



Application of pseudo-diabatic electronic states buried in Hartree–Fock wavefunctions to describe bond dissociation processes



Tomonori Murakami, Katsuhisa Ohta*

Department of Applied Chemistry, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

ARTICLE INFO

Article history:

Received 9 February 2015
Received in revised form 18 April 2015
Accepted 18 April 2015
Available online 8 May 2015

Keywords:

Hartree–Fock
Diabatic electronic states
Ion-pair
Biradical
Bond dissociation

ABSTRACT

Pseudo-diabatic electronic states buried in Hartree–Fock (HF) wavefunctions are applied to describe bond dissociation processes. The limited variational freedom of HF wavefunctions turns to their own advantage to approximately describe the “diabatic” ionic-pair state or the diabatic biradical state. As an application of the pseudo-diabatic states, CH-bond dissociation processes of normal alkanes and their branched isomers are investigated. Reasonable relationships between the diabatic crossing energies and the number of alkyl substituents on a radical center are obtained in accordance with hyperconjugation theory.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The limited variational freedom in Hartree–Fock (HF) wavefunctions is considered to be a deficiency to correctly describe the dissociation of chemical bonds. Correlated wavefunctions, such as the multi-configurational HF (MCHF), or the multi-reference CI (MRCI) wavefunction, are required [1]. However, simple orbital-pictures in HF wavefunctions have provided clear insight into various chemical reactions [2].

In this work, we investigate the pseudo-diabatic electronic states buried in HF wavefunctions to describe bond dissociation processes. It is well-known that “diabatic” electronic wavefunctions are defined as the basis that diagonalizes the nonadiabatic coupling terms. However, there is no generally accepted unique definition of the diabatic representation [3,4]. Compared with correlated wavefunctions, the limited variational freedom of HF wavefunctions turns to their own advantage to describe the diabatic ionic-pair state or the diabatic biradical state while continuously maintaining the electronic character in bond dissociation processes. As an application of such pseudo-diabatic states, CH-bond dissociation reactions of normal alkanes and their branched isomers are investigated.

2. Pseudo-diabatic electronic states buried in Hartree–Fock wavefunctions

The limited variational freedom of HF wavefunctions can describe approximately the diabatic ionic-pair state or the diabatic biradical state. For a qualitative description of the present idea, we use a simple two-electron and two-orbital model for HF wavefunctions [1].

The molecular orbitals for a spin-unrestricted HF (UHF) wavefunction $||\psi_1^\alpha\alpha\psi_1^\beta\beta||$ in the two-electron and two-orbital model are constructed by occupied space-orbitals

$$\psi_1^\alpha = (\cos \theta \phi_\sigma + \sin \theta \phi_{\sigma^*}), \psi_1^\beta = (\cos \theta \phi_\sigma - \sin \theta \phi_{\sigma^*}), \quad (1)$$

and virtual space-orbitals

$$\psi_2^\alpha = (-\sin \theta \phi_\sigma + \cos \theta \phi_{\sigma^*}), \psi_2^\beta = (\sin \theta \phi_\sigma + \cos \theta \phi_{\sigma^*}). \quad (2)$$

The space-orbitals ϕ_σ and ϕ_{σ^*} are expanded by orthonormalized atomic-orbitals χ_A and χ_B as

$$\phi_\sigma = \frac{1}{\sqrt{2}}(\chi_A + \chi_B), \phi_{\sigma^*} = \frac{1}{\sqrt{2}}(\chi_A - \chi_B). \quad (3)$$

Here, we rewrite the “spin-singlet” UHF wavefunction with diabatic electronic states for bond dissociation as

* Corresponding author.

E-mail address: ohta@mmm.muroran-it.ac.jp (K. Ohta).

