

Study on Pair Correlation Energies of Isoelectronic Systems F^- , HF and H_2F^+

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The intrapair and interpair correlation energies of F^- , HF and H_2F^+ systems are calculated and analyzed using MP2-OPT2 method of MELD program with cc-PV5Z* basis set. From the analysis of pair correlation energies of these isoelectronic systems, it is found that the $1s_F^2$ pair correlation energy is transferable in these three isoelectronic systems. According to the definition of pair correlation contribution of one electron pair to a system, the pair correlation contribution values of these three systems are calculated. The correlation contribution values of inner electron pairs and H—F bonding electron pair in HF molecule with those in H_2F^+ system are compared. The results indicate that the bonding effect of a molecule is one of the important factors to influence electron correlation energy of the system. The comparison of correlation energy contributions including triple and quadruple excitations with those only including singles and doubles calculated with 6-311++G(d) basis set shows that the higher-excitation correlation energy contribution gives more than 2% of the total correlation energy for these systems.

Keywords intrapair and interpair correlation, contribution of higher-excitation, pair correlation contribution, chemical bonding effect

Introduction

As a well-known fact, the calculation of electron correlation energy is a bottleneck problem in the calculations of molecular properties and chemical reactions in quantum chemistry.¹ It has attracted great attention of theoretical chemists. Numerous different methods have been used to calculate the correlation energy since Löwdin² give the definition of electron correlation in 1959. In 1960s, Sinanoğlu^{3, 4} defined the exact electron pair correlation energy and developed many-electron theory of atoms and molecules in which the total correlation energy of a system is decomposed into pair correlation energies to simplify the complicated calculation of electron correlation. Nesbet^{5, 6} confirmed the correctness of calculation of pair correlation energies by the variational computation and proposed the method to estimate the total correlation energy by summa-

rizing the pair correlation energies of the atomic systems. He also calculated electron correlation energies of Be—Ne atoms using this method. Bender and Davidson^{7, 8} calculated the pair correlation energies of LiH and HF diatomic molecules. In recent years, Ju and Davidson⁹⁻¹³ carried out the calculations of pair correlation energies of some MX_2 ($M = Li, Na, K; X = F, Cl$). Based on their calculations, they pointed out the absence of logical basis of $E(HLC)$ term in G1, G2 theories developed by Pople *et al.*¹⁴⁻¹⁶ In order to study the general rules and the dissimilarities of the pair correlation energies of the isoelectronic systems, the pair correlation energies of F^- , HF and H_2F^+ systems are calculated using MP2-OPT2 method of MELD program with cc-PV5Z* basis set. For the discussion of chemical bonding effect on the pair correlation energy, according to the definition of pair correlation contribution of one electron pair to a system, the correlation contribution values of these three isoelectronic systems are calculated and analyzed. In addition, the total pair correlation energies $E_{corr}(SD)$ which includes only single and double excitations and $E_{corr}(SDTQ)$ which also include the higher-excitation (triples and quadruples) are calculated for F^- , HF and H_2F^+ systems with 6-311++G(d) basis set using the same method. It is hopeful that these calculation results and analyses could be helpful to understand the essence of chemical bonding from the viewpoint of electron correlation.

Computation method

The electron correlation energy is calculated by^{3, 4}

$$E_{corr} = \Psi_{HF} | H - E_{HF} | \Psi \quad (1)$$

where Ψ_{HF} is the Hartree-Fork wave function with energy E_{HF} , and Ψ is the exact wave function (in intermediate normalization, $\Psi | \Psi_{HF} = 1$). The exact wave function may be expanded in a series of configurations $\Psi_{ij}^{ab} \dots$ with

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Received December 18, 2002; revised March 31, 2003; accepted June 2, 2003.

Project supported by the National Natural Science Foundation of China (Nos. 29873023, 20173027).

electrons excited from orbitals $ij \dots$ to orbitals $ab \dots, i, e$.

$$\Psi = \Psi_{\text{HF}} + \sum C_j^a \Psi_j^a + \sum C_{ij}^{ab} \Psi_{ij}^{ab} + \dots \quad (2)$$

Inserting Eq. (2) into Eq. (1) obtains

$$E_{\text{corr}} = \sum \epsilon_i + \sum_{i < j} \epsilon_{ij} \quad (3)$$

where

$$\epsilon_i = \sum_a \Psi_{\text{HF}} | H | \Psi_i^a C_j^a \quad (4)$$

$$\epsilon_{ij} = \sum_{ab} \Psi_{\text{HF}} | H | \Psi_{ij}^{ab} C_{ij}^{ab} \quad (5)$$

