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Extensions of the Marcus equation for the prediction of approximate transition state geometries in hydrogen transfer and methyl transfer reactions

Paul Blowers*, Richard I. Masel

University of Illinois, 600 S. Mathews, Urbana, IL 61821, USA

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Abstract. The objective of this work is to propose a way to calculate approximate transition state geometries that can then be used as initial guesses in ab initio calculations.

Transition state geometries are calculated for 26 hydrogen transfer reactions and 6 methyl transfer reactions at the MP2/6-31G* and MP2/6-311++G(d,p) levels. Selected cases are also done at other levels including CCSD(T)/6-311++G(d,p). The transition state geometry obeys an equation which arises from an extension of the Marcus equation proposed by Blowers and Masel [8]:

$$\frac{r_B^t + r_F^t}{r_{B,\mathrm{equ}} + r_{F,\mathrm{equ}}} = 1.25 \pm 0.04 \qquad aa$$

In this equation, $r_{B,\mathrm{equ}}$ is the equilibrium bond length for the bond that breaks during the reaction, $r_{F,\mathrm{equ}}$ is the equilibrium bond length for the new bond which forms. r_B^t and r_F^t are the bond lengths at the saddle point in the potential energy surface. r_B^t and r_F^t are found to obey

$$\frac{r_B^t - r_{B,\mathrm{equ}}}{\left(r_B^t + r_F^t - r_{B,\mathrm{equ}} - r_{F,\mathrm{equ}}\right)} = \left(\frac{r_{B,\mathrm{equ}}}{r_{B,\mathrm{equ}} + r_{F,\mathrm{equ}}} + (C_A)^{0.5}\frac{\Delta U_r}{8E_A^0}\right)$$

$$\frac{r_F^t - r_{F,\mathrm{equ}}}{\left(r_B^t + r_F^t - r_{B,\mathrm{equ}} - r_{F,\mathrm{equ}}\right)} = \left(\frac{r_{F,\mathrm{equ}}}{r_{B,\mathrm{equ}} + r_{F,\mathrm{equ}}} - (C_A)^{0.5}\frac{\Delta U_r}{8E_A^0}\right)$$

with an average error of 0.04 Å. In the last two equations above, ΔU is the heat of reaction, E_A^0 is the intrinsic barrier, and C_A is a constant that comes from the model of Blowers and Masel [8].

It is proposed that the above three equations are useful in generating initial guesses for transition state geometries in ab initio calculations. In the cases that were tried, rapid convergence was found when these guesses were used.

Key words: Transition state – ab initio

Introduction

Over the last several years, ab initio methods have become the standard way to estimate transition state properties. Generally one performs the calculation by providing a guess for the transition state geometry and then using one of several techniques to optimize the transition state geometry and energy [1–7].

The speed of the calculation is largely determined by the quality of your first geometry guess. If you take a good guess, the algorithms converge quickly. If a poor guess of the structure is made, the algorithms sometimes never converge to the correct transition state.

Clearly, if one had a good way to calculate approximate transition state geometries, one could improve the speed of ab initio calculation of transition state geometries.

In actual practice, one does not have to do high quality calculations to get good starting geometries for further calculations. For example, in recent papers [8–16] we have used Gaussian [28] to calculate the properties of the transition state for a series of hydrogen and methyl transfer reactions. It was often difficult to get Gaussian to converge to the transition state geometry. Generally, we found that once we have an MP2/6-31G* transition state geometry, it is straightforward to improve the geometry using higher order calculations. However, getting to that first transition state is troublesome. Synchronous transit quasi-Newtonian methods often would not converge. In many cases we were forced simply to guess geometries and hope that the algorithms converged.

If one could calculate approximate transition state geometries, one could find transition states more easily.

