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Analytical form of the interaction energy of radicals at short and long distances

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Abstract. The interaction potential between two planar methyl radicals is investigated based on the available *ab initio* calculations. Two components contribute to this potential: a bonding potential, V_B, an angle-dependent square of the overlap integral for unoccupied p_z orbitals, and a nonbonding potential, V_{NB}, a total of the long-range dispersive and short-range repulsive interactions. The analytical form of the potential, valid at longer distances, can be used for evaluation of the matrix elements of functions describing rotational states.

Key words: Methyl radical – Interaction potential

1 Introduction

Theoretical studies of reaction kinetics involve frequently the use of the potential energy surface of interacting reagents. The details of this surface can be elucidated mostly, although not exclusively, on the basis of *ab initio* calculations. Different analytical forms employing different approximations can be used. The interaction of methane molecules is a good example that has been studied extensively using this approach [1]. Also the reaction $H + CH_3 \rightarrow CH_4$ attracted considerable attention [2].

If quantum mechanical methods are to be used, the form of the V potential that describes the interaction of reactants has to be peculiar, so as to make it possible to calculate easily the matrix elements of the type

$$V_{nm} = \int \cdots \int \psi_n V \psi_m \, d\tau . \tag{1}$$

where ψ_n and ψ_m are the wave functions of the Hamiltonian of the system and $d\tau$ is the element of volume. The potential expressed in this form may be very useful in investigations on weakly interacting systems [3].

For radicals interacting in the gas phase at longer distances, the ψ_n functions refer mainly to the rotational states and can be expressed as linear combinations of products of generalized spherical functions and spherical harmonics [3]. As calculations of the integrals shown in Eq. (1) involve the use of recurrent relations, the derived form of the potential has to be amenable to such a treatment.

It is also of importance that all the forces connected with this potential be strictly Newtonian. The principle of total momentum conservation is thereby satisfied and the recurrent formulae describing addition of momenta in quantum mechanics can be used [3, 4].

As a model system we use the interaction of methyl radicals [5, 6]. There have been many *ab initio* studies of this interaction energy. From our point of view the work of Darvesh et al. [5] is of greatest importance. The method was modeled on those used successfully on the CH_4 system. The energy was estimated using the multireference single- and double-excitation configuration interaction (MRD CI) method. A flat equilateral geometry was selected for CH_3 at a bond length for C–H of 1.079 Å. The orientations and distances r between the radicals were varied. The cases examined are listed in Table 1. The interaction energy V is the difference between the total energy of the system at a given r and the energy at a very long distance (20 Å) when the radicals do not interact for all practical purposes. The values for V are shown in Table 2 in dependence on orientation and distance.

2 Notation and basic relations

The methods described below are general. Adaptation to more or less complicated systems is straightforward. The only requirement imposed is that the potential be separable into the constituents which incorporate the bonded and nonbonded interactions [7]:

$$V = V_{\mathrm{B}} + V_{\mathrm{NB}}. \tag{2}$$

The V_{B} part arises from the overlap of nonfilled orbitals occupied by the unpaired electrons of the radicals. This potential is always attractive at opposed spins and it is involved in the formation of the C–C bond.

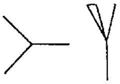
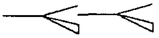
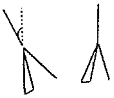
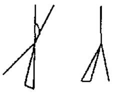
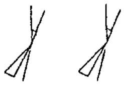
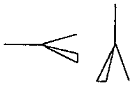
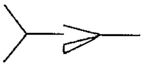
The second component, V_{NB}, is the sum of interactions of the individual pairs:

$$V_{\mathrm{NB}} = \sum_i \sum_j V_{ij}(r_{ij}). \tag{3}$$

These may be, for instance, interactions of the pairs H ⋯ H, H ⋯ C, C ⋯ C and many others. The symbol r_{ij} denotes the distance between the ith component of the first fragment and the jth component of the second fragment. These interactions result from fluctuations of electron densities and repulsions of fully occupied electron orbitals.

