

A Practical Computational Approach to Study Molecular Instability Using the Pseudo-Jahn–Teller Effect

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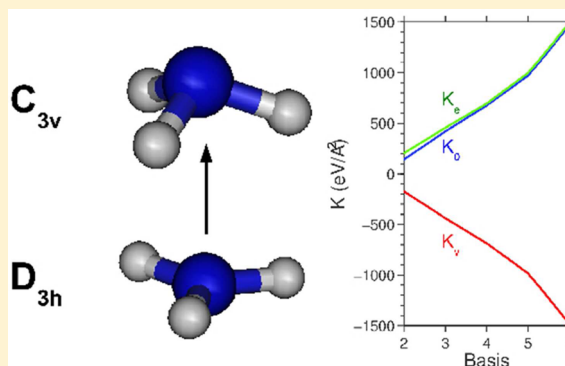
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S Supporting Information

ABSTRACT: Vibronic coupling theory shows that the cause for spontaneous instability in systems presenting a nondegenerate ground state is the so-called pseudo-Jahn–Teller effect, and thus its study can be extremely helpful to understand the structure of many molecules. While this theory, based on the mixing of the ground and excited states with a distortion, has been long studied, there are two obscure points that we try to clarify in the present work. First, the operators involved in both the vibronic and nonvibronic parts of the force constant take only into account electron–nuclear and nuclear–nuclear interactions, apparently leaving electron–electron repulsions and the electron’s kinetic energy out of the chemical picture. Second, a fully quantitative computational appraisal of this effect has been up to now problematic. Here, we present a reformulation of the pseudo-Jahn–Teller theory that explicitly shows the contributions of all operators in the molecular Hamiltonian and allows connecting the results obtained with this model to other chemical theories relating electron distribution and geometry. Moreover, we develop a practical approach based on Hartree–Fock and density functional theory that allows quantification of the pseudo-Jahn–Teller effect. We demonstrate the usefulness of our method studying the pyramidal distortion in ammonia and its absence in borane, revealing the strong importance of the kinetic energy of the electrons in the lowest a_2'' orbital to trigger this instability. The present tool opens a window for exploring in detail the actual microscopic origin of structural instabilities in molecules and solids.



1. INTRODUCTION

A central piece of theoretical chemistry is the interconnection between molecular geometry and electronic structure. In fact, the models behind this correlation are essential to understanding the chemical bond as they include concepts like hybridization,^{1–3} electron-pair repulsions,^{4,5} etc. It seems natural, then, that vibronic coupling theory^{6–8} that describes quantum-mechanically the changes in electronic structure due to distortions in molecular shape and vice versa should be used to quantify these ideas and give them mathematical form. Among the most successful applications of this theory are the Jahn–Teller (JT), the Renner–Teller (RT), and the Pseudo-Jahn–Teller (PJT) effects that encompass all possibilities to describe spontaneous motions that break the symmetry of a molecule or crystal.⁷ Many important phenomena like colossal magnetoresistance in the manganites,⁹ ferroelectricity,^{7,10} spin-crossover,¹¹ reactivity,^{12–14} dynamics,⁸ et cetera are directly associated with these effects, and the theory has inspired significant discoveries like the high-temperature superconductivity in the cuprates.¹⁵ While the appearance of the JT and RT

effects is somewhat constrained by the strong condition that the system must display an orbitally degenerate state, the PJT effect is free from this restriction and is present, to some degree, in all systems.

Although similar in name, the JT and PJT effects are, nevertheless, quite different in how they act. While the first creates nonisotropic forces that distort the system, the second lowers the force constant, leading to a spontaneous instability with an intermediate transition state. However, the most striking difference between both effects resides in their physical meaning. While the JT effect describes the forces that electrons produce when the system displays a degenerate orbital state,^{7,16} the PJT describes the energetics associated with the change in the distribution of electrons¹⁷ (see section 2.1), which can be directly attributed to the transformation of chemical bonding.^{7,18} Thus, even though the nomenclature for both distortion

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mechanisms is similar, the phenomena they are associated with are very different.

The importance of the PJT effect cannot be underestimated. Its most common application is the explanation of the shape of molecules^{7,19,20} and solids,^{7,9,10,21} including linear systems where it has been shown to be stronger than the RT effect and the sole source of instability in this class of molecules.²⁰ Moreover, many interesting phenomena like, for example, the observation of symmetry-forbidden transitions due to vibronic coupling (the so-called Herzberg–Teller effect in spectroscopy²²) or the barrier controlling tunneling in JT systems are directly or strongly influenced by the PJT effect.^{23,24} It has also inspired the concept of order–disorder phase transitions in oxide ferroelectrics,^{7,10,25} used to explain transition states in reactions,^{12–14} and has given rise to the discovery of new materials like the vibronic spin-crossover systems.¹¹

As the PJT effect deals with how electron distribution modifies the molecular structure, it has to be necessarily connected to other chemical theories describing the same phenomena like, for example, Valence-Shell-Electron-Pair-Repulsion (VSEPR) theory.^{4,5} This point requires thorough clarification as various models are based on completely different grounds and are connected to different terms of the molecular Hamiltonian. For instance, interpretation of PJT theory results is usually connected to the electron–nuclear potential; VSEPR theory is largely associated with classical electron–electron repulsions; Ruedenberg’s bonding theory²⁶ puts an emphasis on changes in the kinetic energy, and recent Quantum Theory of Atoms in Molecules simulations associate bonding to the preferred exchange-correlation paths.²⁷ These differences are better observed with the use of a model system. A prototypical example of both VSEPR and PJT theories is the ammonia molecule (Figure 1). In the first case, the triangular to pyramidal distortion is attributed to the electronic repulsion between the bonding electron pairs situated in between nitrogen and hydrogen with the lone-pair directed along the axis of the molecule.⁴ On the other hand, PJT theory claims that the stabilization energy comes from the mixing of the

$N(2p_z)$ orbital with $H(1s)$ ones, something allowed in pyramidal C_{3v} symmetry but not in the triangular D_{3h} one.^{7,28} In this context, the PJT approach has a clear advantage over other theories due to the theorem of instability⁷ (see also ref 28). It states (see below for more details) that upon the separation of the total force constant, K , in nonvibronic (K_0) and vibronic (K_v) contributions:

$$K = K_0 + K_v \quad (1)$$

the nonvibronic ones always yield $K_0 > 0$. One of the main conclusions that can be extracted from this theorem is that the *only* possibility for a molecule to distort is through the JT (for strictly degenerate electronic states in nonlinear systems) or the PJT effects (in any other case including degeneracy in linear systems²⁰). Thus, all symmetry-breaking distortions in non-degenerate systems can be reduced to PJT theory even though in the latter, K_0 and K_v only depend on the operator describing electron–nuclear interactions (see section 2.1). However, in some cases this seems to be in contradiction with an ab initio decomposition of the total energy into kinetic, electron–nuclear, electron–electron, and nuclear–nuclear contributions. In Figure 1 we see that electron–nuclear contributions increase the energy in ammonia as the distortion is performed, while electron–electron ones lower it. This result seems to be in agreement with VSEPR models, but in appearance (see below), it is difficult to explain using PJT theory.

