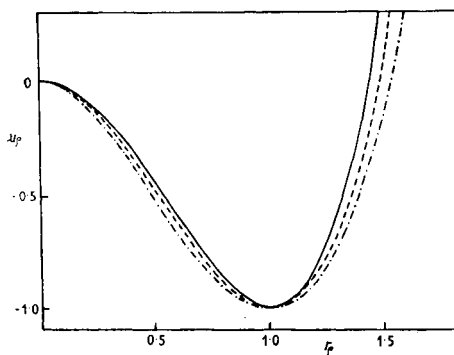

FIG. 1

FM reduced potential curves: ——— NH_3 (Calc. 1), - - - - - PH_3 (Calc. 17), —·—·—· AsH_3 (Calc. 27)
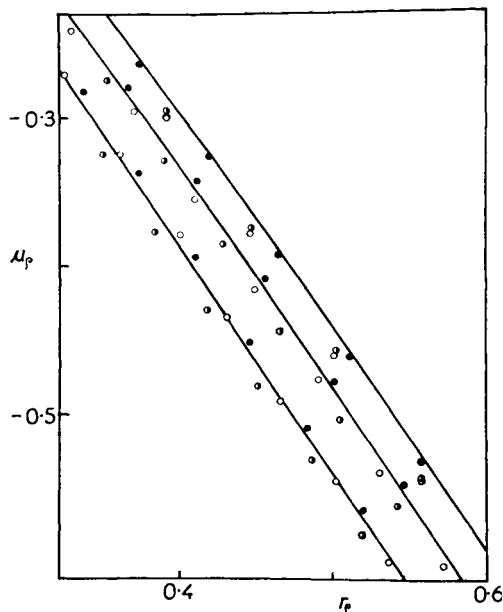
FIG. 2

FM reduced potential curves. First row hydride: 1 NH_3 (Calc. 1), ● NH_3 (Calc. 2), ○ NH_3 (Calc. 3), ◑ OH_3^+ (Calc. 13). Second row hydrides: 2 PH_3 (Calc. 17), ● SiH_3^- (Calc. 23), ○ PH_3 (Calc. 18), ◑ SH_3^+ (Calc. 26). Third row hydrides: 3 AsH_3 (Calc. 27), ● GeH_3^- (Calc. 30), ○ AsH_3 (Calc. 28), ◑ SeH_3^+ (Calc. 32). The lines are from top to bottom: 1, 2, 3

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* The problems arise mainly due to the fact that the standard parametrizations provide too unrealistic barrier heights.

other hand, when relaxing the assumption that x_{ϱ} is a universal constant, a very good coincidence of the second row CNDO-JP curves and the corresponding MBPT curves was obtained for $x_{\varrho} = 4\cdot20$ (Fig. 4). Similarly, the use of $x_{\varrho} = 3\cdot63$ allows for a very close coincidence of the third row CNDO-JP reduced potentials.

The degree of coincidence of the individual CNDO-JP and MBPT-JP reduced curves corresponding to isoelectronic molecules is certainly very high. But, we can see in Figs 3 and 4 that the JP curves of the studied hydrides form three distinct bands of curves (typical representants of these bands of curves are given in Table III). The existence of different JP curves for molecules involving different types of bonding is fully in line with the results obtained in the case of diatomics. This fact implies, in principle, that we are unable to arrive at the universal three-parameter double-
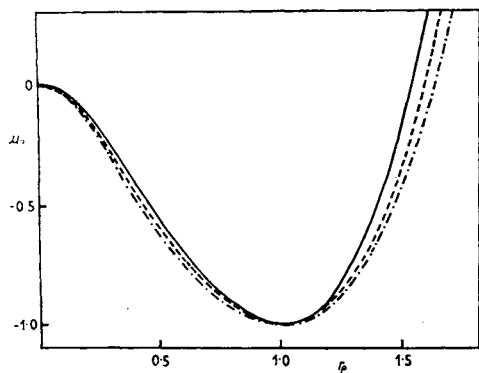

