The adiabatic potential analysis for some carbon containing molecules

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Abstract

In the present paper the procedure to part a molecule into the ion-radicals and bonds, proposed earlier by one of authors within the HF approach, is used. In this procedure the ion-radical occupied orbitals are defined as solutions of HF equations for ion-radical in the basis of occupied MO of the whole molecule. The bond orbitals are constructed to complete the functional space span by the occupied MO of ion-radicals to the functional space span by occupied MO of the whole molecule. In this approach it is easy to calculate the electron density of all ion-radicals and bonds which sum to the total electron density of the whole molecule, the densities overlap being taken into account. Hence the adiabatic potential of the molecule is expressed as a sum of ion-radicals and bonds self-energies and of various intramolecular interaction energies.

The results of *ab initio* adiabatic potential calculations and its decomposition for several carbon containing molecules, such as CH_4, CH_3Li, CH_3F and C_2H_6 , which can be considered as two ion-radicals connected with a single chemical bond, are presented here. The dependence of adiabatic potential components on the bond length is analyzed and simple approximate equations for them are generated. Besides, the electronic structure of ion-radical CH_3^+, common for all calculated here molecules, is considered and its dependence on the molecular environment is analyzed.

1   Introduction

The notion of chemical bond is very useful for the description of various properties of molecules. Besides, chemical bond corresponds to geminal, the two-electron function, which is the next to orbital, the one-electron function, in the group function method [1]. In the Hartree-Fock theory the bond orbital is a non-canonical orbital (linear combination of canonical HF molecular orbitals), localized in the vicinity of two atoms with the electron density maximum in between these atoms. Bonds are responsible for the main part of the molecule cohesion and at the same time bond orbitals are occupied by a small portion of molecular electrons, two electrons at each single bond. Therefore with the help of bond orbitals the calculation and analysis of the molecule adiabatic potential can be made more efficient and simple. It is more efficient because of the great reduction in the number of electrons and it is simpler because each bond mostly depends on the position of two atoms connected with this bond. In the quantum

theory of many-electron systems the exclusion of the core states is usually done with the help of pseudopotential [2, 3, 4, 5, 6]. In this respect the transformation to the core and bond orbitals with subsequent retaining the bond orbitals only can be considered as a particular case of pseudopotential theory specially designed for covalently bonded materials.

However, there is no unique a priori definition of the bond orbital. Bond orbitals are usually obtained with the help of various post HF localization procedures, different localization procedures resulting in different bond orbitals. Recently, a localization procedure convenient to the adiabatic potential analysis was proposed by one of the authors [7]. In this procedure the bond orbital is not localized directly. Instead, a localization procedure is applied to obtain the ion-radical orbitals and then the bond orbital is calculated to complete the functional space span by the occupied MO of ion-radicals to the functional space span by occupied MO of the whole molecule. This procedure is applied here for the adiabatic potential analysis.

In the next section the method of generating the bond orbital is discussed briefly, then in the section 3 the molecule energy decomposition is described, finally in the section 4 the results of adiabatic potential calculations are presented and discussed.

2 Bond orbital

In this section the bond orbital generating method will be discussed in application to the simplest case when a molecule can be considered as consisting of two closed shell ion-radicals R_1 and R_2 connected with a single chemical bond b. It is not difficult to generalize the method for more complex molecules. The bond is assumed to be assigned to the atom A_1 in the ion-radical R_1 and to the atom A_2 in the ion-radical R_2. We also assume that each ion-radical has an even number of electrons, $2n_1$ and and $2n_2$ respectively. The bond has two electrons, so the total number of electron in the molecule is $2n = 2n_1 + 2n_2 + 2$. The nuclei of every atom of the molecule is assigned to the one or to the other ion-radical, the bond has only electrons. Hence each ion-radical has positive charge +1 and the bond has negative charge -2. The ground state of molecule is assumed to be the closed shells singlet state.

