

procedure with respect to rotation of the molecular coordinate system.<sup>24</sup>) The non-orthogonality of atomic eigenvectors on different centers is removed by an "occupancy weighted symmetric orthogonalization" procedure,<sup>23</sup> satisfying

$$\sum_i \bar{w}_i \int |\phi_i - \bar{\phi}_i|^2 d\tau = \text{minimum} \quad (\text{A1})$$

where the weighting factor  $\bar{w}_i = \langle \bar{\phi}_i | \Gamma | \bar{\phi}_i \rangle$  is the occupancy of  $\bar{\phi}_i$ . [In practice, the orthogonalization (A1) is carried out in a 3-step "WSW" procedure, to reduce the implied overcounting that results from employing occupancies of the non-orthogonal  $\bar{\phi}_i$ 's as initial weighting factors.<sup>24</sup>] This generalization of Löwdin's symmetric orthogonalization procedure<sup>61</sup> retains the "maximum resemblance" property for orbitals of high occupancy but allows diffuse orbitals of low occupancy to distort as needed to achieve orthogonality. In this way, the character of the free-atom valence shell (the "natural minimal basis set") of each atom is strongly preserved in the molecular environment, leading to orthonormal functions  $\phi_i$  of high occupancy that are optimal for describing the molecular electron density around each atomic center. Typically, a high percentage (>99%) of the electron density is described by the small number of NAOs of the formal "natural minimal basis" set, with much smaller contributions from the extra-valence-shell "Rydberg" NAOs that complete the span of the input AO basis set. Note that each step in the NAO procedure is based on the "maximum occupancy" criterion that distinguishes "natural" orbitals.

In the orthonormal basis of NAOs, the density matrix provides the occupancies that constitute "natural population analysis". The occupancy (natural population)  $n_i^{(A)}$  of NAO  $\phi_i^{(A)}$  is simply the diagonal expectation value

$$n_i^{(A)} = \langle \phi_i^{(A)} | \Gamma | \phi_i^{(A)} \rangle = (\Gamma^{(A)})_{ii} \quad (\text{A2})$$

The natural populations rigorously satisfy the Pauli principle

$$0 \leq n_i^{(A)} \leq 2 \quad (\text{A3})$$

sum consistently to give the populations  $n^{(A)}$  on each atom

(61) Löwdin, P.-O. *J. Chem. Phys.* 1950, 18, 365-375. Löwdin, P.-O. *Adv. Quantum Chem.* 1970, 5, 185-199. Wannier, O. *Phys. Rev.* 1937, 52, 191-197.

$$n^{(A)} = \sum_i^{\text{on A}} n_i^{(A)} = \text{Tr}(\Gamma^{(A)}) \quad (\text{A4})$$

and are consistent with the total number ( $N$ ) of electrons in the molecule

$$\sum_A^{\text{atoms}} n^{(A)} = N \quad (\text{A5})$$

We have previously shown<sup>24</sup> that the natural populations are efficiently computed, exhibit good stability with respect to basis set changes, and are in satisfactory correspondence with other theoretical and empirical measures of charge distribution.

The NPA method bears some resemblance to Davidson's<sup>62</sup> use of Hartree-Fock AOs to determine orbital occupancies from the molecular density matrix and to Heinzmann and Ahlrichs'<sup>63</sup> use of "modified atomic orbitals" (MAOs) for the same purpose. The MAOs (like the NAOs) take account of the important changes in atomic valence state or AO energy and diffuseness that accompany molecule formation. The Davidson and Heinzmann-Ahlrichs methods satisfy conditions analogous to (A2) and (A3) and would be expected to give results that are qualitatively similar to natural population analysis (significantly improved over Mulliken population analysis in this respect). These methods differ from NPA in being more closely tied to the single-determinant SCF-MO approximation and in generally leaving some portion of the electron density unaccounted for [i.e., inexact satisfaction of (A4) or (A5)]. Very recently, Ehrhardt and Ahlrichs<sup>64</sup> applied the MAO method to SF<sub>6</sub> (using a basis of 5s3p1d on F, 6s4p1d on S) and obtained charges of +2.67 on S and -0.44 on F, quite comparable to the NPA results of this paper.

Registry No. SF<sub>6</sub>, 2551-62-4.

**Supplementary Material Available:** The AO to NAO and NAO to NHO transformation matrices from calculation 8 (14 pages). Ordering information is given on any current masthead page.

