On the origin of dynamic instability of molecular systems

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The vibronic origin of dynamic instability of molecular systems considered earlier, is here given a more complete and rigorous treatment. It is shown that the nonvibronic contribution to the curvature of the adiabatic potential arising due to nuclear displacements under fixed electronic density distribution, is always positive, and hence the only reason for dynamic instability is the pseudo Jahn–Teller effect. For some examples of special interest (planar equilateral NH_3, planar square CH_4 and linear H_3^+) the molecular excited states, responsible for the instability of the ground state, are revealed by means of *ab initio* calculations.

Key words: Pseudo Jahn–Teller effect—vibronic coupling—dynamic instability—excited states

1. Introduction

In the previous papers of one of us [1, 2] (see also Ref. [3]) the problem of the origin of dynamic instability of molecular systems was formulated, and it was shown that this instability is due to the vibronic mixing of the ground state with low-lying excited ones by nuclear displacements in the instability direction (pseudo Jahn–Teller effect [4]). At the points of the adiabatic potential (AP) surface which correspond with the dynamic instability, the interelectronic and internuclear repulsion is compensated by the electron–nuclear attraction and hence all the first derivatives of the AP with respect to the nuclear displacements vanish; but unlike the case of stable configurations, some (or all) of the second derivatives are negative, and any small nuclear displacement decompensates the equilibrium of forces with the repulsion being predominant.

The problem of the origin of such dynamic instability may be reduced to the consideration of the AP curvature K at the extremum in arbitrary directions Q.

The expression for K for the electronic ground state can be easily obtained in the second order perturbation theory with respect to small nuclear displacements Q [5]:

$$K = \langle 0| \left(\frac{\partial^2 H}{\partial Q^2}\right)_0 |0\rangle - 2 \sum_i{}' \frac{|\langle 0|(\partial H/\partial Q)_0|i\rangle|^2}{E_i - E_0}. \tag{1}$$

Here H is the adiabatic electronic Hamiltonian which includes all Coulomb interactions between electrons and nuclei, and $|i\rangle$ and E_i are the electronic wave functions and the energy levels for the equilibrium nuclear configuration, respectively.

In Eq. (1) the curvature K is essentially divided into two terms, $K = K_0 + K_v$. The first one,

$$K_0 = \langle 0| \left(\frac{\partial^2 H}{\partial Q^2}\right)_0 |0\rangle, \tag{2}$$

is the quantum average of the curvature operator in the electronic ground state. It determines the restoring force arising when the nuclei are displaced with respect to the "frozen" electronic distribution. The second term, being always negative, results from vibronic contribution. It takes into account the reduction of the force constant due to the relaxation of electrons making allowance for them to follow the nuclei.

In Refs. [1, 2] a semiquantitative consideration was performed and it was concluded that at least for neutral polyatomic systems the value of K_0 from Eq. (2) is always positive. Note that in all the previous (to Refs. [1–3]) papers (see e.g. [4a] and Refs. in [1–3]) this statement was postulated but not proved. The proof of the inequality $K_0 > 0$ means that the only reason for the dynamic instability of molecular systems is the predominance of the second term above the first one in Eq. (1).

Taking into account the importance of the problem, a more complete and rigorous treatment of the above statement is given in the present paper. First, the analytical deductions are carried out more carefully. Second, for most essential cases *ab initio* calculations were performed in order to reveal the vibronic contribution to the curvature of the AP in more detail. Third, the prevalent part of the vibronic contribution resulting from the interaction of the displaced nucleus with its own inner shell electrons (intraatomic instability) was eliminated by extending the basis set including derivative functions of the occupied atomic orbitals. In this way it becomes possible to single out the excited molecular states, with which the vibronic mixing of the ground state is the most essential reason for the instability.

The systems calculated in their unstable nuclear configuration are: planar equilateral triangular NH_3 (D_{3h} symmetry), planar square CH_4 (D_{4h} symmetry) and linear H_3^+ ($D_{\infty h}$ symmetry). In all these cases it occurs that $K_0 > 0$ as expected from analytical considerations, and the instability results from the pseudo Jahn–

Teller mixing of the electronic ground state with predominantly one excited state. The values of K calculated after Eq. (1) are in qualitative agreement with those evaluated by direct calculation of the energy surface in the nearest neighborhood of the points of instability.

