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Do the VSEPR Points-on-a-Sphere Repulsions Simulate Quantum Interactions?

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The Valence-Shell-Electron-Pair-Repulsion theory, in its Points-on-a-Sphere (POS) variant has been heretofore almost exclusively applied to molecular structure. It is shown that the POS model also implies the form of the potential energy surface for bending deformations of molecules. The extent to which this elementary mechanical model simulates quantum mechanical interactions in binary compounds of main-group elements is investigated using recent EHT molecular orbital calculations to supplement the rather sparse accumulation of experimental and *ab initio* characterizations of potential surfaces. It is found that the POS force field, in the main, parallels quantum quadratic and anharmonic components so closely that it promises to become a useful tool in spectroscopic and diffraction research. A simple effective force law between repelling points, namely $-\partial V_{ij}(r)/\partial r \propto r^{-(s+1)}$, accounts well for the known data. For experiment and *ab initio* theory, the parameter s expressing the hardness of repulsions is about 4, while for EHT computations with frozen VOIP values, interactions are slightly harder with $s \approx 6$. Implications are briefly discussed.

INTRODUCTION

The notion that molecular stereochemistry can be classified, perhaps even understood, in terms of the distribution of mutually avoiding valence-shell electron pairs has attracted attention for a half century. It was recognized from the earliest days of quantum chemistry that the most appropriate hybrid orbitals for bonds and lone pairs radiating from an atom are naturally distributed in space to point away from each other.[1-3] While the relevance of the concept of »molecular-adapted minimal-basis-set atomic orbitals« survives even in today's rigorous quantum treatments,[4] one need not look far to find cases where an unambiguous intuitive decomposition into elementary hybrids for predicting stereochemistry is not at all obvious. In most such cases, however, it has been found unnecessary to speculate about the nature of the hybrid orbitals involved. It is enough merely to count valence-shell electron pairs and to direct the associated bonds/lone pairs in space according to simple rules. One of the first quite general formulations of such rules was articulated by Sidgwick and Powell in 1940.[5] After considerably more structural information had become available, Gillespie and Nyholm[6] extended the rules and gave the stereochemical model the name it is known by today, the »Valence-Shell-Electron-Pair-Repulsion« (VSEPR) theory. Subsequently Gillespie[7] and many others popularized the model and it has become a valuable tool for chemists. Reinforcing the pair-repulsion concept have been recent quantum calculations of molecular electron densities. Regions identifiable with localized electron pairs are plainly evident in the Laplacian of the density, and their spatial distribution agrees with that of the VSEPR theory.[8] One unfortunate pitfall which corrupts the meaning more than the utility of the model is the readiness with which many chemists confuse VSEPR repulsions with simple electrostatic repulsions between electrons. This commonly encountered error will be discussed in a later section.

According to the VSEPR theory, bond angles in molecules are governed by the mutual »repulsions« of Lewis electron pairs[9] in the valence shells of atoms, and these forces are best accomodated when the electron pairs achieve an optimum mutual avoidance. Plausible rules regarding the effects upon pair-repulsions of electronegativity, multiple bonding, *etc.*, have been formulated. For an illustration of the stereochemistry and structural trends correctly predicted by these rules, see Figure 1. So straightforward is the agency of the repulsion envisaged to be that repulsions between electron pairs in a given atomic valence shell have been modeled (successfully) as if they are repelling Points-on-a-Sphere (POS).[7] A voluminous literature[7,10] applies the POS model to stereochemistry and structure. Curiously, little attention has been paid to the fact that a POS model not only implies equilibrium structure—it also implies the shape of the multidimensional potential »surface« for bending deformations of molecules.[11–17] If the VSEPR theory in its POS variant is a bona fide theory yielding correct structures for nonspurious reasons, then, the implied potential surface should closely parallel that revealed by experiment. Although the fact that it actually does in the cases so far examined was at first obscured by misassignments in published vibrational spectra, subsequent work has supported the POS model to a surprising degree.[16,17] That is the principal theme of the present paper.