(62) Davidson, E. R. *J. Chem. Phys.* 1967, 46, 3320-3324. Cf. also: Roby, K. R. *Mol. Phys.* 1974, 27, 81-104.

(63) Heinzmann, R.; Ahlrichs, R. *Theor. Chim. Acta (Berlin)* 1976, 42, 33-45.

(64) Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta (Berlin)* 1985, 68, 231-245.

## Pauli Forces and the Valence Shell Electron Pair Repulsion Model for H<sub>2</sub>O and NH<sub>3</sub>

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**Abstract:** It is shown that the two effects of antisymmetry (Pauli exclusion principle) within the correct SCF wavefunctions cannot "bend" linear H<sub>2</sub>O or planar NH<sub>3</sub> without classical electronic coulombic repulsion (CER) between LMO "charge clouds" in the SCF energy expression. These two effects are the orthogonality of the molecular orbitals (MOs) and the electron-exchange interactions between the LMOs. This result is in direct contradiction to the presently accepted valence shell electron pair repulsion (VSEPR) model, which attributes the geometries of molecules to "Pauli forces" between localized electron pairs. It is argued that the Walsh MO energy correlation diagrams, based on the integral Hellmann-Feynman theorem, are a more correct simple model for molecular geometries.

### I. Computational Tests for the Dominance of Pauli Forces

Large basis set linear combination of atomic orbitals molecular-orbital self-consistent-field (LCAO MO SCF) wavefunctions give good geometries for closed-shell molecules.<sup>1</sup> They appear to be reliable for the initial examination of the physical effects

determining molecular geometries.

The earliest version of the valence shell electron pair repulsion (VSEPR) model of molecular geometries was due to Sidgwick and Powell.<sup>2</sup> They maintained that one critical factor for angular geometries was the *Coulombic* electron repulsion (ER) between the valence-shell electrons. Our results confirm that conclusion.

(1) See, for example: Schaefer, H. F., III *The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results*; Addison-Wesley: Reading, MA, 1972.

(2) Sidgwick, N.; Powell, H. *Proc. R. Soc. London A* 1940, 176, 153.

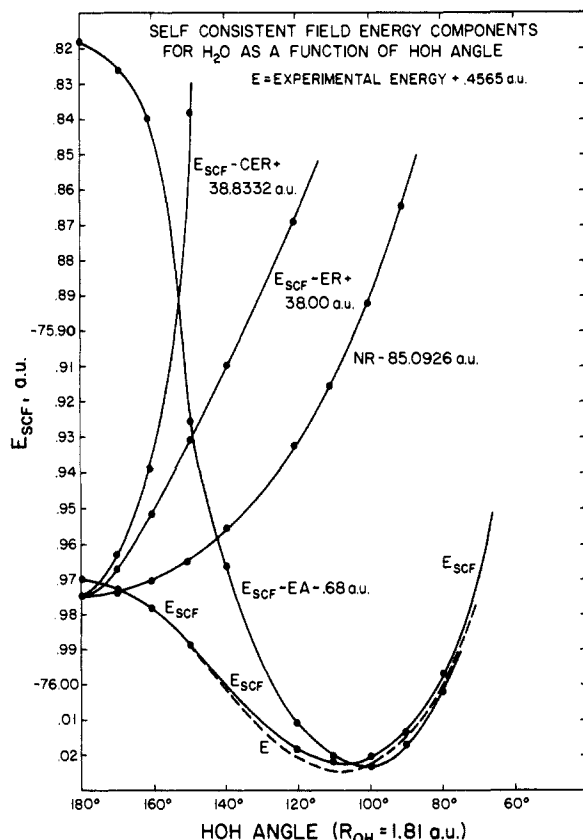


Figure 1. Contributions of EA, ER, and CER to the total energy  $E_{SCF}$  as a function of the HOH angle.

In the later version of the VSEPR model<sup>3</sup> these Coulombic repulsions (ER) have unfortunately been heavily discounted in favor of the so-called "Pauli repulsions" of valence-shell electron pairs, which arise from the antisymmetry of the wavefunction. Our results show that the *correct* SCF wavefunction, with proper antisymmetry but ER *dropped* from the energy,  $E$ , cannot maintain the correct geometry of molecules; e.g.,  $H_2O$  becomes a linear molecule and  $NH_3$  becomes planar. Therefore the antisymmetry of the wavefunction is apparently *not* the *dominating influence* on molecular geometries. This is not to say that antisymmetry of the wavefunction is unimportant. However it is *only one of several important factors* determining molecular angular geometries. It does not deserve the extreme emphasis given to it in the modern version of the VSEPR model.