2. Stability of the nuclear configuration in the frozen electron distribution

Consider for simplicity a closed shell molecule in its ground electronic state, its wave function being represented as a Slater determinant, $|0\rangle = N \det |\varphi_1 \varphi_2 \dots \varphi_n|$, where the molecular orbitals (MO) φ_i are of the LCAO form, $\varphi_i = \sum_\mu C_{\mu i} \chi_\mu$.

The curvature operator in Eq. (2) contains the part of the Hamiltonian dependent on nuclear coordinates only, i.e. $\partial^2 H / \partial Q^2 = \partial^2 V / \partial Q^2$, $V = V_{nn} + V_{en}$, where

$$V_{nn} = \frac{1}{2} \sum_{\alpha,\beta}^{N}{}' \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}; \qquad V_{en} = - \sum_{\alpha=1}^{N} \sum_{i=1}^{n} \frac{Z_\alpha}{|r_i - R_\alpha|}. \tag{3}$$

Here N is the number of atoms, Z_α are the nuclear charges and R_α and r_i are the nuclear and electron coordinates respectively. Let us evaluate the expression of K_0 corresponding to the nuclear displacement along one of the normal coordinates of the molecule Q_κ,

$$Q_\kappa = \sum_{\alpha=1}^{N} \sum_{i=1}^{3} (D^{-1})_{\kappa,\alpha_i} x_{\alpha_i}, \tag{4}$$

where D is the orthogonal matrix transforming the Cartesian coordinates of the nuclei to the normal coordinates Q_κ. With Eq. (3) the K_0 may be written as $K_0 = K_{nn}^0 + K_{en}^0$, where $K_{nn}^0 = (\partial^2 V_{nn} / \partial Q_\kappa^2)_0$, $K_{en}^0 = \langle 0|(\partial^2 V_{en} / \partial Q_\kappa^2)_0|0\rangle$. For the K_{nn}^0 it is easy to obtain that $K_{nn}^0 = K_1 + K_2$, where

$$K_1 = \sum_{(\alpha\beta)} \frac{Z_\alpha Z_\beta}{R_{0,\alpha\beta}^3} \left\{ - \sum_i [1 - 3(\cos \gamma_{\alpha\beta})_i^2] (D_{\kappa,\alpha_i}^2 + D_{\kappa,\beta_i}^2) \right.$$

$$\left. + 3 \sum_{i \neq j} (\cos \gamma_{\alpha\beta})_i (\cos \gamma_{\alpha\beta})_j (D_{\kappa,\alpha_i} D_{\kappa,\alpha_j} + D_{\kappa,\beta_i} D_{\kappa,\beta_j}) \right\}; \tag{5}$$

$$K_2 = 2 \sum_{(\alpha\beta)} \frac{Z_\alpha Z_\beta}{R_{0,\alpha\beta}^3} \left\{ \sum_i D_{\kappa,\alpha_i} D_{\kappa,\beta_i} [1 - 3(\cos \gamma_{\alpha\beta})_i^2] \right.$$

$$\left. - \sum_{i \neq j} D_{\kappa,\alpha_i} D_{\kappa,\beta_j} (\cos \gamma_{\alpha\beta})_i (\cos \gamma_{\alpha\beta})_j \right\}. \tag{6}$$

In Eqs. (5) and (6) R_α^0 are the nuclear coordinates at the equilibrium, $R_{0,\alpha\beta}$ is the equilibrium interatomic distance,

$$R_{0,\alpha\beta} = |R_\alpha^0 - R_\beta^0|, \qquad (\cos \gamma_{\alpha\beta})_i = \frac{(R_\alpha^0 - R_\beta^0)_i}{R_{0,\alpha\beta}}.$$

The sum is carried out over all the pairs of nuclei. Note, that the values of K_{nn}^0 may be both positive and negative depending on the angles $\gamma_{\alpha\beta}$ between the interatomic line and the direction of the corresponding nuclear displacement.