Correspondence to: R. I. Masel
(e-mail: r-masel@uiuc.edu)
**Present address*: Department of Chemical and Environmental Engineering, University of Arizona, 105B Harshbarger, Tuscon, AZ 85721, USA

At present, there is very little information in the literature about how to choose starting guesses for transition state geometries. Recently, Anglada et al. [18] and Ruedenberg and Sun [19] examined the Bell-Evans-Polanyi principle as a way of getting a first guess for a transition state geometry. The technique works, but one needs several preliminary calculations to apply the ideas. There is also some older work of Benson [17] that one could use to get a good first guess for transition state geometries, although it has never been proposed for that purpose. Generally, there are no readily applicable techniques, which makes ab initio calculations of transition state properties much harder than they need to be.

The objective of the work here is to develop some methods to calculate approximate transition state geometries that can be used in further calculations. We are looking for a geometry approximation that is easily calculated using readily available information: equilibrium bond energies, equilibrium bond lengths, and heats of reaction. This work concentrates on predicting MP2/6-31G* geometries for hydrogen transfer and methyl transfer reactions. While MP2/6-31G* geometries are not accurate enough to be used without further optimization at higher levels, they are reasonable starting points for higher level calculations.

In practice, we will actually concentrate on predicting r_B^t, the length of the bond which breaks, and r_F^t, the length of the bond which forms at the transition state geometry. For example, consider the reaction

$$\mathrm{H} + \mathrm{CH_3CH_3} \rightarrow \mathrm{H_2} + \mathrm{CH_2CH_3} \tag{1}$$

In this reaction we will try to predict r_B^t, the length of the C—H bond that breaks, and r_F^t the length of the new H—H bond that forms at the transition state geometry. In our previous work with hydrogen transfer reactions, we have found that the H—H and C—H bonds are usually extended at the transition state, but the rest of bonds in the molecule hardly change during the reaction. The bond lengths are constant to 0.01 Å. The bond angles are always approximately half way between those of the reactants and products. The bonds that break and form are also nearly collinear at the transition state. Generally, r_B^t and r_F^t are the hardest variables to guess so they are the variables we will consider here.

Our approach will be to start with a result from a previous paper, fit the results to ab initio data, and then do a check to see if the result provides useful starting guesses for other ab initio calculations.

Review of our previous results

In a previous paper [8] we considered an extension of the Marcus equation [24] for atom transfer reactions. It was assumed that the potential energy surface for a reaction averaged over all of the coordinates except r_B and r_F can be written as

$$\begin{aligned} V(r_B r_F) = {} & w_B(\exp[1 - \alpha_1(r_B - r_{B,\mathrm{equ}})] - 1)^2 \\ & + w_F(\exp[-\alpha_2(r_F - r_{F,\mathrm{equ}})] - 1)^2 - w_B \\ & + V_o \exp(-\alpha_3 r_F - \alpha_4 r_B) \end{aligned} \tag{2}$$

where $V(r_B,r_F)$ is the potential, $\mathrm{r_B}$ and $\mathrm{r_F}$ are the lengths of the forming and breaking bonds, $r_{B,\mathrm{equ}}$ and $r_{F,\mathrm{equ}}$ are the equilibrium bond lengths, w_B and w_F are the strengths of the bonds, V_o is the strength of the Pauli repulsions between the reactants, and α_1, α_2, α_3, and α_4 are force constants. One can derive an analytical expression for the geometry of the saddle point in the potential energy expression in Eq. (2) by differentiating the equation with respect to r_B and r_F and setting the derivatives equal to zero. The resulting expression for r_B^t and r_B^t appears in the supplemental material for [8].

Extensions of the model to predict transition state geometries

The difficulty with the expressions in [8] is that one will need to know all of the parameters in Eq. (7) in order to use the expressions to predict transition state geometries. Generally, one will not know that information. Here we will try another approach. We will first derive an expression for the transition state position, with adjustable parameters that we can fit to ab initio calculations. We will fit these parameters so we will have an expression that we can use to generate guesses for transition state geometries.

