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ABSTRACT

Non-empirical calculations of the electronic structure of the ammonia molecule are carried out using a "bond-orbital" and a "modified electron-pair" function. The calculated binding energy is 0.348 a.u. (76 o/o of the experimental value) and 0.381 a.u. (83 o/o) respectively. The best theoretical value previously known was 0.378 a.u., the result of an self-consistent LCAO calculation including limited configuration interaction.

It is concluded that the "modified electron-pair" function is an adequate simple approximation, and the "frozen core" approximation employed in the calculation is satisfactory.

The dipole moment is also calculated, and reasonable agreement with the experimental value is obtained.

1. INTRODUCTION

Hurley, Lennard-Jones and Pople 1) and Slater 2) pointed out the merit of using a set of orbitals of the following nature in the calculation of the electronic structure of molecules. Two orbitals which describe one and the same bond are not orthogonal. Orbitals describing different bonds are orthogonal. Thus there is no difficulty connected with non-orthogonality, and energy expressions can be given in a fairly simple closed form. Such orbitals may be said to have pair non-orthogonality.

The idea was further developed by Parks and Parr 3). However, these authors suggested no method of constructing such orbitals with pair non-orthogonality. McWeeny and Ohno 4) proposed one way of doing this. They first obtained a set of orthogonal orbitals and then made the orbitals within each pair non-orthogonal to each other. They carried out calculations of the water molecule using these orbitals. In one of their calculations, they utilized a "modified electron-pair" function which has the form of an ordinary electron-pair-bond function but is constructed from orbitals with pair non-orthogonality. In this method, the water molecule was treated effectively as a four-electron problem, and the wave function contained only two parameters. The calculated total energy was lower than that given by the elaborate self-consistent LCAO method (the SC LCAO method) . 5, 6)

In the modified electron-pair function, McWeeny and Ohno used pre-determined orbitals to describe the inner-shell and the lone pair. This was called the "frozen core" approximation, and it turned out to be quite satisfactory.

Being encouraged by these results in the case of water, we apply the modified electron-pair method to the ammonia molecule in this paper. We adopt the Hartree-Fock atomic orbitals and integral values calculated by Kaplan 7). It is interesting to see whether the differences in the number of lone pairs (one for NH_3, two for H_2O) and in the basic orbitals (Hartree-Fock for NH_3, Slater for H_2O) affect the general features of the result.*

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* It was noted by Kaplan that changing the atomic orbitals from Slater to Hartree-Fock orbitals causes appreciable change in the value of many molecular integrals 7).

A pertinent remark on McWeeny and Ohno's paper was made by Merrifield 8). He pointed out that the work is based on approximate values for three- and four-centre integrals and on single-term Slater orbitals. He seems to feel that errors caused by these two approximations balance one another to produce fortuitous results. In the present ammonia calculation we use Kaplan's integral values which are correct within $\pm 10^{-4}$ a.u. It will be interesting to see whether or not this improvement substantiates Merrifield's criticisms.

We carry out an additional calculation using a "bond-orbital" function, as the bond-orbital function is a special case of the "modified electron-pair" function.

2. ORBITALS AND INTEGRALS

The methods of obtaining the orthonormal hybridized orbitals and of transforming the molecular integrals to integrals of these new basic orbitals are quite similar to the case of water 4). Therefore, we shall only briefly sketch it here.

The co-ordinate system to be used is shown in figure 1.

We start with the set of orbitals used by Kaplan:

$$\mathfrak{a} = (n \; s \; z \; x \; y \; H_0 \; H_x \; H_y), \qquad (2.1)$$

where, n, s, z, x, and y are the Hartree-Fock 1s, 2s, 2pz, 2px and 2py orbitals of the nitrogen atom respectively. The orbitals H_o, H_x and H_y were defined as linear combinations of three hydrogen 1s orbitals h_1, h_2, and h_3 :

$$\begin{aligned} H_0 &= \{ 3(1+2S_h)\}^{-1/2} (h_1 + h_2 + h_3), \\ H_x &= \{ 3(1-S_h)/2\}^{-1/2} (h_1 - \tfrac{1}{2}h_2 - \tfrac{1}{2}h_3), \\ H_y &= \{ 2(1-S_h)\}^{-1/2} (h_2 - h_3), \\ S_h &= (h_1|h_2) = (h_2|h_3) = (h_3|h_1). \end{aligned} \qquad (2.2)$$

It is convenient to go back to the orbitals h_1, h_2 and h_3 instead of H_o, H_x and H_y at this stage:

$$\mathbf{b} = (n\ s\ z\ x\ y\ h_1\ h_2\ h_3) = \mathbf{a}\mathbf{T}, \tag{2.3}$$

where the transformation $\mathbf{T}$ is inverse to the transformation (2.2).