All geometries of the systems studied in this paper were optimized by Gaussian-98 program at HF/6-311++G(d) level. The optimized bonding distance of HF molecule is $R_{\text{H-F}} = 0.08993 \text{ nm}$, and the optimized H_2F^+ geometry structure is $R_{\text{H-F}} = 0.09472 \text{ nm}$, $\angle\text{HFH} = 180.0^\circ$. The molecular orbitals used are ROHF canonical orbitals described in Ref. 17. The calculations of pair electron correlation energy were performed using MP2-OPT2 method^{18,19} of MELD program developed by Davidson *et al.*²⁰ with cc-PV5Z* and 6-311++G(d) basis sets. It should be noted that because the H functions in cc-PV5Z basis set were not included in the present package of MELD program, these H functions were cancelled from cc-PV5Z basis set in calculations of pair correlation energies of the above systems which were denoted in cc-PV5Z* basis set in the text.

Results and discussion

Intrapair and interpair correlation energies of F^- , HF and H_2F^+ systems

Table 1 shows the pair correlation energies E_{ij} calculated for F^- , HF and H_2F^+ systems. As it can be seen in this table, the intrapair correlation energies of $1s_{\text{F}}^2$ in the above three isoelectronic systems are $E(1s^2) = -27.97 \text{ mh}$ in F^- , $E(1a_1^2) = -28.28 \text{ mh}$ in HF molecule and $E(1a_g^2) = -28.28 \text{ mh}$ in H_2F^+ system which are almost a constant. This shows that the $1s_{\text{F}}^2$ electron intrapair correlation is very much alike in the above isoelectronic systems. Such pair correlations change little, which can be considered transferable in these systems. The reason is that because the main components of $1a_1$ in HF and $1a_g$ in H_2F^+ molecular orbital are basically $1s_{\text{F}}$ atomic orbital, which change little during the formation of H—F bonds in HF and H_2F^+ , the intrapair correlation energies of these electron pairs are almost the same value. The interpair correlation energies of inner core electrons with valence electrons such as $1s_{\text{F}}^2 2s_{\text{F}}^2$ and $1s_{\text{F}}^2 2p_{\text{F}}^2$ of these systems are relatively small which are -4.27 , -4.10 and -3.94 mh , respectively. The total of the inner core correlation effects of $1s_{\text{F}}^2 + 1s_{\text{F}}^2 2s_{\text{F}}^2 + 1s_{\text{F}}^2 2p_{\text{F}}^2$ in F^- , $1a_1^2 + 1a_1^2 2a_1^2 + 1a_1^2 3a_1^2 + 1a_1^2 1b_1^2 + 1a_1^2 1b_2^2$ in HF and $1a_g^2 + 1a_g^2 2a_g^2 + 1a_g^2 1b_{3u}^2 + 1a_g^2 1b_{2u}^2 + 1a_g^2 1b_{1u}^2$ in H_2F^+ are -47.75 , -48.39 and -45.96 mh , respectively. These values differ a little in these systems, because the interpair correlation energies between two orbitals whose orbital

Table 1 Pair correlation energies $E_{\text{cor}}(ij)$ and total correlation energies $E_{\text{cor}}(\text{total})$ of H_2F^+ , HF and F^- (—mh)