In order to get a simple expression, it is useful to assume that the force constants for the forming and breaking bonds follow Badger's rule:

$$\alpha_1 = \frac{C_b}{r_{B,\mathrm{equ}}} \tag{3}$$

$$\alpha_2 = \frac{C_b}{r_{F,\mathrm{equ}}} \tag{4}$$

where C_b is a constant which depends on the row in the periodic table of the atoms in the bond. One can then show that to a reasonable approximation:

$$\frac{r_B^{\ddagger} + r_F^{\ddagger}}{r_{B,\mathrm{equ}} + r_{F,\mathrm{equ}}} = C_{BM} \tag{5}$$

In Eq. (5), r_B^t and r_F^t are the lengths of the breaking and forming bonds at the transition state geometry, $r_{B,\mathrm{equ}}$ and $r_{F,\mathrm{equ}}$ are the equilibrium bond lengths and C_{BM} is a constant given by

$$C_{BM} = 1 + \frac{1}{C_b} \ln\left(\frac{2}{1 - C_A\left(\frac{E_A^0}{w_O}\right)}\right) \tag{6}$$

In Eq. (6), E_A^0 is the intrinsic barrier for the reaction, C_b is Badger's constant, and w_O and C_A are constants related to the parameters in the potential energy surface (Eq. 4) by

$$w_O = \frac{W_F + W_B}{2} \tag{7a}$$

$$C_A = \frac{\alpha_3\alpha_4}{\alpha_1\alpha_2} \tag{7b}$$

According to the data in [25], C_b is about 2.7 for C—H and H—H bonds and 3.6 for methyl transfer reactions. Blowers and Masel [12] found that in MP2/6-31G(d), C_A is about 0.5 for hydrogen transfer reactions and 1.0 for methyl transfer reactions. For the hydrogen transfer reactions we will consider later in this paper, E_A^0 is about 10 ± 5 kcal/mol [13] while the bond energies are on the order of 100 kcal/mol. The methyl transfer reactions have bond energies of about 95 kcal/mol and intrinsic barriers of 40 kcal/mol [14]. Plugging into Eq. (6) yields

$$C_{BM} = \left\{ \begin{array}{l} 1.27 \text{ for hydrogentransfer reactions} \\ 1.25 \text{ for methyl transfer reactions} \end{array} \right\} \tag{8}$$

The implication of Eq. (8) is that in MP2/6-31G(d) calculations C_{BM} is almost the same for a variety of reactions. Therefore, one might be able to use Eq. (5) to calculate $r_B^t + r_F^t$.

Once one knows $r_B^t + r_F^t$ one can use previous results to calculate r_B^t and r_F^t. Shaik et al. [21, 26] and Pross [27] note that the Marcus equation/curve crossing model can be used to relate the position of the transition state:

$$\frac{r_B^t - r_{B,\text{equ}}}{\left(r_B^t + r_F^t - r_{B,\text{equ}} - r_{F,\text{equ}}\right)} = \left(0.5 + \frac{\Delta U_r}{8E_A^0}\right) \tag{9}$$

$$\frac{r_F^t - r_{F,\text{equ}}}{\left(r_B^t + r_F^t - r_{B,\text{equ}} - r_{F,\text{equ}}\right)} = \left(0.5 - \frac{\Delta U_r}{8E_A^0}\right) \tag{10}$$

In Eqs. (9) and (10), ΔU, is the heat of reaction. Blowers and Masel's model [8] predicts different values according to whether the potential is in the normal or Marcus inverted regime. The result is

$$\frac{r_B^t - r_{B,\text{equ}}}{\left(r_B^t + r_F^t - r_{B,\text{equ}} - r_{F,\text{equ}}\right)} = \left(\frac{r_{B,\text{equ}}}{r_{B,\text{equ}} + r_{F,\text{equ}}} + (C_A)^{0.5}\frac{\Delta U_r}{8E_A^0}\right) \text{ or 0 whichever is larger} \tag{11}$$

$$\frac{r_F^t - r_{F,\text{equ}}}{\left(r_B^t + r_F^t - r_{B,\text{equ}} - r_{F,\text{equ}}\right)} = \left(\frac{r_{F,\text{equ}}}{r_{B,\text{equ}} + r_{F,\text{equ}}} - (C_A)^{0.5}\frac{\Delta U_r}{8E_A^0}\right) \text{ or 0 whichever is larger} \tag{12}$$

Equations (8)–(12) provide expressions for the transition state geometry in terms of known quantities, plus two parameters C_A and C_{BM}.

