

## HARDNESS AND HOMO–LUMO GAP PROBED BY THE HELIUM ATOM PUSHING THE MOLECULAR SURFACE OF THE FIRST-ROW HYDRIDE MOLECULES

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*Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.*

A molecular surface defined as an isosurface of the valence repulsion energy may be hard or soft with respect to probe penetration. As a probe, the helium atom has been chosen. In addition, the Pauli exclusion principle makes the electronic structure change when the probe pushes the molecule (at a fixed positions of its nuclei). This results in a HOMO–LUMO gap dependence on the probe site on the isosurface. A smaller gap at a given probe position reflects a larger reactivity of the site with respect to the ionic dissociation.

**Keywords:** Hardness; HOMO–LUMO gap; Molecular surface; Valence repulsion; *Ab initio* calculations; Hydrides.

Within the Born–Oppenheimer approximation, the concept of molecular shape (or molecular surface) is often used. The shapes of two molecules in most cases decide about the main characteristics of their interaction<sup>1</sup>. Matching or docking of molecules is important in chemistry (supramolecular complexes) and even more in biology (*e.g.* enzymes and their ligands of the “key-lock” or “hand-glove” types). Despite its evident utility, unfortunately, the shape of the molecular surface cannot have a unambiguous definition<sup>2</sup>.

In the present paper we are interested in how a closed shell molecule responds to penetration of its surface by a closed-shell probe. We will be particularly interested in a special role of the Pauli exclusion principle that forbids two closed shell systems to approach too close, more specifically in the valence repulsion energy of the two closed-shell systems,  $E_{\text{rep}}$ , the later being a direct consequence of the Pauli exclusion principle. Two kinds of the response will be considered, namely the molecular surface hardness as

the first derivative of  $E_{\text{rep}}$  with respect to the coordinate oriented inwards the molecule perpendicularly to the isosurface and in the HOMO–LUMO gap behaviour as a function of the probe position on the molecular surface.

At large intermolecular distances, a dominant contribution to the interaction energy is usually the electrostatic one<sup>3,4</sup>, defined as the Coulombic interaction of the unchanged (frozen) charge distributions of individual molecules. At intermediate distances, the dispersion and induction contributions increase to such an extent that they come additionally into play (as well as some higher-order terms of smaller importance)<sup>5</sup>.

The notions of the electrostatic, dispersion and induction energies come from the polarization approximation in the Rayleigh–Schrödinger perturbational theory of intermolecular forces<sup>6</sup>, in which the zero-order wave function  $\varphi^{(0)}$  is assumed as the product of the normalized solutions to the Schrödinger equation for the individual molecules,  $\varphi^{(0)} = \varphi_A \varphi_B$ . Note, that the  $\varphi^{(0)}$  function does not fulfil the Pauli exclusion principle, since an electron exchange between the subsystems A and B does not change the sign of the function, but leads to a distinct function.

In the so-called symmetry-adapted perturbation theory (SAPT)<sup>7</sup>, the zero-order wave function is taken as the antisymmetrized product  $\psi^{(0)} = N \hat{\mathcal{A}}[\varphi_A \varphi_B]$  (called also the Heitler–London function), where  $N$  is a normalization constant and  $\hat{\mathcal{A}}$  stands for the idempotent ( $\hat{\mathcal{A}}^2 = \hat{\mathcal{A}}$ ) antisymmetrizer. For a moment we assume that  $\varphi_A$  and  $\varphi_B$  represent the exact wave functions for the subsystems that correspond to the exact energies  $E_A$  and  $E_B$ . For two closed-shell systems the SAPT gives the valence repulsion contribution ( $E_{\text{rep}}$ ) as

$$E_{\text{rep}} = E_{\text{HL}} - E_{\text{elst}}, \quad (1)$$

where the Heitler–London interaction energy

$$E_{\text{HL}} = \langle \psi^{(0)} | \hat{H} \psi^{(0)} \rangle - (E_A + E_B) \quad (2)$$

and the electrostatic energy,  $E_{\text{elst}}$ , (identical to that appearing within the polarization approximation) is defined as

$$E_{\text{elst}} = \langle \varphi^{(0)} | \hat{V} \varphi^{(0)} \rangle, \quad (3)$$