At the beginning the ground state electronic structure of the molecule is calculated within one-determinant RHF method with appropriate AO basis and all occupied MO ψ_k, $k = 1, \cdots, n$ are obtained. Then the electronic structure of each ion-radical is calculates twice. First, the ion-radical is calculated in the RHF approximation with the same AO basis, which was used for the total molecule calculations. This produce the orbitals ϕ_k^0 and the total energy E_R^0 of the single ion-radical. Second, this ion-radical is calculated similarly but with another basis, which consists of occupied MO ψ_k of the whole molecule. Thus obtained occupied orbitals ϕ_k and the total energy E_R can be considered as orbitals and energy of the ion-radical in the molecule. In other words, ϕ_k are the non-canonical MO of the whole molecule which correspond to the ion-radical. The difference between E_R and E_R^0 is the ion-radical deformation energy under the influence of the molecular environment. The difference between orbitals ϕ_k and ϕ_k^0 describes the corresponding ion-radical deformation itself.

The occupied orbitals ϕ_k, $k = 1, \cdots, n_1$ of ion-radical R_1 in the molecule and ϕ_k, $k = n_1 + 1, \cdots, n_1 + n_2$ of ion-radical R_2 in the molecule are assumed to be linearly independent. It is really so except some pathological cases. After these orbitals are calculated the bond orbital ϕ_b can be found. For this the density operator $\widehat{\rho}_0$

$$\widehat{\rho}_0 = \sum_{j,k=1}^{n_1+n_2} |\phi_j\rangle \left\{S^{-1}\right\}_{jk} \langle\phi_k|, \qquad S_{jk} = \langle\phi_j|\phi_k\rangle$$

is used. It is evident that all ϕ_k, $k = 1, \cdots, n_1 + n_2$ are eigenfunctions of $\widehat{\rho}_0$ with the same eigenvalue equal to 1. At the same time the trace of $\widehat{\rho}_0$ is $n_1 + n_2 = n - 1$. Therefore there is a non-canonical occupied MO of the molecule which is the eigenfunction of $\widehat{\rho}_0$ with eigenvalue 0. This orbital, orthogonal to all occupied ion-radicals orbitals, can be considered as bond orbital ϕ_b.

3   Energy decomposition

The considered ground state of the molecule is the one-determinant closed shells state and its energy is a well known universal functional of the first order reduced density matrix $\rho(\mathbf{r}|\mathbf{r}')$. It can be written as a sum of four terms

$$E[\rho, \aleph] = E_{kin}[\rho] + E_{en}[\rho, \aleph] + E_{ee}[\rho] + E_{nn}[\aleph]$$

corresponding to the kinetic energy, electron-nucleus interaction energy, electron-electron interaction energy and nuclear repulsion energy. The symbol $\aleph$ here indicates the nucleus subsystem of molecule. The kinetic and the electron-nucleus interaction energies are linear in ρ whereas the electron-electron interaction energy is quadratic in ρ. With the obtained orbitals of ion-radicals and bond the electron density of the molecule can be written as

$$\rho = \rho_1 + \rho_2 + \rho_{12} + \rho_b$$

where

$$\rho_1 = \sum_{k=1}^{n_1} \phi_k(\mathbf{r})\phi_k(\mathbf{r}'), \qquad \rho_2 = \sum_{k=n_1+1}^{n_1+n_2} \phi_k(\mathbf{r})\phi_k(\mathbf{r}'), \qquad \rho_b = \phi_b(\mathbf{r})\phi_b(\mathbf{r}')$$

are ion-radicals and bond densities and

$$\rho_{12} = \rho_0 - \rho_1 - \rho_2$$

is the correction due to the non-orthogonality of ion-radical orbitals. The nucleus are divided between ion-radicals which can be conventionally written as

$$\aleph = \aleph_{R_1} + \aleph_{R_2}$$

Consequently one can calculate the self-energy of various parts of molecule

E_{R_1} - self energy of ion-radical R_1 : $E_{R_1} = E[\rho_1, \aleph_{R_1}]$

E_{R_2} - self-energy of ion-radical R_2 : $E_{R_2} = E[\rho_2, \aleph_{R_2}]$

E_b - self-energy of the bond : $E_b = E[\rho_b, \emptyset]$. (Bond contains no nucleus.)