$$\begin{aligned}
{}^1\Psi_{\text{UHF}}(\theta) &= \|\psi_1^\alpha\alpha\psi_1^\beta\beta\|, \\
&= \cos^2\theta\|\phi_\sigma\alpha\phi_\sigma\beta\| - \sin^2\theta\|\phi_\sigma\alpha\phi_\sigma\beta\| \\
&\quad - \sqrt{2}\cos\theta\sin\theta\|\phi_\sigma\phi_\sigma(\alpha\beta + \beta\alpha)/\sqrt{2}\|, \\
&= \frac{1}{2}\left[\cos 2\theta(\|\chi_A\alpha\chi_A\beta\| + \|\chi_B\alpha\chi_B\beta\|) \right. \\
&\quad \left. + \sqrt{2}\|\chi_A\chi_B(\alpha\beta - \beta\alpha)/\sqrt{2}\| \right. \\
&\quad \left. + \sqrt{2}\sin 2\theta\|\chi_A\chi_B(\alpha\beta + \beta\alpha)/\sqrt{2}\| \right], \\
&= \frac{1}{2}\left[\cos 2\theta({}^1\Phi_{|A^-B^+|} + {}^1\Phi_{|A^+B^-|}) \right. \\
&\quad \left. + \sqrt{2}{}^1\Phi_{|AB|} + \sqrt{2}\sin 2\theta{}^3\Phi_{|AB|} \right].
\end{aligned} \quad (4)$$

Although the spin-symmetry is broken, the wavefunction ${}^1\Psi_{\text{UHF}}(\theta)$ can describe the bond dissociation adiabatically by changing the weight of ionic-pair and biradical states with limited variational-freedom θ .

Conversely, we can extract pseudo-diabatic states from ${}^1\Psi_{\text{UHF}}(\theta)$ by fixing θ to specific values as follows. The value $\theta = 0$ leads to a closed-shell spin-restricted HF (RHF) wavefunction as

$$\begin{aligned}
{}^1\Psi_{\text{UHF}}(\theta = 0) &= \|\psi_1^\alpha\alpha\psi_1^\beta\beta\| = \|\phi_\sigma\alpha\phi_\sigma\beta\| = {}^1\Psi_{\text{RHF}}, \\
&= \frac{1}{2}(\|\chi_A\alpha\chi_A\beta\| + \|\chi_B\alpha\chi_B\beta\|) + \frac{1}{\sqrt{2}}\|\chi_A\chi_B(\alpha\beta - \beta\alpha)/\sqrt{2}\|, \\
&= \frac{1}{2}({}^1\Phi_{|A^-B^+|} + {}^1\Phi_{|A^+B^-|}) + \frac{1}{\sqrt{2}}{}^1\Phi_{|AB|},
\end{aligned} \quad (6)$$

where the ratio [ionic – pair] : [biradical] = $\left[\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2\right] : \left[\left(\frac{1}{\sqrt{2}}\right)^2\right] = 1 : 1$. The RHF wavefunction, which has half ionic-pair character, can be an approximate indication of the ionic-pair state. Although the spin symmetry is broken, the biradical character is also obtained with $\theta = \pi/4$ as

$$\begin{aligned}
{}^1\Psi_{\text{UHF}}(\theta = \pi/4) &= \|\psi_1^\alpha\alpha\psi_1^\beta\beta\| = \frac{1}{2}\|(\phi_\sigma + \phi_{\sigma'})\alpha(\phi_\sigma - \phi_{\sigma'})\beta\| \\
&= \|\chi_A\alpha\chi_B\beta\|, \\
&= \frac{1}{\sqrt{2}}({}^1\Phi_{|AB|} + {}^1\Phi_{|AB|}) = {}^1\Phi_{|AB|}.
\end{aligned} \quad (7)$$

On the other hand, the spin-triplet UHF leads to an open-shell triplet spin-restricted HF (ROHF):

$$\begin{aligned}
{}^3\Psi_{\text{UHF}} &= \|\psi_1^\alpha\alpha\psi_2^\alpha\alpha\| = \|\phi_\sigma\alpha\phi_{\sigma'}\alpha\| = {}^3\Psi_{\text{ROHF}}, \\
&= -\|\chi_A\alpha\chi_B\alpha\| = -{}^1\Phi_{|AB|}.
\end{aligned} \quad (8)$$

The biradical state described by Eq. (8) has pure triplet spin-symmetry.

To correctly describe the bond-dissociation process in adiabatic calculations, we need a MCHF wavefunction. The MCHF in the two-electron and two-orbital model can also be expanded by the diabatic electronic states as

$$\begin{aligned}
{}^1\Psi_{\text{MCHF}} &= c_1\|\chi_A\alpha\chi_A\beta\| + c_2\|\chi_B\alpha\chi_B\beta\| + c_3\|\chi_A\chi_B(\alpha\beta - \beta\alpha)/\sqrt{2}\|, \\
&= c_1{}^1\Phi_{|A^-B^+|} + c_2{}^1\Phi_{|A^+B^-|} + c_3{}^1\Phi_{|AB|},
\end{aligned} \quad (9)$$

where three variational parameters $\{\delta c_i\}_{i=1,3}$ with a normalization condition and the variational freedoms $\delta\chi_A$ and $\delta\chi_B$ for orbitals should be considered. The energies of the adiabatic and diabatic electronic states are summarized in Appendix A.