FIG. 3

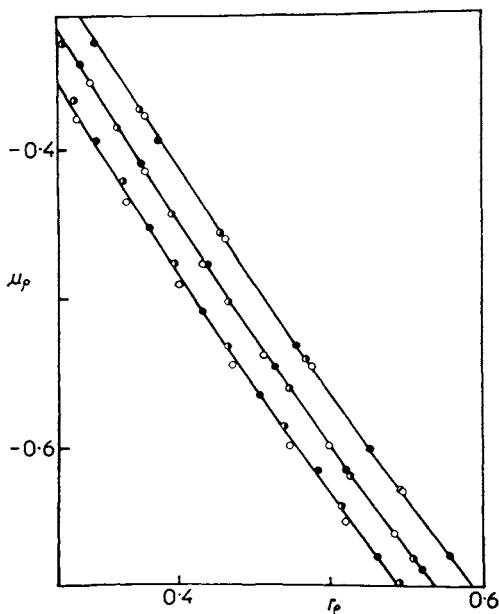JP reduced potential curves: ——— NH_3 (Calc. 1), - - - - - PH_3 (Calc. 17), - · - · - AsH_3 (Calc. 27)

FIG. 4

JP reduced potential curves. First row hydrides: *1* NH_3 (Calc. 1), ● NH_3 (Calc. 2), ○ NH_3 (Calc. 3), ◑ OH_3^+ (Calc. 13). Second row hydrides: *2* PH_3 (Calc. 17J), ● SiH_3^- (Calc. 23), ○ PH_3 (Calc. 18), ◑ SH_3^+ (Calc. 26). Third row hydrides: *3* AsH_3 (Calc. 27), ● GeH_3^- (Calc. 30), ○ AsH_3 (Calc. 28), ◑ SeH_3^+ (Calc. 32). The lines are from top to bottom: *1, 2, 3*

TABLE III

The reduced double-minimum potential curves for the XH_3 pyramidal hydrides

$(CH_3^-, NH_3, OH_3^+)^a$		$(SiH_3^-, PH_3, SH_3^+)^b$		$(GeH_3^-, AsH_3, SeH_3^+)^c$	
r_ϱ	u_ϱ	r_ϱ	u_ϱ	r_ϱ	u_ϱ
0·0446	−0·0044	0·0320	−0·0026	0·0344	−0·0042
0·0857	−0·0178	0·0621	−0·0103	0·0667	−0·0170
0·1238	−0·0398	0·0906	−0·0232	0·0974	−0·0378
0·1601	−0·0702	0·1176	−0·0410	0·1269	−0·0663
0·1955	−0·1085	0·1437	−0·0635	0·1561	−0·1018
0·2308	−0·1540	0·1690	−0·0904	0·1854	−0·1434
0·2670	−0·2061	0·1940	−0·1215	0·2152	−0·1901
0·3048	−0·2639	0·2191	−0·1563	0·2461	−0·2411
0·3446	−0·3264	0·2444	−0·1946	0·2781	−0·2951
0·3868	−0·3927	0·2703	−0·2358	0·3112	−0·3511
0·4314	−0·4615	0·2970	−0·2795	0·3454	−0·4081
0·4783	−0·5316	0·3246	−0·3252	0·3806	−0·4651
0·5272	−0·6018	0·3533	−0·3725	0·4164	−0·5212
0·5778	−0·6707	0·3831	−0·4209	0·4528	−0·5756
0·6297	−0·7369	0·4140	−0·4698	0·4895	−0·6278
0·6826	−0·7989	0·4460	−0·5189	0·5263	−0·6772
0·7361	−0·8552	0·4788	−0·5676	0·5632	−0·7234
0·7899	−0·9044	0·5126	−0·6155	0·6001	−0·7662
0·8437	−0·9449	0·5470	−0·6622	0·6368	−0·8053
0·8976	−0·9753	0·5820	−0·7072	0·6733	−0·8409
0·9512	−0·9942	0·6174	−0·7501	0·7097	−0·8727
1·0046	−0·9999	0·6531	−0·7907	0·7458	−0·9010
1·0577	−0·9912	0·6890	−9·8285	0·7817	−0·9257
1·1104	−0·9666	0·7250	−0·8632	0·8173	−0·9470
1·1627	−0·9248	0·7609	−0·8946	0·8527	−0·9647
1·2146	−0·8647	0·7967	−0·9223	0·8877	−0·9790
1·2661	−0·7849	0·8324	−0·9461	0·9225	−0·9897
1·3170	−0·6845	0·8679	−0·9659	0·9570	−0·9967
1·3676	−0·5623	0·9031	−0·9813	0·9911	−0·9998
1·4176	−0·4175	0·9380	−0·9922	1·0249	−0·9988
1·4671	−0·2491	0·9727	−0·9984	1·0584	−0·9934
1·5161	−0·0565	1·0069	−0·9998	1·0915	−0·9835
1·5646	0·1608	1·0409	−0·9963	1·1243	−0·9687
1·6125	0·4038	1·0744	−0·9878	1·1567	−0·9489
1·6599	0·6726	1·1076	−0·9742	1·1887	−0·9240
1·7067	0·9677	1·1404	−0·9553	1·2203	−0·8939
1·7529	1·2893	1·1727	−0·9312	1·2516	−0·8588
1·7985	1·6375	1·2046	−0·9017	1·2824	−0·8188
1·8435	2·0123	1·2361	−0·8669	1·3128	−0·7742