In the frame of the center-of-mass system, X_1, Y_1, Z_1 and X_2, Y_2, Z_2 refer to the first and second fragments, respectively. The coordinates $x'_{(1)i}$, $y'_{(1)i}$, $z'_{(1)i}$ and $x'_{(2)j}$, $y'_{(2)j}$, $z'_{(2)j}$ determine the location of individual atoms with respect to the radical center-of-mass ($i, j = 1, 2, 3, 4$). From now on the subscripts (1) and (2) will be omitted and retained only for the general coordinates which do not refer to a particular component. Next, we introduce the common center of mass X, Y, Z where $X = (M_1X_1 + M_2X_2)/(M_1 + M_2)$ etc., and the relative coordinates which are expressed in the spherical

Table 1. Values of angles at the different interradical orientations [5]

Geometry	α_1/π	β_1/π	α_2/π	β_2/π	
S	0	$\frac{1}{2}$	1	$\frac{1}{2}$	
A	1	$\frac{1}{2}$	1	$\frac{1}{2}$	
D	$\frac{3}{2}$	0	1	$\frac{1}{2}$	
E	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	
F	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	
G	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	
I	$\frac{1}{6}$	$\frac{1}{2}$	0	$\frac{1}{2}$	
J	$\frac{11}{6}$	$\frac{1}{2}$	0	$\frac{1}{2}$	
K	$\frac{11}{6}$	$\frac{1}{2}$	$\frac{11}{6}$	$\frac{1}{2}$	
P	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	
EP	$\frac{3}{2}$	0	$\frac{3}{2}$	$\frac{1}{2}$	

Other angles are:
$\gamma_1 = 0 \quad \gamma_2 = 0 \quad \theta = \frac{1}{2}\pi \quad \phi = 0$

coordinates r, θ, ϕ where r is the distance between the centers of mass of the fragments:

$$\begin{aligned} X_2 - X_1 &= r \sin\theta \cos\phi, \\ Y_2 - Y_1 &= r \sin\theta \sin\phi, \\ Z_2 - Z_1 &= r \cos\theta. \end{aligned} \tag{4}$$

Table 2. Interaction potential for the methyl radicals estimated by the *ab initio* method [5], $\mathscr{V}$, and for the structures listed in Table 1

Struct.	$\mathscr{V}$ *ab initio*	V fitted first set	V fitted second set	V analytical form eq. (42)
2.5F[a]	28.921	28.927	29.675	
2.5S	– 19.168	– 19.126	– 15.684	
3EP	12.375	11.986	8.871	
3K	– 2.691	– 2.930	– 3.047	
3J	– 5.041	– 5.145	– 5.333	
3I	– 5.289	– 5.373	– 5.455	
3G	47.468	47.467	49.821	
3F	4.410	4.333	4.008	
3E	11.185	11.595	8.439	
3A	– 7.557	– 7.557	– 7.691	
3S	– 7.624	– 7.571	– 7.706	
3.5S	– 2.553	– 2.320	– 2.494	– 2.506
4P	– 0.304	– 0.283	– 0.292	– 0.288
4I	– 0.652	– 0.598	– 0.650	– 0.645
4F	– 0.380	– 0.265	– 0.271	– 0.307
4E	– 0.390	0.012	– 0.049	– 0.307
4D	– 0.249	– 0.168	– 0.236	– 0.288
4A	– 0.810	– 0.699	– 0.767	– 0.764
4S	– 0.813	– 0.699	– 0.767	– 0.764
20S	0.000	0.000	0.000	0.000

[a] A number preceding the name of the structure gives the distance in Å; energy is given in kcal/mol

Also dimensionless variables are introduced:

$$\mathscr{x}_{ij} = \frac{x'_j - x'_i}{r}, \qquad \mathscr{y}_{ij} = \frac{y'_j - y'_i}{r}, \qquad \mathscr{z}_{ij} = \frac{z'_j - z'_i}{r}. \tag{5}$$

The $x'_{(1)}, y'_{(1)}, z'_{(1)}$ coordinates are related to $x''_{(1)}, y''_{(1)}, z''_{(1)}$ coordinates interlinked rigidly with the radicals by the orthogonal transformation

$$\begin{bmatrix} x'_{(1)} \\ y'_{(1)} \\ z'_{(1)} \end{bmatrix} = S_1 \begin{bmatrix} x''_{(1)} \\ y''_{(1)} \\ z''_{(1)} \end{bmatrix}, \tag{6}$$

where

$$S_1 = \begin{bmatrix} \cos\alpha_1 \cos\beta_1 \cos\gamma_1 - \sin\alpha_1 \sin\gamma_1 & -\cos\alpha_1 \cos\beta_1 \sin\gamma_1 - \sin\alpha_1 \cos\gamma_1 & \cos\alpha_1 \sin\beta_1 \\ \sin\alpha_1 \cos\beta_1 \cos\gamma_1 + \cos\alpha_1 \sin\gamma_1 & -\sin\alpha_1 \cos\beta_1 \sin\gamma_1 + \cos\alpha_1 \cos\gamma_1 & \sin\alpha_1 \sin\beta_1 \\ -\sin\beta_1 \cos\gamma_1 & \sin\beta_1 \sin\gamma_1 & \cos\beta_1 \end{bmatrix}. \tag{7}$$