As noted above, our previous MP2/6-31G(d) calculations suggest that C_{BM} should be about 1.25 and C_A should be about 0.5. In the next section we will use ab initio calculations at various levels to find the geometry of the transition state for 26 hydrogen transfer reactions and 6 methyl transfer reactions to see how well they fit Eqs. (5), (11), and (12).

Calculations

The calculations were done using the Gaussian suite of programs [28]. We have calculated the geometry for 26 hydrogen transfer reactions and 6 methyl transfer reactions at the MP2/6-31G* and MP2/6-311+ +G(d,p) levels. We also checked selected structures at the CCSD(T)/6-311+ +G(d,p) level. Energies were calculated using the G-2 method. For each transition state, the geometry was checked to insure that there was only one negative frequency. IRC calculations were also done for selected cases to make sure that the transition states led from the desired reactants to the desired products.

MP2/6-31G* geometries are the old standard. They are not quite good enough for high level calculations, but they are wonderful approximations that one can use to start higher level calculations. That is, if you use MP2/6-31G* geometries as a starting guess for high level calculations, the results almost always converge. MP2(full)/6-31G* geometries are also used directly in G-2 and G-3 calculations and with modifications in CBS calculations. They are the primary geometries in this paper.

We also have included MP2/6-311+ +G(d,p) geometries. In our experience MP2/6-311+ +G(d,p) geometries are not very helpful. They are not good enough to use directly in high level calculations and they take longer to compute than MP2/6-31G* geometries. Still we included them because they are used by other investigators and we could explore the effect of changing basis set on the results.

Lastly, we include some CCSD(T)/ 6-311+ +G(d,p) geometries. CCSD(T)/ 6-311+ +G(d,p) geometries are thought to be quite good. We only computed a few CCSD(T)/ 6-311+ +G(d,p) geometries because we had a limited amount of computer time available. However, selected cases were done to insure that our results are reasonable.

Computational results

Table 1 shows the transition state geometries for a number of reactions computed at the MP2/6-31G* level. The equilibrium bond lengths calculated at the MP2/6-31G* level are also included in the table. Notice that the bond lengths in the transition state vary from 0.799 Å to 1.872 Å. Individual bond extensions vary from 0.15 Å to 0.4 Å. However, $\frac{r_B^t + r_F^t}{r_{B,\text{equ}} + r_{F,\text{equ}}}$ only varies between 1.20 and 1.26. If we assume that

$$\frac{r_B^t + r_F^t}{r_{B,\text{equ}} + r_{F,\text{equ}}} = 1.23 \tag{13}$$

we can estimate $r_B^t + r_F^t$ to within 0.04 Å for all of the cases in the table.

Next we will assume that Eq. (13) is exact and try to use Eqs. (9)–(12) to estimate individual values of r_B^t and r_F^t. First we calculated the heat of reaction for each of the reactions at the G-2 level. We then substituted $r_B^t + r_F^t$ from Eq. (13) into Eqs. (11) and (12) to calculate r_B^t and r_F^t.

Table 2 shows the bond lengths we calculate in this way. The G-2 energies are also included in the table.

Figure 1 compares the values of r_B^t and r_F^t calculated at the MP2/6-31G* level to those predicted by Eqs. (11) and (12). Notice that the values of r_B^t and r_F^t predicted from Eqs. (11) and (12) are usually within 0.1 Å of the MP2/6-31G* geometries for all of the reactions in Table 1. The average error is 0.03 Å, which is about the accuracy of the MP2/6-31G* geometries.