where  $\hat{H}$  is the electronic Hamiltonian,  $\hat{V}$  is the intermolecular interaction operator composed of all Coulombic interactions of particles (electrons and nuclei) of monomer A with those of monomer B. The electrostatic energy may be split into a part that is representable by the multipole–multipole interactions<sup>6</sup> (the permanent multipole moments of the isolated subsystems)  $E_{\text{multipol}}$  and a remainder,  $E_{\text{pen}}$ , the penetration energy that is a correction to the Coulombic interaction coming from interpenetration of the interacting charge distributions (it decays very fast with increasing distance)

$$E_{\text{elst}} = E_{\text{multipol}} - E_{\text{pen}} . \quad (4)$$

These quantities are related to the first-order SAPT energy correction ( $E^{(1)}$ )

$$E^{(1)} = \frac{\langle \varphi^{(0)} | \hat{\mathcal{A}} \hat{V} \varphi^{(0)} \rangle}{\langle \varphi^{(0)} | \hat{\mathcal{A}} \varphi^{(0)} \rangle} \quad (5)$$

through the relation

$$E^{(1)} \equiv E_{\text{HL}} . \quad (6)$$

For large intersystem distances the valence repulsion  $E_{\text{rep}}$  may be approximated by a power series of terms proportional to the overlap of the interacting charge distributions, the first term being of the order of  $S^2$ , where  $S$  is an overlap integral between the orbitals of the interacting subsystems – a measure of their interpenetration in space.

The extent of the molecular interpenetration at the total energy minimum is related not only to the valence repulsion, but also to other contributions, among others all the above mentioned attractive effects. Since the concept of the molecular shape should be related to its repulsive core rather than to interaction with any particular molecule, we introduce a definition of the molecular surface that highlights the valence-repulsion of two subsystems: the molecule under study and a probe. In particular, one of the interacting closed-shell subsystems may be taken following Amovilli and McWeeny<sup>2</sup> as the ground-state helium atom thus representing a simple structureless spherically symmetric atomic probe. The helium atom seems to be quite a particular probe. Helium, which shares a negative electron affinity with all the noble gas atoms (exception among all other elements), has its absolute value the largest (14.4 kcal/mol)<sup>8</sup>, thus minimizing its role as an electron acceptor. At the same time, its ionization potential is the

highest in the periodic table (566.9 kcal/mol), thus minimizing its electron-donor role. One may conclude that such a probe represents probably an atom that is the most inert possible, while when interacting still offers two electrons as a subject of the Pauli exclusion principle. In such a case (zero electric multipole moments of the probe and therefore  $E_{\text{multipol}} = 0$ ), the valence repulsion interaction energy

$$E_{\text{rep}} = E_{\text{HL}} - E_{\text{pen}}. \quad (7)$$

In practice,  $\varphi_A$  and  $\varphi_B$  are never the exact wave functions. If  $\tilde{\varphi}_A$  and  $\tilde{\varphi}_B$  are some approximations to the exact solutions  $\varphi_A$  and  $\varphi_B$ , e.g. the Slater determinant functions, then the  $E_{\text{HL}}$  computed from Eq. (2) and  $E^{(1)}$  of Eq. (5) are not equal anylonger and the difference  $\Delta_{\text{LM}}$  (the Landshoff and Murrell deltas<sup>9,10</sup>,  $\Delta_L$  and  $\Delta_M$ , respectively) can be written in the following form:

$$\begin{aligned} \Delta_{\text{LM}} &= \Delta_L + \Delta_M = E_{\text{HL}} - E^{(1)} = \\ &= \frac{\langle \varphi^{(0)} | \hat{\mathcal{A}}(\hat{H}_A + \hat{H}_B) | \varphi^{(0)} \rangle}{\langle \varphi^{(0)} | \hat{\mathcal{A}} \varphi^{(0)} \rangle} - \langle \varphi^{(0)} | \hat{H}_A + \hat{H}_B | \varphi^{(0)} \rangle, \end{aligned} \quad (8)$$

where  $\hat{H}_A$  and  $\hat{H}_B$  are the Hamiltonians for the A and B subsystems. It has been shown that when the Slater determinants for the isolated monomers are constructed from the exact Hartree–Fock orbitals<sup>9</sup> or when the orbitals are calculated in the dimer atomic basis set<sup>11</sup>, then  $\Delta_L = 0$  and that  $\Delta_M = O(S^4)$ <sup>12</sup>, where  $S$  is an overlap integral. In our calculations the Landshoff  $\Delta_L$  turned out to be as small as  $10^{-8}$  kcal/mol, which is the result of using the dimer basis set, while the Murrell delta is of the order of 0.05 kcal/mol for all the molecules under study.