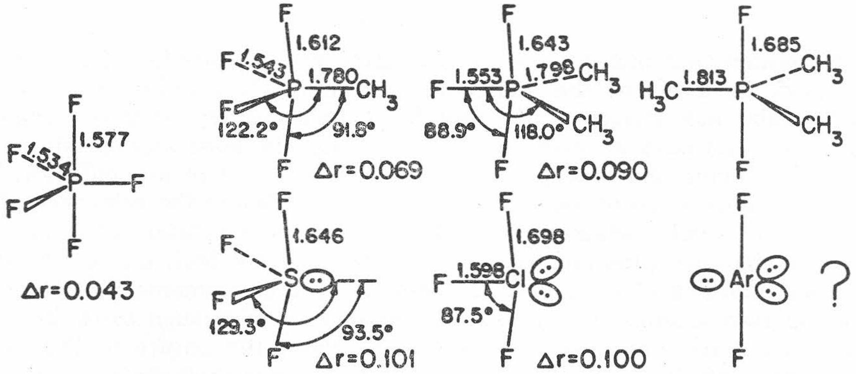

Figure 1. Examples of stereochemistry and structural deformations well accounted for by VSEPR theory.

In the following sections we shall sketch how a potential surface can be extracted from the model of repelling Points-on-a-Sphere, give a few illustrations of the structural chemistry implied, and examine what kind of force law is required to secure realistic harmonic and anharmonic characteristics for the POS force field. Applications in spectroscopy, diffraction, and structural chemistry in general will be evident. In keeping with the early state of development of the ideas involved, some of them heretofore unpublished, we shall concentrate upon binary compounds in order to avoid the complexity of having to introduce multiple parameters to account for different types of electron pairs. Since individual binary compounds (*e. g.* CF_4, IF_7) each require a large number of potential constants to characterize their potential surfaces for bending, they present quite a discriminating test of the POS model. We shall also restrict our attention to compounds of main group atoms. As discussed elsewhere,[14] the substantially different types of bond orbitals utilized by transition metals are modeled less plausibly by points on a sphere.

FORMULATION OF POS FORCE FIELD

For the present surfaces we assume that valence-shell electron pairs *i, j, etc.* can be treated as points constrained to move on the surface of a sphere of radius R under the influence of pairwise additive interaction energies V_{ij}. As a consequence the potential energy for any bending deformation $\tilde{S}_m$ of a molecule AX_n can be expressed by

$$V(\tilde{S}_m) = (\Sigma \underset{j>i}{\Sigma} V_{ij}) - V_0 \qquad (1)$$

where the constant V_0 is the sum over the V_{ij} taken at the equilibrium molecular configuration. It is taken for granted to keep the model elementary that the bond directions radiating from central atom A are centered on the points. In prior work the potential functions V_{ij} have usually been expressed as Kr_{ij}^{-s} or, occasionally, as $C \exp(-\alpha r_{ij})$, where r_{ij} represents the distance between points i and j, and K, s, C, and α are constants. Radius R can be absorbed into parameter K or α. No explicit inclusion of any bending force constants is used to augment equation (1), nor are the undoubtedly appreciable atom-atom nonbonded Urey-Bradley interactions considered.

Minimization of equation (1) with respect to displacements of the points yields the equilibrium bond angles. A Taylor series expansion of equation (1)

$$V = {}^{1}\!/_{2} \sum_{l} \sum_{m} \tilde{f}_{lm} \tilde{S}_l \tilde{S}_m + \frac{1}{6} \sum_{l} \sum_{m} \sum_{n} \tilde{f}_{lmn} \tilde{S}_l \tilde{S}_m \tilde{S}_n + \ldots \qquad (2)$$

leads to the force constants $\tilde{f}_{lm}$, $\tilde{f}_{lmn}$, *etc.*, where the tildes denote that coordinates $\tilde{S}_l$, $\tilde{S}_m$, *etc.*, are *curvilinear*, not *rectilinear*.[18] Explicit formulas have been derived analytically for many of the constants of AX_n for $4 \leq n \leq 7$. It is often simpler to calculate anharmonic constants numerically, however, than to carry out Taylor expansions to higher order terms.

