J. Phys. Chem. A **2005,** *109,* 10121−10128

The Relations of Bond Length and Force Constant with the Potential Acting on an Electron in a Molecule

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Received: July 4, 2005; In Final Form: August 31, 2005

Within a molecule, the potential acting on an electron (PAEM) is defined as the interaction energy of a local electron with the rest of the particles, i.e., all nuclei and remaining electrons. The formalism of the PAEM is first derived, and the calculated PAEMs are then obtained by using the ab initio program based on the MELD program package for a series of diatomic halides, namely, HX, LiX, NaX, and X_2 molecules (X= F, Cl, Br, and I), as well as H_2O and NH_3, and some organic molecules. By comparing the 3D topological graphs of the PAEMs, we found that there is a saddle point along every chemical bond axis. Further, the good linear correlations of the force constant and bond length with the PAEMs are explored through a definition of D_{pb}, which is the absolute value (i.e., the negative) of the PAEM at the saddle point along the chemical bond axis. In addition, the difference between the PAEM and molecular electrostatic potential (MEP) is pointed out by analyzing both their definitions and numerical results.

1. Introduction

The potential describing the interaction between objects or particles that constitute a system plays a basic role in governing the motion of objects or particles of the system. Therefore, exploration and representation of the potential of a system is a fundamental task. For a molecular system consisting of nuclei and electrons, the potential in the usual study mainly involves the Coulomb interaction between them. Nevertheless, the practical solution of the nonrelativistic time-independent Schrödinger equation[1,2] in molecular quantum mechanics is a tremendous work even for simple molecules. A widely used important approximation, a separation of (slow) nuclear motion from (fast) electronic motion, proposed by Born and Oppenheimer,[3] is very often and widely accepted in treating the molecular problem.[4−8] In the Born−Oppenheimer approximation, the potential energy surface (PES), $E(\vec{R})$, which is the molecular total energy at a nuclear configuration ($\vec{R}$ is the nuclear coordinate) on one side and the electronic energy on the other side, is a very important quantity. The investigation of both PES and its reduced form for performing molecular dynamics, as well as giving various indicators of molecular properties and reactivities,[6−8] is extremely important and is a major field of research.

In contrast to the active study of the PES,[1−7] there are few reports on investigation of the potential acting on electrons in a molecule. In fact, as we will see, the electronic state or electronic structure is a different matter from the potential acting on an electron within a molecule, though they are related closely. Just as nuclear motion on a PES can display a chemical reaction vividly, electronic motion on the potential felt by them can determine the properties of the system. Furthermore, the investigation of the potential acting on electrons will provide a new feature about electronic motion and chemical bonding in a molecule. Frankly, since the number of electrons in a molecular system is usually much larger than the number of nuclei, the study about the potential acting on the electrons of the system is certainly a much harder task than that of the PES. Fortunately, we may reduce this many-electron potential to a single-electron potential, i.e., the potential acting on an electron in a molecule (PAEM).

As is well-known, various potentials play an important role in discussing the electronic structure and molecular interaction. In the Hartree−Fock self-consistent field molecular orbital (HFSCF-MO) theory,[9,10] the canonical molecular orbitals (CMOs) satisfy the single-electron HF equation, in which the potential felt by an electron is the interaction energy of this electron at a given CMO with all the nuclei and the remaining electrons. This potential is obviously dependent on the CMO occupied by this electron. In the Kohn−Sham (KS)[11] equation of density functional theory (DFT), an electron at a KS orbital is affected by an effective KS potential which includes the interaction terms from all the nuclei, all other electrons, and the exchange correlation. For the study of metal solids, Slater[12] assumed that all electrons move in the same field, which is formed by all the nuclei and the remaining electrons, and furthermore, he set up Slater average potential field, which is the basis of the energy band theory of solids. The quantity $\{\nabla^2\sqrt{\rho(\vec{r})}\}/\{2\sqrt{\rho(\vec{r})}\}$, termed the one-electron potential (OEP),[13−17] which was introduced by Hunter as a tool for the graphical analysis of electron density in molecules, was included in the one-electron Schrödinger equation defined by him. Chan and Hamilton[18] defined the outmost OEP = 0.0 surface as the molecular envelope and furthermore studied the valence-shell structures of some diatomic molecules at large.

The nuclear potential is a potential of the Coulomb field generated by the atomic nuclei. Tal, Bader, and Erkku[19] had traced the fundamental role of the nuclear potential in determining the topological properties of charge distribution and studied the structural homeomorphism between the electronic charge density and the nuclear potential of a molecular system in terms of their topological properties.

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10.1021/jp053642n CCC: $30.25

The molecular electrostatic potential (MEP) that is created in the space around the molecule by its nuclei and electrons has been proven to be a useful tool in explaining chemical reactivity and molecular interactive behavior (see, for example, refs 20−24 and references therein). It is through this potential that a molecule is first "seen" or "felt" by another approaching chemical species.[20−22] Thus, MEP is often used to discuss reaction, binding, and catalysis mechanisms[20,23,24] or as a descriptor in many research areas such as molecular structure,[25] solvation,[26,27] crystalline state,[28,29] force-field parametrization,[30] quantitative structure−activity relationships (QSAR),[30,31] and molecular similarity studies.[32] It also has a large impact on rational drug design as a tool for "lead" optimization and pharmacophore searches.[33,34]

The potential acting on an electron in an atom or a molecule (PAEM) has been introduced and used in the previous studies,[35−44] for describing and defining a kind of molecular intrinsic characteristic contour (MICC). In this paper, the detailed calculations of PAEMs in terms of the ab initio program based on MELD[45] are presented, and the 3D topological graphs suggest that the PAEMs around a chemical bond relate intimately to its bonding properties, for example, the force constant and bond length. In the remainder of this paper, the derivation of formalism of the PAEM is presented in section 2, followed by the description of the difference between the PAEM and the MEP. The results of the stereoscopic features of the PAEMs for some molecules and the relations of the PAEM with the fundamental bond properties, such as force constant and bond length, are presented and discussed in section 3. Finally, a summary is given in section 4.