Since the nitrogen 1s electrons have much lower energy than the others, we shall retain the nitrogen 1s orbital unchanged. The orbitals h_1, h_2 and h_3 are made orthogonal to the nitrogen 1s orbital by the Schmidt procedure. This yields the set,

$$\mathbf{c} = (n\ s\ z\ x\ y\ h_1^\circ\ h_2^\circ\ h_3^\circ), \tag{2.4}$$

where

$$h_i^\circ = (1 - S_h^2)^{-1/2} (h_i - S_{nh}\, n), \qquad S_{nh} = (n | h_i), \quad i = 1, 2, 3. \tag{2.5}$$

We treat all the valence orbitals, 2s, 2p of N and 1s of H, on an equal basis and apply Löwdin's symmetrical orthogonalization [9]:

$$\mathbf{d} = (n\ \bar{s}\ \bar{z}\ \bar{x}\ \bar{y}\ \bar{h}_1^\circ\ \bar{h}_2^\circ\ \bar{h}_3^\circ) = \mathbf{c}\,\mathbf{S}_c^{-1/2}, \tag{2.6}$$

where $\mathbf{S}_c$ is the overlap matrix for the orbitals $\mathbf{c}$. This orthogonalization procedure has the advantage that the resulting orbitals $\mathbf{d}$ resemble the original orbitals $\mathbf{c}$ most closely in the sense $\sum_i \int | d_i - c_i |^2 dv$ is a minimum [10].

The final step is to get $\bar{s}$, $\bar{z}$, $\bar{x}$, and $\bar{y}$ hybridized. This hybridization is carried out so that the resulting bond hybrids b_1, b_2 and b_3 point along the bond directions:

$$\mathbf{e} = (n\ l\ b_1\ b_2\ b_3\ \bar{h}_1^\circ\ \bar{h}_2^\circ\ \bar{h}_3^\circ) = \mathbf{d}\,\mathbf{U}. \tag{2.7}$$

The transformation $\mathbf{U}$ has the following form,

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -t & -\sqrt{1-t^2}/\sqrt{3} & -\sqrt{1-t^2}/\sqrt{3} & -\sqrt{1-t^2}/\sqrt{3} & 0 & 0 & 0 \\ 0 & \sqrt{1-t^2} & -t/\sqrt{3} & -t/\sqrt{3} & -t/\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2}/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{6} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{2.8}$$

where $t = \sqrt{2} \cot \theta$, and θ is the angle between a bond direction N-H and the -Z axis. In the equilibrium case, $\angle$HNH is 106° 47', and $\cot \theta =$ $= 0.404\,865$.

The final orthonormal hybridized orbitals are related to Kaplan's basic set by

$$\mathbf{e} = \mathbf{a} \mathbf{V}, \tag{2.9}$$

where $\mathbf{V}$ is completely determined by the shape of the molecule and the overlap integrals between the basic atomic orbitals.

The transformation of all integrals to the new basis $\mathbf{e}$ can be carried out in the same way as in the case of water [4].

The numerical calculation is performed for the equilibrium case, the N-H distance being 1.916 a.u. All integrals are taken from Kaplan's paper [7] except for the following [11]:

$(ss|zH_0) = -0.1193$ instead of -0.0864,

$(ns|H_xH_x) = 0.0001$ instead of 0.0014,

$(sH_x|zH_x) = 0.0128$ instead of 0.0060,

$(n|r_H|z) = 0.0070$ instead of 0.0076.

3. THE BOND-ORBITAL APPROXIMATION

The simplest electronic wave function is obtained in the following way. Two electrons are put into the fixed orbitals n and ℓ in order to represent the inner-shell and the lone pair. Each bond is described by using a bond orbital which is a linear combination of b_i and $\bar{h}_i^o$,

$$B_i = (1-\lambda^2)^{1/2} b_i + \lambda \bar{h}_i^o, \qquad i = 1, 2, 3. \tag{3.1}$$

The total wave function is then a single Slater determinant,

$$\begin{aligned} \Phi &= (n^2 \ell^2 B_1^2 B_2^2 B_3^2) \\ &= \frac{1}{\sqrt{10!}} \left| n(1) \bar{n}(2) \ell(3) \cdots \bar{B}_2(8) B_3(9) \bar{B}_3(10) \right|, \end{aligned} \tag{3.2}$$

where the barred orbitals are occupied by an electron with spin β .