H_2F^+		HF		F^-	
$E_{\text{cor}}(1a_g^2)$	28.28	$E_{\text{cor}}(1a_1^2)$	28.28	$E_{\text{cor}}(1s^2)$	27.97
$E_{\text{cor}}(2a_g^2)$	12.28	$E_{\text{cor}}(2a_1^2)$	13.35	$E_{\text{cor}}(2s^2)$	12.48
$E_{\text{cor}}(1b_{3u}^2)$	28.22	$E_{\text{cor}}(3a_1^2)$	32.39	—	—
$E_{\text{cor}}(1b_{2u}^2)$	28.22	$E_{\text{cor}}(1b_1^2)$	28.53	—	—
$E_{\text{cor}}(1b_{1u}^2)$	30.30	$E_{\text{cor}}(1b_2^2)$	28.53	$E_{\text{cor}}(2p^2)$	29.60
$E_{\text{cor}}(1a_g^2 - 2a_g^2)$	3.94	$E_{\text{cor}}(1a_1^2 - 2a_1^2)$	4.10	$E_{\text{cor}}(1s^2 - 2s^2)$	4.27
$E_{\text{cor}}(1a_g^2 - 1b_{3u}^2)$	5.02	$E_{\text{cor}}(1a_1^2 - 3a_1^2)$	4.47	—	—
$E_{\text{cor}}(1a_g^2 - 1b_{2u}^2)$	5.02	$E_{\text{cor}}(1a_1^2 - 1b_1^2)$	5.77	$E_{\text{cor}}(1s^2 - 2p^2)$	5.18
$E_{\text{cor}}(1a_g^2 - 1b_{1u}^2)$	3.70	$E_{\text{cor}}(1a_1^2 - 1b_2^2)$	5.77	—	—
$E_{\text{cor}}(2a_g^2 - 1b_{3u}^2)$	28.96	$E_{\text{cor}}(2a_1^2 - 3a_1^2)$	30.59	—	—
$E_{\text{cor}}(2a_g^2 - 1b_{2u}^2)$	28.96	$E_{\text{cor}}(2a_1^2 - 1b_1^2)$	30.16	$E_{\text{cor}}(2s^2 - 2p^2)$	31.54
$E_{\text{cor}}(2a_g^2 - 1b_{1u}^2)$	31.61	$E_{\text{cor}}(2a_1^2 - 1b_2^2)$	30.16	—	—
$E_{\text{cor}}(1b_{3u}^2 - 1b_{2u}^2)$	41.66	$E_{\text{cor}}(3a_1^2 - 1b_1^2)$	40.73	—	—
$E_{\text{cor}}(1b_{3u}^2 - 1b_{1u}^2)$	38.85	$E_{\text{cor}}(3a_1^2 - 1b_2^2)$	40.73	—	—
$E_{\text{cor}}(1b_{2u}^2 - 1b_{1u}^2)$		$E_{\text{cor}}(1b_1^2 - 1b_2^2)$	43.02	$E_{\text{cor}}(2p^2 - 2p^2)$	43.64
$E_{\text{cor}}(\text{total})$	353.87		366.58		374.60
$E_{\text{cor}}(\text{SD})$	260.32		261.20		272.81
$E_{\text{cor}}(\text{SDTQ})$	265.85		267.50		282.11

energies differ largely or between two orbitals which are far away in space are very small. However, both the intrapair and interpair correlation energies of valence electrons such as $2s_F^2 2s_F^2$, $2s_F^2 2p_F^2$ and $2p_F^2 2p_F^2$ are very large and very different from each other in different systems. For instance, in F^- the intrapair correlation energies of $2s^2$ and $2p^2$ are $E(2s^2) = -12.48$ mh and $E(2p^2) = -29.60$ mh, the interpair correlation energies $E(2s^2 2p^2) = -31.54$ mh and $E(2p^2 2p^2) = -43.64$ mh. The situation is the same in both HF and H_2F^+ systems. The reason is that for valence electrons in high energy orbitals, the interactions among them are strong and these electrons are easy to excite to virtual orbitals to form more effective configurations. According to the perturbation theory, these form more perturbation terms and get more correlation energy for valence electrons.

The sum of intrapair and interpair correlation energies $E_{\text{corr}}(\text{intra})$ and $E_{\text{corr}}(\text{inter})$ of these three systems and the percent of these values in the total correlation energies $E_{\text{corr}}(\text{total})$ are shown in Table 2. From these results, it can be seen that the sum of interpair correlation energy is much larger than that of intrapair correlation energy in each system. For example, in F^- anion, $E_{\text{corr}}(\text{inter}) = -245.35$ mh which is 65.50% of the total correlation energy of F^- . In HF and H_2F^+ , $E_{\text{corr}}(\text{inter})$ are -235.50 mh and -226.58 mh which are 64.24% and 64.03% of the total correlation energies of the respective system, respectively. This indicates that the sum of interpair correlation energy predominates in all the above systems confirming the results in Ref. 9—12.