STRUCTURE IMPLICATIONS OF POS

For binary compounds AX_n without valence shell lone pairs, equilibrium structures implied by Eq. (1) are trivial for $n \leq 6$ inasmuch as they are totally insensitive to the form of the repulsion for any plausible V_{ij}, and follow the rules originally proposed by Sidgwick and Powell.[5] (In cases with nonequivalent valence-shell pairs, structures deviate in predictable ways[19] from the idealized reference structures, as can be seen in Figure 1). Binary compounds with n in excess of 6 present more interesting possibilities. Here the predicted structure depends upon the »hardness« of the repulsion, *i. e.*, upon the magnitude of s if we adopt $V_{ij} = \mathrm{K}r^{-s}$. For example, given seven repelling points[11] with $s < 2.0$ (soft repulsion) a pentagonal bipyramid with D_{5h} symmetry is the most stable static structure. In the range $2 < s < 5$, equatorial repulsions in the tightly packed 5-ring induce an e_2'' ring puckering of greater amplitude, the greater is s. Puckering, in turn, induces an e_1' axial bend coupled in phase with the pucker. The resultant flexible structure is predicted to execute large--amplitude (Pitzer-type) pseudorotations because the barrier between the C_2 and C_s conformers is very small. In the range $5 < s < 5.5$ a C_{2v} structure is optimum. Above $s = 5.5$ a C_{3v} structure becomes lowest in energy. Consequently, even if molecular structure reveals little about repulsion in AX_n molecules with $n \leq 6$, the structures of AX_7 molecules should provide valuable information about valence-shell interactions.

This turns out to be the case for iodine heptafluoride. Of the four possible structure types D_{5h}, C_2/C_s, C_{2v}, and C_{3v} forecast by the POS model for different ranges of s, electron diffraction studies[20] placed IF_7 in the C_2/C_s category ($2 < s < 5$). Moreover, the anharmonic coupling between the e_2'' and e_1' modes predicted by POS was in fact observed and this, together with the magnitude of the ring pucker, further narrowed down the allowed hardness exponent to a value of about 3.5. As we shall show, this hardness is also the value required to fit the *shape* of the potential surface calculated much later by an *ab initio* molecular orbital treatment.[17]

Another $n = 7$ example is XeF_6 which possesses a xenon lone pair in addition to the six bond pairs. In this case the lone pair, apparently endowed with a high degree of s-character, is quite different from the bonding pairs. While the lone pair is observed to be stereochemically active, electron diffraction studies[21,22] indicate that the distortion from O_h symmetry is modest and labile, with the lone pair gliding fairly freely from face to face of the octahedron, repelling adjacent bonds as it migrates. *Ab initio* pseudopotential calculations[23] on XeF_6 suggested a less freely migrating lone pair but otherwise supported the diffraction study. It is worth noting, here, that Gillespie,[24] relying on VSEPR theory, had steadfastly insisted that xenon hexafluoride would be found to be distorted from O_h symmetry even though molecular orbital calculations[25] had suggested that it would not.

Few other structures of molecules with large coordination numbers have been determined in the gas phase. Corresponding solid state structures have been less useful in elucidating VSEPR forces than might be hoped because of packing forces, on the one hand, and the proclivity of nearly spherical molecules to disorder in crystals. A rather large amount of fruitful work, interpreted on the basis of a POS model, has been done on complexes of higher coordination in the solid state, however, particularly with bi- and multidentate ligands.[10] In these cases the bite of the ligands has a strong influence on the stereochemistry.

For the above reasons, molecular structure, while for the most part predicted with admirable sucess by the VSEPR theory, has been of limited value (save for the case of IF_7) in providing insight into the character of the forces involved. An intrinsically more penetrating type of observable, applicable to AX_n molecules with any coordination number greater than 1, is the potential surface for bending as characterized by quadratic, cubic, and higher force constants. This source of information is discussed in the next section.