2. Formalism

2.1. The Potential Acting on an Electron in a Molecule (PAEM). PAEM is defined as the interaction energy of a local electron that belongs to the molecule with the rest of the particles, namely, all the nuclei and the remaining electrons. For a molecule, the Coulomb interaction energy of the first electron at position $\vec{r}_1$ with the rest of the particles is expressed as

$$V'(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R}) = \sum_{\mathrm{A}} \frac{-Z_{\mathrm{A}}}{|\vec{r}_1 - \vec{R}_{\mathrm{A}}|} + \sum_{i=2}^{n} \frac{1}{|\vec{r}_1 - \vec{r}_i|} \quad (1)$$

where $\vec{r}_1$, $\vec{r}_2$, ..., and $\vec{r}_n$ denote the position vectors of the 1st, 2nd, ..., and nth electrons, respectively, $\vec{R}$ denotes the set of nuclear position vectors, $\vec{R}_{\mathrm{A}}$ is the position vector of the nucleus A, and Z_{A} is the nuclear charge of atom A. The summation involving index A is over all the atomic nuclei, and the summation involving index i is over all the remaining electrons. If the molecule is in an electronic state $\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R})$, the first-order reduced average of the potential expressed by eq 1 is

$$V'(\vec{r}_1; \vec{R}) = \int \Psi^*(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R}) V'(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R}) \Psi (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R})\, \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_n = \rho'(\vec{r}_1;\vec{R}) \sum_{\mathrm{A}} \frac{-Z_{\mathrm{A}}}{|\vec{r}_1 - \vec{R}_{\mathrm{A}}|} + (n-1) \int \frac{\rho'_2(\vec{r}_1, \vec{r}_2; \vec{R})}{|\vec{r}_1 - \vec{r}_2|} \mathrm{d}\vec{r}_2 \quad (2)$$

where

$$\rho'(\vec{r}_1; \vec{R}) = \int \Psi^*(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{\mathrm{R}}) \Psi (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R})\, \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_n \quad (3)$$

$$\rho'_2(\vec{r}_1, \vec{r}_2; \vec{R}) = \int \Psi^*(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R}) \Psi (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n; \vec{R})\, \mathrm{d}\vec{r}_3 \cdots \mathrm{d}\vec{r}_n \quad (4)$$

As we know, $\rho'(\vec{r}_1; \vec{R})$ is the probability of finding the first electron at position $\vec{r}_1$, and $\rho'(\vec{r}_1, \vec{r}_2; \vec{R})$ is the probability of finding the first electron at position $\vec{r}_1$ while the second electron is at position $\vec{r}_2$. The potential acting on an electron at $\vec{r}_1$ in a molecule (PAEM) is then expressed as

$$V(\vec{r}_1; \vec{R}) = \frac{V'(\vec{r}_1; \vec{R})}{\rho'(\vec{r}_1; \vec{R})} = -\sum_{A} \frac{Z_{\mathrm{A}}}{|\vec{r}_1 - \vec{R}_{\mathrm{A}}|} + \frac{n-1}{\rho'(\vec{r}_1; \vec{R})} \int \frac{\rho'(\vec{r}_1, \vec{r}_2; \vec{R})}{|\vec{r}_1 - \vec{r}_2|} \mathrm{d}\vec{r}_2 \quad (5)$$

As we know, $\rho(\vec{r}_1; \vec{R}) = n\rho'(\vec{r}_1; \vec{R})$ is the one-electron density function at nuclear configuration $\vec{R}$, and $\rho(\vec{r}_1, \vec{r}_2; \vec{R}) = n(n-1)\rho'(\vec{r}_1, \vec{r}_2; \vec{R})$ is the two-electron density function. Therefore, the PAEM from eq 5 is formulated as

$$V(\vec{r}_1; \vec{R}) = -\sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|\vec{r}_1 - \vec{R}_{\mathrm{A}}|} + \frac{1}{\rho(\vec{r}_1; \vec{R})} \int \frac{\rho_2(\vec{r}_1, \vec{r}_2; \vec{R})}{|\vec{r}_1 - \vec{r}_2|} \mathrm{d}\vec{r}_2 = V_{\mathrm{ne}}(\vec{r}_1; \vec{R}) + V_{\mathrm{ee}}(\vec{r}_1; \vec{R}) \quad (6)$$

where the first term, $V_{\mathrm{ne}}(\vec{r}_1; \vec{R})$, is the attractive potential provided by all the nuclei, and the second term, $V_{\mathrm{ee}}(\vec{r}_1; \vec{R})$, is the potential of the interaction energy for this electron of interest with all the remaining electrons of the molecular system. In each fixed nuclear conformation $\vec{R}$, the spatial one-electron density function, $\rho(\vec{r}_1; \vec{R})$, depends only on one electron coordinate; however, the spatial two-electron density function, $\rho_2(\vec{r}_1, \vec{r}_2; \vec{R})$, depends on two electron coordinates. As usual, we omit $\vec{R}$ from $\rho(\vec{r}_1; \vec{R})$ and $\rho_2(\vec{r}_1, \vec{r}_2; \vec{R})$.

The one-electron density, $\rho(\vec{r}_1)$, can be expressed in the configuration interaction (CI) scheme of quantum chemistry as

$$\rho(\vec{r}_1) = \sum_{I} \sum_{J} \sum_{i_1 \in I} \sum_{j_1 \in J} c_I c_J^* (-1)^{s-t} \delta_{\{I-i_1\}\{J-j_1\}} [f_{i_1}^{\alpha}(\vec{r}_1) f_{j_1}^{*\alpha}(\vec{r}_1) + f_{i_1}^{\beta}(\vec{r}_1) f_{j_1}^{*\beta}(\vec{r}_1)] \quad (7)$$

in which $f_{i_1}^{\alpha}(\vec{r}_1)$ is the i_1th molecular orbital (MO) with α spin corresponding to the sth row in the D_I determinant, $f_{j_1}^{*\alpha}(\vec{r}_1)$ is the complex conjugate of the j_1th MO with α spin corresponding to the tth row in the D_J determinant. The summations involving indexes I and J are over the configurations, and the summations involving indexes i_1 and j_1 are over the molecular orbitals. $\{I - i_1\}$ denotes the cofactor of the D_I determinant, and $\{J - j_1\}$ denotes the cofactor of the D_J determinant. The Kronecker delta, $\delta_{\{I-i_1\}\{J-j_1\}}$, is defined to be unity when $\{I - i_1\}$ equals $\{J - j_1\}$ and is zero otherwise.