Equations in this section are listed in order to show the underlying structure of the present work qualitatively in the two-electron and two-orbital model. As the basis set χ_A and χ_B in Eq. (3), it might be better to use the MCHF active orbitals after the variational calculations with $\delta\chi_A$ and $\delta\chi_B$ in Eq. (9). The consistent quality of the one-electron basis set will be kept along the

bond dissociation process within the MCHF active space. However, one of the purposes of the present work is to show a handy way for the diabatic picture. So, in the following calculations, we use only HF wavefunctions for the pseudo-diabatic states although orbitals of each state are not unitary equivalent.

3. CH-bond dissociation of CH₄

The abstraction of the H atom from saturated alkanes is considered as one of the elementary reactions leading to chain reactions of complex combustion processes [5,6].

As schematically shown in Fig. 1, the adiabatic dissociation of a covalent CH bond proceeds to biradical states along the ground-state energy curve. In the diabatic picture, however, the CH bond goes up along the energy curve to ionic-pair states while continuously maintaining the electronic character. The biradical dissociation path comes down from the singlet or the triplet excited-state while continuously maintaining the electronic character. To follow the biradical dissociation path from the ground-state, we should make a transfer to the biradical dissociation energy curve from the ionic-pair dissociation energy curve at the pseudo-crossing point.

The adiabatic ground-state potential energy to biradical dissociation, without any energy crossing, can be calculated by the spin-singlet UHF wavefunction (5). To describe the diabatic biradical dissociation path from the excited state, the open-shell triplet ROHF is applied. The wavefunction of the spin-restricted closed-shell RHF is used to consider the diabatic ionic-pair state. Results by RHF, however, should be interpreted as an approximate indication of the ionic-pair state, which is only half included in Eq. (6). To verify the adiabatic dissociation process, MCHF wavefunctions with two electrons in two active orbitals ϕ_σ^{CH} and $\phi_{\sigma'}^{\text{CH}}$ were also calculated by optimizing MCHF orbitals at each electronic state. The basis functions for all calculations were DVZ with *d*-polarization and *sp*-diffuse functions in GAMESS [7].

The CH dissociation energy curves for CH₄ are shown in Fig. 2. The optimized bond length $R_{\text{CH}}^{\text{equil}} = 1.084 \text{ \AA}$ was calculated by the close-shell RHF to have a total energy of -40.207775 a.u. in *T_d* symmetry. As a simple reaction-coordinate for the CH dissociation, one of the CH bonds was extended from 1.084 up to 3.000 Å within *C_{3v}* symmetry. Other CH bond lengths and HCH angles were fixed to 1.084 Å and tetrahedral angles (109.47°), respectively.

The total energies and the amount of electrons on the abstracted H atom by Mulliken population analysis at $R_{\text{CH}} = 3.000 \text{ \AA}$ are given in Table 1. As the dissociated biradical-states, the energies from spin-singlet UHF, open-shell triplet ROHF, and the ground singlet state MCHF are similar. The amount of electrons from closed-shell RHF is an approximate

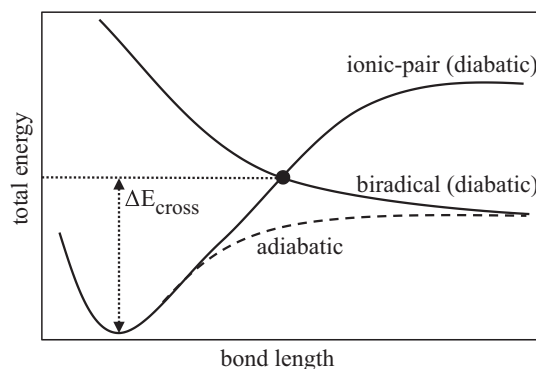


Fig. 1. Schematic diagram of the adiabatic and diabatic energy curves for bond dissociation.

Download English Version:

<https://daneshyari.com/en/article/5393128>

Download Persian Version:

<https://daneshyari.com/article/5393128>

[Daneshyari.com](https://daneshyari.com)