POTENTIAL ENERGY SURFACE

A. *Introductory Remarks*

A single experimental force constant, by itself, sheds no light on the character of VSEPR forces because the magnitude of a given constant can be matched by adjusting either or both the scale factor K and the gauge of hardness, s, in equation (1). If a molecule has several known bending force constants, however, a much more discriminating test is offered, because all should be represented by a single K and s. Moreover, experience suggests that s may reasonably be constrained to a value in the range of, say, 3.5—6. Because the spectrum of force constants often is not extremely sensitive to s in this range it may be adequate to fix s at the outset. Therefore, the POS force field reduces virtually to a single parameter problem (K adjustable) to fit an appreciable number of harmonic and anharmonic bending constants that are usually considered to be independent. Molecules of lower symmetry (*e. g.*, AX_5, AX_7) provide more interesting tests than molecules of higher symmetry (*e. g.*, AX_4, AX_6) because they possess more independent quadratic constants. Anharmonic constants, being much more numerous, seem to offer a richer test than harmonic constants. The fly-in-the-ointment frustrating extensive tests is that few truly *bona fide quadratic* constants are yet available from experiment, and *cubic* and *higher-order* constants are considerably rarer. Even worse, published experimental vibrational assignments and, consequently, assigned force constants were incorrect in the cases first examined for POS tests,[14,16,17] namely AX_5 and AX_7. Clearly, the greater power of the force field diagnosis in comparison with the structure approach is complicated by the greater risk of encountering aberrant data.

If the severely limited amount of reliable spectroscopic information makes the present undertaking seem unpromising and too academic to be of practical use, it should be recognized that there are other sources of information. What precipitated the present scrutiny of the anharmonic components of the bending force field was a recent, quite down-to-earth need. Electron diffraction studies[26] of very hot molecules (CF_4, SiF_4, and SF_6) revealed substantial asymmetries in the radial distribution peaks of the nonbonded distances. Skewing of peaks increased as the temperature was raised and could only be understood on the basis of substantial bond bending anharmonicity.[27] Because too little spectroscopic information was available to confirm this interpretation, a POS force field computation of cubic constants was carried out, for what it was worth, calibrating the scale factor by means of the known quadratic constants. When this approach was found to account for the diffraction intensities of hot molecules,[27] it was decided to compare the mechanical (POS) model with a quantum mechanical model.[28] For initial explorations we applied the semiempirical extended Hückel molecular orbital theory (EHT) which had already been found to give reasonably good potential surfaces for bending. Subsequently, as a check, we carried out SCF *ab initio* computations upon CF_4. *Ab initio* calculations for the quadratic and a few cubic constants had already been performed for PF_5[29] and IF_7.[17]

Accordingly, the remainder of the paper will examine the degree to which the POS model accounts for the potential energy for bending deformations. In those cases where the quadratic field includes a fair number of constants (AX_5, AX_7), only a few key aspects of anharmonicity will be examined. In cases with only two or three quadratic constants (AX_4, AX_6) the cubic field will be explored in detail, as well. Results of the heretofore unpublished molecular orbital calculations[28] are preliminary.

B. AX_2 ($D_{\infty h}$) and AX_3 (D_{3h})

Linear triatomic molecules, which have no cubic and but a single quadratic bending force constant, provide too little information to warrant a POS analysis. Planar AX_3 molecules, with one cubic (in-plane) and two quadratic constants offer somewhat more information but are not a clean test of POS. The best-known stable examples, boron trihalides, confuse the issue by the appreciable π donation of the halogen lone pairs into the a_2'' *p*-orbital of boron. While the associated stiffening of the out-of-plane bend is of the same origin as that handled successfully in ethylene by the POS model,[5] the variable degree of conjugation introduces another parameter and thereby makes the AX_3 system of little interest to treat.