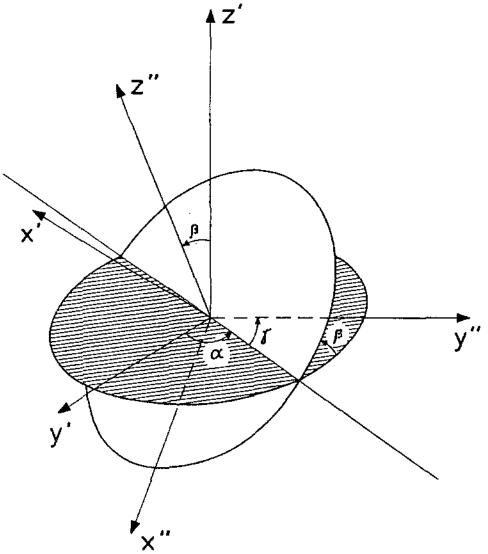


Fig. 1. Euler diagram depicting the location of radicals in the primed system x', y', z'

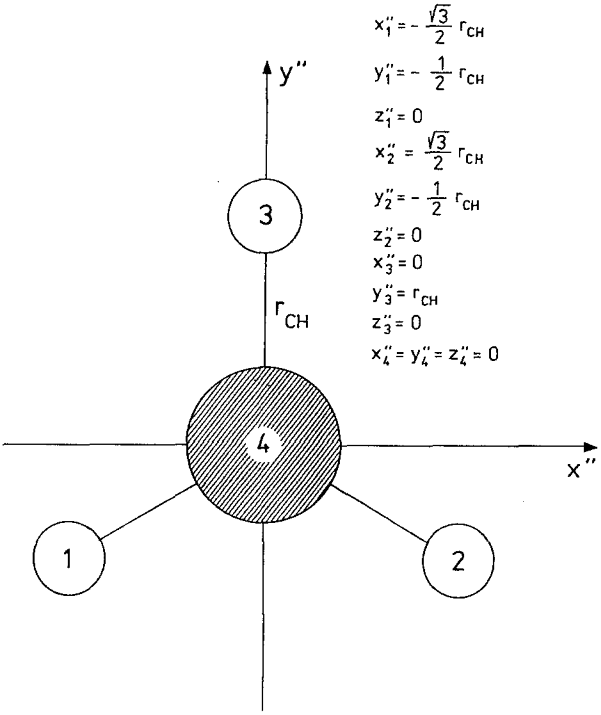


Fig. 2. Location of methyl radicals in the doubly primed system x'', y'', z'' ($r_{CH} = 1.079$ Å)

The Euler angles, α, β and γ, are shown in Fig. 1. The location and coordinates of radicals in the doubly primed system x'', y'', z'' are shown in Fig. 2.

Analogous relations can be written for the second fragment, i.e. $x'_{(2)}, y'_{(2)}, z'_{(2)}$; $x''_{(2)}, y''_{(2)}, z''_{(2)}$; $\alpha_2, \beta_2, \gamma_2$, and S_2.

Taking all these relations into account, the distance r_{ij} can ultimately be transformed into

$$r_{ij} = r\sqrt{(x_{ij} + \sin\theta\cos\phi)^2 + (y_{ij} + \sin\theta\sin\phi)^2 + (z_{ij} + \cos\theta)^2}. \tag{8}$$

3 Bonding interaction V_B

It can be assumed that the carbon atom in the planar methyl radical is in a state of sp^2 hybridization. Thus the orbital p_z occupied by only one electron is located in the plane perpendicular to the plane of the radical. The partially occupied orbitals overlap and the interaction potential V_B is, according to Mulliken [8], proportional to the square of the overlap integral. The overlap integral can be written in the form [9]

$$s = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} p_{z(1)}(x, y, z)p_{z(2)}(x, y, z)\,\mathrm{d}\tau, \tag{9}$$

where $p_{z(1)}$ and $p_{z(2)}$ refer to the first and second fragments, respectively, while $\mathrm{d}\tau = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ is the element of volume of some arbitrarily fixed reference system.