Another important problem with theory is the difficulty to quantify the model parameters. While the theory is presented in terms of well-defined integrals (see section 2.1), in practice these are difficult to obtain and not implemented in standard codes, and the usual way to proceed (see e.g., ref 23) is to fit ab initio energy surfaces with a PJT model. However, these results are strongly dependent on the details of the model and the calculations.¹⁹ In particular, the constants are very dependent on how many states are included in the fit, and the obtained values are, in most cases, unreliable. In the literature, there are several approaches to tackle, at least, part of this problem. An approach used by Cimpoeșu and co-workers^{29,30} involves the use of the coupled-perturbed Hartree–Fock equations to obtain the orbital vibronic constants, leading to the concept of *vibronic orbitals*.⁷ However, application of this method shows that the most important orbital couplings are not those expected from simple arguments, thus making difficult the connection of calculation and chemical intuition. Thus, this approach is unattractive to employ due to the difficulty to extract significant information on the origin of the changes in the bonding pattern. Moreover, Sato et al.³¹ successfully employed the Hartree–Fock equations to calculate the related but more restricted JT vibronic constants providing, at the same time, evidence of the importance of the details of the electron distribution in the active orbitals. Another approach by Bersuker et al.³² reformulates the calculation of the vibronic and nonvibronic contributions to the force constant. While these magnitudes are large compared with the full force constant in ref 32, an attempt to remove a common large factor in K_v and K_0 leads, sometimes, to negative contributions from the new K_0 value (\tilde{K}_0), which complicates the interpretation of instabilities from the idea of the theorem of instability. Finally, Bearpark and co-workers³³ employed symmetry constraints over the CASSCF wave function to restrict excited-state admixture and test for the presence of the PJT effect on organic molecules. While they nicely and very directly show the presence of PJT in the distortion of some molecules, this

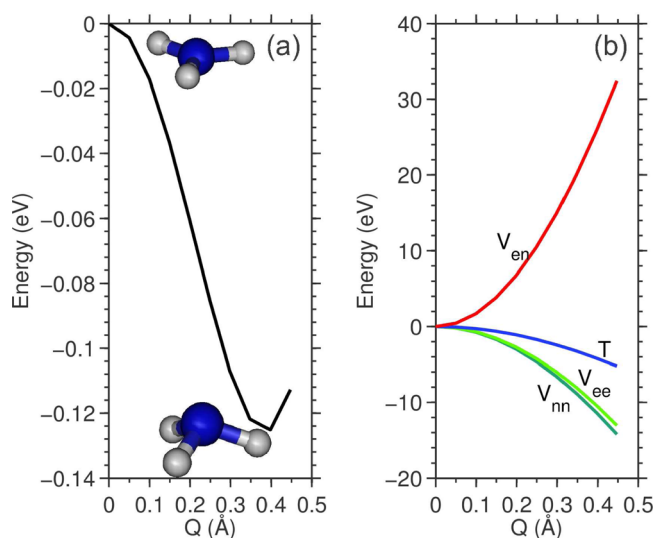


Figure 1. Calculation of the energy surface cross-section along the spontaneous off-plane movement of the N atom in ammonia (a) and the decomposition of the variation of the total energy into electron kinetic, electron–nuclear, electron–electron, and nuclear–nuclear interactions (b).

approach does not allow one to calculate *all* contributions to the PJT effect, and some systems displayed instabilities not described within the approach.

In order to clarify some of these issues, the main objectives of the work are (1) determining where important chemical magnitudes like electron–electron repulsions or the kinetic energy are hidden within the exact PJT expressions so that a connection to usual chemical intuition can be established and (2) producing a practical computational approach that allows determination and quantification of the factors triggering molecular instability in a meaningful way from a chemical point of view.

In order to do so, a brief overview of standard PJT theory is given in section 2.1. In section 2.2, we deduct the exact PJT equations in such a way that their connections with operators like the electron–electron interactions or the kinetic energy are clearly established. In section 2.3, a working scheme to apply PJT theory to one-electron methods, like Hartree–Fock (HF) and Density Functional Theory (DFT), is proposed. Interestingly, it is found that while the formalism is very similar to the exact PJT formulation, the approximations made in *ab initio* methods to the wave function produce some qualitative differences with the canonical theory. Finally, in section 4, this approach is applied to two model systems, the ammonia and borane molecules, to show how it leads to results that are very informative with regard to the effect of electronic structure over the geometry.

2. THEORY

Our starting point is the molecular Hamiltonian containing kinetic energy (T), electron–nuclear (V_{en}), electron–electron (V_{ee}), and nuclear–nuclear (V_{nn}) operators:

$$H = T(\mathbf{r}) + V_{\text{ee}}(\mathbf{r}) + V_{\text{en}}(\mathbf{r}, \mathbf{R}) + V_{\text{nn}}(\mathbf{R}) \quad (2)$$

where \mathbf{r} and \mathbf{R} denote, respectively, the dependency over all electron and nuclear coordinates, respectively. It is customary to set a frozen reference geometry, \mathbf{R}_r , and describe the nuclear position as a distortion from that point, $\mathbf{Q} = \mathbf{R} - \mathbf{R}_r$. Under these premises, it is possible to divide the full Hamiltonian into a reference part, H_r , only valid for the reference configuration, and a vibronic contribution, W , that contains information on the changes occurring with the distortion:

$$H = H_r(\mathbf{r}, \mathbf{R}_r) + W(\mathbf{r}, \mathbf{Q}) \quad (3)$$

where

$$H_r(\mathbf{r}, \mathbf{R}_r) = T(\mathbf{r}) + V_{\text{ee}}(\mathbf{r}) + V_{\text{en}}(\mathbf{r}, \mathbf{R}_r) + V_{\text{nn}}(\mathbf{R}_r) \quad (4)$$

$$W(\mathbf{r}, \mathbf{Q}) = V_{\text{en}}(\mathbf{r}, \mathbf{R}) - V_{\text{en}}(\mathbf{r}, \mathbf{R}_r) + V_{\text{nn}}(\mathbf{R}) - V_{\text{nn}}(\mathbf{R}_r) \quad (5)$$

The JT and PJT models are all based on a perturbative approach to eq 3 where the vibronic operator is expanded over a few symmetrized distortion coordinates \mathbf{Q} and the full Hamiltonian evaluated using the eigenfunctions of H_r that we denote Ψ_i . As seen from eq 4, these functions are the exact electronic wave functions at the reference geometry. In order to simplify the notation, we will now drop all the dependency of the operators on the electronic and nuclear coordinates and call Ψ_0 to the ground state at \mathbf{R}_r and Ψ_i ($i = 1, 2, \dots$) to the excited states for this geometry ordered in increasing energy.