For the standard spin-restricted LCAO MO SCF wavefunctions, the antisymmetry expresses itself in two ways. First, electrons (of opposite spins) doubly occupy *orthogonal* spatial MOs for closed-shell states.<sup>4a</sup> Second, the "classical" electron repulsion of the MO charge densities, CER, is modified by the *exchange attractions*, EA, between electrons of like spins:  $ER = CER + EA$ . Here  $CER = CER_{ij} + CER_{ii} = \sum_i \sum_j \rho_i \rho_j A_{ij} + \sum_i J_{ii}$ ,  $EA = -\sum_i \sum_j \rho_i \rho_j 2K_{ij}$ ,  $J_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_i(1)\phi_j(2) \rangle$ ,  $K_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_j(1)\phi_i(2) \rangle$ . All the above summations are over the  $(N/2)$  doubly occupied spatial MO's for  $N$  electrons. It is

(3) Gillespie, R.; Nyholm, R. *Q. Rev. Chem. Soc.* **1957**, *11*, 339. Gillespie, R. *Molecular Geometry*; Van Nostrand Reinhold: London, 1972; *J. Chem. Educ.* **1974**, *51*, 367.

(4) (a) Antisymmetry requires only that the spatial MOs (and spin MOs) be *linearly independent*, to keep the determinantal wavefunction from vanishing identically. However the simple and visualizable energy expression we discuss ( $E_{SCF} = \sum_i h_i^\circ + \sum_i \sum_j (2J_{ij} - K_{ij}) + NR$ ) requires the *equivalent* wavefunction in terms of orthogonal MOs. Here,  $h^\circ$  is the "bare nuclei" one-electron hamiltonian,  $h_i^\circ = \langle \phi_i(1) | h^\circ(1) | \phi_i(1) \rangle$  and NR is the nuclear repulsion. (b) For this simple collision,  $\psi_T(1,2) = (1/2^{1/2})[\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)] \alpha(1)\alpha(2)$ , for both electrons having spin function " $\alpha$ ". Electrons of "opposite spins" in a closed-shell state (both  $\phi_i$  and  $\phi_j$  doubly occupied) are both "singlet" and "triplet" coupled:  $\psi_s(1,2) = (1/2)[\phi_i(1)\phi_j(2) + \phi_j(1)\phi_i(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ ,  $\psi_T(1,2) = (1/2)[\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ . Therefore there is no *net* exchange effect for the opposite spins.

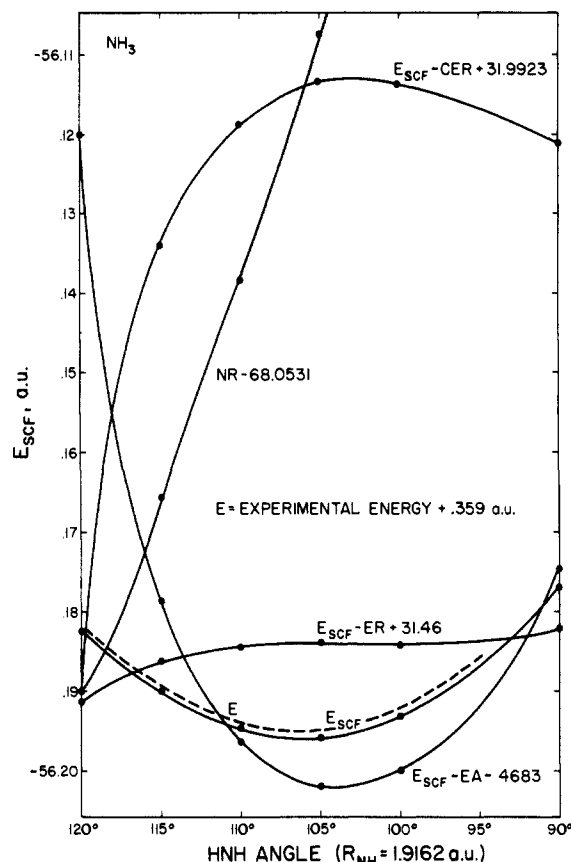


Figure 2. Contributions of EA, ER, and CER to the total energy  $E_{SCF}$  as a function of the HNH angle.

traditional to write the total electronic (Coulombic) repulsion as  $ER = C + EX$ , where  $C = CER + CER_{ii}$  and  $EX = EA - CER_{ii}$ , since  $C$  and  $EX$  are each invariant to an orthogonal (or unitary) transformation of the occupied spatial MOs,  $\phi_i$ .

