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Multiple Ionic-Covalent Couplings in Molecules and Clusters[†]

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The electronic states of molecules made of electropositive and electronegative components result from the interference between the covalent configurations and the ionic configurations. This work shows complex aspects of these ionic-covalent couplings in small molecules such as Li_2H, Li_2F, and Li_4F. The extension of this type of analysis to the adsorption of the electrophilic molecules on the metal clusters or on the metal surfaces is supposed to lead to a radically new interpretation of the observed physical and chemical properties.

Key words: Surface adsorption, Electron transfer, Covalent configuration, Ionic configuration, Electronic state

I. INTRODUCTION

The ionic states are made when the constituents of the molecular system contain an electropositive part, like the metal atoms or small clusters and an electronegative part like the halogen, chalcogen atoms or molecular fragments having high electron affinity. For such a system, an ionic configuration interacts with many covalent configurations in general, and the diabatic coupling involved in those interactions characterizes the given electronic state as a function of the molecular geometry. Those couplings were analyzed previously for the case of molecules made of small number of atoms including one metal atom [1]. The ground states studied in that work all show a strong ionic character around the equilibrium geometry, and each ionic-covalent diabatic coupling was treated as a two-state problem to simplify the analysis. The concerned ionic configuration represents the D^+A^- scheme where D is the electron donor (metal atom) and A is the electron accepter. The asymptote of this ionic configuration lies $IP(D)+EA(A)$ over the lowest covalent dissociation asymptote where IP is the ionization potential and EA is the electron affinity, and the potential energy varies according to approximately $-1/R$ where R is the distance between D and A, except for small R. So the ionic attraction in $-1/R$ exercises its influence over a very wide range of R. The number of the ionic covalent couplings can be precisely known by counting the number of the covalent dissociation asymptotes below the ionic dissociation asymptote [1]. The second ionic asymptote lies in general much higher than

the lowest ionic asymptote, so the second series of the ionic-covalent couplings takes place for highly excited electronic states which are in general out of the scope of the chemical interest.

When the system contains many electron donors, like large metal clusters or bulk metal, then the number of the ionic configurations as well as the number of the covalent configurations increases rapidly as a function of the number of metal atoms. We may then expect a large number of the ionic-covalent couplings taking place at low enough potential energy ranges. In this work, I show that it is indeed the case even for small metal clusters, by doing high level quantum chemical calculations applied to small molecular systems, namely Li_2H, Li_2F, and Li_4F. The lithium metal clusters were chosen for the simplicity for calculation, and the hydrogen atom and the fluorine atom were chosen for comparison as they have a moderate and a strong electron affinity, respectively. The ionic-covalent couplings in LiH [1] and LiF [2] were analyzed previously. It might have been good to study furthermore larger metal clusters, but the current limitation of *ab intio* calculation should be taken into account if one requires the acceptable accuracy.

II. METHOD OF CALCULATION

The electronic states of four molecules were calculated with high level quantum chemical methods including the multi-configuration complete-active-space self-consistent-field (CAS-SCF) and the multi-reference singles and doubles configuration interaction (MRCI). The atomic basis sets were optimized to faithfully represent the lowest covalent configurations and the lowest ionic configurations, using atomic and molecular calculations. The basis set used for lithium atom consists of 12s7p1d Gaussian type orbitals (GTOs) which is flex-

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ible enough to describe the lowest electronic states of the neutral clusters as well as the cationic species. The basis set for hydrogen atom consists of 7s3p2d GTOs and for fluorine atom 12s8p3d GTOs were used, which are large enough to describe the anionic states as well as the neutral states. Those GTOs were directly used as the atomic basis functions (ABFs) without contraction.

For the molecular calculations the MOLCAS program package [3] was used. The molecular orbitals (MOs) were obtained in the CAS-SCF calculations where many roots (states) were sought and the MOs were averaged for those states. The active valence MO space and the number of roots were varied to find as many roots as possible without loosing accuracy. Then the resulting set of MOs were used to do MRCI calculations for Li_2H and Li_2F molecules. The MRCI calculation could not be done for the Li_4F molecule because of too many states (60 bound states) to calculate even for the modern computer systems, thus only CAS-SCF calculations were done for this molecule.