For the system x'', y'', z'' the orbitals p_z are given by [9]

$$p_{z(1)} = Nz''_{(1)}\exp\left(-\frac{Zr''_{(1)}}{2a_0}\right), \tag{10}$$

$$r''_{(1)} = \sqrt{x''^2_{(1)} + y''^2_{(1)} + z''^2_{(1)}}, \tag{11}$$

$$p_{z(2)} = Nz''_{(2)}\exp\left(-\frac{Zr''_{(2)}}{2a_0}\right), \tag{12}$$

$$r''_{(2)} = \sqrt{x''^2_{(2)} + y''^2_{(2)} + z''^2_{(2)}}, \tag{13}$$

where N is the normalization constant, Z is the nucleus charge and a_0 is the radius of the Bohr orbit [9].

Using transformation reciprocal to Eq. (7) the orbitals $p_{z(1)}$ and $p_{z(2)}$ become

$$p_{z(1)} = N[x'_{(1)}\cos\alpha_1\sin\beta_1 + y'_{(1)}\sin\alpha_1\sin\beta_1 + z'_{(1)}\cos\beta_1]\exp\left(-\frac{Zr'_{(1)}}{2a_0}\right), \tag{14}$$

$$p_{z(2)} = N[x'_{(2)}\cos\alpha_2\sin\beta_2 + y'_{(2)}\sin\alpha_2\sin\beta_2 + z'_{(2)}\cos\beta_2]\exp\left(-\frac{Zr'_{(2)}}{2a_0}\right). \tag{15}$$

Using the substitution $x'_{(1)} = x_M - X_1 + X$; $x'_{(2)} = x_M - X_2 + X$ etc., the system of the center of mass for both the fragments is introduced.

If $M_1 = M_2$ we obtain

$$\begin{aligned} x'_{(1)} &= x_M + \tfrac{1}{2}r\sin\theta\cos\phi, \\ y'_{(1)} &= y_M + \tfrac{1}{2}r\sin\theta\sin\phi, \\ z'_{(1)} &= z_M + \tfrac{1}{2}r\cos\theta \end{aligned} \tag{16}$$

and

$$x'_{(2)} = x_M - \tfrac{1}{2}r \sin\theta \cos\phi,$$
$$y'_{(2)} = y_M - \tfrac{1}{2}r \sin\theta \sin\phi,$$
$$z'_{(2)} = z_M - \tfrac{1}{2}r \cos\theta. \tag{17}$$

Substitution from Eqs. (16) and (17) into (14) and (15) followed by rotation of the system X_M, Y_M, Z_M through the angles θ and ϕ leads to

$$\begin{bmatrix} x_M \\ y_M \\ z_M \end{bmatrix} = \begin{bmatrix} \cos\theta\cos\phi & -\sin\phi & \sin\theta\cos\phi \\ \cos\theta\sin\phi & \cos\phi & \sin\theta\sin\phi \\ -\sin\theta & 0 & \cos\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}. \tag{18}$$

Finally we obtain

$$p_{z(1)} = \{x[\cos\theta \sin\beta_1 \cos(\phi - \alpha_1) - \sin\theta\cos\beta_1] - y\sin\beta_1 \sin(\phi - \alpha_1) + (z + \tfrac{1}{2}r)[\cos\theta\cos\beta_1 + \sin\theta\sin\beta_1\cos(\phi - \alpha_1)]\} \exp\left(-\frac{Zr_{(1)}}{2a_0}\right), \tag{19}$$

$$p_{z(2)} = \{x[\cos\theta \sin\beta_2 \cos(\phi - \alpha_2) - \sin\theta\cos\beta_2] - y\sin\beta_2 \sin(\phi - \alpha_2) + (z - \tfrac{1}{2}r)[\cos\theta\cos\beta_2 + \sin\theta\sin\beta_2\cos(\phi - \alpha_2)]\} \exp\left(-\frac{Zr_{(2)}}{2a_0}\right), \tag{20}$$

where

$$r_{(1)} = \sqrt{x^2 + y^2 + (z + \tfrac{1}{2}r)^2}, \tag{21}$$
$$r_{(2)} = \sqrt{x^2 + y^2 + (z - \tfrac{1}{2}r)^2}. \tag{22}$$