The SCF LCAO MO approximations to the wave functions of the isolated interacting species ( $\tilde{\varphi}_A$  and  $\tilde{\varphi}_B$ ) have been used and therefore, according to Eq. (8), the valence repulsion energy has been computed from Eq. (1) with

$$E_{\text{HL}} = E^{(1)} - \Delta_{\text{LM}}. \quad (9)$$

The basis sets employed are the Dunning's d-aug-cc-pVDZ<sup>13</sup>. The geometries of all the molecules under study have been first optimized. The optimized methane geometry corresponds to  $r_{\text{CH}} = 1.086$  Å, for the ammonia molecule  $r_{\text{CH}} = 0.9979$  Å and the HNH angle is equal to 108.11°, the water

molecule geometry corresponds to  $r_{\text{OH}} = 0.94085 \text{ \AA}$  and  $\alpha_{\text{HOH}} = 104.69^\circ$ , while the hydrogen fluoride bond length is equal to  $0.8972 \text{ \AA}$ .

#### THE SURFACE DISTRIBUTION OF THE PAULI HARDNESS AND OF THE HOMO-LUMO GAP

Having defined the molecular shape as the valence repulsion isosurface, one may be interested in how easily the probe penetrates the isosurface, *i.e.* in the hardness of a particular spot on the isosurface. The Pauli hardness  $h^{(1)}(\mathbf{P})$  is defined<sup>15</sup> as the first derivative of the valence repulsion energy computed at a given point of the valence repulsion +5 kcal/mol isosurface (the value has been chosen to be consistent with the convention adopted in ref.<sup>2</sup>) in the direction  $\nabla E_{\text{rep}}$  (*i.e.*, normal to this isosurface) with the corresponding coordinate  $r > 0$  meaning the probe penetrating the molecular volume:

$$h^{(1)}(\mathbf{P}) = \left( \frac{\partial}{\partial r} E_{\text{rep}} \right) \Big|_{r=0}, \quad (10)$$

where  $r = 0$  corresponds to the point of the isosurface (higher-order hardnesses, or hyperhardnesses can be defined as well).

The probe entering the isosurface makes an electron cloud flow, which changes the energy spectrum. In the acceptor-donor reaction rate theory<sup>16</sup>, collision of two molecules constitutes a perturbation which leads to an avoided crossing. When the reaction begins, one of the diabatic surfaces involved corresponds to the ground electronic state, the other to an excited state (with an electronic charge distribution resembling that of the reaction products), whereas when the reaction ends, their energies order is reversed. It is shown<sup>16</sup> that the key excited state that resembles the products corresponds to the HOMO→LUMO single excitation. Therefore, the HOMO-LUMO gap

$$\Delta\varepsilon = \varepsilon(\text{LUMO}) - \varepsilon(\text{HOMO}), \quad (11)$$

where  $\varepsilon$  means the orbital energy, may be considered as related to the energy barrier to overcome. Two reacting molecules or a single molecule with a probe may undergo such a HOMO-LUMO intersection just by mechanical pushing (molecule-molecule or molecule-probe). The larger the  $\Delta\varepsilon$  the larger the deformation needed to overcome the barrier and the larger the barrier itself. Both HOMO and LUMO of the first-row hydride molecule-probe system are localized on the molecule, not on the probe (the probe orbital

energy is equal to  $-0.88$  a.u., while the HOMO and LUMO energies for, *e.g.*, the hydrogen fluoride molecule are much higher in the energy scale:  $-0.65$  and  $0.01$  a.u., respectively; for other molecules studied, the probe orbital energy separation is even larger) and therefore the  $\Delta\varepsilon$  as a function of the probe position on the energy isosurface may be viewed as a surface reactivity (with respect to the intramolecular electron transfer) distribution of the molecule under study

$$\Delta\varepsilon(\mathbf{r}_S) = [\varepsilon(\text{LUMO})(\mathbf{r}_S) - \varepsilon(\text{HOMO})(\mathbf{r}_S)], \quad (12)$$

where  $\mathbf{r}_S$  is the probe position on the valence repulsion  $+5$  kcal/mol isosurface.