The spatial two-electron density function, $\rho_2(\vec{r}_1,\vec{r}_2)$, can practically be expressed by the following

$$\begin{aligned}\rho_2(\vec{r}_1, \vec{r}_2) = \sum_{I,J} c_I c_J^* \sum_{\substack{i_1,i_2 \in I\\ j_1,j_2 \in J\\ i_1 < i_2\\ j_1 < j_2}} (-1)^{s+t-u-v}\, \delta_{\{I-i_1-i_2\}\{J-j_1-j_2\}}\\
\{f^{\alpha}_{i_1}(\vec{r}_1)f^{\alpha}_{j_1}(\vec{r}_1)f^{\alpha}_{i_2}(\vec{r}_2)f^{\alpha}_{j_2}(\vec{r}_2) + f^{\alpha}_{i_1}(\vec{r}_1)f^{\alpha}_{j_1}(\vec{r}_1)f^{\beta}_{i_2}(\vec{r}_2)f^{\beta}_{j_2}(\vec{r}_2)\\
- f^{\alpha}_{i_1}(\vec{r}_1)f^{\alpha}_{j_2}(\vec{r}_1)f^{\alpha}_{i_2}(\vec{r}_2)f^{\alpha}_{j_1}(\vec{r}_2) - f^{\alpha}_{i_1}(\vec{r}_1)f^{\alpha}_{j_2}(\vec{r}_1)f^{\beta}_{i_2}(\vec{r}_2)f^{\beta}_{j_1}(\vec{r}_2)\\
- f^{\alpha}_{i_2}(\vec{r}_1)f^{\alpha}_{j_1}(\vec{r}_1)f^{\alpha}_{i_1}(\vec{r}_2)f^{\alpha}_{j_2}(\vec{r}_2) - {}^{\alpha}_{i_2}(\vec{r}_1)f^{\alpha}_{j_1}(\vec{r}_1)f^{\beta}_{i_1}(\vec{r}_2)f^{\beta}_{j_2}(\vec{r}_2)\\
+ f^{\alpha}_{i_2}(\vec{r}_1)f^{\alpha}_{j_2}(\vec{r}_1)f^{\alpha}_{i_1}(\vec{r}_2)f^{\alpha}_{j_1}(\vec{r}_2) + f^{\alpha}_{i_2}(\vec{r}_1(f^{\alpha}_{j_2}(\vec{r}_1)f^{\beta}_{i_1}(\vec{r}_2)f^{\beta}_{j_1}(\vec{r}_2)\\
+ f^{\beta}_{i_1}(\vec{r}_1)f^{\beta}_{j_1}(\vec{r}_1)f^{\alpha}_{i_2}(\vec{r}_2)f^{\alpha}_{j_2}(\vec{r}_2) + f^{\beta}_{i_1}(\vec{r}_1)f^{\beta}_{j_1}(\vec{r}_1)f^{\beta}_{i_2}(\vec{r}_2)f^{\beta}_{j_2}(\vec{r}_2)\\
- f^{\beta}_{i_1}(\vec{r}_1)f^{\beta}_{j_2}(\vec{r}_1)f^{\alpha}_{i_2}(\vec{r}_2)f^{\alpha}_{j_1}(\vec{r}_2) - f^{\beta}_{i_1}(\vec{r}_1)f^{\beta}_{j_2}(\vec{r}_1)f^{\beta}_{i_2}(\vec{r}_2)f^{\beta}_{j_1}(\vec{r}_2)\\
- f^{\beta}_{i_2}(\vec{r}_1)f^{\beta}_{j_1}(\vec{r}_1)f^{\alpha}_{i_1}(\vec{r}_2)f^{\alpha}_{j_2}(\vec{r}_2) - f^{\beta}_{i_2}(\vec{r}_1)f^{\beta}_{j_1}(\vec{r}_1)f^{\beta}_{i_1}(\vec{r}_2)f^{\beta}_{j_2}(\vec{r}_2)\\
+ f^{\beta}_{i_2}(\vec{r}_1)f^{\beta}_{j_2}(\vec{r}_1)f^{\alpha}_{i_1}(\vec{r}_2)f^{\alpha}_{j_1}(\vec{r}_2) + f^{\beta}_{i_2}(\vec{r}_1)f^{\beta}_{j_2}(\vec{r}_1)f^{\beta}_{i_1}(\vec{r}_2)f^{\beta}_{j_1}(\vec{r}_2)\}\end{aligned} \tag{8}$$

where $\delta_{\{I-i_1-i_2\}\{J-j_1-j_2\}}$ is equal to 1, if the cofactor $\{I - i_1 - i_2\}$ of the D_I determinant is equal to the cofactor $\{J - j_1 - j_2\}$ of the D_J determinant, and otherwise is zero.

On the basis of the expressions of $\rho(\vec{r}_1)$ in eq 7 and $\rho_2(\vec{r}_1, \vec{r}_2)$ in eq 8, we can then obtain the concrete expression of PAEM in eq 6, which can be numerically calculated by using an ab initio method. Practically in this paper, the SDCI calculations were performed by the MELD program package developed by Davidson et al. with the near Hartree−Fock quality Gaussian-type orbital basis sets;[46] the molecular integrals in eqs 7 and 8 were then calculated. Furthermore, the PAEM and the electron density were implemented in terms of a program of our own. All calculations were carried out on SGI Octane2 workstation and SGI O300 server.

2.2. The Difference Between the PAEM and the Molecular Electrostatic Potential (MEP). To compare the PAEM and the MEP more clearly, the PAEM in eq 6 is reformulated (termed PAEM (RHF)) in the spin-restricted HFSCF-MO as follows

$$\begin{aligned}V(\vec{r}_1) &= -\sum_{A} \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\, d\vec{r}_2 - \frac{1}{\rho(\vec{r}_1)} \int \frac{\rho_1(\vec{r}_2; \vec{r}_1)\rho_1(\vec{r}_1; \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\, d\vec{r}_2\\
&= V_{ne} + V_{es} + V_{ex}\end{aligned} \tag{9}$$

where $\rho_1(\vec{r}_1; \vec{r}_2)$ and $\rho_1(\vec{r}_2; \vec{r}_1)$ are the first-order reduced matrix. V_{ne} represents the nuclear−electron attraction terms, depending on one electron coordinate and one nuclear coordinate, V_{es} is the electrostatic Coulomb repulsion energy, depending on two electron coordinates without considering the electron spin, and V_{ex} is the exchange potential felt by the electron with other electrons of the same spin.

As mentioned in the Introduction, MEP, $\phi(\vec{r})$, is often used in various studies of molecular interaction and reactivity. It is defined as the electrostatic energy acting on a unit charge caused by all the nuclei and all the electrons of the considered molecule, and can be calculated for one particular point in space $\vec{r}_1$, according to the following equation:

$$\begin{aligned}\phi(\vec{r}_1) &= \phi_{nucl}(\vec{r}_1) + \phi_{el}(\vec{r}_1)\\
&= \sum_{A} \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} - \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\, d\vec{r}_2\end{aligned} \tag{10}$$

with $\phi(\vec{r}_1)$, the electrostatic potential at point $\vec{r}_1$; $\phi_{nucl}(\vec{r}_1)$, the electrostatic potential arising from the nuclei; $\phi_{el}(\vec{r}_1)$, the electrostatic potential arising from the electrons; $\vec{R}_A$, the position of nucleus A; and $\rho(\vec{r}_2)$, the electron density at point $\vec{r}_2$.