Intrashell and intershell correlation energies of F^- , HF and H_2F^+ systems

Table 2 also shows the total intrashell and intershell correlation energy contributions of these three systems. The total KK and KL correlation energy is small and only about 12%—14% of the total correlation energy of each system, but the valence intrashell correlation $E_{\text{corr}}(\text{LL})$ dominates. That is because the valence intrashell correlation includes all the intrapair and interpair correlations of valence electrons and as discussed above it is known that both of them are large. This result is applicable for all substances. Based on this fact, some computation theories like G1, G2 adopt "frozen-core" model to calculate the energy and get reasonable results (the error is less than 8.36 kJ/mol). This "inner-shell" cancellation is basic to much of the quantum chemistry. The most important is that because most of chemical reactions are only the transformations of valence electrons, it is useful to investigate the energy change of a reaction from the viewpoint of the correlation energy change of valence electrons.

Effect of chemical bonding on pair correlation energies of F^- , HF and H_2F^+ systems

Although all these three isoelectronic systems F^- , HF

and H_2F^+ have ten electrons in the systems, the different chemical bonding in each system results in different electronic cloud distributions and different wavefunctions, so that correlation pattern changes a lot in these three isoelectronic systems. In order to investigate the effect of chemical bonding on the pair correlation energies of a molecular system clearly, we defined the pair correlation contribution of one electron pair to a system as the sum of the intrapair correlation energy plus half of the sum of the interpair correlation energies of one electron pair in the system, *i. e.*,²¹

$$E_{\text{corr}}(i) = E_{\text{corr}}(ii) + 1/2 \sum_j E_{\text{corr}}(ij) \quad (6)$$

where $E_{\text{corr}}(i)$ is the pair correlation contribution of i th electron pair to the system, $E_{\text{corr}}(ii)$ is the intrapair correlation energy of i th electron pair and $E_{\text{corr}}(ij)$ is the interpair correlation energy between i th and j th electron pairs in the system. In this way, the total correlation energy of a system can be obtained by summarizing the pair correlation contributions of all electron pairs in the system, *i. e.*,

$$E_{\text{corr}}(\text{total}) = \sum_i E_{\text{corr}}(i) \quad (7)$$

According to Eq. (6), the pair correlation contribution values of each electron pair in F^- , HF and H_2F^+ systems were calculated and given in Table 2. As shown in Table 2, the correlation contribution values of $1s^2$ electron pairs in F^- , HF and H_2F^+ are -37.88 , -38.33 and -37.12 mh, respectively, and the correlation contribution values of $2s^2$ electron pairs in F^- , HF and H_2F^+ are -59.79 , -60.86 and -59.02 mh, respectively. These values change little in the three systems indicating that the chemical bonding has relatively small effect on the electron correlation of the inner electron pairs. Also it can be seen in Table 2 that the correlation contributions of three $2p^2$ electron pairs in F^- are -91.60 mh, while the correlation contributions of $2p^2$ lone electron pair of F in HF and H_2F^+ are -88.37 and -86.80 mh, respectively. This indicates that H—F bond has somewhat influence on $2p^2$ electron pairs in HF and H_2F^+ systems. Compared with F^- anion, with the formation of H—F bonds, the correlation contributions of $2p^2$ electron pairs in HF and H_2F^+ decrease. Analyzing the correlation contribution values of H—F bonding electron pair in HF and H_2F^+ systems, as it is shown in Table 2 that $E_{\text{corr}}(\text{H—F}) = -90.65$ mh in HF and $E_{\text{corr}}(\text{H—F}) = -85.46$ mh in H_2F^+ , this indicates that the overlapping of $2p_z$ orbital of F atom with $1s$ orbital of H atom is very large which form strong covalent bond in HF and H_2F^+ systems. The further comparison of $E_{\text{corr}}(\text{H—F})$ value in HF with that in H_2F^+ shows that H—F covalent bond in H_2F^+ system is less strong than that in HF molecule, indicating that the relativity of the correlation energy of the bonding electron pair is related to the strength of the chemical bonds.