2.1. Brief Pseudo Jahn–Teller Theory Overview. The concept of the PJT effect can be illustrated over a simple two-state model using eq 3 and expanding the vibronic operator to

second-order along a single nontotally symmetric coordinate, Q

$$W \approx H'Q + \frac{1}{2}H''Q^2 + \dots \quad (6)$$

where the prime symbol ($'$) denotes derivatives with respect to the nuclear coordinates (i.e., $H' \equiv (dH)/(dQ)$, $H'' \equiv (d^2H)/(dQ^2)$). The linear term in eq 6 will produce an interaction between two states, i and j , only if the product $\Psi_i \otimes \Psi_j$ spans the irrep of Q . In order to quantify this effect, the Hamiltonian of eq 3 can be evaluated with these two states to find the vibronic matrix:

$$\langle \Psi_i | H | \Psi_j \rangle = \begin{pmatrix} E_i + \frac{1}{2}K_i Q^2 & F_{ij}Q \\ F_{ji}Q & E_j + \frac{1}{2}K_j Q^2 \end{pmatrix} \quad (7)$$

where $E_i = \langle \Psi_i | H_r | \Psi_i \rangle$, $K_i = \langle \Psi_i | H'' | \Psi_i \rangle$, and $F_{ij} = F_{ji} = \langle \Psi_i | H' | \Psi_j \rangle$ are, respectively, the energy of each state at the reference configuration, the primary force constants, and the linear PJT coupling constant between states i and j . In order to find the energy of the states as the geometry is changed, the matrix eq 7 must be diagonalized. In this process, as the coupling constant F_{ij} is nonzero, the final wave functions will become an admixture of Ψ_i and Ψ_j . It is important to note that in the absence of PJT coupling the electronic wave functions and all their derived properties (electron density, etc.) would remain frozen to their values at the reference geometry.

In order to check whether the mixing with excited states can trigger the instability of a system, the force constant of the ground state, K , is obtained with the help of the Hellmann–Feynman theorem⁷ that states that the force is independent of the derivative of the wave function with respect to nuclear coordinates:

$$K = \langle \Psi_0 | H'' | \Psi_0 \rangle + \langle \Psi_0 | H' | \Psi' \rangle + \langle \Psi' | H' | \Psi_0 \rangle \quad (8)$$

From the arguments above, it is clear that the first term found in eq 8 corresponds with the nonvibronic (K_0) contribution described in eq 1 and the other two with the vibronic one (K_v). Using the solutions of eq 7 and generalizing it to account for many excited states (α), the vibronic contribution can be written

$$K_v = -2 \sum_{\alpha} \frac{|F_{0\alpha}|^2}{E_{\alpha} - E_0} \quad (9)$$

The above definition clearly proves that $K_v < 0$ for the electronic ground state and thus shows that the vibronic terms favor instability. However, we have no *a priori* indication of the sign of K_0 . This brings the second important concept in PJT theory: the theorem of instability^{7,28} shows that the value of the primary force constant in the ground state, K_0 , is always positive. Thus, the only possibility for the appearance of a spontaneous instability that breaks the symmetry of a system is

$$K_0 < |K_v| \quad (10)$$

From a chemical point of view, the presentation of the theory above is not without problems. In particular, through the definitions of K_0 and $F_{0\alpha}$, we see that the former can be written as a combination of all the terms of the Hamiltonian that depend on the nuclear coordinates (V_{en} and V_{nn}) while the linear coupling constant only depends on the operator V_{en} ,

since V_{nn} does not depend on the electronic coordinates. It is surprising, then, that while this formulation of the PJT effect is exact and K_0 and K_v are related to the change of the expected value of the energy, the equations considered here do not provide any information about the influence of the interelectronic repulsions or electronic kinetic energy over the total energy when they should sensibly be there *taking into account that the electron density is changing with the distortion*. Thus, the PJT effect expressed in this manner does not allow direct comparison with important chemical models like VSEPR since, for example, it does not provide explicit information about electron–electron contributions (although it should be noted that it is contained *implicitly* in its exact formulation). In the following section, we will develop the theory in a way that will show how PJT theory takes into account these contributions to the total energy and that, in a second step, will allow us to compare with the formulation typically found in *ab initio* calculations and thus obtain numerical estimations of the factors involved in the spontaneous distortion of a molecule.

2.2. Full Variational-Perturbational Approach. We are going to apply the Hylleraas variational³⁴ approach over the PJT problem. Our starting point is the expansion of the Hamiltonian (eq 2) and its ground eigenfunction to second order in Q :

$$H(\mathbf{r}, \mathbf{Q}) = H_r + H'Q + \frac{1}{2}H''Q^2 + \dots \quad (11)$$

$$\Psi_g(\mathbf{r}, \mathbf{Q}) = \Psi_0 + \Psi'Q + \frac{1}{2}\Psi''Q^2 + \dots \quad (12)$$

We now obtain the ground state energy surface calculating the expected value of the Hamiltonian with the wave function:

$$\begin{aligned} \langle \Psi_g | H | \Psi_g \rangle &= \langle \Psi_0 | H_r | \Psi_0 \rangle + Q[\langle \Psi' | H_r | \Psi_0 \rangle + \langle \Psi_0 | H' | \Psi_0 \rangle \\ &+ \langle \Psi_0 | H' | \Psi' \rangle] + Q^2[\frac{1}{2}\langle \Psi_0 | H'' | \Psi_0 \rangle \\ &+ \langle \Psi_0 | H' | \Psi' \rangle + \langle \Psi' | H' | \Psi_0 \rangle + \langle \Psi' | H_r | \Psi' \rangle \\ &+ \frac{1}{2}\langle \Psi'' | H_r | \Psi_0 \rangle + \frac{1}{2}\langle \Psi_0 | H'' | \Psi'' \rangle] \end{aligned} \quad (13)$$

We will also calculate the variation of the norm of the wave function:

$$\begin{aligned} \langle \Psi_g | \Psi_g \rangle &= \langle \Psi_0 | \Psi_0 \rangle + Q[\langle \Psi' | \Psi_0 \rangle + \langle \Psi_0 | \Psi' \rangle] \\ &+ Q^2[\langle \Psi' | \Psi' \rangle + \frac{1}{2}\langle \Psi'' | \Psi_0 \rangle + \frac{1}{2}\langle \Psi_0 | \Psi'' \rangle] \end{aligned} \quad (14)$$

We will now proceed to calculate the force constant of the ground state using the term in Q^2 from eq 13. To simplify the resulting expression, we use the fact that $H_r\Psi_0 = E_0\Psi_0$ and employ the two equations obtained from making the linear and quadratic terms of eq 14 equal to zero to conserve the norm of the wave function during the distortion. After some simple algebra, we get

$$\begin{aligned} K &= \langle \Psi_0 | H'' | \Psi_0 \rangle + 2(\langle \Psi_0 | H' | \Psi' \rangle + \langle \Psi' | H' | \Psi_0 \rangle) \\ &+ 2\langle \Psi' | H_r - E_0 | \Psi' \rangle \end{aligned} \quad (15)$$

which, identifying terms, can be written in the following way:

$$K = K_0 + 2K_v + K_e \quad (16)$$

where

$$K_e = 2\langle \Psi' | H_r - E_0 | \Psi' \rangle \quad (17)$$

We can now compare eq 16 with the one employed in PJT theory (eq 8). We find that while the first term, corresponding with K_0 , is the same in both equations, the contribution of K_v in eq 16 is twice that in eq 8, while the term given by eq 17 describing the energy changes due to second-order variations in the wave function is completely missing in the usual PJT formulation.⁷ It is important to note that since the operator in K_e does not contain any derivative with respect to Q , it incorporates all the information on the variation of the electron–electron and kinetic energy with distortion, which is one of the points we wanted to clarify. Since the physical interactions in this term have a purely electronic nature, as opposed to K_0 and K_v , we denote this contribution K_e . The rest of the section will be devoted to show that if we had access to all wave functions, Ψ_i (something impossible in any practical situation), eqs 8 and 16 would lead to exactly the same value of the total force constant. In order to find the relationship between eq 8 and eq 15, we will now optimize the energy with respect to the wave function derivative (i.e., following Hylleraas variational principle³⁴), and from eq 15 we get

$$(H_r - E_0)|\Psi'\rangle = -H'|\Psi_0\rangle \quad (18)$$

If we now express Ψ' in terms of the eigenfunctions of H_r (i.e., Ψ_i),

$$|\Psi'\rangle = \sum_{n \neq 0} D_n |\Psi_n\rangle \quad (19)$$

and we substitute in eq 18 and multiply on the left by $\langle \Psi_n |$, we get

$$D_n = -\frac{\langle \Psi_n | H' | \Psi_0 \rangle}{E_n - E_0} \quad (20)$$

This equation shows the way that the wave functions mix due to distortions in the geometry of the system. Since the operator on the right-hand side involves derivatives with respect to the nuclear coordinates, it is exclusively determined by the V_{en} operator. Now, taking K_e and using eqs 19 and 18, we get

$$K_e = 2 \sum_{n \neq 0} |D_n|^2 (E_n - E_0) \quad (21)$$

The above expression shows that the second-order change in energy, due to the change of the electronic wave function without a change in the nuclear part of the Hamiltonian, is strictly positive. Thus, even though the total force constant, eq 15, contains the extra term K_e with respect to the usual PJT expression, we see that, as this contribution is positive, the origin of the instability still corresponds (eq 1) to the vibronic contribution, K_v . In order to find the relationship between the two expressions of the force constant, we substitute eq 20 into 21 to find

$$K_e = 2 \sum_{n \neq 0} \frac{|\langle \Psi_n | H' | \Psi_0 \rangle|^2}{E_n - E_0} = -K_v \quad (22)$$

Therefore, we can recover the PJT force constant (eq 1) from the more complete eq 16 when we use the infinite states solution of H_r . Since K_e is positive, one could be tempted to say that electron–electron and kinetic energy terms contained in it cannot be mainly responsible for a distortion. However, this interpretation is rather questionable as what eq 22 really does is establish that K_v and K_e are fully exchangeable (i.e., equivalent),

both measuring how sensitive the total energy (and each of its contributions) is to a change of the wave function when following a nuclear motion. This equivalency explains why, while the electron density is changing, as do electron–electron, electron–nuclear, and kinetic energy terms, commonly formulated PJT theory can focus just on electron–nuclear interactions. Moreover, eq 22 opens the possibility to study an instability from different points of view, knowing that all lead to the same physical result, a negative force constant. Also, and from a chemical perspective, it is more important to establish what favors instability in a particular compound when compared to others than to know why it simply distorts. In order to do so, it is advantageous to be able to select the most distinctive interactions, something that eq 22 allows us to do. Finally, we would like to note that while K_v is sometimes approximated by a few excitations between the frontier orbitals, eq 22 clearly shows that since all electrons are involved in the K_e (which is the expected value of $H_r - E_0$ for Ψ_r), they are as well in K_v .

In the next section, we will develop a quantitative approach to obtain all these magnitudes using Hartree–Fock or Density-Functional-Theory (DFT) calculations as implemented in many popular codes. While similar approaches exist in the literature,^{29,30} none of them explain the role of interactions other than electron–nuclear, which is a central point in this work. Moreover, we would like to raise a number of warnings on how some quantities, while obtainable, do not really provide a chemical insight since they are strongly dependent on the details of the calculation like the basis-set.

2.3. Pseudo Jahn–Teller Effect in the One-Electron Approximation. We will first focus on the Hartree–Fock approximation expressed in terms of a localized atomic orbital (AO) basis set. Our objective will be to find an expression for the second derivative of the total energy that can be compared to the expressions in the previous section. The starting point, then, is the total energy that can be written as³⁵

$$E = \sum_{\alpha\beta}^{\text{AO}} D_{\alpha\beta} [F_{\alpha\beta} - (V_{ee})_{\alpha\beta}] \quad (23)$$

where $D_{\alpha\beta}$, $F_{\alpha\beta}$, and $(V_{ee})_{\alpha\beta}$ are, respectively, the density, Fock, and electron–electron interaction matrices expressed in the AO basis set (denoted by Greek indexes). The Fock matrix contains the typical contributions to the molecular Hamiltonian (eq 2):

$$F_{\alpha\beta} = T_{\alpha\beta} + (V_{en})_{\alpha\beta} + 2(V_{ee})_{\alpha\beta} \quad (24)$$

In order to relate our approach to the PJT effect, we must describe how the ground state mixes with excited ones along the distortion coordinate, Q . In one-electron theories, this state mixing is translated into orbital mixing which, in principle, is described by the Roothan–Hartree–Fock equation:

$$F(Q) A(Q) = S(Q) A(Q) \epsilon(Q) \quad (25)$$

where S is the overlap matrix between the AO functions, ϵ the diagonal matrix containing the eigenvalues of the Fock matrix expressed in AO, F_{AO} , and A is the matrix for the canonical orbitals in this basis. However, the main difficulty here lies in how to describe the orbital mixing when the AO basis is also changing with the position of the atoms. This problem is similar to constructing a diabaticization scheme, where it is well-known that the transformation from adiabatic to diabatic states is not unique.³⁶ Our solution to this problem is using a floating basis

set that follows the nuclei and which is defined by the transformation,

$$A(Q) = S^{-1/2}(Q) L_0 C(Q) \quad (26)$$

The first matrix ($S^{-1/2}$) in eq 26 transforms the AOs into Löwdin orbitals while L_0 , which does not depend on the distortion, contains the coefficients describing the canonical orbitals at the high-symmetry configuration ($Q = 0$) in the Löwdin basis set. Finally, $C(Q)$ are the coefficients for the orbitals in the new basis. It is important to note here that, while Löwdin orbitals are not uniquely defined, our transformation must be unique (except for orbital phases). In order to do so, we take a random set of Löwdin orbitals at the high-symmetry configuration ($Q = 0$), and for $Q \neq 0$, we choose them to be maximally similar to the initial ones. Since we transform to the canonical molecular orbitals at the high-symmetry configuration using L_0 , the final transformation is unique. Thus the Roothan–Hartree–Fock equation in the new basis reads

$$F(Q) C(Q) = C(Q) \epsilon(Q) \quad (27)$$

This equation is very important, and the new basis provides some key differences with eq 25: (a) the orbital coefficient matrix, $C(Q)$, is the identity at the high-symmetry point, and (b) for $Q \neq 0$, the off-diagonal terms describe the mixing of the orbitals with the distortion. Thus, study of the matrix $C(Q)$ provides full information on how the wave function is changing and where PJT is most important. Obviously, the Fock matrix in eq 27 is different from that in eq 25 due to the change in basis (under the new basis, we will denote all matrix indexes with Latin letters). We can now take the second derivative of eq 23 with respect to the distortion coordinate Q to obtain the force constant:

$$K = \sum_{ij}^{\text{MO}} [D_{ij}(F - V_{ee})''_{ij} + 2D_{ij}'(F - V_{ee})'_{ij} + D_{ij}''(F - V_{ee})_{ij}] \quad (28)$$