$E_{R_1 \oplus R_2}$ - self-energy of the union of ion-radicals R_1 and R_2 : $E_{R_1 \oplus R_2} = E[\rho_0, \aleph]$

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$E_{R_1 \oplus b}$ - self-energy of the union of ion-radical R_1 and bond : $E_{R_1 \oplus b} = E[\rho_1 + \rho_b, \aleph_{R_1}]$ (orbitals of ion-radical R_1 and bond are orthogonal)

$E_{R_2 \oplus b}$ - self-energy of the union of ion-radical R_2 and bond : $E_{R_2 \oplus b} = E[\rho_2 + \rho_b, \aleph_{R_2}]$ (orbitals of ion-radical R_2 and bond are orthogonal)

Then the total energy of the molecule can be written as

$$E = E_{R_1} + E_{R_2} + E_b + E_{int}(R_1, R_2) + E_{int}(R_1, b) + E_{int}(R_2, b) + E_{int}(R_1, R_2, b) \qquad (1)$$

Here the interaction energies can be expressed with the defined above self-energies of various parts of molecule

$$E_{int}(R_1, R_2) \quad = E_{R_1 \oplus R_2} - E_{R_1} - E_{R_2}$$

$$E_{int}(R_1, b) \quad = E_{R_1 \oplus b} - E_{R_1} - E_b$$

$$E_{int}(R_2, b) \quad = E_{R_2 \oplus b} - E_{R_2} - E_b$$

$$E_{int}(R_1, R_2, b) \quad = E - E_{R_1 \oplus R_2} - E_{R_1 \oplus b} - E_{R_2 \oplus b} + E_{R_1} + E_{R_2} + E_b$$

The first three terms are the two-body interaction energies. The last term is the three-body interaction energy. It would be equal to zero if orbitals of one ion-radical were orthogonal to orbitals of another ion-radical. All terms in the equation (1) are well defined. However it was found more convenient to decompose the molecule energy in a different way. For this the ion-radical self-energy was written as a sum of the single ion-radical energy and its deformation energy. Besides, all three species we divided our molecule into, namely ion-radical I, ion-radical II, and bond, are charged and therefore there is the Coulomb tail in their interaction energy, which makes problems in the extended systems and must be treated separately. Therefore the ion-radicals interaction energy was divided into the long-range and short-range parts

$$E_{int}(R_1, R_2) = E_{lr}(R_1, R_2) + E_{sr}(R_1, R_2).$$

The short-range part was left in the energy equation explicitly, while the long-range part together with the bond – ion-radical interaction energies and the three-body energy were combined into a quantity which we refer to as the bond energy

$$E_{bond} = E_b + E_{int}(R_1, b) + E_{int}(R_1, b) + E_{lr}(R_1, R_2) + E_{int}(R_1, R_2, b)$$

Hence the energy of the molecule was written as

$$E = E_{R_1}^0 + E_{R_2}^0 + E_{R_1}^{def} + E_{R_2}^{def} + E_{sr}(R_1, R_2) + E_{bond} \qquad (2)$$

The long-range part of the interaction energy has no unique definition. Every distributed in space charge (electron cloud or nuclei array) can be described with an infinite sequence of multiple moments, hence the interaction energy can be expressed as an infinite sum of various point multipoles interactions, multipoles being calculated with respect to a given reference point. The division of the whole multipole expansion into the long-range and the short-range parts is always conditional and any expression is open for discussion. In the present paper only the interaction between point charges at reference points was included into the long-range

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part. The atoms A_1 and A_2 nucleus positions were taken for the reference points of ion-radicals. For the The reference point, corresponding to zero dipole moment, was taken for bond. The ion-radicals charges we denote as q_1 and q_2, the bond charge as q_b.

4   Results and discussion

In this section the results of the adiabatic potential calculations are presented and discussed. The following molecules were chosen as the test objects: $H–CH_3$, $Li–CH_3$, $CH_3–CH_3$, and $F–CH_3$. Each molecule was calculated as it was described in sections 2 and 3, and for all of them the ion-radicals and bond densities, adiabatic potential and its constituents were obtained. Then, the obtained densities and the total energy constituents were analyzed to check how well the proposed procedure is justified. Besides some simple equations were generated to fit various energy constituents for future applications.

As it is impossible to display all the obtained results, we chose the CH_4 molecule to be the representative object in the analysis. The other molecules behave similarly to CH_4 so only the final numerical results are presented for them.