The functions $p_{z(1)}$ and $p_{z(2)}$ are now substituted into Eq. (9). With the use of elliptical coordinates the integral in Eq. (9) acquires an elementary form which can be computed. We obtain

$$s = N^2 \exp\left(-\frac{Zr}{2a_0}\right) [f_1(r)\cos\theta_{12} - f_2(r)\cos\theta_1\cos\theta_2], \tag{23}$$

where

$$\cos\theta_1 = \cos\beta_1\cos\theta + \sin\beta_1\sin\theta\cos(\phi - \alpha_1), \tag{24}$$
$$\cos\theta_2 = \cos\beta_2\cos\theta + \sin\beta_2\sin\theta\cos(\phi - \alpha_2), \tag{25}$$
$$\cos\theta_{12} = \cos\beta_1\cos\beta_2 + \sin\beta_1\sin\beta_2\cos(\alpha_1 - \alpha_2) \tag{26}$$

and

$$f_1(r) = 1 + \tfrac{1}{15}a[15 + a(6 + a)], \tag{27}$$
$$f_2(r) = a^2\tfrac{1}{5}[1 + a(1 + \tfrac{1}{3}a)], \tag{28}$$
$$a = \frac{Zr}{2a_0}. \tag{29}$$

As the energy V_B is proportional to the square of the overlap integral we can write

$$V_B = -A \exp\left(-\frac{Zr}{a_0}\right)[f_1(r)\cos\theta_{12} - f_2(r)\cos\theta_1\cos\theta_2]^2, \tag{30}$$

where A is the constant expressed in terms of energy.

Our result differs somewhat from that obtained earlier by Darvesh et al. [5]. The common feature is the exponential decrease in V_B with increasing r. The angle dependencies are not the same, however. Darvesh et al. single out the σ-overlap (structures S, A, I, J, K) and the π-overlap (structures E, F, G); some of their structures, such as D, P and EP, do not exhibit any overlap at all. In our approach the separation of overlaps into the σ and π type is less emphasized. It is likely that this reflects better the real course of events.

While the number of adjustable parameters in Ref. [5] amounts to 4, it is restricted to 2 in our approach: the constant A and the charge on the nucleus Z. Both have precise physical meaning, as Z results from the screening of the carbon nucleus by electrons.

4 Nonbonding interaction V_{NB}

Attractive and repulsive components are singled out in the nonbonding potential [7, 10]. The attractive part arises from dispersive interactions and at longer distances is best approximated by a term proportional to r_{ij}^{-6}. Such a proportionality is well established both by experiment and theory [9]. The repulsive part of the potential presents more problems. Wardlaw and Marcus [7] opted for the Lennard-Jones 6–12 potential whilst Darvesh et al. [5] used a modified form of the Morse potential. The Lennard-Jones potential is known to be a rather coarse approximation. Introduction of the Morse potential involves additional adjustable parameters. Since quantum mechanics indicates that the exponential character of the repulsive part predominates [11, 12], we chose a Buckingham exp-6 potential [10].

$$V_{ij}(r_{ij}) = a_{ij}\exp(-n_{ij}r_{ij}) - \frac{b_{ij}}{r_{ij}^6}. \tag{31}$$

The parameters a_{ij} and b_{ij}, hence a_{HH}, a_{CH}, a_{CC} and b_{HH}, b_{CH}, b_{CC}, are expressed by the depth of the potential well ε_{ij}, i.e. $\varepsilon_{HH}, \varepsilon_{CH}, \varepsilon_{CC}$, and by the radii r_{0ij} ($r_{0HH}, r_{0CH}, r_{0CC}$) which determine the location of a minimum on the curve $V_{ij}(r_{ij})$. These functions can be found taking into account the criteria for the occurence of a minimum [10]. The parameters n_{ij} are treated in this procedure as fixed.

Thus V_{NB} is assumed to arise from the separate contributions of interactions between individual atoms. Such an assumption was also adopted in Refs. [5, 7].

5 Fitting of parameters

The parameters n_{HH}, n_{CC} and n_{CH} are selected to be varied in V_{NB}. Thus, altogether five adjustable parameters are necessary; others are fixed and taken from the literature, mostly from Ref. [7]. All the quantities used are assembled in Table 3.