The EA terms arise because of the indistinguishability of two electrons of *like spins* in a region where the two spatial MOs  $\phi_i$  and  $\phi_j$  appreciably penetrate. The same type of exchange integral,  $K_{ij}$ , arises in simple particle-beam collision theory for collision of two electrons of like spins. It represents a "softening" of the "classical repulsion",  $J_{ij}$ , due to the zero probability of finding both electrons (of like spin) at the same point in physical space.<sup>4b</sup>

For energy-localized "localized MOs",<sup>5</sup> the EA term is minimized. Since the orthogonal transformation from the "canonical MOs" to the LMOs does not change the overall wavefunction; this EA can be considered to be the *necessary* (true) "exchange attraction" for the system. We have shown the contribution of this EA to the total energy,  $E_{SCF}$ , as a function of HOH and HNH angles in the figures. EA is the difference between the  $E_{SCF}$  and the  $E_{SCF} - EA$  curves. We see that EA is larger in magnitude for the linear  $H_2O$  or planar  $NH_3$  due to the greater penetration of the LMOs. Thus the EA arising from the antisymmetry principle tends to favor the *linear*  $H_2O$  or *planar*  $NH_3$ .

In the figures we also show the effect of removing the total electronic (Coulombic) repulsion, ER, from  $E_{SCF}$ , with no change in the MOs. A linear  $H_2O$  or planar  $NH_3$  then has minimum energy. Thus although the MOs remain as the proper SCF LMOs,  $H_2O$  becomes linear and  $NH_3$  planar. The addition of EA only reinforces this tendency. The  $(E_{SCF} - CER)$  strongly favors linear  $H_2O$  and planar  $NH_3$ . We see that the two effects of the antisymmetry principle (on the SCF wavefunction) are not able to "bend"  $H_2O$  from the linear or  $NH_3$  from the planar configuration without the classical Coulombic repulsion (CER) being also present. Therefore it is incorrect to *attribute* the equilibrium

(5) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.

angular structure of H<sub>2</sub>O or NH<sub>3</sub> to "Pauli forces": effects of the antisymmetry.

In an important earlier work Bills and Snow<sup>6</sup> showed that if electron Coulombic repulsion (ER) is neglected in the calculation of the SCF wavefunction a linear H<sub>2</sub>O results. However, the system then becomes essentially that of an O<sup>-2</sup> ion (with hydrogenic atomic orbitals (AOs) of effective nuclear charge +8) and two nearly bare protons. It is not then surprising that a linear H<sub>2</sub>O is obtained, in that the repulsion of the "bare protons" is thereby minimized. Our results show that even if the SCF MO wavefunctions are left unchanged, when ER is dropped from  $E_{SCF}$ , H<sub>2</sub>O will still become linear and NH<sub>3</sub> planar.

All the effects that act to determine the total energy are, of course, extremely closely linked. For example the deletion of the nuclear repulsion  $NR_{HH}$  of protons would cause the two protons of H<sub>2</sub>O or three protons of NH<sub>3</sub> to collapse together. The kinetic energy  $T$  of the electrons changes as much as does the total energy, with opposite sign ( $T = -E$ ), as HOH changes from  $\angle HOH = 180^\circ$  to  $\angle HOH = 105^\circ$ , if optimum  $R_{OH}$  is used at each angle. This follows from an extension of the diatomic virial theorem to polyatomics, due to Nelander and Parr.<sup>7</sup> Thus the changes in the kinetic energies of the electrons are also crucial to the final geometry. However, the VSEPR model as presently formulated attributes the angular structures of molecules primarily to only one factor.<sup>2,3</sup> In spite of considerable empirical success, this is an untenable position. As Drago<sup>8</sup> has pointed out, there are in fact more empirical exceptions to the VSEPR model than was originally thought.