Table 1. r^t_B and r^t_F for a number of reactions calculated at the MP2/6-31G* level

Reaction	r^t_F, Å	r^t_B, Å	$r_{F,\mathrm{equ}}$, Å	$r_{F,\mathrm{equ}}$, Å	$\frac{r^t_B+r^t_F}{r_{B,\mathrm{equ}}+r_{F,\mathrm{equ}}}$
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	0.8920	1.4049	0.7376	1.0928	1.255
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	0.8897	1.4100	0.7376	1.0992	1.252
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	0.8905	1.4111	0.7376	1.1001	1.252
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	0.8775	1.4008	0.7376	1.0922	1.245
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	0.8833	1.4143	0.7376	1.0965	1.253
$H + CH_3OH \rightarrow H_2 + CH_2OH$	0.9273	1.3734	0.7376	1.0896	1.259
$H + CH_3OH \rightarrow H_2 + CH_3O$	0.8667	1.2493	0.7376	0.9701	1.239
$H + CH_4 \rightarrow H_2 + CH_3$	0.8784	1.4230	0.7376	1.0897	1.259
$H + CH_3CH_2OH \rightarrow H_2 + CH_2CH_2OH$	0.8927	1.4103	0.7376	1.0921	1.259
$H + NH_3 \rightarrow H_2 + NH_2$	0.8812	1.3168	0.7376	1.0168	1.253
$H + H_2O \rightarrow H_2 + OH$	0.8409	1.2932	0.7376	0.9687	1.251
$H + HF \rightarrow H_2 + F$	0.7993	1.3219	0.7376	0.9339	1.269
$OH + CH_4 \rightarrow H_2O + CH_3$	1.2259	1.2689	0.9687	1.0897	1.212
$OH + CH_3CH_3 \rightarrow H_2O + CH_2CH_3$	1.2088	1.3067	0.9687	1.0928	1.22
$OH + NH_3 \rightarrow H_2O + NH_2$	1.3081	1.1257	0.9687	1.0168	1.226
$OH + CH_3 \rightarrow H_2O + CH_2$	1.2519	1.2171	0.9687	1.0783	1.206
$OH + CH_2 \rightarrow H_2O + CH$	1.1070	1.3640	0.9687	1.0776	1.208
$O + CH_4 \rightarrow OH + CH_3$	1.1820	1.3065	0.9791	1.0827	1.207
$O + CH_3CH_3 \rightarrow OH + CH_2CH_3$	1.2099	1.2818	0.9791	1.0928	1.203
$O + NH_3 \rightarrow OH + NH_2$	1.2051	1.1963	0.9791	1.0168	1.203
$O + NH \rightarrow OH + N$	1.4659	1.0995	0.9791	1.0395	1.271
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	1.3319	1.3319	1.0897	1.0897	1.222
$CH_3 + CH_3OH \rightarrow CH_4 + CH_3O$	1.2516	1.2320	1.0897	0.9701	1.206
$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH$	1.3859	1.2999	1.0897	1.0896	1.232
$CH_3 + NH_3 \rightarrow CH_4 + NH_2$	1.3078	1.2591	1.0897	1.0168	1.219
$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3522	1.3155	1.0897	1.0928	1.222
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	1.3819	1.8740	1.0897	1.5243	1.246
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3855	1.8686	1.0897	1.5449	1.235
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	1.4153	1.8723	1.0897	1.5479	1.246
$H + CH_3CH_2CN \rightarrow CH_4 + CH_2CN$	1.3596	1.8593	1.0897	1.5306	1.228
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	1.3736	1.8674	1.0897	1.5437	1.231
$H + CH_3OH \rightarrow CH_4 + OH$	1.3528	1.7136	1.0897	1.423	1.220

Figure 2 compares the values of r^t_B and r^t_F calculated at the MP2/6-31G* level to those predicted by Eqs. (9) and (10). In this case, the errors are slightly larger. The average error is 0.05 Å. Still, the transition state geometries predicted from Eqs. (9) and (10) are always within 0.15 Å of the MP2/6-31G* geometries for all of the reactions in Table 1.

The results in Figs 1 and 2 show that Eq. (8) can be used to get a reasonable approximation to the geometry calculated at the MP2/6-31G* level. Next we want to address whether the close agreement between theory and experiment was due to a fortuitous cancellation of errors in the MP2/6-31G* calculations, or whether the equations will work in higher level calculations. We also want to see if the parameters in the model change if the level of the calculations change.