The total energy and its constituents in the equation (2) are shown in Figure 1 as a function of the bond length, which is the distance between nucleus of atoms A_1 and A_2 in ion-radicals R_1 and R_2 respectively. The points represent the calculated values, solid lines show the developed approximations. The main energy constituents responsible for the molecule formation are E_{bond} and $E_{sr}(R_1, R_2)$, the deformation energies are less significant. The E_{bond} itself has no minimum. Using the sum $E_{bond} + E_{sr}(R_1, R_2)$ as an approximate adiabatic potential one will obtain the equilibrium bond length 2.0 a.u and the energy at equilibrium position -1.095 a.u . The corrections due to the deformation energy are 0.076 a.u. to the equilibrium bond length and $+0.1$ a.u. to the energy at equilibrium. Such behaviour show us that ion-radicals obtained with the proposed procedure are to a good approximation a rather tightly bounded units, so all ion-radicals electrons can be excluded from the molecule electronic structure calculations, the latter being confined to the bond electrons only. The equation for the bond orbital has been developed in [7] and the solution of this equation will produce E_{bond}. The ion-radicals repulsion, necessary to provide the stable state of the molecule, can be considered as a fixed potential energy function to be added to the HF energy of the bond. The ion-radicals deformation energy is a small correction.

Having this in mind we generates simple approximations for the ion-radicals short-range interaction and deformation energies. The ion-radicals interaction energy and its short-range and long-range parts are shown in Figure 2 as functions of the bond length. The short-range part is closely related to the ion-radical orbitals overlap, the latter being well localized. Therefore the oftenly used exponential function

$$E_{sr} = C_{sr}e^{-\alpha_{sr}z}$$

was chosen as an approximation. Here z is the bond length. This approximation was found to yield satisfactory results in all considered molecules, in spite of the fact that it approximates the repulsion energy between groups of atoms and not between two single atoms. The obtained values of parameters C_{sr} and α_{sr} for all considered molecules are given in the Table 1.

Next we consider the ion-radical deformation. As it was said above, the deformation energy was found to be a small correction. However it is not negligible and needs analysis as the whole

scheme is meaningful only if the ion-radical deformation is small enough. Various competitive processes different for inner and outer ion-radical electrons are responsible for the ion-radical deformation but most of them have similar response function which helps the parametrization. The closed shells RHF method used here fails to correctly describe the chemical bond at large interatomic separation and its results has physical meaning in the vicinity of the equilibrium geometry only. Still for the deformation energy parametrization in this region one can use the equation

$$E^{def} = D_0 + (C_0 + C_1 z)^2 e^{-\alpha z}$$

where z is the bond length. Would this equation be valid up to infinity the parameter D_0 will be the energy difference between CH_3^+ in CH_4 and the single CH_3^+. As it is, D_0 is the parameter which together with the rest of the equation for E^{def} reproduces the CH_3^+ deformation energy at the equilibrium geometry. This parametrization was successful in all considered molecules except CH_3F where the parametrization accuracy is rather poor. The obtained values of parameters D_0, C_0, C_1, and α are given in the Table 1.

Sometimes reasonable description of deformation can be provided by a simple model where the deformation itself is described with a single parameter Δ, the self-energy of the deformed state $\Delta^2/2\beta$ is quadratic in deformation parameter and the energy in the potential causing deformation $\Delta f(z)$ is linear in the deformation parameter. In this model

$$E^{def} = \frac{\beta}{2} f^2(z).$$

Hence from the dependence of the deformation energy on z one can extract the dependence on z of the potential responsible for deformation. In our case the ion-radical deformation is due to the joint influence of the bond and another ion-radical and the separation of $f(z)$ into these two interactions needs special analysis.

The set of molecules selected for calculations was chosen to investigate the dependence of the ion-radical deformation on its molecular environment. For the quantitative description the electron density of CH_3^+ ion-radical in different molecules was calculated along two lines, one corresponding to the bond between ion-radicals and another corresponding to the inner bond of CH_3^+. The results are shown in Figures 4 and 5, the innermost 1s orbital of C being excluded as it results in the same sharp narrow peak in all molecules. In these figures the region is shown where the density change is the most pronounced. In this region the density itself is comparatively small. From these figures it follows that the ion-radical deformation is small. It corresponds to the diminishing the density in the region of the bond between ion-radicals when the second ion-radical is changed from Li^+ to F^+ and to the increasing the density in the inner part of CH_3^+, both in the region of the inner bond and in between the inner bonds.