C. AX_4 (T_d)

Although the π bond contributions in tetrahalides are often considered to be significant, especially in shortening the bond lengths in CF_4 and SiF_4, the effects on bending force constants are, presumably, modest. The two independent quadratic force constants, by themselves, afford meager fare for study but, when the three cubic force constants are also brought into the comparison, the tetrahedral case becomes more illuminating. Unfortunately, there exist virtually no reliable experimental data on bending anharmonicity in these molecules. Therefore, we have carried out EHT calculations and, in the case of CF_4, *ab initio* computations. For methane both *ab initio* and experimental values are available from the literature.[30]

Shown in Figure 2 are profiles for several tetrahedral molecules, of relative force constants, »normalized« to unit mean quadratic force constants. The conformity of POS profiles to quantum profiles is, while imperfect, more noteworthy than the disparity. Methane is conspicuously the worst case, particularly in the constant $\tilde{f}_{222}$ for which the observed and MO values agree while being quite out of line with the pattern of the other molecules studied. Why methane, the only case with no core or lone pair electrons in the ligands, is so different is not altogether clear.

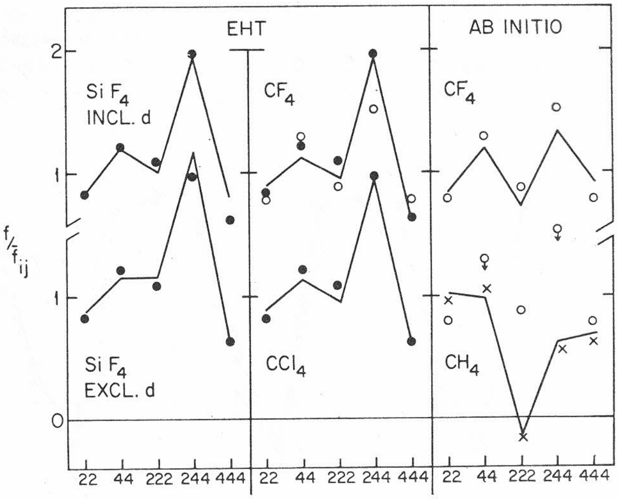

Figure 2. Quadratic and cubic bending force constants for representative tetrahedral molecules, labeled by symmetry coordinate sequence. Lines, molecular orbital calculations. Solid points and open circles, POS force field with $s = 6$ and 4, respectively. Crosses, experiment. For display purposes the sign convention of reference 30 was changed for $\tilde{S}_2$. Symmetry coordinates in radians.

One systematic feature also encountered in other systems is that EHT force fields with standard parameter appear to correspond to slightly harder valence shell repulsions ($s \approx 6$, say) than do *ab initio* repulsions ($s \approx 4$).

D. AX_5 (D_{3h})

As outlined elsewhere[16,31–33] the vibrational properties of pentacoordinated compounds of main group elements display a common theme. We shall consider a single prototype case, PF_5, first studied in this manner a decade ago. Sketched in Figure 3 are the profiles of the five independent quadratic force constants as computed or measured in various ways. Again, provided that the correct vibrational assignment is made, the POS model is seen to work pleasingly well.

Little information is available about the anharmonic components of the force field beyond the influence they have on the barrier to Berry pseudorotations.[34,35] If the barrier is inferred solely from the quadratic bending force constants, a value perhaps four-fold too high is obtained, according to the POS model[14] and to estimates by Holmes[31] based on spectroscopy. If the POS scale factor is adjusted to fit the quadratic constants, the quadratic components of the force field imply a barrier of about 22 kcal/mol while the full accounting of POS anharmonicity reduces the barrier to 5.5 kcal/mol [$n \approx 4$, calibrating scale factor with $f(e_1{}'\ \mathrm{eq})$]. *Ab initio* molecular orbital values of Strich and Veillard[36] are 4.8 (or 8.5) kcal/mol for basis sets including (or excluding) *d*