In earlier work<sup>9</sup> we have shown that the constraint of the  $1a_1$  and  $2a_1$  SCF MOs of CH<sub>4</sub> to be exactly the  $1s$  and  $2s$  SCF AOs of the C atom has no effect on the angular conformation of CH<sub>4</sub>. In fact this constraint slightly increases the angular rigidity of CH<sub>4</sub>: the angular force constants increase in value due to the constraint. About one-fourth of the molecular binding energy is lost, and the C-atom LMO hybrid-AO component changes from  $\sim s^{1.13}p^{2.87}$  to  $\sim sp$ . The above is not surprising when we realize that the nuclear framework of CH<sub>4</sub> is, on the whole, angularly more rigid than is the molecule. The symmetry force constants are 0.486 and 0.458 md/Å for the  $S_2(E)(C_{2v})$  and  $S_4(F_2)(C_{3v})$  symmetry modes of the molecule, whereas the corresponding values for the "bare" nuclear framework are 0.406 and 0.961 md/Å. Since any angular movement of a single proton is a linear combination of these symmetry modes, the nuclear framework is, on the whole, more rigidly tetrahedral than is the molecule. The presence of the electrons acts to "soften" the tetrahedral rigidity of CH<sub>4</sub>. The use of the same constraint ( $1a_1 = 1s$  and  $2a_1 = 2s$ ) for H<sub>2</sub>O and NH<sub>3</sub> led to decreased bond angles. This is in accord with the "electron-promotion and AO-hybridization theory" which has long been used.<sup>10</sup>

Palke<sup>11</sup> has used LMOs to show that the "Pauli forces" due to

the orthogonality between the LMOs have strengths in inverse order to that proposed in the present version of the VSEPR model:  $bp-bp > bp-lp > lp-lp$ , with  $bp$  = bond pair, and  $lp$  = lone pair. That could be an important consideration for the  $\angle HOH \approx 112^\circ$  bond angle of H<sub>3</sub>O<sup>+</sup>, which does not "fit" with the VSEPR ideas.

It is well-known that, since left-right (along the bond) correlation of a localized bonding electron pair is not described by SCF wavefunctions, valence-bond-theory ionic terms are not properly weighted. Nevertheless good basis set SCF wavefunctions do give quite good geometries for nearly all molecules so far examined. Therefore it seems likely that the present results would not be greatly changed if separated pair wavefunctions were used, which include these correlations in the two OH bonds. We are presently investigating this by using the first two pair natural orbitals (PNOs) for each OH LMO.<sup>16</sup> Conversely it seems unlikely that complete neglect of the "ionic terms", as in a simple valence bond (Heitler-London) wavefunction, would qualitatively change our conclusions, if such a wavefunction would give a good geometry for HOH. It is difficult to visualize the VSEPR model "Pauli repulsions" being the dominant effect in the true wavefunctions, if not in the SCF ones, in view of the success of the latter for molecular angular geometries. The "experimental" energy curves of the figures are estimates based on experimental bending force constants and barrier heights, with shapes adjusted from large configuration interaction (CI) calculations. Our barrier for H<sub>2</sub>O is 0.0521 au compared to 0.0542 au from a large scale CI calculation.<sup>18</sup> Our NH<sub>3</sub> barrier is 0.0105 au (for optimized NH bond distances) compared to the "experimental" value of about 0.0092 au.<sup>19</sup>

From the standpoint of teaching elementary chemistry courses, it is perhaps unfortunate that there is no one dominant effect determining molecular geometries, e.g., "Pauli repulsions" of electron pairs. Since any student can easily calculate the angular rigidity of the "bare" CH<sub>4</sub> nuclear framework and compare this with the experimental CH<sub>4</sub> force constants, we should be cautious with the use of the VSEPR ideas to the exclusion of others. Many otherwise sophisticated chemists depend too heavily on the VSEPR model in their thinking.

The Gaussian basis set we have used<sup>9b</sup> is described in detail in ref 9a.

## II. Walsh Correlation Diagrams as a Conceptually Simple Alternative

Walsh-Mulliken molecular orbital energy ( $E_i$ ) correlation diagrams appear to offer a correct model for understanding of molecular geometries, when they are based on first- and second-order perturbation theory<sup>12</sup> or the integral Hellmann-Feynman theorem (IHFT).<sup>13</sup> In both these cases the electronic repulsions (ER) and electronic kinetic energy ( $T$ ) are cancelled between the two Hamiltonians:  $H - H^0 = \Delta H$  contains only the

(6) Bills, J. L.; Snow, R. L. *J. Chem. Phys.* **1975**, *97*, 6340.

(7) Nelander, B. *J. Chem. Phys.* **1970**, *51*, 469. Parr, R. G.; Brown, J. E. *J. Chem. Phys.* **1968**, *49*, 4849.

(8) Drago, R. S. *J. Chem. Educ.* **1973**, *50*, 244.