Since the five orbitals in (3.2) are orthogonal to each other, the total electronic energy is expressed by a simple formula which contains only one variational parameter λ .

The total energy reaches a minimum when $\lambda^2 = 0.42$, and the binding energy is 0.348 a.u. = 9.47 eV which is 96 o/o of the binding energy calculated by the SC LCAO method. The experimental binding energy is 0.459 a.u. = = 12.49 eV . The effect of variation of λ^2 on the energy is illustrated in figure 2.

The calculated dipole moment for $\lambda^2 = 0.42$ is 1.84 Debye while that by the SC LCAO method is 1.82 Debye and the experimental value is 1.46 Debye.

It is remarkable that this simple wave function produces almost as good results as the elaborate SC LCAO function. It is also interesting to note that the optimum value of λ^2 , which is a measure of the bond polarity, is very close to the value (0.43) for the O-H bond in water.

Kaplan constructed his equivalent orbitals from his SC LCAO molecular orbitals in the following way,

$$\left.\begin{aligned} n' &= \psi_{I}, \\ l' &= \psi_{III}, \\ B_1' &= -\tfrac{1}{\sqrt{3}}\,\psi_{II} + \sqrt{\tfrac{2}{3}}\,\psi_{IV}, \\ B_2' &= -\tfrac{1}{\sqrt{3}}\,\psi_{II} - \tfrac{1}{\sqrt{6}}\,\psi_{IV} + \tfrac{1}{\sqrt{2}}\,\psi_{V}, \\ B_3' &= -\tfrac{1}{\sqrt{3}}\,\psi_{II} - \tfrac{1}{\sqrt{6}}\,\psi_{IV} - \tfrac{1}{\sqrt{2}}\,\psi_{V}, \end{aligned}\right\} \qquad (3.3)$$

where ψ_I , ψ_{II} , ψ_{III} , ψ_{IV} and ψ_V are the molecular orbitals in the order of increasing orbital energy.*

We may compare our orbitals n , l , B corresponding to the inner shell, lone pair and bond orbitals respectively with Kaplan's equivalent orbitals. In terms of the basic set $\mathfrak{a}$, they are expressed as

$$\left.\begin{aligned} n &= n, \\ l &= 0.020\,n - 0.700\,s + 0.781\,z - 0.210\,H_o, \\ B_1 &= -0.025\,n - 0.292\,s - 0.231\,z + 0.530x + 0.249\,H_o + 0.371\,H_x, \end{aligned}\right\} (3.4)$$

---

* The choice of pure ψ_{III} as the lone-pair orbital is rather arbitrary. In the C_{3v} case, we cannot determine equivalent orbitals by symmetry consideration only.

and

$$\left.\begin{aligned} n' &= 1.000\,n - 0.003\,s - 0.002\,z - 0.001\,H_o, \\ \ell' &= 0.026\,n - 0.442\,s + 0.896\,z - 0.258\,H_o, \\ B'_1 &= -0.017\,n - 0.438\,s - 0.093\,z + 0.560\,x + 0.157\,H_o + 0.397\,H_x \end{aligned}\right\} \quad (3.5)$$

We can see a marked resemblance between these two sets of orbitals although the methods of construction are entirely different.

4. THE MODIFIED ELECTRON-PAIR APPROXIMATION

As for the inner-shell and the lone pair, we use the same "frozen-core" approximation as in the previous section. The description of the three bonds is improved by using the following two functions for a bond instead of just B_i ,

$$\left.\begin{aligned} \tilde{b}_i &= (1-\lambda^2)^{1/2} b_i + \lambda \bar{h}_i^\circ, \\ \tilde{h}_i &= (1-\lambda'^2)^{1/2} b_i + \lambda' \bar{h}_i^\circ, \end{aligned}\right. \qquad i = 1,\ 2,\ 3\ . \qquad (4.1)$$

We use the electron-pair function

$$[\tilde{b}_i \tilde{h}_i] = \{2(1+S^2)\}^{-1/2}\{\tilde{b}_i(1)\tilde{h}_i(2) + \tilde{h}_i(1)\tilde{b}_i(2)\}\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2), \quad (4.2)$$

to describe a bond and thus the total wave function is written in an abbreviated form as

$$n^2\,\ell^2\,[\tilde{b}_1\tilde{h}_1]\,[\tilde{b}_2\tilde{h}_2]\,[\tilde{b}_3\tilde{h}_3]\,. \qquad (4.3)$$

The orbitals $\tilde{b}_i$ and $\tilde{h}_i$ are not orthogonal any more, and this non-orthogonality within a bond is necessary for a single spin-paired "structure" to be a reasonably good approximation. However, the non-orthogonalities are limited within bonds, and we can still express the total electronic energy in a fairly simple closed form 1, 2, 3).