Since V_{en} is a sum of one-particle operators, we have:

$$K_{en}^0 = -\sum_\alpha Z_\alpha \sum_{i,j} D_{\kappa,\alpha_i} D_{\kappa,\alpha_j} \frac{\partial^2}{\partial x_{\alpha_i} \partial x_{\alpha_j}} (\Phi_\alpha^{(1)} + \Phi_\alpha^{(2)}), \tag{7}$$

where

$$\Phi_\alpha^{(1)} = \sum_{\mu \in \alpha} q_\mu \int \frac{[\chi_\mu(r - R_\alpha^0)]^2}{|r - R_\alpha|} dv,$$

$$\Phi_\alpha^{(2)} = \sum_{\beta \neq \alpha} \sum_{\mu \in \beta} q_\mu \int \frac{[\chi_\mu(r - R_\beta^0)]^2}{|r - R_\alpha|} dv. \tag{8}$$

In evaluating Eq. (8), as in Refs. [1, 2], the Mulliken formula

$$\chi_\mu \chi_\nu \approx \tfrac{1}{2} S_{\mu\nu}[\chi_\mu^2 + \chi_\nu^2], \tag{9}$$

was used giving rise to the orbital populations $q_\mu = \sum_\nu P_{\mu\nu} S_{\mu\nu}$, where $P_{\mu\nu}$ are the density matrix elements and $S_{\mu\nu}$ are the overlap integrals of the atomic orbitals. As it was pointed out in Refs. [1, 2], this approximation is correct up to $S_{\mu\nu}^2$.

The potential $\Phi_\alpha^{(1)}$ in Eq. (8) describes the intra-atomic electron-nuclear interactions, whereas $\Phi_\alpha^{(2)}$ represents the sum of the potentials at the points R_α generated by the electron distributions centered at the nuclei β. Using, for example, Slater type orbitals, rather simple analytical expressions for the nuclear attraction integral can be easily obtained [6], and then the second derivatives of the $\Phi_\alpha^{(1)}$ and $\Phi_\alpha^{(2)}$ can be evaluated. It can also be shown that for the atomic core $1s$-orbitals the second derivative of the $\Phi_\alpha^{(1)}$ yields the positive contribution to K_{en}^0 (because it describes the occurrence of the restoring force acting on the nuclei displaced from the center of the selfconsistent electron distribution) and its value is equal to $4/3\, q_{1s}\xi_{1s}^3$, where q_{1s} is the core orbital population ($q_{1s} \approx 2$) and ξ_{1s} is the Slater exponent of the $1s$ AO (Refs. [1, 2]). Since $\xi_{1s} \approx Z_\alpha$ the contribution to K_{en}^0 from the core electrons of the α-nucleus is approximately equal to $8/3 Z_\alpha^4$ and rapidly increases with Z_α. For example for the out-of-plane displacement of the N atom of the planar NH_3 molecule this value is very large (194.1 mdyn/Å) as compared with the resulting force constant for this displacement (≈ -0.26 mdyn/Å). As for the p-type AO, the maximum of its electron density $[\chi_\mu(r - R_\alpha^0)]^2$ is somewhat displaced from the point R_α^0, thus the contribution to K_{en}^0 of p orbitals may be both negative (equal to $-\tfrac{4}{15} q_p\xi_p^3)^1$, if the nucleus is displaced along the axis of the corresponding p orbital, and positive (equal to $\tfrac{2}{15} q_p\xi_p^3$), if the nucleus is displaced perpendicularly to the axis of the p function. Similar estimations may be performed also for other types of AO's (d, f etc.). The corresponding contributions to K_0 may be both positive and negative.

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1   In Refs. [1, 2] the minus in this term was omitted by mistake (this was pointed out by M. M. Mestechkin). This, however does not affect the main conclusion that $K_0 > 0$ for the ground state. Indeed the positive contributions of the $1s$ orbitals to K_0 are always much larger than that of the negative contribution of the p functions. Furthermore, even in the case of the MO consisting of atomic p orbitals only (as it may occur, for example, in the excited state of the hydrogen molecule) $K_0 > 0$ at the equilibrium point due to the positive contribution to K_0 from nuclear Coulomb repulsion

Nevertheless, due to the difference between the Slater exponents the contribution to K_0 from the d, f and other types of AO's are much less than the very large positive contribution of the core orbitals.