(9) (a) Jarvie, J.; Willson, W.; Doolittle, J.; Edmiston, C. *J. Chem. Phys.* **1973**, *59*, 3020. (b) For the O and N atoms we have used Whitten's<sup>9c</sup>  $10s$ ,  $5p$  Gaussian basis contracted to  $4s$ ,  $3p$  groups, with the two lowest exponent  $s$  and  $p$  Gaussians being groups in themselves. Also  $3d$  groups were used for polarization effects. These  $3d$  groups consist of four  $s$ -type (lobe-type) Gaussians. This  $d$  polarization is necessary for good HOH and HNH angles. The hydrogen atom basis is Whitten's basis with all exponents multiplied by  $2^{1/2}$  and the  $5s$  Gaussians contracted to three groups (with the two lowest exponent Gaussians being groups in themselves). (c) Whitten, J. *J. Chem. Phys.* **1966**, *44*, 359; *J. Chem. Phys.* **1963**, *39*, 349.

(10) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367. Slater, J. *Phys. Rev.* **1931**, *37*, 481.

(11) Palke, W. E. *J. Chem. Phys.* **1979**, *71*, 4664. Palke, W. E.; Kirtman, B. *J. Am. Chem. Soc.* **1978**, *100*, 5717.

(12) Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754. Pearson, R. G. *J. Chem. Soc.* **1969**, *91*, 1252, 4947. Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976.

(13) Kim, H. J.; Parr, R. G. *J. Chem. Phys.* **1964**, *41*, 2892. Parr, R. G. *J. Chem. Phys.* **1964**, *40*, 3726. Takahata, Y.; Parr, R. G. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1380. Epstein, S. T. In *Force Concept in Chemistry*; Deb, B. M., Ed.; Van Nostrand Reinhold: New York, 1981.

(14) Edmiston, C.; Jarvie, J.; Bartleson, J. *J. Chem. Phys.*, in press.

(15) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17.

(16) Edmiston, C.; Krauss, M. *J. Chem. Phys.* **1968**, *49*, 192; **1966**, *45*, 1833; **1965**, *42*, 1119.

(17) This equation follows immediately upon substitution of  $\Delta\psi = (\psi/\eta) - \psi^0$  into  $\Delta E^{IHFT} = \Delta E = \langle \psi^0 | \Delta H | \psi \rangle / \eta$ . The latter follows from  $H\psi = E\psi$  and  $H^0\psi^0 = E^0\psi^0$ , so  $\langle \psi^0 | H | \psi \rangle - \langle \psi^0 | H^0 | \psi^0 \rangle = \langle \psi^0 | H - H^0 | \psi \rangle = (E - E^0) \langle \psi^0 | \psi \rangle = \eta \Delta E$ , since  $\langle \psi | H^0 | \psi^0 \rangle^* = \langle \psi^0 | H^0 | \psi \rangle = E^0 \langle \psi | \psi^0 \rangle^* = E^0 \langle \psi^0 | \psi \rangle$ , because  $H^0$  and  $H$  are Hermitian operators, and  $E^0$  and  $E$  are real. The orbital approximation equation follows by substitution of Slater determinants for  $\psi$  and  $\psi^0$  (with  $\phi_i = \eta_i(\phi_i^0 + \Delta\phi_i)$ ) and the neglect of all terms containing more than one  $\Delta\phi_i$ . (See ref 14 for more details). An accurate SCF wavefunction obeys the ordinary Hellmann-Feynman theorem but not exactly the IHFT theorem used here. Nevertheless for small distortions of molecules we have found very good accuracy compared to the more reliable SCF MO variational results. The analysis must be carried out at a succession of small distortions, but the method we developed<sup>14</sup> involves trivial computation beyond that needed for the LCAO MO SCF results. The results of the IHFT theorem are often quite sensitive to errors in the wavefunction. However it is inconceivable that this  $\langle 1\pi_x | \Delta N A | 1\pi_x \rangle$  term would not remain highly negative for the completely accurate  $1\pi_x$  MO. This is because the protons are approaching one lobe of the  $1\pi_x \approx 2p_z(\text{O atom})$  instead of lying on the nodal plane of the  $1\pi_x$  as in linear H<sub>2</sub>O.

(18) Hennig, P.; Kraemer, W.; Dierksen, G. H. F.; Strey, G. *Theor. Chim. Acta* **1978**, *47*, 233.