The function contains two variational parameters λ and λ' , and for $\lambda = \lambda'$ the present approximation reduces to the bond orbital approximation.

The calculated results are shown in Table I. The dependence of the

TABLE I. Total and binding energies and dipole moment in various approximations.

	Total energy (a.u.)	Binding energy (a.u.)	Dipole moment (Debye)
Bond orbital ($\lambda^2 = 0.42$)	-56.250	0.348	1.84
Modified electron pair ($\lambda^2 = 0.20$, $\lambda'^2 = 0.65$)	-56.283	0.381	1.89
SC LCAO 7)	-56.266	0.364	1.82
SC LCAO + CI 7)	-56.280	0.378	-
Experimental 7)	-56.595	0.459	1.46

energy on λ^2 and λ'^2 is illustrated in figure 3.

The resulting binding energy is 0.381 a.u. = 10.37 eV which is 0.90 eV better than the bond orbital value and is 83 o/o of the experimental value.

This simple treatment, in which we reduce the problem effectively to that of six-electrons, gives an energy 0.46 eV better than the ten-electron SC LCAO calculation. The optimum values of the parameters λ^2 and λ'^2 are again not so different from those for water, the latter being 0.17 and 0.72.

It is interesting to note that the energy value calculated with the modified electron-pair function is slightly better than that obtained by the limited configuration interaction calculation 7). In the latter, thirteen configurations were carefully selected from the total ninety-eight configurations.

The modified electron-pair method seems to be a nice compromise between accuracy and ease of use.

5. DISCUSSION

We have used orthogonalized atomic orbitals as our basis. The aim of this was not only to circumvent the non-orthogonality difficulty but also to emphasize the localization of bonds and lone pairs. Whether the present basic orbitals $\mathfrak{e}$ (2.7) are localized or not is difficult to say. For example, the orbital $\bar{h}_1^0$ is expressed as

$$\bar{h}_1^0 = -0.080\, n + 0.379\, s + 0.117\, z - 0.352\, x + + 1.365\, h_1 - 0.123\, h_2 - 0.123\, h_3 .^{*} \tag{5.1}$$

This looks more delocalized than the original hydrogen orbital h_1 at the first sight. However, the coefficients of the other atomic orbitals are such that they reduce the electron density near the nitrogen atom and hydrogen atoms 2 and 3, so that the orbital $\bar{h}_1^0$ may well be more localized than h_1. We cannot compare the degree of localization unless we introduce a certain measure. Hall suggested the use of self-Coulomb integral $(\varphi\varphi|\varphi\varphi)$ for this measure $^{12)}$. The values for $\bar{h}_1^0$ and h_1 are

$$\left.\begin{aligned} (\bar{h}_1^0 \bar{h}_1^0 | \bar{h}_1^0 \bar{h}_1^0) &= 0.6899 \text{ a.u.} \\ (h_1 h_1 | h_1 h_1) &= 0.6250 \text{ a.u.} \end{aligned}\right\} \tag{5.2}$$

This criterion, therefore, shows that $\bar{h}_1^0$ is the one more localized.

The modified electron-pair function is satisfactory in that it gives lower total energy than either the SC LCAO method or the limited configuration interaction method. Thus the present orthogonalization procedure to keep the nitrogen 1s orbital unperturbed is justified. To describe the inner shell and lone pair by the fixed orbitals n and ℓ respectively - this may be called the "frozen-core" approximation - proves also satisfactory.

The wave function furnishes, at the same time, a clear-cut picture of bonding and lone-pair electrons.