To simulate the adsorption phenomena of the hydrogen and fluorine atom to the metal surface, we have chosen the isosceles triangular C_{2v} geometries for the Li_2H and Li_2F molecules, and the pyramidal C_{4v} geometries for the Li_4F molecule. Only two geometrical parameters were varied, the internuclear distance between the lithium atoms (r) and the intermolecular distance between the lithium cluster and the ad-atoms (R).

III. RESULTS

A section of the potential energy surfaces of Li_2H for Li−Li internuclear distance (r) of 5 Bohr, which is close to the experimental value for the Li_2, 5.051 Bohr [4], as functions of the metal-hydrogen distance (R) is shown in Fig.1(a). Seven lowest electronic states appearing in this figure show the unusual shape of the potential surfaces made from ionic and covalent configurations. The first series of avoided crossings occur between the covalent configurations of Li_2−H, namely the $Li_2(X^1\Sigma_g^+)$−H, $Li_2(a^3\Sigma_u^+)$−H, $Li_2(A^1\Sigma_u^+)$−H, $Li_2(b^3\Pi_u)$−H, etc., and the Li_2^+−H$^-$ ionic configuration where the Li_2^+ moiety is correlated to the ground cationic state $X^2\Sigma_g^+$. This series of avoided crossings is similar to the $^1\Sigma_g^+$ electronic states of LiH where the covalent configurations, Li(2s)−H, Li(2p)−H, Li(3s)−H, $\cdots$, Li(4f)−H, interact with the only one ionic configuration, Li$^+$−H$^-$, the asymptote of the latter being situated between Li(4f)−H and Li(5s)−H [5,6].

In the Li_2H molecule, however, there are many other series of avoided crossings. The second series involves the before-mentioned covalent states and the Li_2^+−H$^-$ ionic configuration where the Li_2^+ moiety is correlated to the first excited cationic state $1^2\Pi_u$ which lies 0.1125 Hartree higher than the $X^2\Sigma_g^+$ state of Li_2^+ according to the separate calculations done for
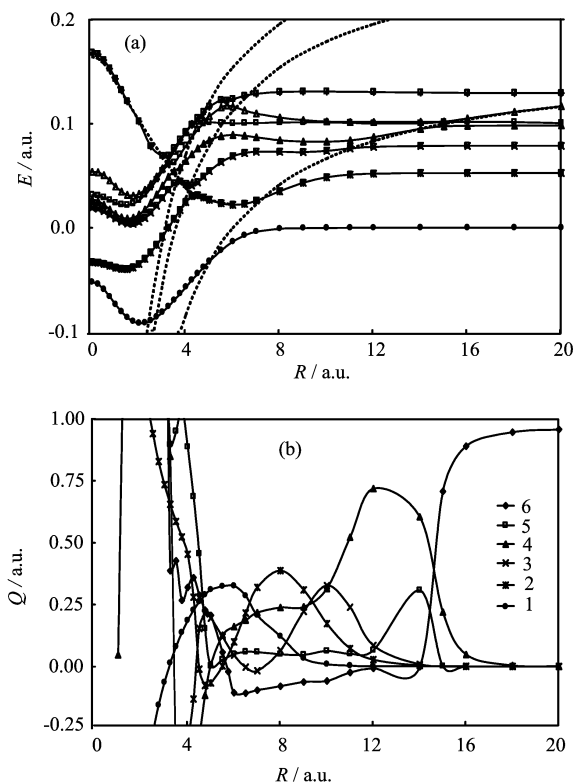
FIG. 1 A section of the potential energy surfaces of the lowest 7 electronic states as functions of the Li_2−H intermolecular distance, R, (a) and the effective charges of the corresponding states (b) for the Li_2H molecule (Li−Li distance equals 5 Bohr). See text for the 3 attractive dotted curves representing the ionic configurations and one repulsive dotted curve representing the lowest covalent configuration in (a).