If eqs 9 and 10 are compared, the two potentials, PAEM and MEP, have an essential difference. First, from the very meaning, the PAEM describes the interaction energy of an internal electron with the remaining part of the molecule, the $n - 1$ electrons, and all the nuclei, but the MEP represents the interaction energy of an external unit charge with the whole molecule, i.e., including n electrons and all the nuclei. Second, an obvious distinction is the fact that PAEM contains the exchange energy of the considered electron with the remaining electrons of the same spin, a quantum effect, in contrast to the observation that in MEP there is no such exchange effect between the unit charge and the whole molecule. Third, to clarify, if we consider the interaction of an external electron with the molecule, its interaction potential is just the negative of $\phi(\vec{r}_1)$ in eq 10, which seems to be the first two terms of the PAEM in eq 9; however, the third term of eq 9 not only contains the exchange potential but also includes an implicit self-interaction of this electron with itself that is canceled by that which is contained in the second Coulomb term. The difference of the PAEM from the MEP will be described further by the numerical calculation results and presented in section 3.

3. Results and Discussion

3.1. 3D Topological Representation of the PAEM. Using the formalism and computational method mentioned above, we have performed the calculations of the PAEMs for a series of diatomic halides, namely, HX, LiX, NaX, and X_2 molecules ($X = F$, Cl, Br, and I), as well as H_2O, NH_3, and some organic molecules. Their 3D topological representations have been depicted and explored in detail and discussed as follows.

3.1.1. The PAEM of the HBr Molecule. To calculate the PAEM for a HBr molecule, we put the Br atom at the origin of the coordinate system and the H atom at the X-axis; the equilibrium bond length of the HBr molecule is chosen to be 2.673 au (experimental value).[47] Since a HBr molecule belongs to the $C_{n\infty}$ group with a symmetry axis along the molecular axis that contains the two nuclei, it is sufficient to only represent the PAEM, $V(\vec{r}_1)$, on a plane where $\vec{r}_1$ passes through the molecular axis.

First, we chose some points along the Br−H axis, i.e., the X-axis. The molecular integrals of eqs 7 and 8 for these points were then calculated by using the SDCI calculation in MELD program with the near Hartree−Fock quality Gaussian-type orbital basis sets, here, the Partridge (22s17p11d) and (18s9p) Gaussian basis sets used in Br and H atoms, respectively. A separate program was made in order to evaluate one-electron density, $\rho(\vec{r}_1)$, and two-electron density, $\rho_2(\vec{r}_1, \vec{r}_2)$. The values of the PAEM (CI) ($V(x)$), electron density (Den(CI)), V_{ee} (CI), as well as the electron−nuclear interaction, V_{ne}, are listed in Table 1. It can be seen from the table that these values vary gradually as x increases. The functions of the PAEM and the Den (electron density) with electronic coordinate are also shown

TABLE 1: Electronic Physical Quantities along the Br−H Bond Axis in HBr Molecule[a]

x	PAEM (CI)	V_{ee} (CI)	Den (CI)	PAEM (RHF)	MEP (RHF)	V_{ne}
−0.2000	−92.7159	82.6322	76.0957	−92.6996	85.6865	−175.3495
−0.1000	−244.2165	106.1442	344.3885	−244.1996	233.8221	−350.3622
0.0000	−34860.2457	140.1284	26757.3629	−34860.2287	34824.1985	−34860.2287
0.1000	−244.2326	106.1561	343.4188	−244.2168	233.8497	−350.3905
0.2000	−92.7281	82.6762	76.0889	−92.7135	85.7044	−175.4063
0.3000	−47.8641	69.2240	24.1760	−47.8501	43.5226	−117.0902
0.4000	−28.7266	59.2134	16.3106	−28.7132	24.9575	−87.9423
0.5000	−18.9443	51.5159	10.6010	−18.9316	15.4930	−70.4627
0.6000	−13.3566	45.4591	6.0706	−13.3446	10.3227	−58.8185
0.7000	−9.9059	40.6010	3.2405	−9.8944	7.3113	−50.5099
0.8000	−7.6143	36.6696	1.6982	−7.6032	5.4294	−44.2873
0.9000	−5.9865	33.4664	0.9173	−5.9755	4.1685	−39.4567
1.0000	−4.7718	30.8259	0.5391	−4.7605	3.2722	−35.6020
1.1000	−3.8559	28.5980	0.3608	−3.8444	2.6066	−32.4588
1.2000	−3.1834	26.6622	0.2771	−3.1720	2.0987	−29.8511
1.3000	−2.7019	24.9496	0.2369	−2.6909	1.7060	−27.6578
1.4000	−2.3576	23.4280	0.2165	−2.3470	1.4029	−25.7930
1.5000	−2.1105	22.0754	0.2054	−2.0999	1.1728	−24.1947
1.6000	−1.9367	20.8703	0.1992	−1.9255	1.0055	−22.8175
1.7000	−1.8241	19.7919	0.1962224	−1.8117	0.8951	−21.6288
1.8000	−1.7683	18.8216	0.1959763	−1.7537	0.8400	−20.6059
1.8026	−1.7676	18.7974	0.1960	−1.7530	0.8393	−20.5811
1.8079	−1.7663	18.7491	0.1961	−1.7515	0.8381	−20.5317
1.8158	−1.7647	18.6772	0.1962	−1.7497	0.8365	−20.4585
1.8316	−1.7626	18.5351	0.1965	−1.7472	0.8344	−20.3149
1.8382	−1.7621	18.4765	0.1966	−1.7465	0.8340	−20.2561
1.8408	−1.7619231	18.4532	0.1967	−1.7463	0.8339	−20.2328
1.8461	−1.7619167	18.4067	0.1968	−1.7461	0.8337848	−20.1864
1.8474	−1.7619207	18.3951	0.1968	−1.7461	0.83379300	−20.1749
1.8487	−1.7619	18.3836	0.1969	−1.7460	0.83381170	−20.1634
1.8500	−1.7620	18.3720	0.1969	−1.7460280	0.8338	−20.1520
1.8513	−1.7620	18.3605	0.1969	−1.7460252	0.8339	−20.1405
1.8526	−1.7620	18.3490	0.1970	−1.7460329	0.8339	−20.1291
1.8553	−1.7622	18.3260	0.1970	−1.7461	0.8341	−20.1063
1.8579	−1.7623	18.3030	0.1971	−1.7462	0.8342	−20.0837
1.8632	−1.7628	18.2573	0.1973	−1.7465	0.8347	−20.0387
1.8658	−1.7631	18.2346	0.1973	−1.7467	0.8350	−20.0163
1.8737	−1.7642	18.1666	0.1976	−1.7476	0.8362	−19.9499
1.8763	−1.7647	18.1441	0.1977	−1.7480	0.8367	−19.9280
1.8803	−1.7655	18.1104	0.1978	−1.7486	0.8375	−19.8953
1.8829	−1.7661	18.0880	0.1979	−1.7491	0.8381	−19.8736
1.8855	−1.7667	18.0656	0.1980	−1.7497	0.8387	−19.8520
1.8868	−1.7670	18.0545	0.1980	−1.7500	0.8390	−19.8412
1.8882	−1.7674	18.0433	0.1981	−1.7503	0.8394	−19.8305
1.8895	−1.7677	18.0322	0.1981	−1.7506	0.8397	−19.8198
1.8908	−1.7681	18.0211	0.1982	−1.7509	0.8401	−19.8091
1.8921	−1.7685	18.0100	0.1982	−1.7512	0.8405	−19.7985
1.8934	−1.7689	17.9989	0.1983	−1.7516	0.8409	−19.7879
1.8947	−1.7693	17.9879	0.1983	−1.7519	0.8413	−19.7773
1.8961	−1.7697	17.9768	0.1984	−1.7523	0.8417	−19.7667
1.8987	−1.7705	17.9548	0.1985	−1.7531	0.8426	−19.7456
1.9000	−1.7710	17.9438	0.1986	−1.7535	0.8430	−19.7351
2.0000	−1.8409	17.1450	0.2042	−1.8197	0.9134	−19.0129
2.1000	−1.9974	16.4145	0.2133	−1.9718	1.0711	−18.4492
2.2000	−2.2804	15.7429	0.2264	−2.2499	1.3561	−18.0783
2.3000	−2.7758	15.1226	0.2444	−2.7402	1.8552	−17.9875
2.4000	−3.6995	14.5469	0.2680	−3.6587	2.7849	−18.4148
2.5000	−5.7703	14.0101	0.2979	−5.7248	4.8652	−20.2112
2.6000	−13.6532	13.5070	0.3358	−13.6036	12.7621	−29.8550
2.7000	−36.9671	13.0329	0.3451	−36.9144	36.0962	−38.6040
2.8000	−7.7895	12.5846	0.2651	−7.7347	6.9451	−19.6942
2.9000	−4.3134	12.1608	0.2033	−4.2571	3.4995	−16.2531
3.0000	−2.9639	11.7609	0.1561	−2.9065	2.1825	−14.6165
3.1000	−2.2487	11.3836	0.1199	−2.1908	1.5006	−13.5682
3.2000	−1.8074	11.0276	0.0924	−1.7493	1.0924	−12.7928
3.3000	−1.5092	10.6917	0.0711	−1.4513	0.8265	−12.1710
3.4000	−1.2951	10.3745	0.0547	−1.2375	0.6434	−11.6473
3.5000	−1.1343	10.0749	0.0422	−1.0772	0.5123	−11.1919
3.6000	1.0094	9.7916	0.0327	−0.9531	0.4156	10.7872
3.7000	−0.9097	9.5235	0.0254	−0.8543	0.3425	−10.4219
3.8000	−0.8284	9.2694	0.0198	−0.7741	0.2862	−10.0885