The contribution to K_{en}^0 resulting from the $\Phi_\alpha^{(2)}$ magnitude may be expressed by the following general formula:

$$
-\sum_\alpha Z_\alpha \sum_{i,j} D_{\kappa,\alpha_i} D_{\kappa,\alpha_j} \frac{\partial^2}{\partial x_{\alpha_i} \partial x_{\alpha_j}} \Phi_\alpha^{(2)}
$$

$$
= -(1-C)K_1 + (1-C) \sum_{(\alpha\beta)} \frac{1}{R_{0,\alpha\beta}^3} \left\{ \sum_i [1 - 3(\cos \gamma_{\alpha\beta})_i^2] \right.
$$

$$
\times (Z_\alpha \Delta Z_\beta D_{\kappa,\alpha_i}^2 + Z_\beta \Delta Z_\alpha D_{\kappa,\beta_i}^2)
$$

$$
\left. -3 \sum_{i \neq j} (\cos \gamma_{\alpha\beta})_i (\cos \gamma_{\alpha\beta})_j (Z_\alpha \Delta Z_\beta D_{\kappa,\alpha_i} D_{\kappa,\alpha_j} + Z_\beta \Delta Z_\alpha D_{\kappa,\beta_i} D_{\kappa,\beta_j}) \right\}, \quad (10)
$$

where K_1 is given by Eq. (5), ΔZ_α is the value of the charge transfer from the α atom due to the chemical bonding, $\Delta Z_\alpha = Z_\alpha - \sum_{\mu \in \alpha} q_\mu$, and C is a constant which, as a rule is less than unity, if the interatomic distance has the order of magnitude of the usual chemical bond ($R_{0,\alpha\beta} \approx 2.0$ a.u.). It can be shown that some terms in K_{en}^0 and K_{nn}^0 cancel in pairs. The remaining terms in Eqs. (6) and (10) are proportional to $\sum_{(\alpha\beta)} Z_\alpha Z_\beta / R_{0,\alpha\beta}^3 \sum_{i,j} D_{\kappa,\alpha_i} D_{\kappa,\beta_j}$, and with Z_α, $Z_\beta > 1$, $R_{0,\alpha\beta} \approx 2.0$ a.u. these terms are much less than the positive contribution to K_0 due to the interaction of the nuclei with their own core electrons (proportional to $\sum_\alpha Z_\alpha^4 \sum_{i,j} D_{\kappa,\alpha_i} D_{\kappa,\alpha_j}$).

Thus, for the displacement of the nuclei having fulfilled inner shells the value of K_0 is positive. It is obvious that the most "unfavorable" for the above proof are the cases when only hydrogen atoms (with minimal value of Z_α and without inner electrons) are involved in the normal displacement under consideration. For these cases the above estimations are rather rough. In Sect. 4 we consider several "unfavorable" molecules for which the value of K_0 at the unstable nuclear configuration was obtained by use of *ab initio* MO-LCAO-SCF wave functions. In all considered cases the value of K_0 is positive.

3. Two types of the electron relaxation: the "floating" of the atomic orbitals and the change of the LCAO coefficients

In carrying out the SCF calculations of the potential energy surface of the many electron system one finds the adiabatic one-electron MO's $\{\varphi_i(r, Q)\}$ which depend on the nuclear coordinates Q parametrically. For small Q value

$$
\varphi_i(r, Q) = \varphi_i(r, 0) + \left(\frac{\partial \varphi_i(r, Q)}{\partial Q} \right)_0 Q + \cdots . \quad (11)
$$

In several works (e.g. see Refs. [7–9]) it was suggested to use the "floating" basis set for vibronic calculations. Within this approach the many electron wave

functions are constructed from the AO's floating with the nuclei, $\chi_\mu = \chi_\mu(r, Q)$. With the use of the MO-LCAO approximation one obtains

$$\left(\frac{\partial\varphi_i(r, Q)}{\partial Q}\right)_0 = \sum_{\mu=1}^{m} C_{\mu i}(0)\left(\frac{\partial\chi_\mu(r, Q)}{\partial Q}\right)_0 + \sum_{\mu=1}^{m}\left(\frac{\partial C_{\mu i}}{\partial Q}\right)_0 \chi_\mu(r, 0). \tag{12}$$

The first term in Eq. (12) describes the floating of the basis orbitals with the nuclei, whereas the second one represents the corresponding change of the shape of the MO due to the changes in the LCAO coefficients.