Comparison of eq 28 with eqs 15 and 16 suggests that if we assign the role of the changes in the wave function and Hamiltonian respectively to the density matrix and $F - V_{ee}$, the Hartree–Fock values of K_0 , K_v , and K_e should, respectively, be

$$K_0 = \sum_{ij}^{\text{MO}} D_{ij}(F - V_{ee})''_{ij} \quad (29)$$

$$K_v = \sum_{ij}^{\text{MO}} D_{ij}'(F - V_{ee})'_{ij} \quad (30)$$

$$K_e = \sum_{ij}^{\text{MO}} D_{ij}''(F - V_{ee})_{ij} \quad (31)$$

Let us now study how well these terms compare with those found in usual PJT schemes (i.e., K_0 and PJT coupling constants). Let us start with K_0 :

$$K_0 = \langle \Psi_0 | H'' | \Psi_0 \rangle = \int \rho(\vec{r}) V_{en}'' d\vec{r} + V_{nn}'' \quad (32)$$

Noting that in the one-electron approximation the electron density is $\rho = \sum_i^{\text{occ}} n_i |\phi_i|^2$ (n_i is the orbital occupation), we get

$$K_0 = \sum_i^{\text{occ}} n_i \int |\phi_i|^2 V_{\text{en}}'' d\vec{r} + V_{\text{nn}}'' \quad (33)$$

This expression, essentially the same as given in ref 32, can be very favorably compared to eq 29 realizing that, for the chosen basis, the density matrix is $D_{ij} = n_i \delta_{ij}$. Then,

$$K_0 = \sum_i^{\text{MO}} n_i (F - V_{\text{ee}})_{ii}'' \quad (34)$$

In conclusion, we find that the definition of K_0 given by eq 29 seems fully consistent with the general one (eq 32) and that only occupied orbitals play a role in it. On the other hand, it is important to note that while H'' does not depend on electron–electron interactions the operator in our approach does, revealing a clear difference between them due to the use of approximate wave functions to find eq 29.

In a similar fashion, we can obtain the equivalent to the vibronic coupling constants describing the mixing of the states (eq 20) by using the coupled-perturbed Hartree–Fock equations (essentially deriving eq 27 and denoting the matrix at the reference configuration with an r subindex):

$$F_r C' + F' C_r = C_r \varepsilon' + C' \varepsilon_r \quad (35)$$

To simplify the above equation, we are going to suppose that there are no degenerate orbitals coupled to the symmetry-breaking distortions, so that $\varepsilon' = 0$, and remember that in our basis $F_r = \varepsilon_r$, and C_r is the identity. Thus,

$$\varepsilon_r C' - C' \varepsilon_r = -F' \quad (36)$$

Expressing the above equation in terms of the individual orbitals, we obtain

$$C_{ij}' = -\frac{F_{ij}'}{\varepsilon_i - \varepsilon_j} \quad (37)$$

This equation is completely equivalent to eq 20 when the Hamiltonian is substituted by the Fock matrix. However, when we use eq 37 to calculate the derivative of the density matrix and obtain K_v , we get

$$\begin{aligned} K_v &= \sum_{i,j} D_{ij}' [F - (V_{\text{ee}})]_{ij}' \\ &= \sum_{i,j} (n_j - n_i) \frac{(F_{ij}')^2}{\varepsilon_i - \varepsilon_j} - (n_j - n_i) \frac{F_{ij}'}{\varepsilon_i - \varepsilon_j} (V_{\text{ee}})_{ij}' \end{aligned} \quad (38)$$

The first term in eq 38 is simply an orbital version of the usual PJT expression, eq 9. However the second one, as we will see below, is associated with the presence of a basis set that changes with the system geometry. It is important to note that eq 38 predicts that the stabilization energy will only be produced when an occupied–unoccupied pair of orbitals interact vibronically. So when $n_j - n_i \neq 0$, this gives rise to the formation of a bonding–antibonding orbital pair with respect to the distortion, as in the usual PJT interpretation.

We would like to note here that while the formulas above allow studying of the individual orbital couplings (as performed in ref 29), these do not have chemical significance. First, unoccupied HF orbitals are too diffuse, making the low energy unoccupied valence orbitals yield small vibronic contributions when compared to high-energy orbitals coming from localized polarization functions. The latter functions are not usually taken into account in qualitative chemical models, and as

shown later, they should not participate in interpretation. Also, and as we will see, the individual K_0 , K_v , and K_e contributions are very large when compared with K and strongly dependent on the basis set; thus, a small relative numerical variation of any of them could erroneously be identified as the origin of the distortion. Useful quantities to study the instability are those which have a similar magnitude to K and change significantly from one system to another. One such quantity is the total contribution to the force constant by an occupied orbital. This quantity can be obtained from eq 23 noting that the density matrix can be expressed as a sum to all occupied orbitals ($D_{ij} = \sum_l n_l C_{il} C_{jl}$), which allows one to naturally find the contribution of each occupied orbital (l) to K , K_0 , K_v , and K_e

$$k_0^{(l)} = n_l \sum_{i,j} C_{il} C_{jl} (F - V_{\text{ee}})_{ij}'' \quad (39)$$

$$k_v^{(l)} = n_l \sum_{i,j} (C_{il} C_{jl})' (F - V_{\text{ee}})_{ij}' \quad (40)$$

$$k_e^{(l)} = n_l \sum_{i,j} (C_{il} C_{jl})'' (F - V_{\text{ee}})_{ij} \quad (41)$$

and thus pinpoint those orbitals more strongly participating in the instability. We demonstrate this application in section 4. We would like to note here that, while related to the above, the calculation of canonical orbital energy derivatives by Yamaguchi et al.³⁷ includes all the occupied–occupied orbital interactions (raising and lowering pairs of contributions while not altering the total force constant) instead of the net orbital contribution given by the equations above, making the search for the orbitals that participate in the distortion more difficult.

The same one-electron theory can be applied to DFT calculations. The main difference is that the energy cannot be separated in an orbital sum like in eq 23 since the exchange–correlation functionals are strongly nonlinear functions of the electron density

$$E = \sum_{ij} D_{ij} [T + V_{\text{en}} + V_{\text{ee}}^{(cl)}] + V_{\text{xc}} \quad (42)$$

Here, $V_{\text{ee}}^{(cl)}$ is the classical part of the electron–electron interaction and V_{xc} is the exchange–correlation energy. Calculation of the force constant from eq 42 is trivial and the division of the result into K_0 , K_v , and K_e relatively straightforward except for the V_{xc} term. Considering that K_e contains all changes in electron–electron energies, it seems reasonable to ascribe the second derivative of V_{xc} to this term. Thus, application of the PJT theory described above is possible for both Hartree–Fock and DFT methods.