Isosurfaces are bound to have a certain arbitrariness in their definition. One may ask, whether the hardnesses obtained depend qualitatively on a particular definition. To check that we have used additionally the isosurface definition that is based on the Hartree–Fock interaction energy  $E_{\text{int}}^{\text{HF}}$  (calculated with the Boys–Bernardi counterpoise correction for the basis set superposition). The corresponding isosurface may be penetrated perpendicularly by the helium probe and the corresponding Hartree–Fock hardness may be computed using  $E_{\text{int}}^{\text{HF}}$

$$h^{(1)\text{HF}} = \left( \frac{\partial}{\partial r} E_{\text{int}}^{\text{HF}} \right) \Bigg|_{r=0}. \quad (13)$$

## RESULTS AND DISCUSSION

The valence repulsion isosurface itself as well as the  $\Delta\varepsilon(\mathbf{r}_S)$  and  $h^{(1)}$  functions of the position on the isosurface exhibit, of course, the symmetry of the molecule *i.e.* transform according to its fully symmetric irreducible representation.

Figures 1a–1d show the positions  $\mathbf{r}_S$  of the helium atoms at the 5 kcal/mol isosurface of the valence repulsion energy  $E_{\text{rep}}$  together with the values  $\Delta\varepsilon(\mathbf{r}_S)$  and the Pauli maximum and minimum hardnesses  $h^{(1)}(\text{P})$  for the four molecules under study: HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>.

The 5 kcal/mol isosurface is convex for all the molecules studied, the overall shape is roughly spherical, but its anisotropy is well marked for all the molecules. The distance from the heavy atom nucleus to the isosurface ( $r$ ) depends significantly on the direction chosen. Interestingly<sup>15</sup>, the amplitude  $\Delta r = r_{\text{max}} - r_{\text{min}}$  is very much the same ( $0.37$  Å) for NH<sub>3</sub>, H<sub>2</sub>O and HF molecules, while the methane molecule is an exception with  $\Delta r = 0.49$  Å.