In what follows we show how the floating of the electron distribution with the nuclear displacements can be taken into account with a space-fixed basis set of functions commonly used in the crude adiabatic (Born–Oppenheimer) approximation. This approach, distinguished from direct calculation of AP surface with the floating basis set, allows for a more efficient use of symmetry considerations resulting in the reduction of computational work. It reveals not only the direction of instability and curvature of the AP as such, but also the structural details responsible for their origin.

Consider for simplicity the hydrogen atom placed at the origin in its ground state $\varphi_{1s}(r, 0) = N e^{-\alpha r}$. Displace the proton from the origin by a small value Q. It is obvious that the electron follows the nucleus and its wave function becomes $\varphi_{1s}(r, Q) = N e^{-\alpha|r-Q|}$. Presenting $\varphi_{1s}(r, Q)$ as a perturbation series in Q,

$$\varphi_{1s}(r, Q) = \varphi_{1s}(r, 0) + \sum_j{}'\varphi_j(r, 0)\frac{\langle\varphi_{1s}(r, 0)|(\partial H/\partial Q)_0|\varphi_j(r, 0)\rangle}{\varepsilon_{1s} - \varepsilon_j}Q + \cdots \tag{13}$$

one finds that about 93% of the last term in (13), describing the electron relaxation, is due to the contribution of the excited states of the continuum [10]. On the other hand, $\varphi_{1s}(r, Q)$ may be expressed as a power series in Q, $\varphi_{1s}(r, Q) = \varphi_{1s}(r, 0) + (\partial\varphi_{1s}(r, Q)/\partial Q)_0 Q + \cdots$. Comparing it with Eq. (13) one obtains

$$\left(\frac{\partial\varphi_{1s}(r, Q)}{\partial Q}\right)_0 = \sum_j{}'\varphi_j(r, 0)\frac{\langle\varphi_{1s}(r, 0)|(\partial H/\partial Q)_0|\varphi_j(r, 0)\rangle}{\varepsilon_{1s} - \varepsilon_j}. \tag{14}$$

It can be seen that the function $(\partial\varphi_{1s}(r, Q)/\partial Q)_0$ effectively serves as an excited state of the hydrogen atom the mixing of which allows the electron to follow the nucleus. On the other hand, this function is certainly not a real excited state of the hydrogen atom and cannot be observed spectroscopically or in any other way; it may be called "*arti* AO".

For the many electron wave function an expression similar to Eq. (14) may be presented. If the wave function can be represented in the form of a single Slater determinant, then

$$\left(\frac{\partial}{\partial Q}\Psi(r, Q)\right)_0 = \sum_{i=1}^{n} \det\left|\varphi_1(r, 0)\cdots\left(\frac{\partial\varphi_i(r, Q)}{\partial Q}\right)_0\cdots\varphi_n(r, 0)\right|. \tag{15}$$

From Eq. (12) it follows that, if the basis set is extended including the functions $\tilde{\chi}_\kappa = (\partial\chi_\kappa(r, Q)/\partial Q)_0$, then $(\partial\varphi_i(r, Q)/\partial Q)_0 = \sum_\kappa d_\kappa\varphi_\kappa(r, 0)$ and the derivative of

the many electron function is a sum of single-excited configurations. Thus the extension of the basis set including the functions $\tilde{\chi}_\kappa$ allows to construct excited configurations which may effectively take account of the part of the electron relaxation resulting from the electron (intraatomic) floating with the nuclei. Note that, as for the above case of the hydrogen atom, the excited configurations formed by the excitation of the electron to the MO's mainly composed from $\tilde{\chi}_\kappa$ do not correspond to any real excited state of the molecular system. These *arti* MO's merely serve to substitute the infinite sum over the all excited states in Eq. (1) and thereby effectively take into account the vibronic mixing of these states with the ground one. The need of extension of the basis set with such additional *arti* AO's in calculations of nonadiabatic matrix elements was pointed out by Habitz and Votava [11]. In this paper it was also shown that the role of higher order derivatives of the basis functions is not essential.