2.4. Effect of the Basis Set. As noted above, evaluation of many vibronic properties is strongly dependent on the basis set. To show how this dependency influences the vibronic constants, let us now obtain the value of the first derivative of the Fock matrix, F' , using the Hartree–Fock expression. The Fock matrix is³⁵

$$(F) = \langle \chi_\alpha | \hat{h} + \sum_j^{\text{occ}} [\hat{J}_j - \hat{K}_j] | \chi_\beta \rangle \quad (43)$$

Here, \hat{h} is the one-electron operator that contains the kinetic and electron–nuclear terms, and \hat{J}_j and \hat{K}_j are the usual direct and exchange Coulomb operators. The first derivative of the Fock matrix is

$$\begin{aligned}
 (F') &= \langle \chi_\alpha | \hat{h} + \sum_j^{\text{occ}} [\hat{J}_j - \hat{K}_j] | \chi_\beta \rangle + \langle \chi_\alpha | \hat{h}' \\
 &+ \sum_j^{\text{occ}} [\hat{J}_j' - \hat{K}_j'] | \chi_\beta \rangle + \langle \chi_\alpha | \hat{h} + \sum_j^{\text{occ}} [\hat{J}_j - \hat{K}_j] | \chi_\beta' \rangle \\
 &= \langle \chi_\alpha | \chi_\beta \rangle \epsilon_\beta + \langle \chi_\alpha | \chi_\beta' \rangle \epsilon_\alpha + \langle \chi_\alpha | \hat{h}' \\
 &+ \sum_j^{\text{occ}} [\hat{J}_j' - \hat{K}_j'] | \chi_\beta \rangle
 \end{aligned} \quad (44)$$

In eq 44, we have three terms, the first two depending on the overlap of the basis functions and the third on the derivative of the operators. Ideally, we would like F' to be independent of the change of the basis functions, χ , as they are simply auxiliary, used to perform the calculation, and should not impact the chemical interpretation. However, we find that the two first terms in eq 44, which are related to Pulay forces,³⁸ can be very strong, particularly when many polarization functions are included in the calculations. These functions yield very high vibronic constant values as the derivative of a basis function is closely related to its polarization. Thus, these terms are responsible for the very high value of the vibronic contributions to the force constant from the coupling to highly excited orbitals in, for example, ref 29. This shows that special care should be taken using orbital vibronic constants due to their dependency on the basis set, which, as stressed above, should not alter the interpretation of the calculation.

3. COMPUTATIONAL DETAILS

We have used the molpro code³⁹ to perform HF and DFT calculations. Various standard basis sets^{40,41} have been employed. We developed our own code (PJTTTOOLS, see ref 42) to extract the information from the molpro output. We are currently improving the program to accept a general file that can be generated by many codes associated with the calculation of the natural bonding orbitals (NBO).

4. RESULTS

In order to test our computational approach and find its dependence on various factors like basis set or level of calculation, we have applied the method to study the $D_{3h} \rightarrow C_{3v}$ distortion of ammonia (see Figure 2) and compare the results

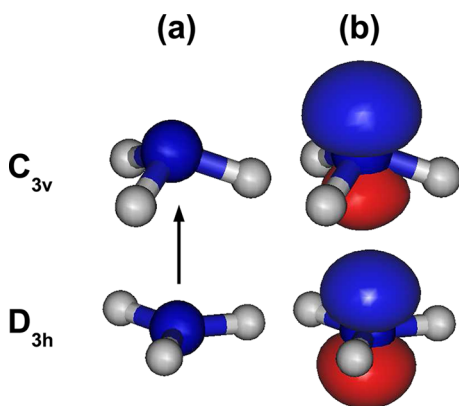


Figure 2. (a) Representation of the a_2'' normal mode responsible for the distortion of ammonia and (b) the change in the HOMO in ammonia when going from the D_{3h} to the C_{3v} configurations.

with those of borane where this instability is not realized. In a first step, we optimized the ammonia molecule for the high-symmetry (D_{3h}) and distorted (C_{3v}) configurations using the cc-pvtz basis at HF and Local Density Approximation (LDA) levels, while results for other DFT functionals can be found in the Supporting Information. Similar results are obtained for other bases, so we take these geometries as a reference for all of our calculations. The only imaginary mode in the high-symmetry configuration of NH_3 is the a_2'' one shown in Figure 2 that drives the $D_{3h} \rightarrow C_{3v}$ distortion. This vibration is the only a_2'' one in the system, so it can be uniquely defined from symmetry considerations and the atom masses and is exactly the same for all methods and basis sets employed here. We present a brief summary of these results in Table 1.

Table 1. Basic Structural and Energetic Results on XH_3 ($X = \text{N, B}$) Molecules^a

system	method	$R_{\text{X-H}}(D_{3h})$	$R_{\text{X-H}}(C_{3v})$	$\alpha_{\text{H-X-H}}$	$K(a_2'')$	ΔE
NH_3	HF	0.985	0.999	107.7	-1.65	0.232
NH_3	LDA	1.006	1.023	106.5	-3.31	0.198
BH_3	HF	1.187	1.187	120.0	7.12	0.0
BH_3	LDA	1.197	1.197	120.0	5.36	0.0

^aThe distance between the central atom and hydrogen ($R_{\text{X-H}}$) is given in Å. The H-X-H angle ($\alpha_{\text{H-X-H}}$) is given in degrees, and the force constant of the a_2'' mode, K , and stabilization energy, ΔE , are, respectively, given in $\text{eV}/\text{\AA}^2$ and eV.

In order to study the origin of the distortion in ammonia, the values of K_0 , K_v , and K_e (eqs 29–31), associated with the a_2'' mode, are calculated with increasing quality basis sets. In Figure 3a, we see that, as expected from PJT theory, K_0 and K_e are

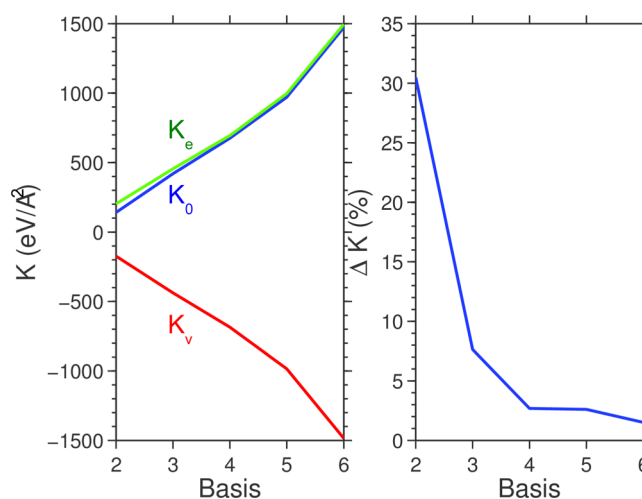


Figure 3. Calculation of the total contributions to the force constant, K_0 (blue), K_v (red), and K_e (green) (a) varying the basis quality along the series cc-pvXz ($X = \text{d}(2), \text{t}(3), \text{q}(4), 5, 6$) in the ammonia molecule. (b) Comparison of the absolute value of K_v and K_e , $\Delta K = |K_v/K_e| - 1$, varying the basis quality.