[a] Note: x denotes the electronic coordinate, Den denotes electron density, RHF is the spin-restricted Hartree−Fock method, and CI is configuration interaction method. All quantities are in atomic units.

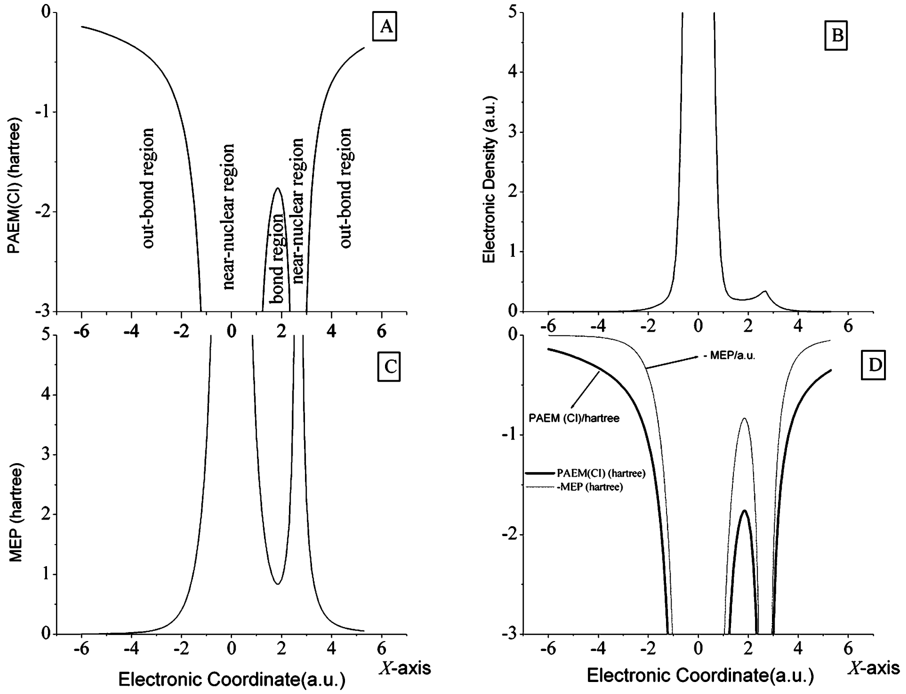

Figure 1. The curves of PAEM, electron density, and MEP with the electronic coordinates for a HBr molecule. (A) PAEM. (B) Electronic density. (C) MEP. (D) Comparison of PAEM with minus MEP.

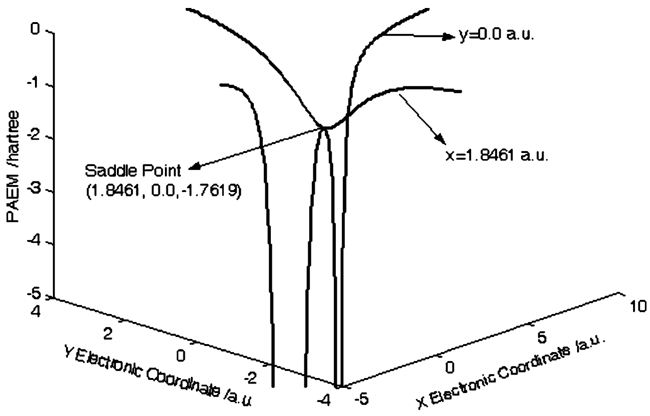

Figure 2. The saddle point of the saddle surface is displayed around the H$-$Br chemical bond region of HBr.