The explicit form of the functions $\tilde{\chi}_\kappa$ may be obtained by direct differentiation of $\chi_\kappa(r, Q)$ with respect to the displacements Q. Thus, for example, the differentiated Slater $1s$-type AO is $\tilde{\chi}_{1s} = \partial \varphi_{1s}^{Sl}/\partial z|_0 = N'(z/r) e^{-\alpha r}$, so the angular part of the resulting function is like that of the p type AO, while its radial distribution corresponds to the $1s$ type AO. The differentiated Gaussian s function is similar to the corresponding Gaussian p function possessing the same Gaussian exponent as the s function.

If the functions $\tilde{\chi}_\kappa$ are added to the complete basis set, an overcompleteness of the basis set occurs. However in the quantum chemical calculations restricted basis sets are usually employed. The problem of the overcompleteness of such basis sets may be reduced to the analysis of the positive definiteness of the matrix of the overlap integrals [12]. In so far as functions $\tilde{\chi}_\kappa$ and the occupied AO's are differently localized in space, the overlap matrix remains, as a rule, positively defined.

4. Numerical results

In this Section the results of *ab initio* calculations of some molecular systems in their unstable nuclear configurations are presented. For each system the value of K_0 and values of various relaxation contributions to the curvature of the AP surface K are evaluated. The calculations of the electron wave functions and of the energy levels were carried out by the restricted Hartree–Fock method with the use of STO-3G basis set. The excited states were formed by electron excitation within the approximation of "frozen" orbitals. The energies of the excited states were evaluated as differences between the energies of the corresponding MO's taking account of corrections due to the change in Coulomb and exchange interactions.

4.1. Planar equilateral NH_3

The planar NH_3 molecule is considered at the configuration of an equilateral triangle (D_{3h} symmetry). It is known that in this configuration the NH_3 molecule
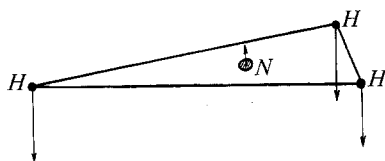
Fig. 1. Out-of-plane A_2'' distortion of planar equilateral NH_3 molecule

is unstable with respect to the low symmetry A_2''-type out-of-plane distortion (Fig. 1). The ground state wave function of $^1A_1'$ symmetry corresponds to the electron configuration $1a_1'^2 2a_1'^2 e_x'^2 e_y'^2 1a_2''^2$. The value of K_0 obtained with the use of this wave function in accordance with Eq. (2) is equal to 201.11 mdyn/Å, the largest part of this great positive value (equal to 194.12 mdyn/Å) owing to the interaction of the frozen core $1s$-electrons of the N atom with the nucleus. The resulting value of K obtained by the direct calculation of the potential energy surface along the normal coordinate of the A_2'' symmetry is equal to -0.26 mdyn/Å. If the basis set is extended by including the derivatives of the occupied AO's, then the vibronic mixing of the corresponding configurations of the A_2'' symmetry takes into account the intraatomic electron floating with the nuclear displacement. The sum of the negative contribution to K resulting from these configurations is equal to -200.68 mdyn/Å. Thus, after excluding the strong positive contribution to K_0 due to the electron following its own nuclei, the value of K_0 becomes equal to 0.43 mdyn/Å. The calculations show that the energy of the above excited states appropriate to the *arti* AO's is rather large. For example, the energy of the excited state formed by the electron excitation from the inner shell $1s$ AO of the N atom to the $\partial\chi_{1s_N}/\partial Q_{A_2''}$ orbital is approximately equal to 5000 eV. However, in spite of the fact that the corresponding denominator in Eq. (1) is very large, the matrix element $\langle\chi_{1s_N}|(\partial H/\partial Q_{A_2''})_0|(\partial\chi_{1s_N}/\partial Q_{A_2''})_0\rangle$, being the numerator of the respective term, is large, too, so the vibronic contribution of this term in K is significant. Thus it can be seen that the including of the artifunctions $\tilde{\chi}_\kappa$ in the basis set is a convenient method of taking account of the electron intraatomic floating with the nuclear displacements.