(19) Stevens, R. M. *J. Chem. Phys.* **1974**, *61*, 2086; **1971**, *55*, 1725.

changes in the electron-nuclear attractions ( $\Delta NA$ ) and nuclear-nuclear repulsions ( $\Delta NR$ ). Thus a  $\Delta E_i$  term for each occupied MO,  $\phi_i$ , is given approximately as  $\Delta E_i = \langle \phi_i^\circ | \Delta NA | \phi_i^\circ \rangle + \langle \phi_i^\circ | \Delta NA | \Delta \tilde{\phi}_i \rangle$ . The corresponding *exact* expression from the IHFT,<sup>14,17</sup> is  $\Delta E^{IHF} = \langle \psi^\circ | \Delta NA | \psi^\circ \rangle + \langle \psi^\circ | \Delta NA | \Delta \tilde{\psi} \rangle + \Delta NR$ , where  $\Delta \tilde{\psi} = (\psi/\eta) - \psi^\circ$ , and  $\psi^\circ$  and  $\psi$  are the *exact*  $N$ -electron wavefunctions for the undistorted and distorted geometries. Here,  $\eta = \langle \psi^\circ | \psi \rangle$ ,  $\Delta \tilde{\phi}_i = (\phi_i/\eta_i) - \phi_i^\circ$  and  $\eta_i = \langle \phi_i^\circ | \phi_i \rangle$ . Then  $\Delta E = \Delta E^{IHF} \approx \sum_i^N \Delta E_i + \Delta NR$ . If we let  $\Delta H \approx SH' + (S^2/2)H''$  and  $\Delta \tilde{\phi}_i \approx S\phi_i'$ , then this becomes the usual first- and second-order perturbation-theory formulas based on MO wavefunctions.<sup>12</sup>

Now, the  $\Delta E_i$ s can be physically *understood* in terms of the Hellmann-Feynman force acting along the path between the two confirmations (of  $\psi^\circ$  and  $\psi$ ), via the two components given above. The first component  $\langle \phi_i^\circ | \Delta NA | \phi_i^\circ \rangle$  gives the energy change for motion of the nuclei, relative to  $\phi_i^\circ$ , with no change in  $\psi^\circ_{SCF}$ . This should be a conceptual component of the thinking of chemists. The term  $\langle \phi_i^\circ | \Delta NA | \Delta \tilde{\phi}_i \rangle$  gives the modification of the first term due to relaxation of  $\phi_i^\circ$  (to  $\phi_i$ ) which arises from the *mixing* of the *occupied* MOs with the *unoccupied* MOs ( $\phi_k^\circ$ ,  $k > N$ ). This is also an important conceptual component in the thinking of chemists, giving rise to the Woodward-Hoffmann HOMO-LUMO "frontier MO" mixing ideas.<sup>15</sup> (Only occupied and unoccupied MOs of *like* symmetry, along the "reaction coordinate", can "mix" to form the new MOs,  $\phi_i$ .) Although the  $\langle \psi^\circ | \Delta NA | \psi^\circ \rangle$  term is nearly always positive it can contain some very negative  $\langle \phi_i^\circ | \Delta NA | \phi_i^\circ \rangle$  components. For example for the "spontaneous bending" of linear H<sub>2</sub>O, planar NH<sub>3</sub> and planar CH<sub>4</sub>,  $\langle 1\pi_z | \Delta NA | 1\pi_z \rangle \approx \lambda \langle 1\pi_z | \tilde{H}'' | 1\pi_z \rangle$  is *very negative* ( $1\pi_z \rightarrow 3a_1$ ) and more than accounts for the molecular energy lowering  $\Delta E_{SCF}$ .<sup>14</sup> (Here  $\Delta NA = \Delta \tilde{H} = \Delta H - \Delta NR \approx SH' + \lambda \tilde{H}''$ ,  $\lambda = S^2/2$ .) It is the major component of  $\Delta E(3a_1)$  of the Walsh-Mulliken diagram. BeH<sub>2</sub> and BH<sub>3</sub>, for which the  $1\pi_z$  MO is unoccupied, do not spontaneously bend from linear and planar, respectively.