positive and K_v negative, the latter being the cause of instability. Moreover, in Figure 3b we see that the relative difference between K_v and K_e , $\Delta K = |K_v/K_e| - 1$, quickly decreases when increasing the quality of the basis set approaching the ideal limit $\Delta K = 0$ (eq 22). However, these quantities pose serious problems when used to analyze an instability. First, we can observe in Figure 3a that the absolute value of each of these

force constant contributions is much larger (at least 2 orders of magnitude) than the total force constant (see Table 1). These contributions present, qualitatively, the same behavior in ammonia and borane, and thus, extracting any physical information of why ammonia distorts and borane does not from these quantities is almost impossible. In particular, the distortion cannot be attributed to any particular change in K_0 , K_v , or K_e as their variations when changing the molecule are again larger than the force constant itself. Second, from a calculation standpoint, these quantities are very difficult to obtain, as shown in Figure 3a, where even the use of very large basis sets (cc-pv5z, cc-pv6z) does not allow reaching even moderately converged results in their absolute values. The reason behind the divergence in the values is the fact that better basis sets allow describing the changes in the electron density with more detail. In particular, the Dunning basis sets⁴¹ employed to obtain Figure 3 include in each step a much larger amount of polarization functions that, in turn, are those that have a larger overlap with the derivative of the valence basis functions (see eq 44). LDA results (in the Supporting Information) display the same behavior as HF ones.

In order to avoid the previous difficulties, we now turn to the analysis of the force constant in terms of the occupied orbital contributions as shown in Figure 4 and Table 2. At difference

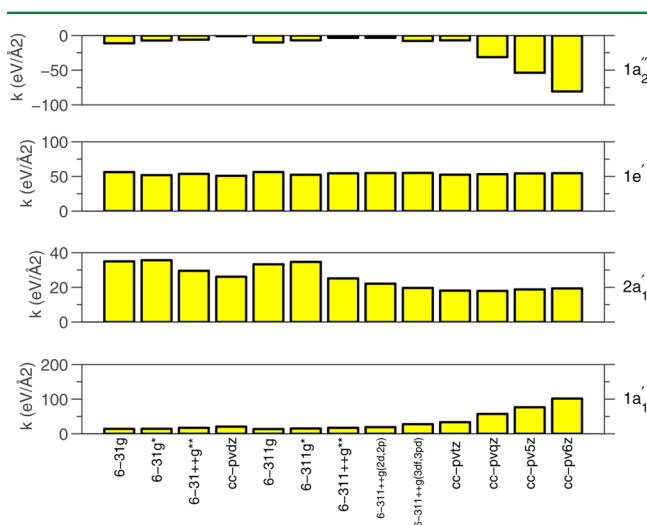


Figure 4. Calculation of the orbital contributions for each of the occupied orbitals of ammonia (see Figure 2) to the total force constant for several basis sets.

with K_0 , K_v , and K_e , we see here that these contributions have the same order of magnitude as the total constant and are, as a consequence, significant to establishing the origin of the distortion. Furthermore, they are much more stable with respect to the variation of the basis set. As shown in Figure 4, the contributions for all the orbitals are stable for Pople basis sets and moderately sized Dunning basis sets (cc-pvdz to cc-pvtz). A deviation is still observed for $1a_1'$ and $1a_2''$ when using very large basis sets containing many polarization functions (cc-pv5z and cc-pv6z) for $1a_1'$ and $1a_2''$ orbitals, but they are much smaller than in the case of the global contributions to the force constant and are not significant for the most usual basis sets. From the instability point of view, the picture arising from the orbital decomposition is totally consistent when varying the basis set; all orbitals yield positive contributions except the one for $1a_2''$ that is negative. Due to the stability of the results, we

present numerical values of the orbital contributions obtained using the cc-pvtz basis set in Table 2 for both NH_3 and BH_3 .

In both molecules the orbitals $1a_1'$, $2a_1'$, and $1e'$ yield positive contributions to the force constant. We observe that while reasonable numerical differences arise between HF and LDA approaches, the qualitative picture emerging from both sets of values is the same. In ammonia, the values listed on the tables are higher than in borane due to the larger nuclear charge of nitrogen when compared to boron. If we now analyze the results, we first note that the contribution from the $1e'$ orbital is the largest as this orbital contains the $N(2p_x, 2p_y)$ orbitals involved in σ bonding and actively oppose the out-of-plane motion of the nitrogen atom. In both cases, the sum of the contributions of these orbitals is larger in absolute value than the one coming from the repulsion among the nucleus of nitrogen and the three protons when we try to move the former out of the plane. This gives rise to a negative contribution to the total force constant, thus favoring the distortion. In conclusion, our calculations indicate that in the absence of the a_2'' orbital contribution, NH_3 would remain in the high-symmetry D_{3h} configuration as BH_3 . However, and in full agreement with chemical intuition, the small, negative contribution of the a_2'' orbital that is only occupied in ammonia allows this latter molecule to distort.

A fundamental question now is what drives this orbital to lower the force constant of the molecule. In order to correctly answer this key query, it is important to recall that in an off-center phenomenon the changes in electron density play a crucial role.^{43,44} Accordingly, the values of kinetic energy, electron–electron repulsion, or electron–nuclei attraction associated with a given orbital are modified along the distortion. Owing to this fact, the force constant, k , corresponding to a given orbital can be written as a sum of contributions arising from the variations of such different quantities along the distortion. The result of such an analysis for the a_2'' orbital of ammonia is given in Table 3 where the different orbital contributions to the global K_0 , K_v , K_e , and K are collected. First, we observe that both orbital k_0 and k_e contributions to the total force constant are positive, k_v being the only global negative contribution. From all the contributions to the orbital k_v , we see that only the electron–nuclear and kinetic energy contributions are negative, while the electron–electron and exchange ones are positive. However, considering the contribution of each interaction globally to the orbital force constant (i.e., $k_0 + 2k_v + k_e$), only the electron–electron and kinetic energy produce total negative contributions. Thus, the picture emerging from Table 3 is that while the electron–nuclear interactions contribute strongly to K_v , they are not responsible for the distortion of ammonia. On the other hand, electron pair repulsions characterized by the electron–electron interactions certainly favor the distortion, but their global contribution is very similar to that of the kinetic energy (one is larger in HF and the other in LDA). Now the question is, why would the kinetic energy favor the distortion of ammonia? The answer can be found in Figure 5 where we show the electron distribution associated with the $a_2''(a_1)$ orbital at the $D_{3h}(C_{3v})$ conformations. In D_{3h} , the $N(2p_z)$ orbital does not overlap with the $H(1s)$ ones, and so the electrons in this orbital are strongly confined to the close surroundings of the N atom (Figure 5a). After the distortion, the $N(2p_z)$ orbital overlaps with $H(1s)$, giving rise to an expansion of the orbital,¹⁷ as clearly seen in Figure 5b. As is well-known, an increase of volume implies a reduction of kinetic energy due to the smaller confinement of