Now, the low-lying excited states giving the largest contribution to the nuclear instability may be revealed. The lowest excited state of the A_2'' symmetry ($E^{calc.} = 4.6$ eV), formed by the electron excitation from the lone pair $1a_2''(|2p_{z_N}\rangle)$ MO to the Rydberg $3s$ AO of the N atom, gives a negligibly negative contribution to the curvature of AP surface equal to -0.06 mdyn/Å. The most significant negative contribution to K equal to -0.62 mdyn/Å results from the excited state corresponding to the electron excitation from the $1a_2''(|2p_{z_N}\rangle)$ MO to the antibonding $a_1'(C_1|2s_N\rangle - C_2|1s_{H_1}\rangle - C_2|1s_{H_2}\rangle - C_2|1s_{H_3}\rangle)$ MO. Although the energy of this excited state is rather large ($\Delta E^{calc.}$ read off the ground state is equal to 14 eV), it is the vibronic mixing with this state that leads to the negative curvature of the AP (equal to -0.25 mdyn/Å) and, thereby, to the instability of the planar NH_3 molecule (see Fig. 2). This confirms the statement that the most important contribution to the vibronic effects comes from strongly bonding or antibonding orbitals.
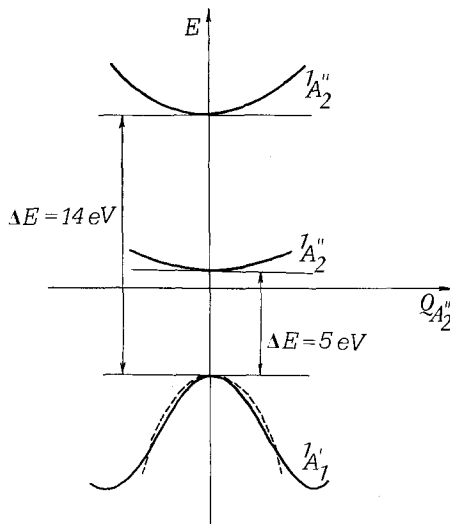
Fig. 2. Adiabatic potential energies of NH_3 molecule versus A_2'' type nuclear displacements. Dotted line is $KQ_{A_2''}^2/2$ with K taken from Eq. (1). Solid line schematically represents the results of direct *ab initio* calculations of the ground state energy surface

4.2. Planar square CH_4

Another example is the planar square CH_4 molecule of D_{4h} symmetry. It is unstable with respect to the propeller type B_{2u} nuclear displacement which distorts the initial configuration toward the tetrahedron shape (Fig. 3). This is one of the unfavorable cases for the general theory of Section 2, because only the hydrogen atoms with small Z_α and without inner shells are involved in B_{2u} displacement. The electron configuration appropriate to the $^1A_{1g}$ ground state wave function is $1a_{1g}^2 2a_{1g}^2 e_u^4 a_{2u}^2$. The value of K_0 calculated with this wave function is equal to 2.86 mdyn/Å. The sum of the negative contributions of the relaxation due to the electron floating with the nuclei is equal to -2.82 mdyn/Å. Among the excited states arising from the valence-shell excitations the most essential vibronic mixing contribution is given by the excited state formed by the electron transfer from the nonbonding MO of the a_{2u} ($|2p_{z_C}\rangle$) symmetry to the MO $b_{1g}(|1s_{H_1}\rangle - |1s_{H_2}\rangle + |1s_{H_3}\rangle - |1s_{H_4}\rangle)$ which is 11 eV above the ground state. The corresponding negative contribution, equal to -0.55 mdyn/Å, causes the instability of the planar square configuration of the CH_4 molecule with respect to the B_{2u} type displacement. The magnitude of the resulting negative curvature of the AP qualitatively agrees with the value of K obtained by the direct calculation of the AP energy surface (Fig. 4).
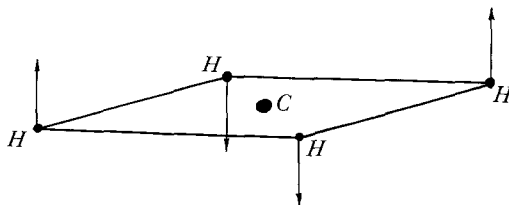