In conclusion, the energy-driven localization enables one to decompose the molecule into the ion-radicals and bond with ion-radicals being the comparatively tightly bounded objects. The ion-radical electronic structure depends only a little on its molecular environment. At the same time the ion-radicals interaction must be included in the molecule adiabatic potential to provide the accurate equilibrium geometry.

Acknowledgment

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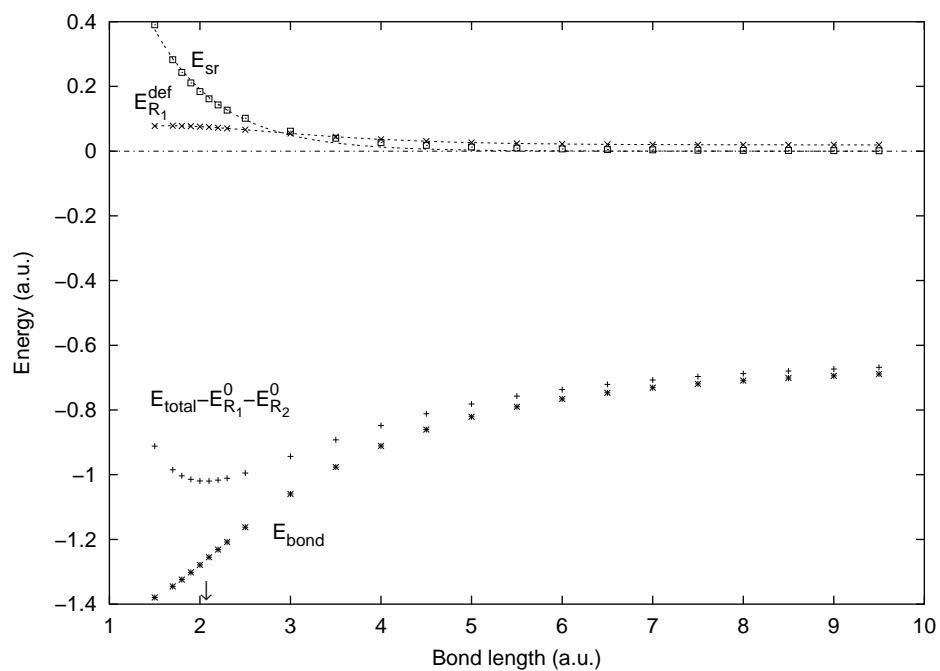
Figure 1: The total energy and its constituents in CH_4 as a function of the bond length. The arrow indicates the equilibrium bond length.
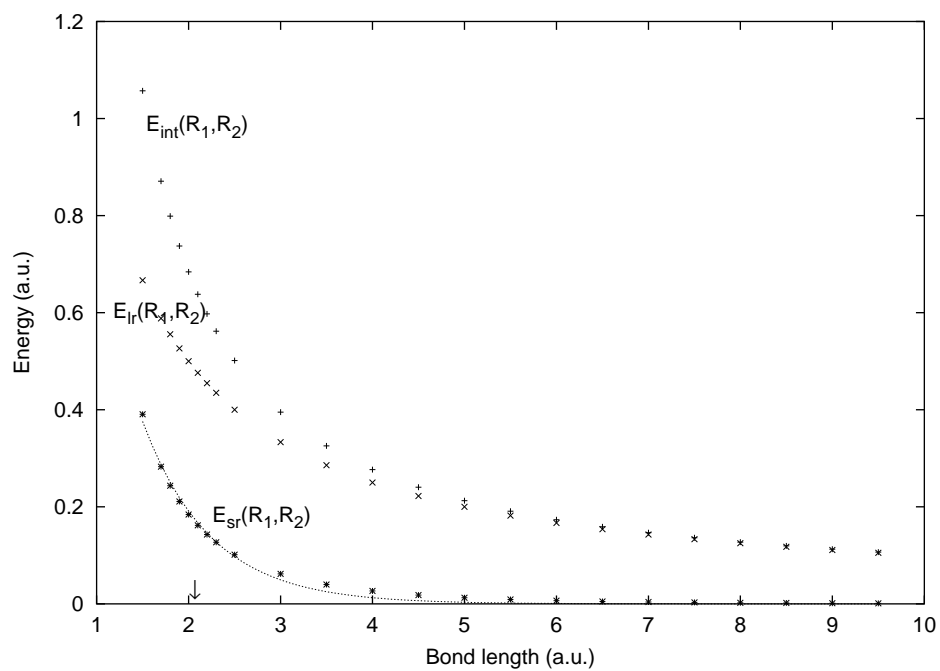

