The relations of bond length and force constant with the potential acting on an electron in a molecule

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The potential acting on an electron in a molecule (PAEM) is defined as the interaction energy of a local electron with the rest particles, i.e. all nuclei and remaining electrons. The substantial difference of the PAEM from the molecular electrostatic potential (MEP) is analyzed and discussed. PAEM has been introduced and used in the previous studies,[1-4] for describing and defining a kind of molecular intrinsic characteristic contour. PAEM at $\vec{r}_1$ in a molecule can be expressed as

$$V\left(\vec{r}_1\right) = -\sum_A \frac{Z_A}{\left|\vec{r}_1 - \vec{R}_A\right|} + \frac{1}{\rho(\vec{r}_1)}\int \frac{\rho_2\left(\vec{r}_1, \vec{r}_2\right)}{\left|\vec{r}_1 - \vec{r}_2\right|}d\vec{r}_2$$
$$= V_{ne}\left(\vec{r}_1\right) + V_{ee}\left(\vec{r}_1\right) \qquad (1)$$

The SDCI calculations were performed by the MELD[5] program package developed by Davidson et al. and a program of our own, and then the PAEM was obtained with the near Hartree-Fock quality Gaussian-type orbital basis sets[6]. The PAEMs for a series of diatomic halides, HX, LiX, NaX and X_2 (X=F, Cl, Br, and I), as well as H_2O and NH_3 and some organic molecules have been studied. The 3D graph of the PAEM for HBr on *XY* plane (Molecular Plane) is depicted in Figure 1.

We have illustrated and compared the 3D topological graphs of the PAEMs. All these 3D graphs of the PAEMs are topologically similar along the chemical bond axes, which are divided into three regions, the near-nucleus, bond and out bond regions. However, it should be noted that we can distinguish them from each other by two points: one is the well width which mainly reflects the nuclear charge, and the other is the height of the PAEM barrier

along the bond axis around the bond region, or equivalently the depth D_{pb} of the PAEM curve on the plane that passes through the saddle point and perpendicular to the bond axis. We have found that the D_{pb} inherently correlates with the bond length and force constant, which are two fundamental bond properties characterizing the strength of a chemical bond. Figure 2 shows the linear relationship between the D_{pb} and bond lengths for H-X (X=F, Cl, Br, I) chemical bond. Thus, it is demonstrated that the PAEM value D_{pb} at the saddle point characterizes the strength of the chemical bond.
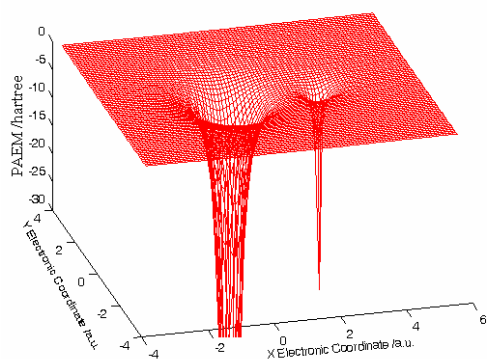
Figure 1 The three-dimensional graph of the PAEM for HBr on *XY* plane (Molecular Plane).
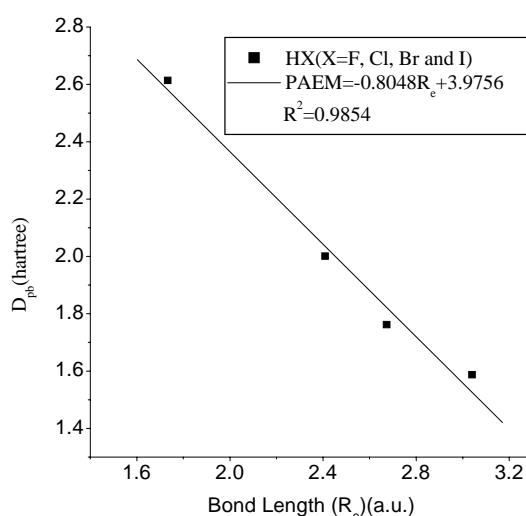
Figure 2. The linear relationship between the D_{pb} and bond lengths for H-X (X=F, Cl, Br, I) chemical bond

Reference

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