In the electron-pair function, correlation between the two electrons with

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* It should be noted that the sign of the 2s orbital of nitrogen is opposite to the usual one.

spin α and β in each bond is taken into account to some extent. On the other hand, this correlation is not at all taken into account in the bond orbital function. The optimum values of λ^2 and λ'^2 differ considerably from that in the bond orbital function, and this means that correlation affects the electron distribution appreciably. The energy drop of 0.033 a.u. = 0.90 eV going from the bond orbital function to the modified electron-pair function may be regarded as resulting from this intra-bond correlation.

The calculated value of the dipole moment is close to that obtained by the SC LCAO method, and agreement with the experimental value is not excellent but reasonable.

Comparing these results with those for water [4), one can see that their general features are almost the same. Thus, we may conclude that the success of the modified electron-pair method is bona fide. The change of the basic atomic orbitals - from Slater orbitals to SCF - and the change of the number of bonds and lone-pairs do not affect the results.

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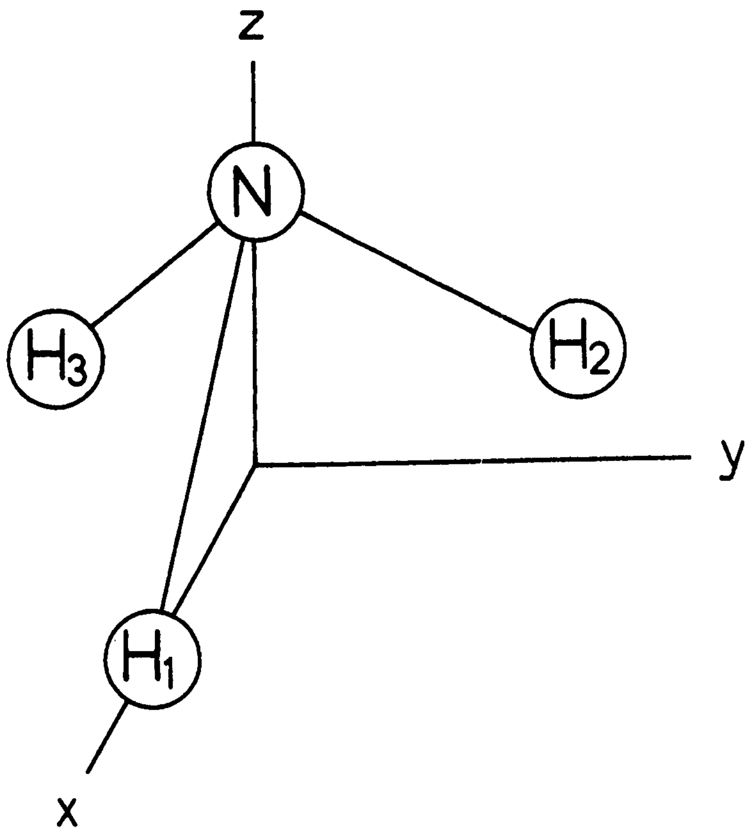

Figure 1. The co-ordinate system.