Figure 2: Ion-radicals interaction energy decomposition: the Coulomb tail and the short range part.
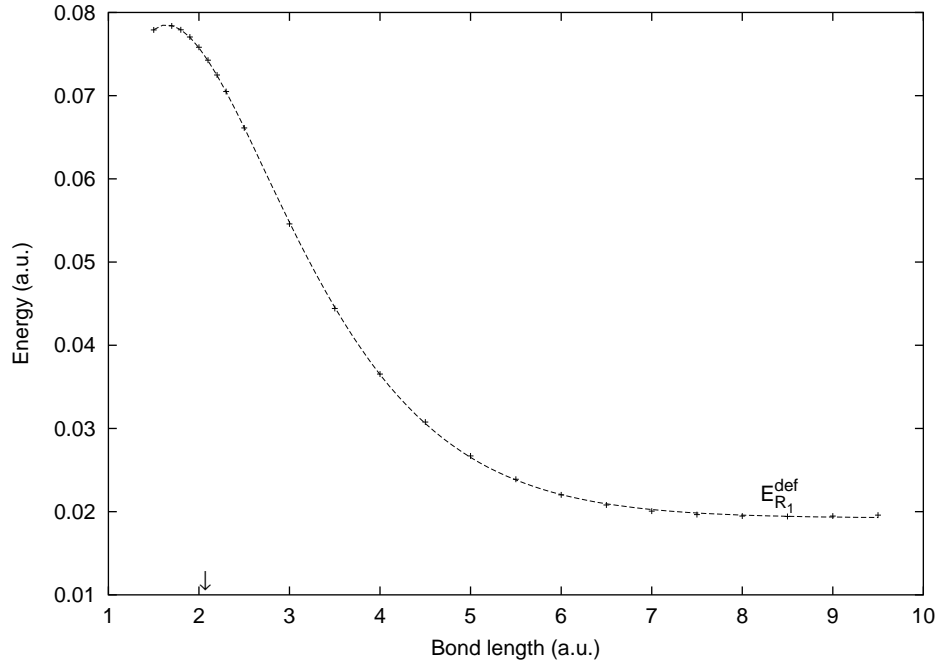
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Figure 3: Ion-radical deformation energy in detail.

Table 1: Summary of the fitting parameters.

Property	CH_3–H	CH_3–Li	CH_3–F	CH_3–CH_3
C_{sr}	2.860	0.910	12.662	9.852
α_{sr}	1.353	0.867	1.379	1.253
C_3	0.000	-3.457	-14.641	-9.374
α_3	0.000	2.733	2.518	1.975
D_0^1	0.019	0.065	0.003	0.033
C_0^1	-0.063	-0.133	0.916	0.731
C_1^1	0.477	0.376	0.000	0.000
α^1	1.323	0.957	0.987	0.769
D_0^2	0.000	0.000	0.244^a	0.033
C_0^2	0.000	0.162	-7117.371^a	0.731
C_1^2	0.000	0.000	4135.459^a	0.000
α^2	0.000	1.221	8.151^a	0.769