TABLE III

(Continued)

(CH$_3^-$, NH$_3$, OH$_3^+$)^a		(SiH$_3^-$, PH$_3$, SH$_3^+$)^b		(GeH$_3^-$, AsH$_3$, SeH$_3^+$)^c	
r_ϱ	u_ϱ	r_ϱ	u_ϱ	r_ϱ	u_ϱ
1·8878	2·4137	1·2672	− 0·8267	1·3428	−0·7252
1·9315	2·8414	1·2978	− 0·7811	1·3723	−0·6722
1·9746	3·2953	1·3279	− 0·7300	1·4014	−0·6155
2·0170	3·7748	1·3576	− 0·6733	1·4300	−0·5554
2·0587	4·2796	1·3968	− 0·6111	1·4582	−0·4917
2·0997	4·8050	1·4155	− 0·5432	1·4859	−0·4244
2·1399	5·3624	1·4437	− 0·4696	1·5132	−0·3527
2·1795	5·9390	1·4714	− 0·3901	1·5399	−0·2756
2·2183	6·5379	1·4986	− 0·3046	1·5662	−0·1913
2·2564	7·1581	1·5253	− 0·2129	1·5919	−0·0975
2·2937	7·7986	1·5514	− 0·1148	1·6171	0·0090
2·3303	8·4583	1·5770	−0·0101	1·6418	0·1322
2·3661	9·1359	1·6021	0·1015	1·6660	0·2770
2·4011	9·8300	1·6266	0·2205	1·6897	0·4493
2·4353	10·5395	1·7615	1·1074	1·7574	1·2019
2·4686	11·2626	1·8575	2·1097	1·8200	2·4889

^{a} Calc. 1 (see Table II); ^{b} Calc. 12; ^{c} Calc. 29.
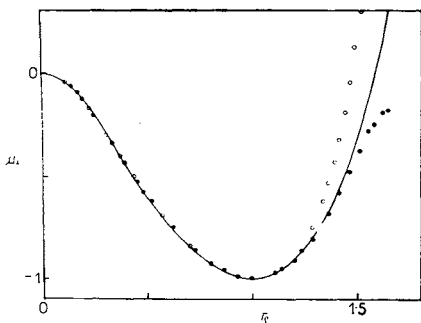

FIG. 5

JP reduced potential curves of the PH$_3$ molecule: ——— MBPT 2 Curve (Calc. 17), ● "Experiment" (Calc. 15), ○ MO-SCF (Calc. 16)
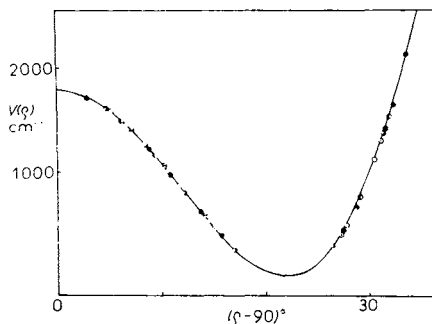

FIG. 6

The inversion potential function of ammonia: ——— Experiment (ref.[11]), ⊙ (Calc. 2), ● (Calc. 6), ◑ (Calc. 3), ◐ (Calc. 4), ○ (Calc. 7), ⊖ (Calc. 8)

-minimum potential function within our reduction scheme. In practice, however, the results indicate that a rather good approximation to such a function can be constructed separately for a group of molecules involving the same type of bonding.

There is still one result of our calculations which is in full accord with the results collected by Jenč for diatomic molecules. We can see in Fig. 3 that even highly dedicated MO-SCF calculations might be wholly inadequate to our requirements.