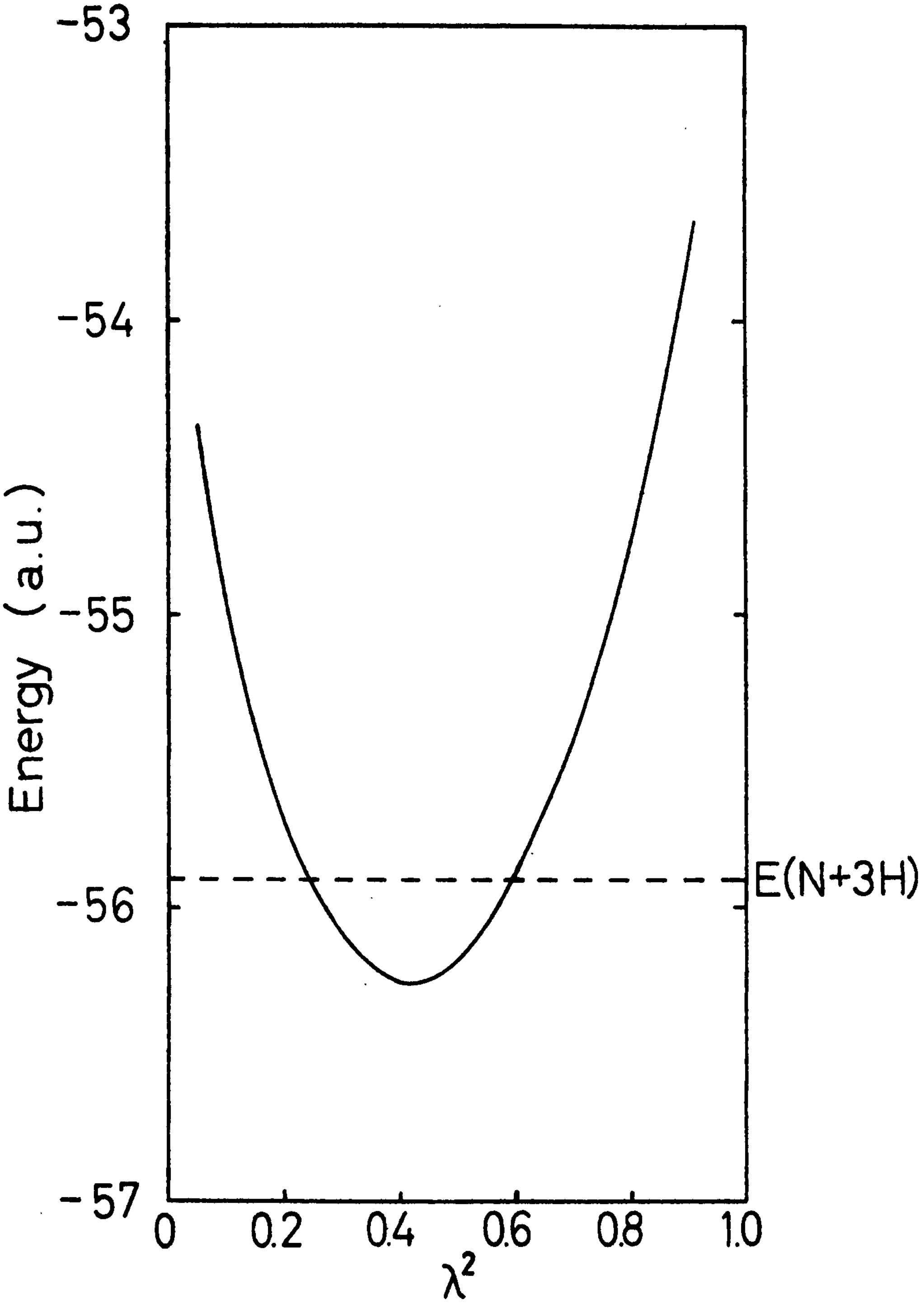

Figure 2. Energy as a function of λ^2.

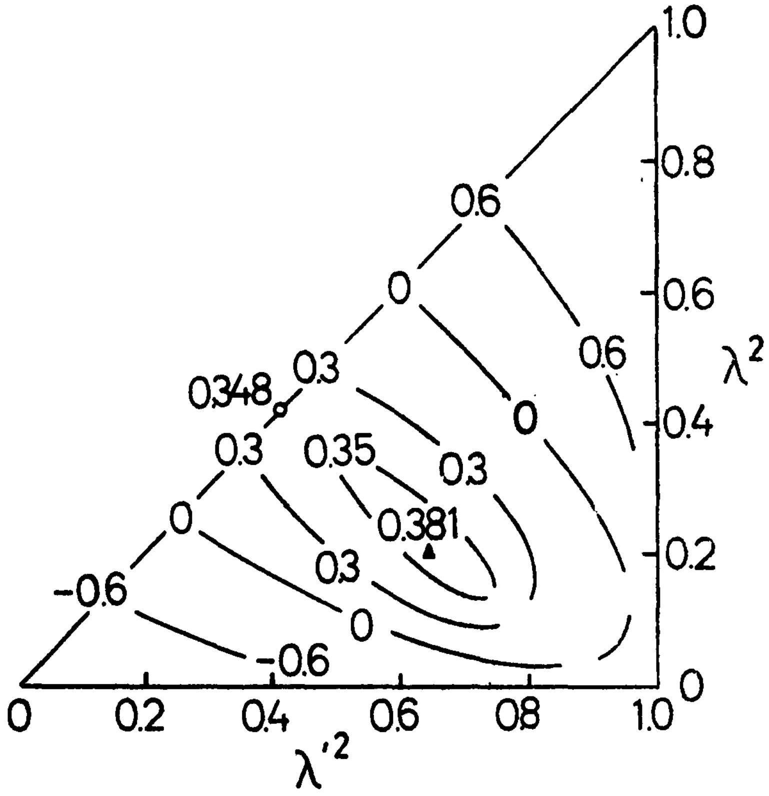

Figure 3. Contour map of binding energy (in a.u.)

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