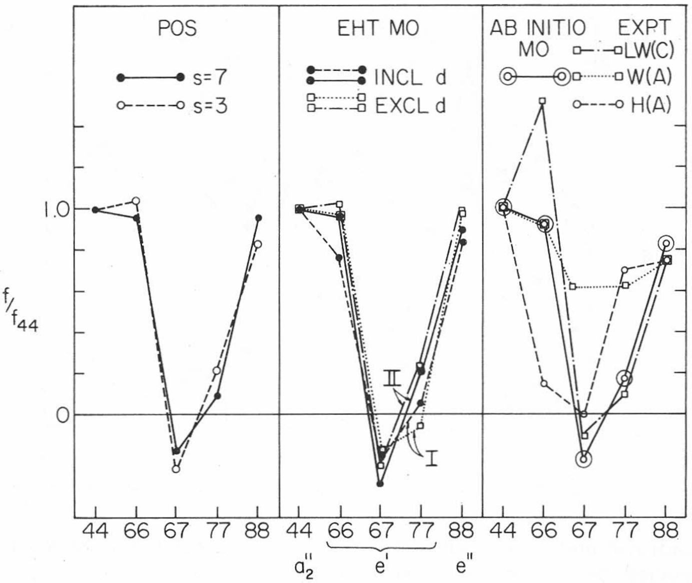

Figure 3. Profile of quadratic force constants for bending of PF_5 according to POS, molecular orbital, and various experimental force fields. See reference 14 for details.

functions on phosphorus. Full accounting of anharmonicity was built into the treatment. It appears, then, that the anharmonic aspect of the POS field is of the correct order of magnitude.

E. *AX_6 (O_h)*

Octahedral binary compounds are of little interest unless their small set of three bending quadratic force constants is supplemented by anharmonic constants. Comparisons are available for only one example to date, that of SF_6. For this example, however, not only are the quadratic constants known from experiment but also one of the cubic constants.[37] Portrayed in Figure 4 are the relevant profiles. All but one POS constant, $\breve{f}_{555}$, are in reasonably satisfactory agreement with calculations and/or experiment. This constant, for which only EHT values are so far available for comparison,[28] turns out to be unstable with respect to charge iteration, unlike the others, and must be regarded as unsettled.

F. *AX_7 (D_{5h} Reference)*

For pentagonal bipyramids there are seven bending quadratic constants that can cover a wide range of values as shown in Figure 5 for IF_7. If a diagonal valence force field had been plotted, the profile ratios for pure $\breve{S}_4$, $\breve{S}_7$, $\breve{S}_{10}$, and $\breve{S}_{11}$ would all have been unity, while those for $\breve{S}_6$ and $\breve{S}_9$ would have been equal

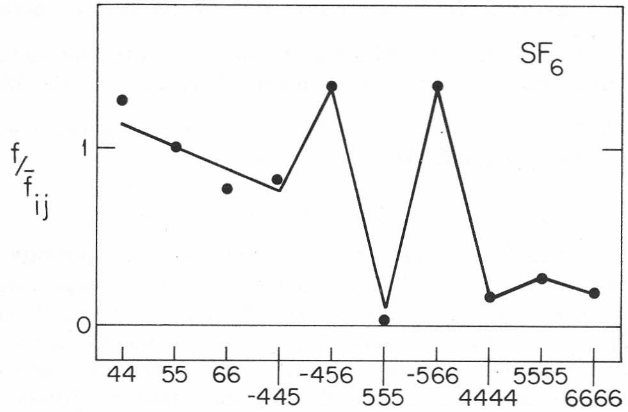

Figure 4. Quadratic, cubic, and diagonal quartic bending force constants for SF_6. Lines, extended Hückel molecular orbital theory. Points, POS force field with $s = 4$.