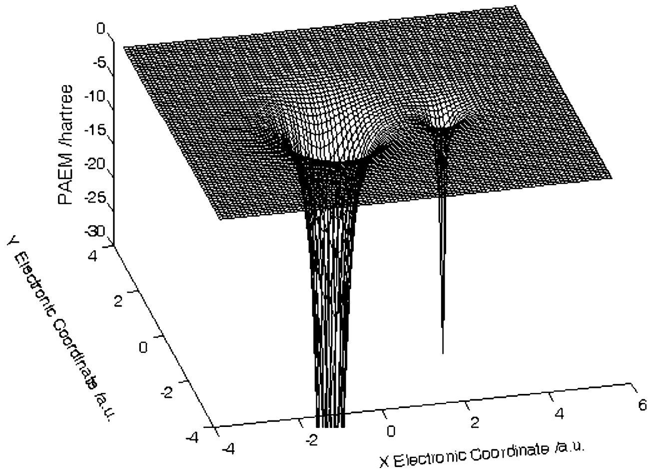

Figure 3. The three-dimensional graph of the PAEM for HBr on the XY-plane (molecular plane).

in Figure 1A,B. Obviously, the curve $V(x)$, the potential acting on an electron in the HBr molecule along the molecule axis, has two wells around the two nuclei (a wide one around the Br nucleus and a narrow one around the H nucleus), a hill around the H$-$Br bonding region, and two "plateaus". These three regions can be called near-nuclear, bond, and out-bond regions, respectively. Special attention may be paid where along the Br$-$H chemical bond axis there is a point $x = 1.8461$ au at which the $V(x)$ takes its maximum value, $V(x = 1.8461) = -1.7619$ hartree.

The PAEM in eq 9 and the MEP in eq 10 corresponding to each point were obtained numerically on the basis of the RHF of MELD program and listed in Table 1. The curve of the MEP is shown in Figure 1C. For a further comparison, the curves of the PAEM (CI) and the minus MEP are plotted in Figure 1D. It is obvious that the PAEMs calculated with CI and RHF are slightly different for this case, while the curve of minus MEP is much different from that of the PAEM.

Next, we make a straight line perpendicular to the Br$-$H axis and pass through the point $x = 1.8461$ au. With this line of $x = 1.8461$ au and y being a variable, the potential $V(x = 1.8461, y)$ curve shows a local minimum value at the point ($x = 1.8461$, $y = 0.0$). This can be seen from Figure 2, where the curve along the X-axis is also plotted. In the bond region of the PAEM, there is a local maximum point along the chemical bond axis, and at the same time, it is a local minimum along the Y-axis. This implies that the PAEM surface has a saddle point at $x_1 = 1.8461$, $y_1 = 0.0$, with $V(1.8461, 0.0) = -1.7619$ hartree.

When $\vec{r}_1$ runs on the molecular plane (the XY-plane), i.e., grids the XY-plane, the calculated $V(\vec{r}_1)$ (PAEM) values corresponding to these points are displayed in the Z-axis, then a 3D topological representation of the PAEM is brought out and drawn in Figure 3. Apparently, the PAEM curve along the bond axis may be divided into three regions which can be called, respectively, the bond region, the out-bond region, and the near-nucleus region. In the bond region, the PAEM has a local maximum from which the curve goes down toward both sides. The highest point of the PAEM curve on the XZ-cross-section is just the lowest point of the PAEM curve on *the vertical plane* (perpendicular to the XZ-plane), and hence, this point is the

TABLE 2: Values of Bond Lengths (BL), PAEM, D_{pb}, and k_f (force constant) for Some Diatomic Molecules

molecule	bond	BL/mw (a.u.)	PAEM (SDCI)	D_{pb}	k_f/(N/cm)
HF	F−H	1.733	−2.614	2.614	9.66
HCl	Cl−H	2.409	−2.001	2.001	5.16
HBr	Br−H	2.673	−1.762	1.762	4.12
HI	I−H	3.040	−1.587	1.587	3.14
LiF	Li−F	3.011	−1.168	1.168	2.50
LiCl	Li−Cl	3.819	−0.996	0.996	1.43
LiBr	Li−Br	4.101	−0.923	0.923	1.20
LiI	Li−I	4.520	−0.868	0.868	0.97
NaF	Na−F	3.640	−0.921	0.921	1.76
NaCl	Na−Cl	4.461	−0.813	0.813	1.09
NaBr	Na−Br	4.728	−0.795	0.795	0.94
NaI	Na−I	5.124	−0.752	0.752	0.76
I_2	I−I	5.038	−1.084	1.084	1.72
Br_2	Br−Br	4.311	−1.374	1.374	2.46
Cl_2	Cl−Cl	3.756	−1.631	1.631	3.23
F_2	F−F	2.668	−2.016	2.016	4.70

saddle point of the PAEM saddle-shaped surface around the bond region.

As a metaphor, the topological graph of the PAEM in Figure 3 shows that the Br nucleus is located at a wider lake, while the H nucleus is at a narrower lake, and the bond region is the river channel connecting the two lakes. Here, the "water" is just the electrons in the lake and the channel. The electrons moving around the two nuclei through the channel make the two atoms combine into a stable molecule. We might say that a PAEM provides a geography for the electronic motion in a molecule just as a PES (potential energy surface) gives a geography for a chemical reaction.

3.1.2. The PAEMs of Some Molecules. In a similar way, we have performed systematic studies on the 3D topological representation of the PAEMs for some other diatomic halides, including HX (X = F, Cl, I), LiX, NaX, and X_2 (X = F, Cl, Br, and I) molecules. Their equilibrium bond lengths are taken from the experimental values.[47] On a molecular plane, the halogen atom nucleus in each diatomic halide molecule mentioned above is chosen as the origin of the coordinate system, where the line along the nuclear axis of this molecule is chosen as the *X*-axis, a line perpendicular to the molecular axis (*X*-axis) is defined as the *Y*-axis, and the *Z*-axis represents the PAEM calculated by an ab initio method based on the MELD package and a separate program.

We have also obtained the PAEMs of H_2O, NH_3, and some organic molecules at their equilibrium geometries using the method mentioned above. Some common features of the PAEMs of these molecules can be drawn: (1) In the near-nucleus region, there is a deep potential well which originates from the nuclear attraction and is wider for the atom with a larger atomic number; (2) in the out-bond region, the potential increases with increasing distance between the electron and the nucleus and approaches zero at infinity, which is quite similar to the potential for an isolated atom; (3) the feature of the PAEMs of these molecules is that there is a saddle point for every bond region. It can obviously be seen that the coordinates and heights of the saddle points for different molecules are different. An interesting question arises: Does this PAEM potential barrier relate to the property of the chemical bond? The answer is positive. We will explore how the PAEM potential relates to the chemical bonding and molecular properties in the following.