In order to answer that question, we decided to compute transition state geometries at the MP2/6-311++G(d,p) level. Table 3 shows the geometries calculated at the MP2/6-311++G(d,p) level. Again we find that the model fits the calculations very well. We find for all cases except $H + HF \rightarrow H_2 + F$, that the ab initio values of r^t_B and r^t_F are within 0.08 Å of the value calculated via Eq. (13).

Table 4 and Fig. 3 compare the values of r^t_B and r^t_F from the MP2/6-311++g(d,p) calculations to those from Eqs. (11) and (12). We find that if we choose $C_A = 0.5$, as expected from our MP2/6-31G(d), we only obtain fair agreement between the MP2/6-311++g(d,p) calculations and Eqs. (11) and (12). However, if we increase C_A to 1.0, we obtain excellent agreement between the ab initio calculations and the model. Equations (11) and (12) predict values of $r^{\mathrm{t}}_{\mathrm{B}}$ and $r^{\mathrm{t}}_{\mathrm{F}}$ with an average error of 0.039 Å and a maximum error of 0.097 Å.

Finally, Table 5 shows a few cases we have evaluated to see if the results change at the CCSD(T)/6-311++G(d,p) level. We picked cases where the agreement between the model and the experiment were not particularly good at the MP2/6-311++g(d,p) level and did tests to see what happens at the CCSD(T)/6-311++G(d,p) level.

We find that for the cases shown, the agreement between the ab initio calculations and Eqs. (11) and (12) improves at the CCSD(T)/6-311++G(d,p) level. Equations (11) and (12) fit the MP2/6-311++G(d,p) for the cases shown with an average error of 0.052 Å. The error decreases to 0.031 Å at the CCSD(T)/6-311++G(d,p) level.

Another observation is that $\frac{r^t_B+r^t_F}{r_{B,\mathrm{equ}}+r_{F,\mathrm{equ}}}$ is slightly higher in CCSD(T) calculations than in the corresponding MP2 calculations. The best fit to the CCSD(T)/6-311++G(d,p) results came with $\frac{r^t_B+r^t_F}{r_{B,\mathrm{equ}}+r_{F,\mathrm{equ}}} = 1.27$, which is also the value predicted via Blowers and Masel's model [8].

Finally it is interesting to note that the average difference between r^t_B and r^t_F predicted from Eqs. (11) and (12) and those predicted by the CCSD(T)/

Table 2. A comparison of r_B^t and r_F^t calculated at the MP2/6-31g* level to those calculated from Eqs. (11) and (12) with $C_A = 0.5$, $C_{BM} = 1.23$, and $E_A^0 = 10$ kcal/mol for the hydrogen transfer reactions and $C_A = 1$, $C_{BM} = 1.23$, and $E_A^0 = 40$ kcal/mol for the methyl transfer reactions. In the table the heats of reaction were estimated via the G2 method