Table 3. Parameters of the potential energy surface

Parameter	Magnitude	Literature
Fixed parameters		
$r_{0\mathrm{HH}}$ [Å]	3.37	[7]
$r_{0\mathrm{CC}}$ [Å]	3.88	[7]
$r_{0\mathrm{CH}}$ [Å]	$\frac{1}{2}(r_{0\mathrm{HH}} + r_{0\mathrm{CC}})$	[7, 10]
$\varepsilon_{\mathrm{HH}}$ [kcal/mol]	0.01	[7]
$\varepsilon_{\mathrm{CC}}$ [kcal/mol]	0.095	[7]
$\varepsilon_{\mathrm{CH}}$ [kcal/mol]	$\sqrt{\varepsilon_{\mathrm{HH}}\varepsilon_{\mathrm{CC}}}$	[7, 10]
Adjusted parameters		
	Set First	Second
n_{HH} [Å^{-1}]	3.7557 ∓ 0.001	3.7895 ∓ 0.029
n_{CC} [Å^{-1}]	3.2575 ∓ 0.034	3.8112 ∓ 0.377
n_{CH} [Å^{-1}]	2.9395 ∓ 0.018	2.3254 ∓ 0.252
Z	2.7525 ∓ 0.012	2.7212 ∓ 0.017
A [kcal/mol]	578.99 ∓ 17.54	564.25 ∓ 67.59

The procedure of fitting these parameters to the *ab initio* results is based on the mean quadratic approximation extended on nonlinear systems [13]. The results of fitting are shown in Table 3. Two variants are examined. The whole set of 19 *ab initio* points is used in the first and second variant of approximation.

The first one uses a criterion of minimization of the sums of the squared deviations between the value computed accurately [5], $\mathscr{V}_k$, and the value fitted, V_k, where the subscript k ($k = 1, 2, \ldots, 19$) stands for the number of a given structure.

$$S = \sum_k [\mathscr{V}_k - V_k]^2. \tag{32}$$

The agreement with the individual *ab initio* structures is very good at short distances 2.5–3.5 Å (see Table 2). The magnitude of the potential is large at such short distances, however. With r surpassing 3.5 Å, the potential decreases on the average by an order of magnitude. Consequently, the agreement deteriorates to become less satisfactory for some structures.

Especially, the 4E structure exhibits the worst performance. Enhancement in the number of fitting parameters as well as the use of the modified form of the 6-exp potential [14] offers no remedy. Also complete deletion of the 4E geometry does not lead to any significant improvement. The reasons for such a discrepancy are not clear. As can be seen in Table 2, at a distance of 3 Å the E geometry is definitely less energetically favorable than the F geometry. However, a small change in the distance, by only 1 Å, leads to a complete reversal of the situation; the 4E structure becomes more favourable than the 4F one. Such a dramatic change is unlikely to occur at such short a distance. Moreover, our potential approximates to all of the other geometries quite satisfactorily. Apparently, there is some error in the calculations of the 4E structure even though it cannot be inferred explicitly on the basis of our results.

Generally, provided that the disagreement with the 4E structure is ignored, the results of approximation are satisfactory; the mean standard deviation is

0.168 kcal/mol.For instance, the difference between the structures 3E and 3EP is shown clearly; while the parts V_{NB} are almost equal, the parts V_B definitely are not. The structure 3E exhibits pure overlap of the π type; no overlap at all can be detected in the structure 3EP. As the overlap of partially occupied orbitals exerts a stabilizing influence, the energy for 3E is smaller by more than 1 kcal/mol than that for 3EP on the basis of *ab initio* results. The fitting procedure reproduces this trend. Most satisfactory agreement occurs also for both energetically unfavorable 3G and 2.5F structures and favorable 2.5S, 3S, 3A structures and for many others.

Comparison with former works [5, 7, 12] does not reveal marked discrepancies, even though the forms of approximation functions were different. Darvesh et al. [5] estimated $n_{HH} = 3.44$ Å^{-1} which is not very different from our estimate 3.75 Å^{-1}. The best agreement with SCF atomic orbitals for the carbon atom is achieved at $Z = 3.136$ [11]. Our value, $Z = 2.752$, is substantially smaller; however, the carbon atom considered in this work is linked with three hydrogen atoms which increases the screening effect and decreases Z.

To obtain good approximation at longer distances, $r > 3.5$ Å, the relative square of deviations was applied as the fitting criterion in the second variant. Such a procedure yields reliable results for large interradical separations [1]

$$S = \sum_k \left[\frac{\mathcal{V}_k - V_k}{\mathcal{V}_k} \right]^2 . \tag{33}$$

Obviously, the agreement at shorter distances, $r < 3.5$ Å, suffers under the use of such a criterion. At longer distances the agreement becomes excellent, which is noteworthy, as long distances are of special significance. We elaborate on this in Sect. 6. All in all, the parameters fitted in variant II do not differ much from those fitted in variant I; the worst agreement is for n_{CH} and n_{CC}.