3.2. Quantitative Relationship Between Bond Properties and PAEMs. It is noted that the PAEM for a usual molecule has a negative value everywhere. Thus, we define the absolute value of the PAEM at the saddle point as the depth of the PAEM at the saddle point along a chemical bond axis, denoted D_{pb}, i.e., the energy gap from this point to the energy level of zero. The D_{pb} characterizes how easily the electrons transfer from one nuclear (atomic) region to another nuclear (atomic) region through the bond region, or in other words, how high a PAEM barrier the electrons should overcome from one nuclear (atomic) region to the other nuclear (atomic) region through the bond region. The characteristic descriptors of PAEM in the bond region, D_{pb}, are listed respectively in Tables 2 and 3 for some diatomic halide molecules and for some polyatomic molecules containing A−H bonds (A = C, N, O) and CC single, double, and triple bonds.

It is well-known that bond length and uncoupled vibrational stretching frequency (or force constant for general cases, because coupled vibrations are common in complex molecules) are two important physical qualities, which characterize the strength of the chemical bond. Should the strength of the chemical bond be related to the quantity D_{pb} issued from the PAEM? We will answer this in the following sections.

By the way, as shown in Figure 1D, the shapes of PAEM and the negative of MEP have some topological resemblance; thus, it is natural to question whether the negative of MEP also have a similar correlation as the PAEM does. However, the PAEM and the MEP are different in nature, as we have pointed out in section 3.1.1. The correlation of −MEP with those physical quantities does not have a clear meaning and so is not what we are concerned with here.

TABLE 3: Values of Bond Lengths (BL) and D_{pb} for X−H Bonds (X = C, N, O) and CC Single, Double, and Triple Bonds[a]

molecule	bond	BL	D_{pb}	molecule	bond	BL	D_{pb}
ethane	C−C	2.900	1.6070	H_2O	O−H	1.809	2.4094
propane	C−C	2.895	1.6185	CH_3OH	O−H	1.786	2.4127
n-butane(C2−C3)	C−C	2.893	1.6319	HCOOH	O−H	1.837	2.3693
n-butane(C1−C2)	C−C	2.893	1.6330	CH_4	C−H	2.060	1.8366
acetone	C−C	2.872	1.7070	CH_3CH_3	C−H	2.067	1.8271
cyclopropane	C−C	2.857	1.7277	$CH_3CH_2CH_2{-}H$	C−H	2.092	1.7950
trans-2-butene	C−C	2.850	1.6934	$CH_3(CH_2)_2CH_2{-}H$	C−H	2.111	1.7820
propene	C−C	2.846	1.7074	$H_2C{=}CH_2$	C−H	2.054	1.8762
2-butyne	C−C	2.774	1.8088	$HC{\equiv}CH$	C−H	2.003	2.0024
propyne	C−C	2.757	1.8429	CH_3OH	C−H	2.067	1.8649
benzene (o)	C−C	2.644	1.9480	benzene	C−H	2.081	1.8432
trans-2-butene	C=C	2.544	2.0874	H_3COCH_3	C−H	2.118	1.7899
propene	C=C	2.534	2.1121	$H_3C(CO)CH_3$	C−H	2.084	1.8234
ethylene	C=C	2.530	2.1216	$H_3C{-}C{\equiv}C{-}H$	C−H	1.996	1.9954
2-butyne	C≡C	2.294	2.5157	$H{-}CH_2{-}C{\equiv}CH$	C−H	2.088	1.8420
propyne	C≡C	2.279	2.5587	$H_3C{-}C{\equiv}C{-}CH_3$	C−H	2.109	1.8054
acetylene	C≡C	2.274	2.5866	NH_3	N−H	1.912	2.1161

[a] Note: All quantities are in atomic units.

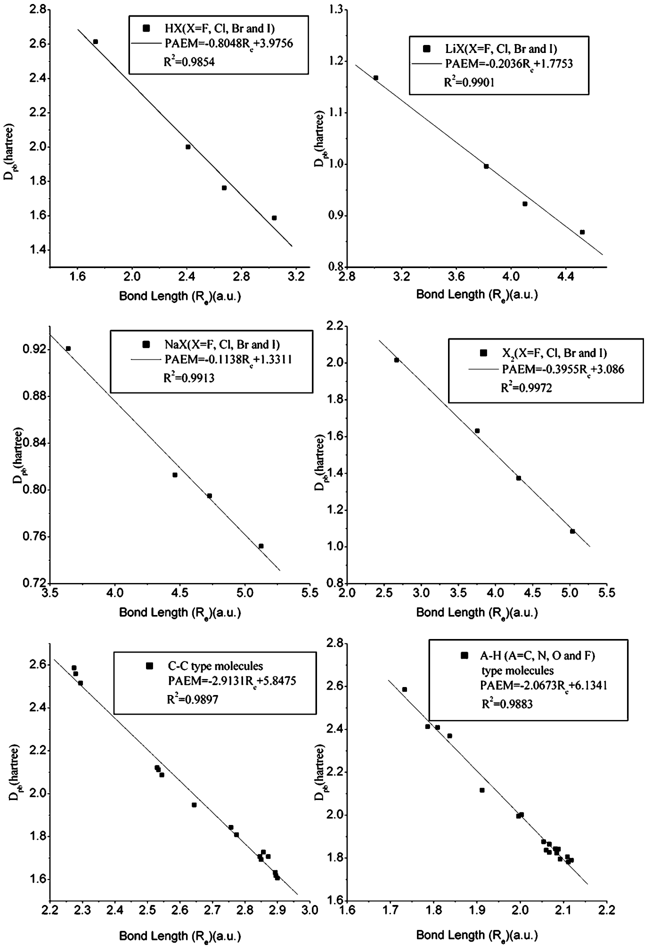

Figure 4. The linear relationship between D_{pb} and bond lengths for a variety of chemical bonds, including HX, LiX, NaX, XX (X = F, Cl, Br, I), AH (F, O, N, C), and CC single, double, and triple bonds.