Reaction	r_F^t, Å (MP2/6-31G*)	r_B^t, Å (MP2/6-31G*)	r_F^t, Å (Eq. 12)	r_B^t, Å (Eq. 11)	ΔU_r, kcal/mol (G2)
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	0.8920	1.4049	0.9209	1.3305	−3.66
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	0.8897	1.4100	0.9178	1.3415	−2.83
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	0.8905	1.4111	0.9184	1.342	−2.99
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	0.8775	1.4008	0.8887	1.362	5.00
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	0.8833	1.4143	0.9141	1.3418	−1.84
$H + CH_3OH \rightarrow H_2 + CH_2OH$	0.9273	1.3734	0.9587	1.2887	−13.86
$H + CH_3OH \rightarrow H_2 + CH_3O$	0.8670	1.2493	0.9095	1.191	−0.64
$H + CH_4 \rightarrow H_2 + CH_3$	0.8784	1.4230	0.9085	1.3391	−0.33
$H + CH_3CH_2OH \rightarrow H_2 + CH_2CH_2OH$	0.8927	1.4103	0.9155	1.335	−2.23
$H + NH_3 \rightarrow H_2 + NH_2$	0.8812	1.3168	0.9003	1.2576	1.95
$H + H_2O \rightarrow H_2 + OH$	0.8409	1.2932	0.8598	1.2389	13.68
$H + HF \rightarrow H_2 + F$	0.7993	1.3219	0.7672	1.2888	41.23
$OH + CH_4 \rightarrow H_2O + CH_3$	1.2259	1.2689	1.2436	1.2882	−12.45
$OH + CH_3CH_3 \rightarrow H_2O + CH_2CH_3$	1.2088	1.3067	1.2642	1.2715	−17.34
$OH + NH_3 \rightarrow H_2O + NH_2$	1.3081	1.1257	1.2388	1.2033	−11.73
$OH + CH_3 \rightarrow H_2O + CH_2$	1.2519	1.2171	1.2261	1.2917	−8.31
$OH + CH_2 \rightarrow H_2O + CH$	1.1070	1.3640	1.2744	1.2426	−19.92
$O + CH_4 \rightarrow OH + CH_3$	1.1820	1.3065	1.1874	1.3486	4.03
$O + CH_3CH_3 \rightarrow OH + CH_2CH_3$	1.2099	1.2818	1.2079	1.3405	−0.86
$O + NH_3 \rightarrow OH + NH_2$	1.2051	1.1963	1.185	1.2699	4.75
$O + NH \rightarrow OH + N$	1.4659	1.0995	1.3161	1.1667	−27.26
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	1.3319	1.3319	1.3403	1.3403	0
$CH_3 + CH_3OH \rightarrow CH_4 + CH_3O$	1.2516	1.2320	1.3348	1.1987	1.31
$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH$	1.3859	1.2999	1.3742	1.3063	−7.65
$CH_3 + NH_3 \rightarrow CH_4 + NH_2$	1.3078	1.2591	1.3372	1.2537	0.72
$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3522	1.3155	1.362	1.3225	−4.89
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	1.3819	1.8740	1.3721	1.8432	−16.89
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3855	1.8686	1.3724	1.8682	−16.93
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	1.4153	1.8723	1.3851	1.8591	−23.62
$H + CH_3CH_2CN \rightarrow CH_4 + CH_2CN$	1.3596	1.8593	1.3668	1.8562	−14.05
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	1.3736	1.8674	1.362	1.877	−11.47
$H + CH_3OH \rightarrow CH_4 + OH$	1.3528	1.7136	1.363	1.7276	−12.54

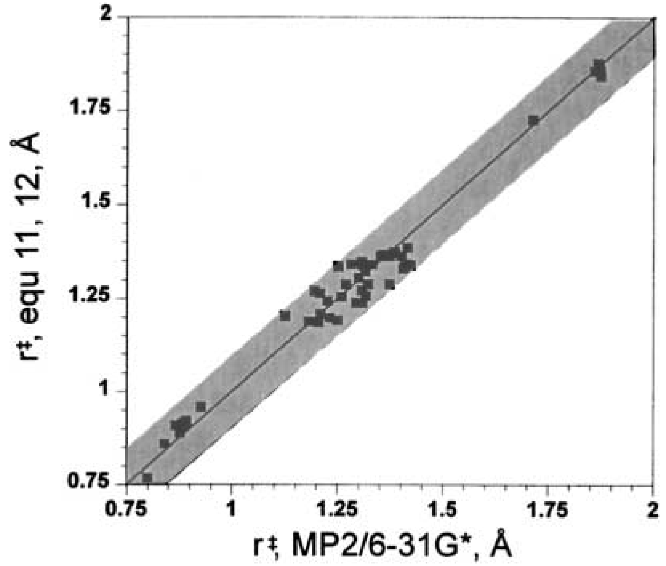

Fig. 1. A comparison of r_B^t and r_F^t for a number of reactions calculated at the MP2/6-31G* level to those estimated from Eqs. (11) and (12) with $C_A = 0.5$ and $E_A^0 = 10$ kcal/mol for the hydrogen transfer reactions and $C_A = 1$ and $E_A^0 = 40$ kcal/mol for the methyl transfer reactions. The *shaded area* represents a maximum error of 0.1 Å