the Li_2^++H system with the hydrogen atom separated from the cation of Li_2 at large distance ($R=10^4$ Bohr). The third series of avoided crossings occur between the before-mentioned covalent states and the third (second excited) ionic state correlated to the $2^2\Sigma_g^+$ state of Li_2^+ which lies 0.1543 Hartree higher than the $X^2\Sigma_g^+$ state of Li_2^+. From the asymptotes of the ground and excited states of the ion-pair Li_2^+−H$^-$ at infinite separation, we can draw a series of $-1/R$ curves that appear in Fig.1(a) as attractive dotted lines. We can see a good agreement between the lowest $-1/R$ curve and the adiabatic electronic curves in particular for long intermolecular distances as in the LiH case. With the second and the third $-1/R$ curves, we can also see that these curves coincide with the avoided crossing region so helping to find the nature of the electronic states according to the ionic or covalent characters. Thus this illustrates that around each crossing point between the potential curve of an ionic configuration and the potential curve of a covalent configuration should be an avoided crossing.

The effective charge defined as the dipole moment divided by the intermolecular distance (R, taken to be

the distance between the hypothetical metal surface to the ad-atom, *i.e.* from the midpoint of Li_2 dimer to the nucleus of the ad-atom) of the electronic states of Li_2H for each state as a function of R is plotted in Fig.1(b). This figure shows a widely varying effective charge as a function of R, and a careful cross examination of Fig.1 shows the relationship between the ionicity (more or less ionic character) and the effective charge. In particular there is a nice correlation between the lowest series of the ionic-covalent avoided crossings and the exchange-variation of the effective charge.

Our previous works comparing the covalent-ionic coupling in LiH [1] and LiF [2] have shown that the avoided crossings occur more sharply in the latter than in the former, meaning that the covalent-ionic couplings in LiF are much weaker than in LiH. (The weak diabatic coupling is characterized by a very localized and closely avoided crossing, while the strong diabatic coupling shows a largely avoided crossing spanning a wide range of geometry.) A section of the adiabatic potential surfaces and the effective charges of Li_2-F are drawn in Fig.2 (a) and (b). With the guide of three ionic diabatic curves in $-1/R$, we can see the same feature as in the Li_2-H case but with much sharper avoided crossings in the Li_2-F case.

The 60 lowest electronic states of Li_4F molecule were calculated on the CAS-SCF level using 14 MOs in the active space for 9 active electrons (5 from F atom and 1 from each Li atom) generating 237.706×10^3 configuration state functions (CSFs). All 60 states have negative potential energy with respect to that of the dissociation into the ground state of Li_4+F. It is possible that more states can be stable if we could increase further the number of roots but it was not practicable with the given limitations of the software and the hardware. Most of the lowest states have the minimum potential on the surface (at the four-fold centre of the square made of four Li atoms) and the potential changes little for small intermolecular distance (R). The potential energies and the dipole moments of the 60 states for $R=0.5$ Bohr are shown in Fig.3. The ground state has the binding energy of 6.0 eV and has a dipole moment close to zero. So it can be called a covalent state. For high-lying states, the dipole moment varies a lot spanning from +4 a.u. (atomic units) where the fluorine atom has a large negative charge to −4 a.u. where the fluorine atom has a large positive charge. The section of the potential energy surfaces with the Li−Li distances (r) fixed to 5 Bohr shows a complex avoided crossing pattern depending on R. It is a manifestation of complex ionic-covalent couplings between the metal cluster and the adatom.