6 Potential at long distances

As formerly discussed, the V_{NB} potential fails to be correct at both longer and shorter distances. This failure involves especially the attractive term proportional to r_{ij}^{-6}. It is known that this relation holds very well at long distances [9] when the mutual overlap of wave functions of the interacting bodies can be ignored on the basis of the so-called polarization approximation. No wonder that our approximation works better, the longer the distance between the radicals; the best results are those obtained by using criterion 33 in the second variant shown in Table 3.

There is another reason to be concerned with longer distances. Such distances are of special significance in the description of the initial stage of radical recombination; perturbation calculus can be used under such circumstances [3]. Our potential is to be used to compute the matrix elements of the type 1 with functions ψ_n that refer to the rotational states and are indispensable in the above-mentioned calculations. The V_B potential resulting exclusively from the overlap of unoccupied orbitals is amenable to such a treatment. The V_{NB} part, however, depends on the internal structure of reactants, for instance, on the bond lengths between the individual atoms. With a shortening of the distance, rotational motion becomes more and more hindered and finally full rotations stop altogether.

It can therefore be assumed that the centers of mass of reacting radicals are separated by a distance that is long compared with the radical dimensions. The variables defined in Eq. (5) have to satisfy the relations

$$
\begin{aligned}
|x_{ij}| &< 1,\\
|y_{ij}| &< 1,\\
|z_{ij}| &< 1.
\end{aligned}
\tag{34}
$$

Under such an assumption, the V_{NB} potential can be expanded into a series around a point $p \equiv (x_{ij} = 0,\ y_{ij} = 0,\ z_{ij} = 0)$:

$$
\begin{aligned}
V_{ij}(r_{ij}) \approx V_{ij}(r) &+ \frac{1}{1!}\left[\frac{\partial V_{ij}}{\partial x_{ij}}\right]_p x_{ij} + \frac{1}{1!}\left[\frac{\partial V_{ij}}{\partial y_{ij}}\right]_p y_{ij} + \frac{1}{1!}\left[\frac{\partial V_{ij}}{\partial z_{ij}}\right]_p z_{ij}\\
&+ \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial x_{ij}^2}\right]_p x_{ij}^2 + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial x_{ij} y_{ij}}\right]_p x_{ij} y_{ij} + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial x_{ij} z_{ij}}\right]_p x_{ij} z_{ij}\\
&+ \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial y_{ij} x_{ij}}\right]_p y_{ij} x_{ij} + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial y_{ij}^2}\right]_p y_{ij}^2 + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial y_{ij} z_{ij}}\right]_p y_{ij} z_{ij}\\
&+ \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial z_{ij} x_{ij}}\right]_p z_{ij} x_{ij} + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial z_{ij} y_{ij}}\right]_p z_{ij} y_{ij} + \frac{1}{2!}\left[\frac{\partial^2 V_{ij}}{\partial z_{ij}^2}\right]_p z_{ij}^2\\
&+ \cdots
\end{aligned}
\tag{35}
$$

Based on this expansion the V_{NB} can, after some transformations, be reduced to the form

$$
\begin{aligned}
V_{\text{NB}} = \sum_{ij} V_{ij}(r)&\\
&+ \sum_{ij} r \frac{\partial V_{ij}(r)}{\partial r}\left[x_{ij} \sin\theta \cos\phi + y_{ij} \sin\theta \sin\phi + z_{ij} \cos\theta\right]\\
&+ \sum_{ij} \tfrac{1}{2} r^2 \left[\frac{\partial^2 V_{ij}(r)}{\partial r^2} - \frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}\right]\\
&\times \left[x_{ij} \sin\theta \cos\phi + y_{ij} \sin\theta \sin\phi + z_{ij} \cos\theta\right]^2\\
&+ \sum_{ij} \tfrac{1}{2} r \frac{\partial V_{ij}(r)}{\partial r}\left[x_{ij}^2 + y_{ij}^2 + z_{ij}^2\right].
\end{aligned}
\tag{36}
$$