[a] Doesn't really make sense since the fitting not converged. In fact the F^+ deformation energy can be expressed as the Morse potential.
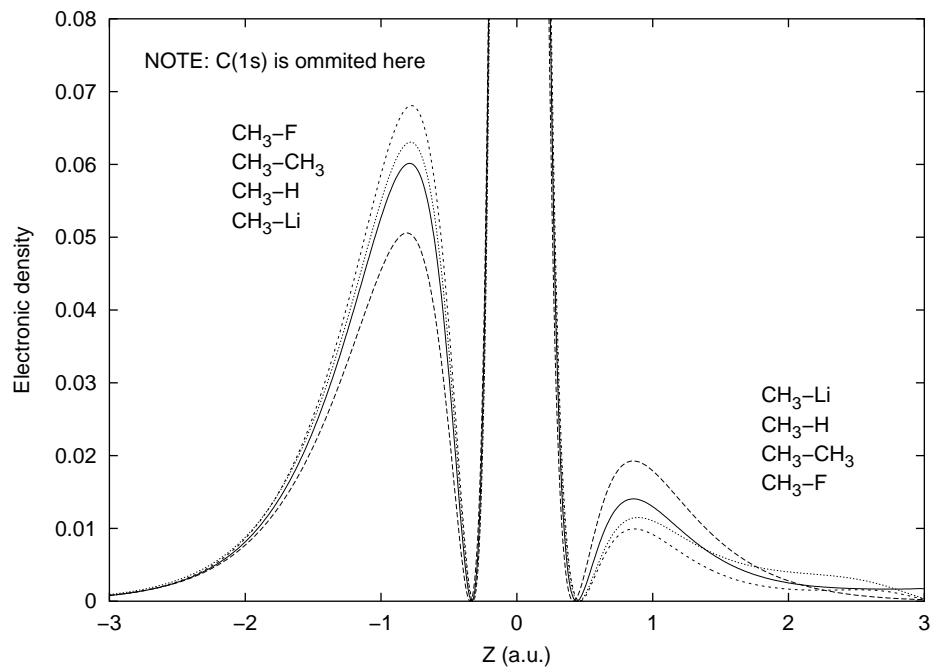
Figure 4: CH_3^+ density along the bond axis built on all its functions except C(1s). The right part of the plot covers bond region, while the left the inner.
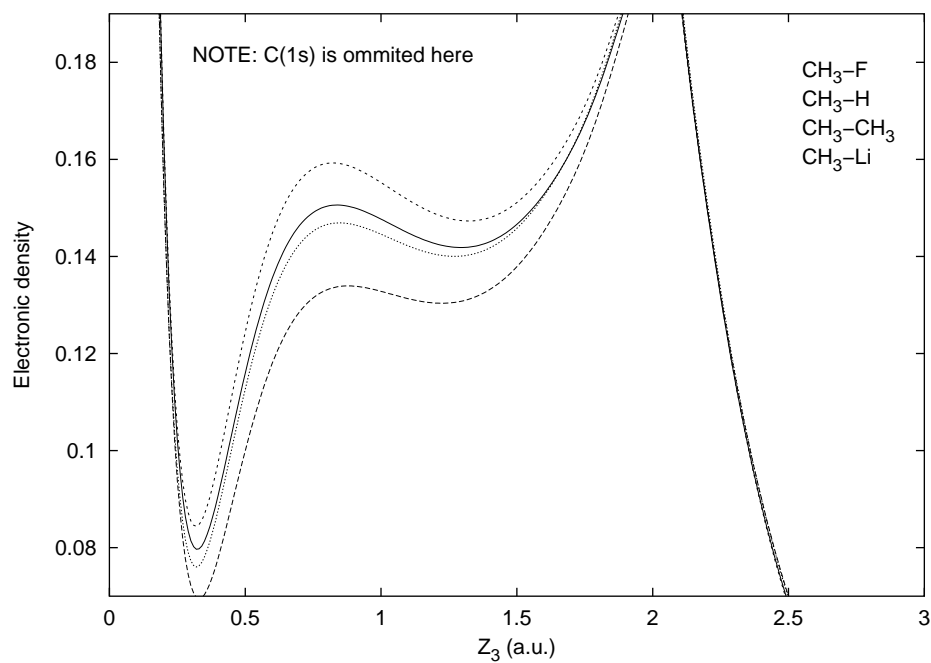

Figure 5: CH_3^+ density along the inner C–H axis built on all its functions except C(1s). The carbon is at 0 while the hydrogen is at 2.