IV. DISCUSSION

It is not easy to find the reliable potential energy surfaces for many electronic states over a wide domain of geometry. To obtain Fig.1, the active space in the CAS-SCF calculations consisted of 12 MOs for 3 active electrons which generated 296 CSFs and 12 lowest states were optimized. The MRCI calculation using the same number of active orbitals and including the core-valence correlation generated in all 932.531×10^3 CSFs.
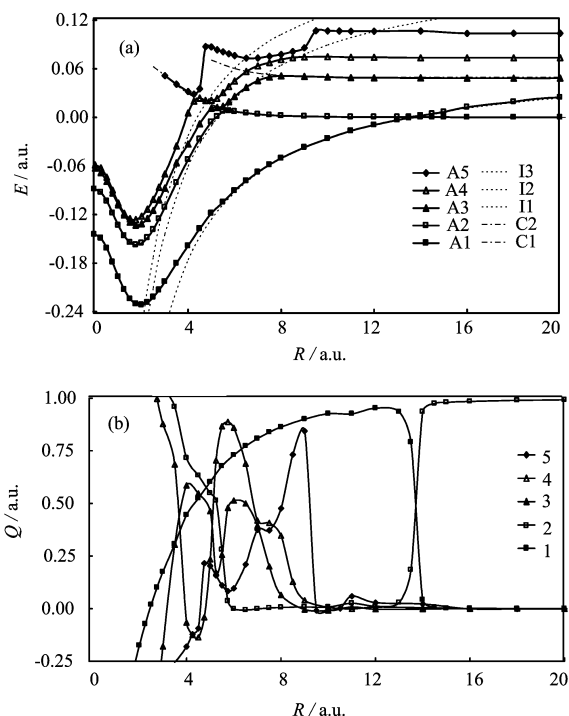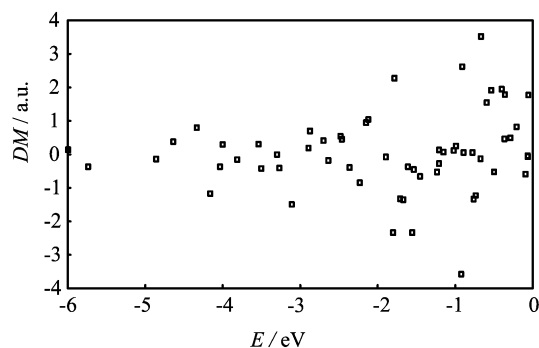

FIG. 2 A section of the potential energy surfaces of the lowest 7 electronic states as functions of the Li_2-F intermolecular distance, R, (a) and the effective charges of the corresponding states (b) for the Li_2F molecule (Li−Li distance equals 5 Bohr). See text for the 3 attractive dotted curves representing the ionic configurations and one repulsive broken curve representing the lowest covalent configuration in (a).

FIG. 3 The potential energies and the dipole moments of the lowest 60 electronic states of Li_4F molecule (for Li−Li distances equal to 5 Bohr, and the fluorine atom from the Li_4 surface equal to 0.5 Bohr).

Among 12 roots obtained from the MRCI calculation, we can consider at least the lowest 7 states to be correct. In the course of finding the best method to obtain a reliable data, smaller active spaces were tested. When 5 active orbitals for 3 valence electrons were used in the CAS-SCF, and solved the problem for the lowest 3 roots (*i.e.* optimize the MOs for the three lowest states), we obtained only two states which were correct when we compared with the final result shown in Fig.1. The third state followed the lowest repulsive diabatic curve appearing in broken line in this figure (which represents the lowest diabatic covalent curve), so looking like the seventh state, for $R<4.5$ Bohr, and for $R>4.5$ Bohr it looked like the third adiabatic curve of Fig.1 but with many second order discontinuities (*i.e.*, the discontinuities in the first derivative with respect to R). In general, it is better to have as large active space as possible for sufficiently large number of the roots to optimize, then taking only the lowest states resulting from the CAS-SCF and MRCI. For the system which undergoes a large change in the character of each state as a function of the geometrical variation, there occurs many interchanges regarding the energy order for the high-lying roots, and that's why the solution for the high-lying states cannot be trusted in any CAS-SCF or MRCI calculation.

V. CONCLUSION

There exist a large number of bound states with a wide variety of ionicity in the metal/ad-molecule systems which is caused by complex interactions between the multiple ionic configurations and the multiple covalent configurations. The increasing density of state of the neutral metal clusters and their cations can be seen in the example of small sodium clusters [7]. Considering the symmetry breaking in the real system originated from the local imperfections of the metal substrate, there can be many ways of making state-to-state changes from a given adiabatic state. The actual evolution of the state will depend very much upon the initial conditions and the subsequent change in the environment, for example, the fluctuation of the thermal reservoir, via the phonon-electron coupling. This means that what one calls as the surface adsorbed state is not a unique state but could be a large number of states, which are more or less bound and which are more or less ionic (in either sense, anionic or cationic) or covalent. Many disparities seen in different experimental studies of the surface adsorption may be understood in this context.

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