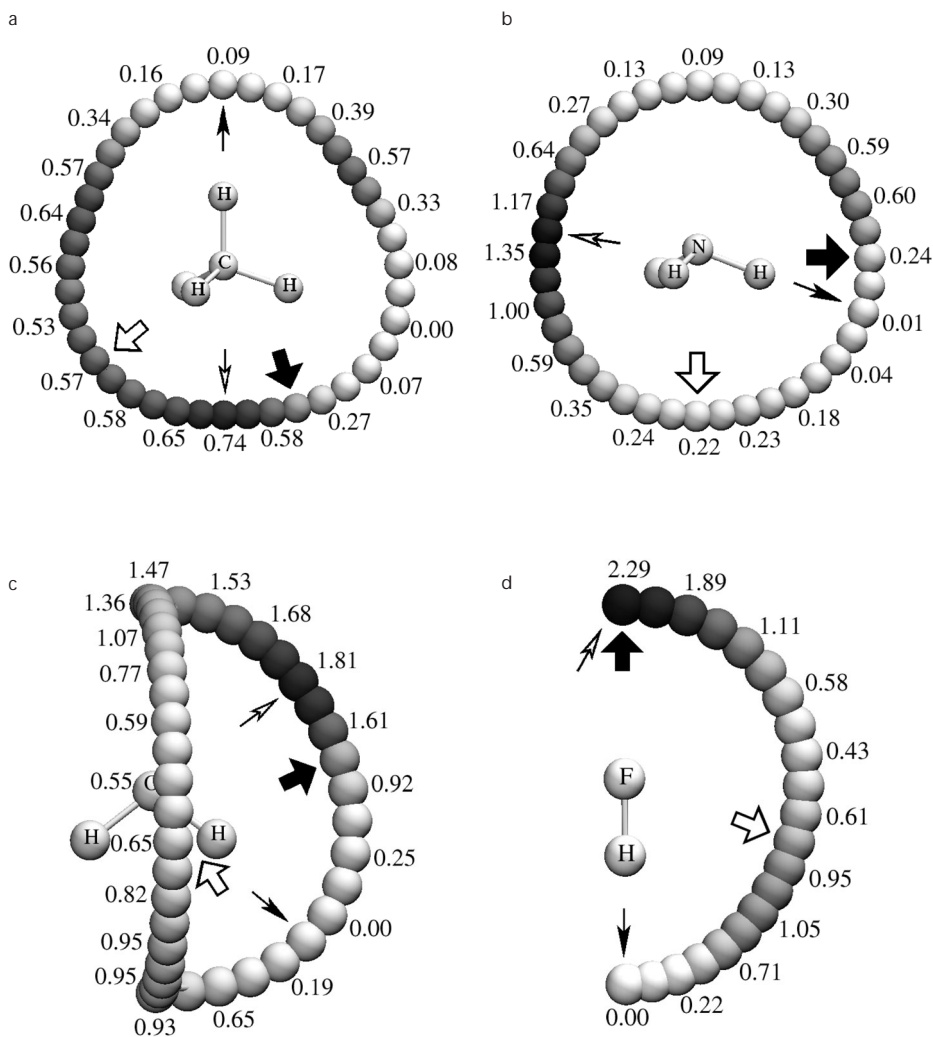


FIG. 1

The helium atomic probe positions on the +5 kcal/mol isosurface of the valence repulsion energy,  $E_{\text{rep}}$ , for CH<sub>4</sub> (a), NH<sub>3</sub> (b), H<sub>2</sub>O (c) and HF (d). The shadow of the helium probe corresponds to the value of the HOMO-LUMO gap, when the probe penetrates the molecule in the direction normal to the isosurface. The white (black) color corresponds to the lowest (largest) gap. The numbers shown correspond to the HOMO-LUMO gap (in kcal/mol) relative to the HOMO-LUMO gap minimum for a given molecule reported in column 7 of Table I (in a.u.). The narrow arrows show the points of the isosurface that are the closest to ( $r_{\text{min}}$ , white arrow) and most distant from ( $r_{\text{max}}$ , black arrow) the heavy atom. The wide black (white) arrow shows the surface point that corresponds to the maximum (minimum) Pauli hardness

In order to make the two isosurfaces (of  $E_{\text{rep}}$  and  $E_{\text{int}}^{\text{HF}}$ ) comparable, we have assumed that they have a common point opposite to the heavy atom and corresponding to the 5 kcal/mol valence repulsion energy (therefore they are tangent one to the other). The isosurface of the Hartree–Fock interaction energy differs only by about 0.05 Å. The corresponding electronic density isosurface, which also has been computed, deviates a little more by about 0.12 Å.

As shown in Table I the computed numerical values of  $h^{(1)}(\text{P})$  and  $h^{(1)}(\text{HF})$  obviously differ, the  $h^{(1)}(\text{HF})$  is roughly twice as small as the  $h^{(1)}(\text{P})$ .

TABLE I

Hardnesses ( $h^{(1)}$  in kcal/mol Å) and the HOMO–LUMO gaps  $\Delta\varepsilon$  for the methane, ammonia, water and hydrogen fluoride molecules in their equilibrium Hartree–Fock geometries calculated for the +5 kcal/mol isosurface of the valence repulsion (a) as well as for the corresponding (see the text) isosurface of the Hartree–Fock interaction energy (b). In columns 2 and 3 the maximum ( $h_{\text{max}}^{(1)}$ ) and minimum ( $h_{\text{min}}^{(1)}$ ) values of the hardness  $h^{(1)}$  are given, the column 4 contains their difference (anisotropy  $\Delta h^{(1)}$ ), all the quantities in kcal/mol Å. In the column 5 the HeXH angles  $\alpha$  (in °; X means the heavy nucleus) are reported, where the helium atom position corresponds to the maximum hardness. Columns 6–9 contain the maximum  $\Delta\varepsilon$ , the minimum  $\Delta\varepsilon$  (in hartree) and their difference  $\Delta(\text{gap})$  (in kcal/mol) as well as the angle  $\beta$  (in °) that corresponds to that helium position that exhibits the minimum of  $\Delta\varepsilon$

## a) Isosurface of the valence repulsion energy

Molecule	$h_{\text{max}}^{(1)}(\text{P})$	$h_{\text{min}}^{(1)}(\text{P})$	$\Delta h^{(1)}(\text{P})$	$\alpha_{\text{HeXH}}$	$\Delta\varepsilon_{\text{max}}$	$\Delta\varepsilon_{\text{min}}$	$\Delta(\text{gap})$	$\beta_{\text{HeXH}}$
CH <sub>4</sub>	18.66	18.08	0.58	43	0.5485	0.5474	0.73	3
NH <sub>3</sub>	19.94	16.71	3.23	44	0.4326	0.4305	1.34	6
H <sub>2</sub> O	20.96	18.53	2.43	44	0.5173	0.5145	1.77	4
HF	22.14	20.66	1.48	180	0.6601	0.6565	2.29	0