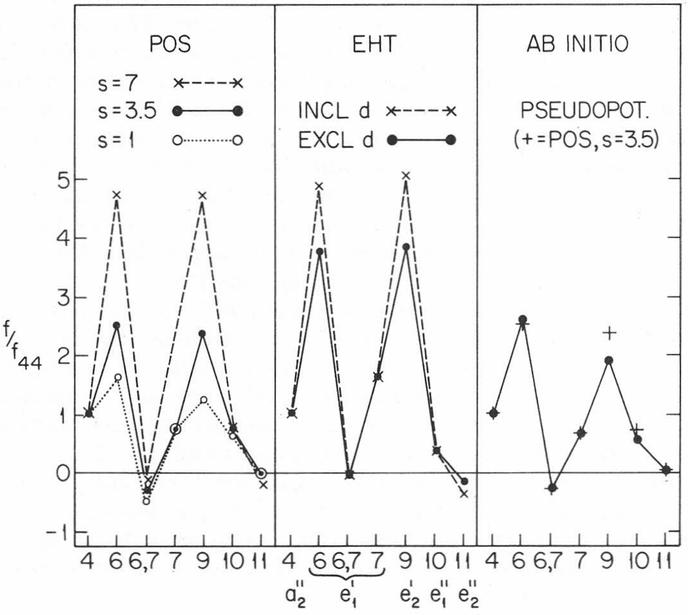

Figure 5. Profile of quadratic force constants for bending of IF_7 according to POS and molecular orbital calculations. See reference 17 for details.

to each other but different from unity. Such an approximation fails to exhibit the trends of the MO calculations that are so faithfully followed by the POS model. It is noteworthy that the electron diffraction structural data,[20] analyzed a dozen years before the *ab initio* computations were carried out,[17] implied, as explained in a previous Section, an $r^{-3.5}$ POS force law. This can be seen in Figure 5 to correspond, as well, to the hardness required to fit the *ab initio* quadratic force constants. Only one cubic force constant for bending has been studied, namely $\breve{F}_{7,11,11}$, the important constant coupling the axial bend to the ring pucker. Expressed in the convention of reference 17, the POS value -0.11 mdyn Å/Å^3 (for $s = 3.5$, scale factor to fit $\breve{f}_{77}$) agrees well with the *ab initio* value,[17] -0.13 mdyn Å/Å^3.

DISCUSSION

As shown in the foregoing sections for binary compounds, the Valence-Shell-Electron-Pair-Repulsion theory in its elementary repelling Points-on-a-Sphere formulation mimics the behavior of molecules too successfully to be dismissed as spurious. This is compelling evidence that occupied bond orbitals are guided by quantum laws to avoid each other in space. Such a repulsion of valence electron pairs is, unfortunately, all too often confused with a simple electrostatic repulsion. The present paper is not the place to expound upon this fallacy in detail but a few words are appropriate. According to the Hellmann-Feynman theorem,[38,39] to be sure, the forces acting upon the atomic nuclei are identically the *electrostatic* forces exerted in the molecule with its quantum mechanically governed electron distribution. This is not at all similar to summing the repulsive coulomb forces acting between a few localized bits of the electron distribution and ignoring forces associated with the remainder of the electron distribution and the nuclei. In this vein it is important to note that the POS model conforms to observed intramolecular force fields only when the repulsions are made considerably harder than electrostatic repulsions. As has been noted elsewhere,[40,41] in molecules the mutual avoidance of filled orbitals correlates one-to-one with the striving to achieve the best possible all-round bonded overlap of atoms (and, where applicable, the most effective lone pair occupancy of low-energy orbitals) consistent with the constraints of orbital use imposed by the exclusion principle.[42] In short, the POS »Pauli force« is not the vague, hypothetical force so often set up as a straw man to be knocked down; in molecules it is manifestly covalent in origin. In the not unrelated illustrative case of electron pair avoidance, the nonbonded repulsion of two helium atoms, the role of the exclusion principle is transparent, for it prohibits the second electron pair from populating the low-energy bonding molecular orbital occupied by the first. Mulliken[43] has aptly referred to nonbonded repulsions as »covalent antibonding.« As successive electron pairs are fed into molecules, successively less stable orbitals with progressively more nodes must be called upon. Nodes are the link between avoidance of localized orbitals and governance of energy.

Lest the foregoing seem to attribute the POS repulsions, say, in SiF_4 to F... F *atom-atom* repulsions (which indeed are *much* harder than coulombic) instead of to bond-bond repulsions, it is pertinent to discuss the matter explicitly. In all of the AX_n cases discussed above, precisely the same type of POS force-field behavior could be obtained by invoking atom-atom instead of electron pair repulsions. The most obvious evidence that this is not an appopriate interpretation is that the VSEPR repulsions required to reproduce the observed force fields do *not* fall off as rapidly as the expected X... X repulsions when the size of A increases, lengthening the X... X distances. Plausible estimates[17,44] make X... X repulsions too small to correspond to POS repulsions, though in some cases with small central atoms or large n, the atom-atom forces may make quite a significant (Urey-Bradley) contribution.