The  $\langle 3a_1^\circ | \Delta NA | 4a_1^\circ \rangle$  term ( $\langle 1\pi_z | \Delta NA | 3\sigma_g^* \rangle$ ) for linear H<sub>2</sub>O is very small, so HOMO-LUMO mixing is not of much importance to the "allowed" spontaneous bending of linear H<sub>2</sub>O and planar NH<sub>3</sub> and CH<sub>4</sub>. Frontier MO ideas are *not always* the total explanation for an "allowed" or "forbidden" nuclear arrangement.<sup>15</sup>

Here again, within the context of the Hellmann-Feynman theorem or second-order perturbation theory, we *could* say that

H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> have "bent" equilibrium structures *because* of the  $\langle 1\pi_z | \Delta NA | 1\pi_z \rangle$  term.<sup>17</sup> However, this is only one of the many important effects determining the equilibrium structures. We see that every supposedly general *simple* idea of the explanation of molecular geometries and "allowed" nuclear rearrangements is "doomed to failure" in some situations, because many very strong effects determine potential energy surfaces. Perhaps there is some simple general idea, yet to be discovered, which will do this, but it will not be found without careful examination of *all* the important effects such as we have begun here.

Both the high barrier for H<sub>2</sub>O and low barrier for NH<sub>3</sub> are "HOMO-LUMO symmetry-allowed" inversion barriers. Because of *three* interproton repulsions in NH<sub>3</sub>,  $\Delta NR$  is very large and nearly destroys an otherwise high inversion barrier. We believe that the quite different behavior of ( $E - ER$ ) in the figures for H<sub>2</sub>O and NH<sub>3</sub> is closely related to these very different  $\Delta NR$ s. Again we see the tremendous complexity of *understanding* the energy surfaces of even these very simple molecules.

Note that ( $E_{SCF} - EA$ ) gives fairly good geometries but too small bond angles and much too high inversion barriers. This corresponds to *distinguishable* electrons occupying orthogonal SCF LMOs. Certainly without the orthogonality (i.e., linear independence) of the MOs the electrons would all tend to "collapse" into a somewhat expanded inner shell on the O atom. Thus antisymmetry does have a great deal of importance to the structure of all atoms and molecules. However, it is not *the* dominating influence for the *angular* structures of H<sub>2</sub>O and NH<sub>3</sub>. The classical repulsion of the MO charge clouds (CER), nuclear repulsions, electronic kinetic energies, etc., are also of critical importance. Although  $\Delta E^{IHF} \approx \Delta E_{SCF}$  is sensitive to errors in  $\psi_{SCF}$  (to first order),<sup>17</sup> we have found it to be reliable for small distortions (e.g., bending of H<sub>2</sub>O and NH<sub>3</sub>) and highly visualizable in its MO components.<sup>14</sup>  $\Delta E^{IHF}$  seems to provide a good beginning toward a *correct* understanding of energy surfaces. Because of the difficulty of accurate quantum calculations for large molecules and activated complexes, this understanding is badly needed. Although the Woodward-Hoffmann HOMO-LUMO terms must be augmented by the  $\langle \phi_i^\circ | \Delta NA | \phi_i^\circ \rangle$  terms for a complete understanding of MO correlation diagrams, the widespread success of the former shows the power of this approach.

Registry No. H<sub>2</sub>O, 7732-18-5; NH<sub>3</sub>, 7664-41-7.

## Molecular PO<sub>2</sub>Cl: Matrix IR Investigations and ab Initio SCF Calculations<sup>1a</sup>

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**Abstract:** PO<sub>2</sub>Cl produced by a photochemical reaction between O<sub>3</sub> and POCl in solid Ar has been studied by IR spectroscopy. The same species is formed in a high-temperature reaction between POCl<sub>3</sub>, O<sub>2</sub>, and Ag. IR spectra including <sup>16</sup>O/<sup>18</sup>O and <sup>35</sup>Cl/<sup>37</sup>Cl shifts show that the OPO angle is about 135° and that the PCl bond is unexpectedly strong ( $f(\text{PCl}) = 3.7 \text{ mdyn } \text{Å}^{-1}$ ). These results are confirmed by ab initio SCF calculations. Bonding in PO<sub>2</sub>Cl is compared with that of similar molecules.

Some of us have recently detected analogues of NOCl, for example, the high-temperature molecules POCl,<sup>2</sup> PSCl,<sup>3</sup> AsOCl,<sup>4</sup>

(1) (a) Presented in part at Chemie-Dozententagung, 1984, Konstanz, Verlag Chemie; International Matrix Conference, 1985, Fontevraud. (b) Universität Karlsruhe. (c) Universität Münster.

(2) Binnewies, M.; Lakenbrink, M.; Schnöckel, H. Z. Anorg. Allg. Chem. 1983, 497, 7.

etc., and investigated their structures. In addition to such molecules, in which a group Va element has a formal oxidation state of three and a coordination number of two, there is increasing interest in compounds of phosphorus(V) with a coordination

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