## b) Isosurface of the HF interaction energy

Molecule	$h_{\text{max}}^{(1)}(\text{HF})$	$h_{\text{min}}^{(1)}(\text{HF})$	$\Delta h^{(1)}(\text{HF})$	$\alpha_{\text{HeXH}}$	$\Delta\varepsilon_{\text{max}}$	$\Delta\varepsilon_{\text{min}}$	$\Delta(\text{gap})$	$\beta_{\text{HeXH}}$
CH <sub>4</sub>	8.03	7.80	0.23	57	0.5485	0.5472	0.82	6
NH <sub>3</sub>	7.82	6.52	1.30	44	0.4327	0.4306	1.29	16
H <sub>2</sub> O	8.64	7.55	1.09	37	0.5173	0.5144	1.86	7
HF	9.37	8.68	0.69	180	0.6601	0.6556	2.83	0



The Pauli hardnesses differ widely within a single molecule (the upper part of Table I), thus exhibiting a strong anisotropy (the same pertains to the Hartree–Fock hardness)<sup>15</sup>. However, for both definitions of the hardness, the anisotropy is the largest for the ammonia molecule, it decreases monotonically with the heavy atom atomic number with a remarkable exception for the methane molecule. Interestingly, it turned out that the hardest parts of the valence repulsion isosurface often correspond to the global minimum of the interaction energy<sup>15</sup>.

Figure 1 shows the surface distribution of  $\Delta\varepsilon(\mathbf{r}_g)$ , while in Table I are collected the maximum and minimum values of  $\Delta\varepsilon$  of Eq. (12) for each of the molecules and the two definitions of the isosurface (columns 6–9). It turns out that the trends obtained are independent of the isosurface definition, the gap increases with the atomic number of the heavy atom. As seen from Table I (column 9, upper part of the Table) for all the  $\text{XH}_n$  molecules under study and practically independently of the particular isosurface, the smallest gap corresponds to the probe pushing almost along a H–X bond (within the accuracy of about  $6^\circ$ ) right towards the protruding hydrogen atom (see  $\beta_{\text{HeXH}}$ ). On the other hand, the maximum gap in all cases corresponds to the opposite direction, which means pushing the X atom. Similar results correspond to the Hartree–Fock isosurface (column 9, lower part of the Table). The probe pushing the molecular electron cloud (due to the Pauli exclusion principle) makes the pushed site to play a role of the forced electron donor. According to the interpretation given above, the lowest gap means that the intramolecular electron transfer reaction occurs more easily (larger reactivity). Therefore the problem of the gap may be understood when considering whether it is easier to force the  $\text{H}^+(\text{XH}_{n-1}^-)$  polarization when pushing the probe towards the hydrogen atom along the HX bond, or to force the  $\text{H}^-(\text{XH}_{n-1}^+)$  polarization when pushing the probe from the X side. Since the hydrogen atom electronegativity is lower than any of the X atoms considered, the HOMO–LUMO gap is smaller for the hydrogen atom head-on pushing by the helium atom probe. In conclusion, the probe that pushes a particular site of a molecule makes the site acting as a forced electron donor. The probe when pushing lowers the energy of that excited state which resembles the new electronic distribution with the site positively charged.

As one can see from Table I (column 8), the largest as well as the smallest HOMO–LUMO gap increases monotonically with the atomic number of the X atom except for the methane molecule. Despite the methane exception the gap amplitude  $\Delta(\text{gap})$  changes monotonically.

As seen from Figs 1a–1d, the maximum hardness position coincides roughly with the HOMO–LUMO gap maximum except for ammonia molecule.

## CONCLUSIONS

One may conclude that for the homologous series under study

- the valence repulsion isosurface although roughly of spherical shape exhibits a significant anisotropy. The isosurface exhibits the site-dependent Pauli and Hartree–Fock hardness

- the HOMO–LUMO energy gap varies up to 1% for a given molecule (the HOMO–LUMO gap anisotropy), when subject to pushing by the helium probe (at the 5 kcal/mol valence repulsion isosurface and the corresponding isosurface of  $E_{\text{int}}^{\text{HF}}$ )

- the anisotropy of the HOMO–LUMO gap changes monotonically with the atomic number of the X atom and attains the maximum value for the HF molecule, while it is the smallest for the  $\text{CH}_4$  molecule

- for a given molecule, the lowest HOMO–LUMO energy gap corresponds to the head-on probe approach to the hydrogen atom nearly along the H–X bond direction

- for a given molecule, the largest HOMO–LUMO energy gap corresponds to the head-on probe approach to the X atom nearly along the X–H bond direction

- these directions are related to the expected polarization of the molecule forced by pushing by the helium probe atom (easier for the direction from the less negative to more negative atom than the other way round).

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