TABLE IV

Calculated[a] and experimental wavenumbers of PH_3 transitions

Calc. No (see Table II)	ν_2	$2\nu_2$	$3\nu_2$	$4\nu_2$	$5\nu_2$	$6\nu_2$	$7\nu_2$	$8\nu_2$
13[b]	992	1 972·5	2 941·2	3 895·9	4 836	5 760	6 666	7 553
14[c]	991·8	1 972·5	2 940·9	3 985·9	4 835	5 758	6 663	7 548
12[d]	992	1 972·5	2 940·8	3 895·9	4 837	5 762	6 669	7 557
1[e]	992·5	1 972·5	2 940·3	3 896·0	4 837	5 770	6 686	7 586
Exp. wavenumbers	992	1 972·5	2 940·8	3 895·9				

[a] $\mathscr{R}_e = 2\cdot29817$ Å (1 Å $= 10^{-10}$ m, 1 cm$^{-1} \hat{=} 1\cdot196256 . 10^{-2}$ kJ mol^{-1});[b] $B = 11\ 618$ cm^{-1}, $\varrho_{ij} = 0\cdot8813$ Å^2, $\varkappa_{\varrho} = 4\cdot20$; [c] $B = 11\ 733$ cm^{-1}, $\varrho_{ij} = 0\cdot8372$ Å^2, $\varkappa_{\varrho} = 4\cdot20$; [d] $B = 11\ 762$ cm^{-1}, $\varrho_{ij} = 0\cdot8375$ Å^2, $\varkappa_{\varrho} = 4\cdot20$; [e] $B = 11\ 565$ cm^{-1}, $\varrho_{ij} = 0\cdot4509$ Å^2, $\varkappa_{\varrho} = 5\cdot06$.
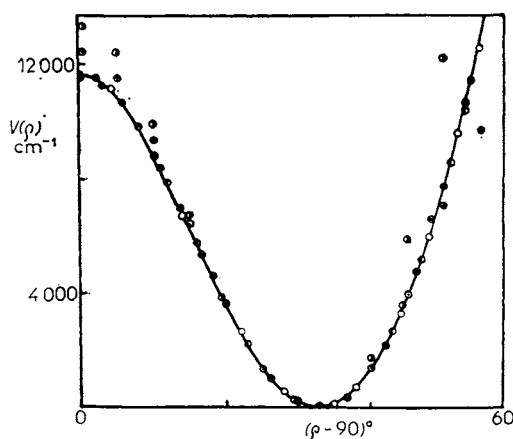

FIG. 7

The inversion potential function of phosphine: ——— (Calc. 19), ● (Calc. 18), ○ (Calc. 20), ◖ (Calc. 26), ⊖ (Calc. 1), ⊙ (Calc. 15), ◑ (Calc. 16)

The Inversion Potential Function of Phosphine

We see in Fig. 5 that there is a rather good coincidence between the calculated JP curves of phosphine and the corresponding experimental curve (ERC) for $|r_\varrho| \in$ $\in \langle 0, \approx 1.35 \rangle$. Outside this interval the ERC behaves "pathologically". This is obviously due to the unrealistic asymptotic behaviour of the experimental potential (see Fig. in ref.[16]).

Let us assume now that there is a calculated JP curve which coincides closely with the ERC inside the "equilibrium" region. Then, it is quite natural to expect that this curve will also coincide closely outside this region. In such case, an asymptotically correct potential may be obtained within the RPC scheme (the mappings $r_\varrho - u_\varrho$ and $\mathcal{A} - V$ are obviously one-to-one). This certainly important assertion seems to be justified by numerical experiments we have done for the ammonia CNDO potentials. For instance, by keeping $\mathcal{A}_e$, B and ϱ_{ij} fixed at their experimental values, the theoretical potentials have been constructed from the individual CNDO-JP curves. The overall coincidence between the resulting potentials and the experimental potential is remarkable (Fig. 6).

To estimate the prospects of the RPC approach in the case of phosphine the corresponding theoretical potentials have been constructed from a set of different CNDO-JP curves. The results of our calculations, performed with the same model Hamiltonian as in ref.[16] and for $\mathcal{A}_e$ fixed at the experimental value, are collected in Table IV and illustrated by Fig. 7. Despite the fact that it is hard to assess how reliably the theoretical potentials have been determined, we believe that they are reasonable approximants to the genuine potential.

CONCLUSIONS

A reduced potential curve method permitting three-parameter studies of double--minimum potential functions of XY_3 pyramidal molecules has been proposed in this paper.

In view of the present results it appears that a close theoretical approximation to the experimental reduced potential curve may be obtained by means of the standard CNDO/2 semiempirical method. This heuristic evidence leads us to expect a practical use of the proposed approach. The arguments contained in this paper were suggested by the results obtained in calculations on the pyramidal XH_3 hydrides only and, of course, still have to be verified by more extensive calculations.

The construction of the reduced potential curves for other types of vibrational coordinates is, undoubtedly, an important problem and will be the subject of our further investigations.

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