3.2.1. Relationship Between Bond Length and PAEM for Chemical Bonds in Diatomic and Polyatomic Molecules. Bond length is an observable quantity, which can be measured accurately by modern spectroscopic and diffraction techniques. Data about bond lengths in Table 2 are mostly from commonly available sources, for example, the CRC Handbook[47] for R_e. Zavitsas has nicely shown the good correlation of bond length with other fundamental bond properties, such as bond dissociation energy and infrared vibrational frequency.[48,49] Theoretically, the bond order defined and calculated by some quantum chemical methods is employed to characterize the bond multiplicity or strength, but it depends on the orbital overlap and so has various definitions.[50,51]

We correlate bond length with the D_{pb}, the characteristic descriptor of the PAEM in the bond region. Tables 2 and 3 list the bond lengths (BL) of a number of H−X, Li−X, Na−X, X−X (X = F, Cl, Br, and I), A−H (A = C, N, O), and CC chemical bonds, with their respective D_{pb}. By plotting the D_{pb} values for those bonds versus the bond lengths for the different series of bond types, we can easily obtain a quite good linear relationship as shown in Figure 4. In addition, stronger bonds are shorter, and the bond lengths of HX (X = F, Cl, Br, and I) are in the inverse order of D_{pb}. The PAEM of HF molecule has the largest depth for the series of hydrogen halides, and correspondingly, its bond length is the shortest, i.e., the chemical bond of HF is the strongest.

3.2.2. Relationship Between Force Constant and PAEM for Diatomic Molecules. As we know, if the forces between bonded atoms are very strong, then a large magnitude of energy is required to force a bond to deviate significantly from its equilibrium value. This is reflected in the magnitude of the force constant for the bond stretching. Some values of force constants derived from experimental values[47] of the harmonic vibration

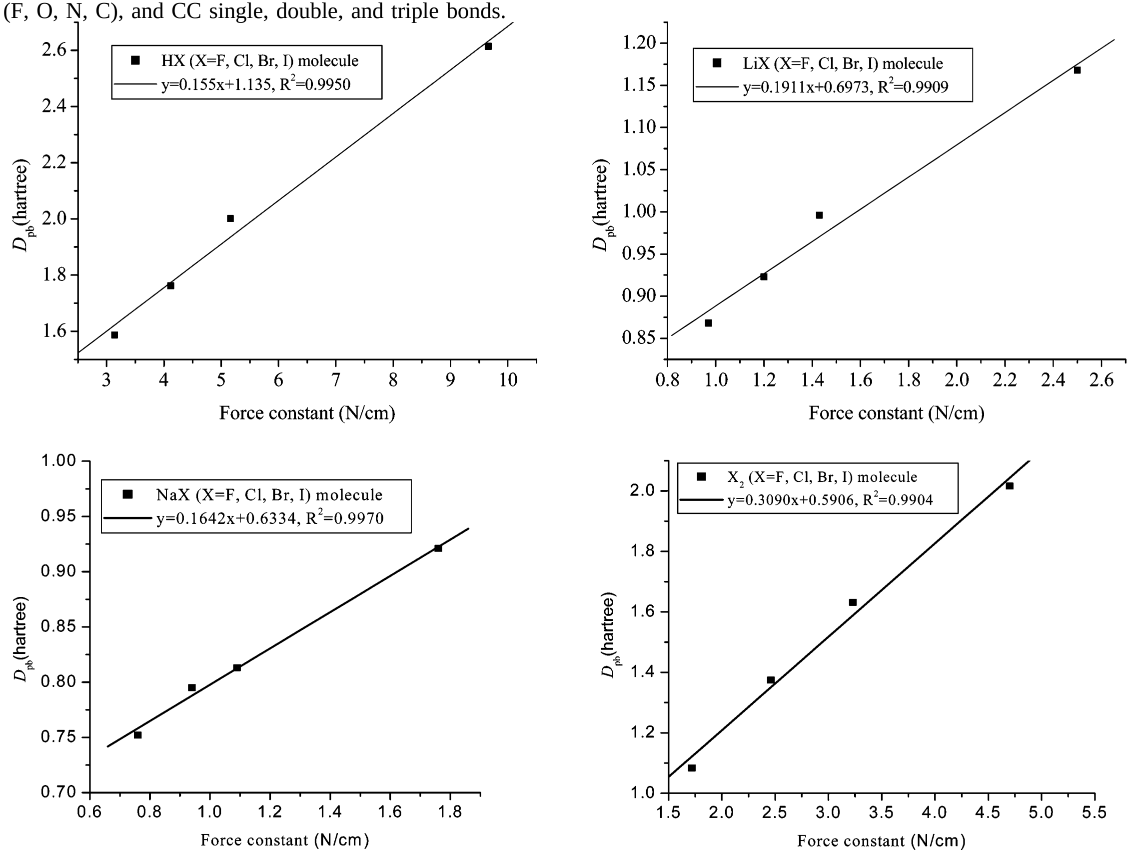

Figure 5. The linear relationship between D_{pb} and the force constants for a variety of chemical bonds, such as HX, LiX, NaX, and XX (X = F, Cl, Br, and I).

frequencies are given in Table 2, where it can be seen that those bonds that one would intuitively expect to be stronger have larger force constants.

We have studied the correlation of the force constants with the D_{pb}, the characteristic descriptor of the PAEM, at the saddle point in the bond region for these diatomic molecules. We just plot the D_{pb} versus the force constants for these bonds, then four quite good linear relationships (the correlation coefficients are 0.9950, 0.9909, 0.9970, and 0.9904 for HX, LiX, NaX, and X_2 molecules (X = F, Cl, Br, I), respectively) depicted in Figure 5 are obtained. It is obvious that the larger the D_{pb} is, the larger the force constant is. Since the value of the force constant is proportional to the strength of the chemical bond, we can conclude that the larger the D_{pb} is, the stronger the chemical bond is. As we know, for HX (X = F, Cl, Br, I) molecules, the strengths of these chemical bonds are in the order H−F > H−Cl > H−Br > H−I. For other series of diatomic halide molecules, the order and strength of these chemical bonds is the same as that for the HX (X = F, Cl, Br, I) molecules.

To conclude, the electronic motion along a chemical bond through the saddle-type region of the potential acting on an electron in a molecule (PAEM), which is related to chemical bonding, is to some extent likened to the motion of reactants along the IRC through the reaction barrier on the PES, which relates to the chemical reaction. The study of PAEM relating to other aspects of molecular physicochemical properties is in progress.

4. Summary

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 and computed on the basis of the MELD program package and our own program. 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, and the graphs 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 reflects mainly 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 of the PAEM curve on the plane that passes through the saddle point and is perpendicular to the bond axis, i.e., D_{pb}. We have found that D_{pb} inherently correlates with the bond length and the force constant, which are two fundamental bond properties characterizing the strength of the chemical bond. Thus, it is demonstrated that the characteristic descriptor of the PAEM, D_{pb}, at the saddle point characterizes the strength of the chemical bond.

Acknowledgment. The authors are very grateful to Professor E. R. Davidson for providing us the MELD package and other kinds of help. The research is supported by the grants (no. 20403007) from National Science Foundation of China.

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