Table 2. Orbital Contributions (k , k_0 , k_v , k_e) to the Total Force Constant, K , and Its Constituents K_0 , $2K_v$, and K_e for NH_3 and BH_3 Using the cc-pvtz Basis Set^a

system contribution		HF				LDA			
		k_0	$2k_v$	k_e	k	k_0	$2k_v$	k_e	k
NH_3	$1a_1'$	57.15	−66.78	43.05	33.41	52.15	−64.84	39.92	27.22
	$2a_1'$	90.66	−118.39	45.79	18.06	79.79	−107.99	42.15	13.95
	$1e'$	117.73	−166.95	101.68	52.46	103.63	−150.92	92.51	45.22
	$1a_2''$	187.62	−357.48	162.75	−7.11	168.34	−321.31	150.17	−2.78
	nuclear	−150.88	0.00	0.00	−150.88	−150.88	0.00	0.00	−150.88
	DFT XC					0.00	0.00	18.88	18.88
BH_3	total	420.01	−876.55	454.95	−1.60	356.48	−795.67	436.98	−3.31
	$1a_2''$	21.45	−25.36	13.24	9.33	25.02	−24.57	12.82	13.27
	$2a_1'$	34.03	−37.51	15.35	11.88	27.93	−27.16	8.09	8.86
	$1e'$	60.77	−80.81	47.53	27.53	53.48	−71.25	39.15	21.37
	nuclear	−69.15	0.00	0.00	−69.15	−69.15	0.00	0.00	−69.15
	DFT XC					0.00	0.00	9.64	9.64
total		107.86	−224.42	123.65	7.12	90.76	−194.23	108.85	5.36

^aThe orbital contributions are given per individual orbital; i.e., the e' orbital total contribution is twice the one in the table due to the degeneracy. Units are $\text{eV}/\text{\AA}^2$.

Table 3. Orbital Contributions (k_0 , k_v , k_e , k) of the $1a_2''$ Orbital in NH_3 to K_0 , K_v , and K_e and Their Decomposition in Kinetic Energy Electron–Electron Repulsion, Electron–Nuclear Interactions at the HF/cc-pvtz and LDA/cc-pvtz Levels of Theory^a

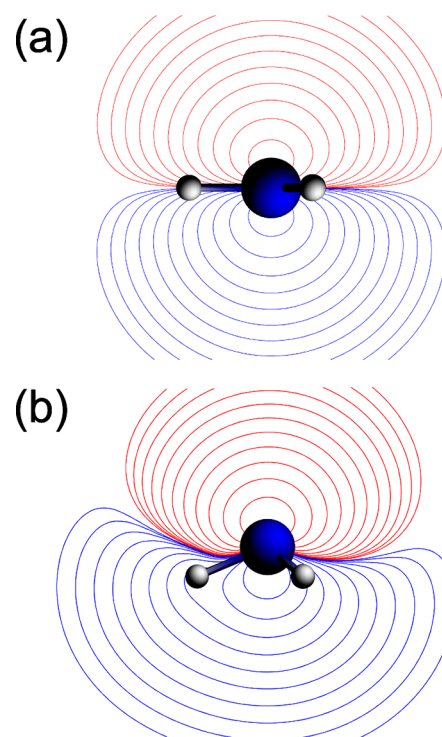
		k_0	k_v	k_e	k
HF	T	128.72	−321.48	117.65	−15.11
	V_{en}	94.82	−47.13	−17.44	30.25
	V_{ee}	−49.68	37.98	−7.44	−19.14
	V_{x}	13.76	−26.86	9.99	−3.11
	total	187.62	−357.48	162.75	−7.12
LDA	T	125.14	−307.94	166.51	−29.45
	V_{en}	93.30	−51.80	−1.51	54.49
	V_{ee}	−50.09	38.43	−14.83	−27.47
	total	168.34	−321.31	150.17	−2.78

^aUnits are $\text{eV}/\text{\AA}^2$.

the wave function.⁴⁵ It is important to note that this mechanism is completely equivalent to that usually employed in PJT theory⁷ to explain the distortion of NH_3 where symmetry breaking allows creating new covalencies (in this case $N(2p_z) - H(1s)$). However, with our method, we are able to reveal that, in fact, the kinetic energy is producing the stronger stabilization during the distortion of ammonia. It is very important to note here that this mechanism does not violate any of the usual rules of PJT as the global values of K_0 (and K_e introduced here) are positive while K_v is negative.

5. CONCLUSIONS

In this work, we have shown that, while the usual pseudo-Jahn–Teller formula for the calculations of the force constant, $K = K_0 + K_v$, is exact, it does not allow one to extract the contribution of the different interactions to the expected value of the change of the total energy or that corresponding to a particular orbital. In particular, it leads to the overlooking of terms that yield the variation of the kinetic energy and electron–electron repulsions in the distortion and that are usually key elements in chemical reasoning. We show that, by using an alternative expression of K , it is possible to connect the PJT theory with other chemical bond models, like pair repulsion theory, that are based on electron–electron repulsions, or the Ruedenberg models²⁶ that

**Figure 5.** Density plot for the a_2'' orbital in LDA calculation (a) when the symmetry is D_{3h} and (b) when the symmetry is C_{3v} .

highlight the role of the kinetic energy of the electrons in bond formation.

In order to overcome the extraordinary difficulty of achieving a perfect knowledge of the whole wave function, we also propose a practical method to calculate the PJT contributions to an instability at the Hartree–Fock and DFT levels of theory. We have shown that since the values of either K_0 , K_v , or K_e are, at least, 2 orders of magnitude larger than the total K and extremely sensitive to the computational details, they are less useful than the contributions extracted from an orbital decomposition of the force constant. Using this approach, we show that the stabilization of D_{3h} ammonia with the distortion does not come from a lowering of the expectation value of the

electron–nuclear operator, as one would expect when using naively the usual pseudo-Jahn–Teller arguments or just electron–electron repulsion as envisioned in the VSEPR model, since the kinetic energy relaxation in the a_2'' orbital, associated with the umbrella distortion, has a contribution at least as sizable as the repulsion of the lone pair with the bonding pairs.

We have shown that the present method and the open code employed for this analysis are useful in understanding the interesting chemical problems associated with structural instabilities in molecules and solids. The extension of the present approach to solids and non-geometry-dependent basis sets is currently in development in our groups.

■ ASSOCIATED CONTENT

■ Supporting Information

Calculation of the total contributions to the force constant at the LDA level; calculation of the orbital contributions for each of the occupied orbitals of NH_3 to the total force constant for several basis sets at the LDA level of theory; orbital contributions for NH_3 and BH_3 at the GGA (BLYP and PBE)/cc-pvtz level of theory; contributions of K_0 , K_v , and K_e to the force constant of the orbital $1a_2''$ of NH_3 and their decomposition in kinetic energy, electron–electron repulsion, and electron–nuclear interactions at the GGA (BLYP and PBE)/cc-pvtz level of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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