Next, the primed system x', y', z' is replaced by the doubly primed system x'', y'', z'' using transformation (7). As the radicals are symmetrical tops, there are many symmetry elements and the form of the potential can be simplified considerably. For instance, all the sums of the $\sum x_i''$, $\sum y_i''$, $\sum x_i'' y_i''$ type, and similar others vanish; only those sums that feature doubly primed coordinates squared and $\sum z_i''$, $\sum z_j''$ and $\sum z_i'' z_j''$ remain different from zero. Also the relationship $\sum x_i''^2 = \sum y_i''^2$

is obeyed. All this taken into account leads, after onerous but not difficult transformations, to the form

$$\begin{aligned}
V_{\mathrm{NB}} = {} & \sum_{ij} V_{ij}(r) \\
& - \left[\cos\theta_1 \sum_{ij} \frac{\partial V_{ij}(r)}{\partial r} z_i'' - \cos\theta_2 \sum_{ij} \frac{\partial V_{ij}(r)}{\partial r} z_j''\right] \\
& - \sum_{ij} \tfrac{1}{4}\left[\frac{\partial^2 V_{ij}(r)}{\partial r^2} - \frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}\right] \\
& \times [(x_i''^2 + y_i''^2 - 2z_i''^2)\cos^2\theta_1 + (x_j''^2 + y_j''^2 - 2z_j''^2) \\
& \times \cos^2\theta_2 + 4z_i'' z_j'' \cos\theta_1 \cos\theta_2 - (x_i''^2 + y_i''^2 + x_j''^2 + y_j''^2)] \\
& + \sum_{ij} \tfrac{1}{2}\frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}[x_i''^2 + y_i''^2 + z_i''^2 + x_j''^2 + y_j''^2 + z_j''^2 - 2z_i'' z_j'' \cos\theta_{12}].
\end{aligned} \tag{37}$$

The meaning of the symbols $\cos\theta_1, \cos\theta_2, \cos\theta_{12}$ is the same as in Eqs. (24)–(26). The values for the doubly primed coordinates x_i'', y_i'' and so forth are shown in Fig. 2.

The first term in Eq. (37) corresponds to the zero term of expansion, the second term is the first term of expansion while the third and fourth terms correspond to the second term of expansion for V_{NB} around the point $p \equiv (\mathscr{x}_{ij} = 0,\ \mathscr{y}_{ij} = 0,\ \mathscr{z}_{ij} = 0)$.

Equation (37) holds for all the molecules of symmetrical top type. For the planar methyl radicals the coordinates z_i'' and z_j'' are zero which leads to further simplifications. Only the zero and second terms are different from zero. Were the umbrella structure of CH_3 taken into account, the first term would not have vanished as well. But even under such circumstances the second term need be accounted for, as the restriction to the first approximation is too inaccurate.

Ultimately, V_{NB} at larger distances becomes

$$V_{\mathrm{NB}} = \varepsilon_0 - \varepsilon_1 \cos^2\theta_1 - \varepsilon_2 \cos^2\theta_2, \tag{38}$$

where

$$\varepsilon_0 = \sum_{ij} V_{ij}(r) + \sum_{ij} \frac{1}{4}\left[\frac{\partial^2 V_{ij}(r)}{\partial r^2} + \frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}\right](x_i''^2 + y_i''^2 + x_j''^2 + y_j''^2), \tag{39}$$

$$\varepsilon_1 = \sum_{ij} \frac{1}{4}\left[\frac{\partial^2 V_{ij}(r)}{\partial r^2} - \frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}\right](x_i''^2 + y_i''^2), \tag{40}$$

$$\varepsilon_2 = \sum_{ij} \frac{1}{4}\left[\frac{\partial^2 V_{ij}(r)}{\partial r^2} - \frac{1}{r}\frac{\partial V_{ij}(r)}{\partial r}\right](x_j''^2 + y_j''^2). \tag{41}$$

As both the reacting radicals are identical, further symmetries occur as, for instance, $\varepsilon_1 = \varepsilon_2$. In order not to lose generality these simplifications are not introduced.

The derived form of V_{NB} can be used starting from a distance of about 3.5 Å. At so short a distance it fails, however, for some very energetically unfavorable orientations, such as *G*, *F*, *EP*. Starting from about 4.5 Å, Eq. (38) works very well for all orientation angles.

7 Conclusions

The interaction energy of the radicals at the distance $r > 3.5$ Å is obtained ultimately in the form

$$V = \varepsilon_0 - \varepsilon_1 \cos^2 \theta_1 - \varepsilon_2 \cos^2 \theta_2 - A \exp\left(-\frac{Zr}{a_0}\right) [f_1(r) \cos \theta_{12} - f_2(r) \cos \theta_1 \cos \theta_2]^2, \quad (42)$$

which is very convenient for computation of the matrix elements (Eq. (1)) for the rotational states as discussed in paper [3]. By no means do we claim by this statement that the problem of the V potential and its components is definitely solved. There is room for improvement especially if more *ab initio* calculations of the radical interactions at longer distance, $r \geq 3.5$ Å, become available.

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