Table 2 Sum of intra-, intershell, intra-, interpair correlation energies and pair correlation contributions $E_{\text{corr}}(i)$ [Eq. (6)] of H_2F^+ , HF and F^- (—mh)

	$E_{\text{corr}}(1s_{\text{F}}^2)$	$E_{\text{corr}}(2s_{\text{F}}^2)$	$E_{\text{corr}}(2s_{\text{p}}^2)$	$E_{\text{corr}}(\text{H—F})$	$E(\text{KK})$	$E(\text{KL})$	$E(\text{LL})$	$E_{\text{corr}}(\text{intra})$	$E_{\text{corr}}(\text{intra})$
H_2F^+	37.12	59.02	86.80	85.46	28.28	17.68	307.19	127.29	226.58 (64.03%)
HF	38.33	60.86	88.37	90.65	28.28	20.11	318.19	131.08	235.50 (64.24%)
F^-	37.88	59.79	91.60	—	27.97	19.81	326.82	129.25	245.35 (65.50%)

In addition, as shown in Table 2, the percents of the sum of interpair correlation energies in total correlation energy of F^- , HF and H_2F^+ systems are 65.50%, 64.24% and 64.03%, respectively. Because of the bonding effects in HF and H_2F^+ , both of the percentage values of HF and H_2F^+ decrease in comparison with that of F^- though all of them have ten electrons. The reason is that compared with F^- anion, HF and H_2F^+ are poly-centered systems so that the electron clouds of H—F bonding electron pairs in HF and H_2F^+ are more dispersed than $2p^2$ electron pair in F^- anion. This results in the decreases of the interpair correlation energies between H—F bonding electron pair and the other electron pairs in HF and H_2F^+ systems. For example, the interpair correlation energy between two $2p^2$ electron pairs in F^- is $E_{\text{corr}}(2p^2 2p^2) = -43.64$ mh, while the interpair correlation energies between H—F bonding electron pair and $2p^2$ lone electron pair in HF and H_2F^+ are -40.73 and -38.85 mh, respectively. The calculation of the percent of the sum of interpair correlation energies in the total correlation energy only including valence shell electrons also shows the greater decrease tendency in HF, H_2F^+ and F^- which are ten electron systems, respectively. The reason is that the pair correlation energies of valence electrons are greatly influenced by the bonding effect of HF and H_2F^+ systems.

Correlation contribution of higher excitations of F^- , HF and H_2F^+ systems

In order to study the contributions of triple and quadruple excitations, we have carried out calculations of total pair correlation energies of these three systems including these higher-excitation terms denoted in $E_{\text{corr}}(\text{SDTQ})$ using MP2-OPT2 method with 6-311++G(D) basis set, for comparison, the total pair correlation energies only including single and double excitations $E_{\text{corr}}(\text{SD})$ are also calculated using the same method with same basis set. The results of $E_{\text{corr}}(\text{SDTQ})$ and $E_{\text{corr}}(\text{SD})$ are given in the two bottom lines in Table 1. Comparing the two calculation results of $E_{\text{corr}}(\text{SDTQ})$ and $E_{\text{corr}}(\text{SD})$ of F^- , HF and H_2F^+ systems respectively, it is found that the triple and quadruple excitation contributions contribute 3.30% in F^- , 2.36% in HF and 2.08% in H_2F^+ to the total correlation energy of the respective system, all of which are more than 2% of total correlation energy. Thus, these higher-excitation contributions can not be negligible in the accurate calculations of quantum chemistry.²²

Conclusions

On the basis of our results, the principle conclusions can be obtained as follows:

The $1s_{\text{F}}^2$ electron pairs are very much alike in these isoelectronic systems and such pair correlation energy is transferable. In F^- , HF and H_2F^+ systems, the inner core correlation effects differ a little and the total inner intrashell and intershell correlation energies are small. However the interpair correlation and intrashell correlation energies of the valence electron pairs are large and differ a lot. The valence intrashell correlation energy dominates in all the above systems.

Based on the definition of pair correlation contribution of one electron pair to a system, the correlation contribution values were calculated for F^- , HF and H_2F^+ systems. The calculation results show that the pair correlation contribution of H—F covalent bond in HF is larger than that in H_2F^+ system. With the formation of H—F bond in HF and H_2F^+ , the pair correlation energies of bonding electrons change somewhat compared with F^- anion. It is shown that the correlation contribution values of inner electron pairs are relatively little influenced, however both of the percent of the sum of interpair correlation energy in total correlation energy only including valence electrons and the percent of the sum of interpair correlation energy in total correlation energy decrease in HF and H_2F^+ . Therefore it can be concluded that the bonding effect of a molecule is one of the important factors to influence electron correlation energy of the system.

From the calculation of triple and quadruple excitation contributions in F^- , HF and H_2F^+ systems, it is found that the contribution of higher-excitations are more than 2.00% in these three isoelectronic systems which should not be negligible in the accurate calculations in quantum chemistry.

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(E0212185 LI , L. T. ; ZHENG , G. C.)