Another feature of the POS model deserves comment. In constructing the model, the points on a sphere symbolically representing localized electron pairs are assumed to be placed on the straight lines connecting bonded atoms. In bending deformations, then, the angular displacements of the points are the same as the angular displacements of the atoms. In short, POS bond lines are never bent. This restriction is purely a convention for book-keeping and cannot be assumed to imply anything about the physical details of covalent bonds. There is evidence that bonds tend to bend in vibrational displacements,[45–48] with central atom hybrids not closely following ligand motions. Some molecular properties are well accounted for by bond bending even in equilibrium structures.[8,49,50] Presumably, endowing a POS model with more flexible bond lines would not change the correlations already established; it would simply encumber a plain, neat treatment with (perhaps) pointless complexity.

Limitations of the POS model, in its simplest form at least, include its poor applicability to compounds of transition metals. Another problem (causing little trouble in practice) is encountered in systems such as AX_5 and AX_7. In these systems the bonds spontaneously organize into an equatorial girdle pierced by two axial bonds. Since axial and equatorial bonds are intrinsically different, the POS axial and equatorial points might be expected to follow different effective force laws. In practice the difference can be absorbed into the hardness parameter s. Another limitation of the POS treatment is its inability to account for a (so far) small fraction of the potential constants of main group compounds. Viewed from another perspective, this shortcoming of POS might be of some use in helping to identify atypical interactions of potential interest.

Despite the above imperfections of the POS model, the most important fact is that it manages to reproduce quite well a large body of information. That it can interrelate so many constants without parameter adjustment purely on the basis of the geometric properties of space suggests some underlying authenticity. It appears that the model may have a number of applications in helping to diagnose molecular behavior. It seems to offer a simpler yet more reliable scheme[14–17] than those customarily adopted by spectroscopists in assigning molecular vibration frequencies. It can provide quick estimates of anharmonic potential constants for bending if the harmonic constants are known. Here, in the limited studies we have made,[28] it handles the quartic and higher constants as well as the cubic. It is promising in its ability to characterize certain dynamic properties of molecules such as Berry pseudorotation[34] (in trigonal bipyramids) and Pitzer pseudorotation[51] (in pentagonal bipyramids), including the coupling of modes of different symmetry that can lend intensity to overtones of nominally inactive modes.[20] It was able to account for puzzling anomalies seen in diffraction patterns of very hot molecules.[27] It even characterizes in a rather appealing physical way the systematic imperfection to be expected in EHT molecular orbital computations of the potential surface for bending. Although these surfaces are surprisingly good, when calculated (as is customary) with frozen matrix elements instead of elements adjusted to compensate for the flow of charge in molecular deformations, the implied valence-shell-electron-pair repulsions are somewhat too »hard«.

What significance underlies the concept of »hardness of repulsions« in VSEPR theory and, indeed, why quantum interactions in molecules are simulalted so realistically by a simple mechanical model, are questions that have not been analyzed searchingly. Whatever the basis of the correlations turns out to be, however, the model itself is ripe for exploitation. Its heretofore practically unnoticed virtues offer food for thought for experimentalists and theorists, alike.

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SAŽETAK

Da li odbijanja VSEPR »točaka na kugli« simuliraju kvantne interakcije?

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Model odbijanja parova velentnih elektrona u svojoj varijanti »točaka na kugli« (POS) rabio se do sada isključivo za određivanje ravnotežnih struktura molekula. U ovom radu pokazano je da POS daje i potencijalne plohe za deformacije kutova veza, koje se mogu usporediti s plohama dobivenima kvantno-kemijskim metodama (*ab initio,* EHT). Proizlazi da model POS postaje koristan pribor za spektroskopska i difrakcijska istraživanja. Efektivna sila koja djeluje između »točaka na kugli« može se izraziti kao $\sim r^{-(s+1)}$, gdje je $s \cong 4$.