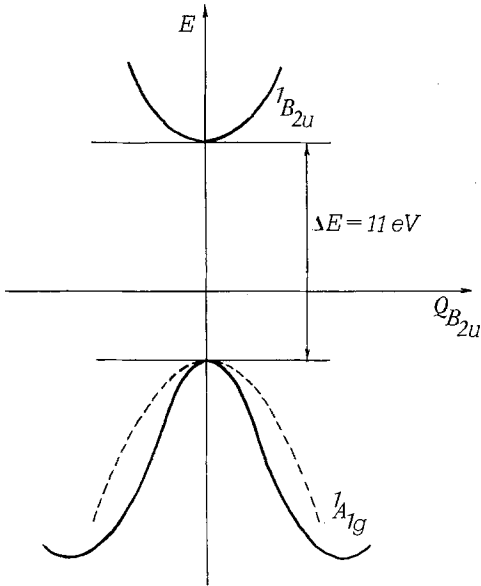**Fig. 3.** Propeller type B_{2u} distortion of planar square CH_4 molecule

E

$^1B_{2u}$

$\Delta E = 11\,eV$

$Q_{B_{2u}}$

$^1A_{1g}$

Fig. 4. The same as in Fig. 2 for CH_4 molecule versus B_{2u} type nuclear displacements.

4.3. Linear H_3^+

The linear H_3^+ molecule ($D_{\infty h}$ symmetry) is unstable with respect to the bending distortion of the Π_u type which leads to the stable equilateral triangle configuration (Fig. 5). This is also an unfavorable case for the above proof of the positiveness of K_0, since only hydrogen atoms are involved in the Π_u displacement and it is a system with a scarceness of electron density at the nuclei. The calculations

H H

H

Fig. 5. Bending type Π_u distortion of linear H_3^+ molecule

E

$^1\Pi_u^+$

$\Delta E = 12\,eV$

Q_{Π_u}
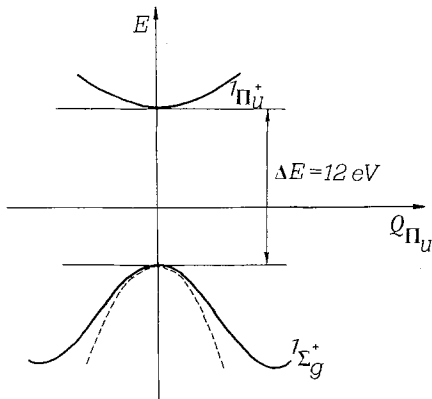
$^1\Sigma_g^+$

Fig. 6. The same as in Fig. 2 for H_3^+ molecule versus Π_u type nuclear displacements

indicate that in this case K_0 is positive, too (the value of K_0 with account of the electron floating with the nuclei is equal to 0.13 mdyn/Å). The pseudo Jahn–Teller mixing of the excited state of Π_u symmetry formed by the p-functions of the hydrogen atoms results in the negative curvature of AP, the value of K being equal to $-0,11$ mdyn/Å, while the evaluation of K by means of the direct calculations of the AP energy surface yields K equal to $-0,10$ mdyn/Å (Fig. 6).

Thus in the unfavorable cases, as in general, it occurs that $K_0 > 0$, and the dynamic instability of the above molecules is also due to the pseudo Jahn–Teller coupling of the ground state with one of the excited states.

5. Conclusions

The present work results in following conclusions.

1. *Ab initio* calculations of the molecular systems and extended general analytical estimations completely confirm the earlier statement of one of us that *the only reason of dynamic instability of polyatomic molecular systems is the pseudo Jahn–Teller effect*, i.e. *the vibronic mixing of the ground state with the excited ones* [1, 2].

2. With the use of *ab initio* calculations it was shown that, in contrast to the widespread thinking, *the pseudo Jahn–Teller effect may be essential* (in the sense that it may lead to instability of molecular systems with all the consequences for the observable properties of such systems [5]) *even for electronic states with large energy level gaps* of about $10 \div 15$ eV. The vibronic effects are most essential when the mixing states (not necessarily being the nearest in energy) involve strongly bonding or antibonding orbitals.

3. The floating of the atomic inner (core) electrons, not directly related to the vibronic effects under consideration, can be eliminated by means of including derivatives of the occupied AO's (additional *arti* AO's) into the basis set of MO calculations.

In carrying out the numerical calculations some approximations were introduced. In particular, the excited states were taken within the assumption of "frozen" orbitals. Even within this approximate treatment the qualitative features of the AP and, especially, the vibronic origin of the molecular instability were evaluated and proved with great trustworthiness, and this confirms the correctness of the above listed conclusions.

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