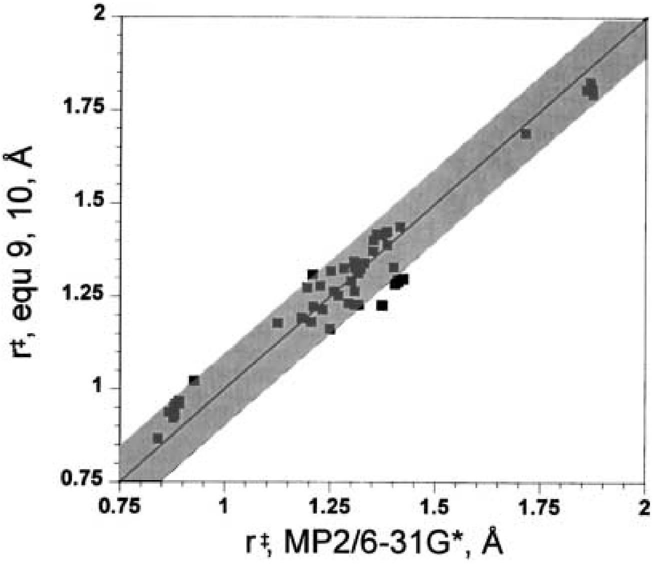

Fig. 2. A comparison of r_B^t and r_F^t for a number of reactions calculated at the MP2/6-31G* level to those estimated from Eqs. (9) and (10) with $E_A^0 = 10$ kcal/mol for the hydrogen transfer reactions and $E_A^0 = 40$ kcal/mol for the methyl transfer reactions. The *shaded area* represents a maximum error of 0.1 Å

Table 3. r_B^t and r_F^t for a number of reactions calculated at the MP2/6-311 + + G(d,p) level

Reaction	r_F^t, Å	r_B^t, Å	$r_{\mathrm{F,equ}}$, Å	$r_{\mathrm{B,equ}}$, Å	$\frac{r_B^t+r_F^t}{r_{B,\mathrm{equ}}+r_{F,\mathrm{equ}}}$
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	0.8884	1.3836	0.7383	1.0934	1.240
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	0.8861	1.3896	0.7383	1.0939	1.240
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	0.8877	1.3906	0.7383	1.0952	1.242
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	0.8781	1.3999	0.7383	1.0926	1.244
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	0.8802	1.3945	0.7383	1.0920	1.243
$H + CH_3OH \rightarrow H_2 + CH_2OH$	0.9608	1.3441	0.7383	1.0959	1.257
$H + CH_3OH \rightarrow H_2 + CH_3O$	0.8411	1.2657	0.7383	0.9593	1.241
$H + CH_4 \rightarrow H_2 + CH_3$	0.8737	1.4055	0.7383	1.0903	1.246
$H + CH_3CH_2OH \rightarrow H_2 + CH_2CH_2OH$	0.8927	1.4103	0.7383	1.0938	1.257
$H + NH_3 \rightarrow H_2 + NH_2$	0.8593	1.3289	0.7383	1.0132	1.249
$H + H_2O \rightarrow H_2 + OH$	0.8125	1.3319	0.7383	0.9686	1.256
$H + HF \rightarrow H_2 + F$	0.7749	1.3962	0.7383	0.9166	1.312
$OH + CH_4 \rightarrow H_2O + CH_3$	1.3207	1.1908	0.9686	1.0903	1.220
$OH + CH_3CH_3 \rightarrow H_2O + CH_2CH_3$	1.3067	1.2088	0.9686	1.0934	1.220
$OH + NH_3 \rightarrow H_2O + NH_2$	1.3108	1.1086	0.9686	1.0132	1.221
$OH + CH_3 \rightarrow H_2O + CH_2$	1.2939	1.1869	0.9686	1.0795	1.211
$OH + CH_2 \rightarrow H_2O + CH$	1.2406	1.2067	0.9686	1.0787	1.195
$O + CH_4 \rightarrow OH + CH_3$ (forces converged)	1.2408	1.2679	0.9686	1.0903	1.218
$O + CH_3CH_3 \rightarrow OH + CH_2CH_3$	1.2371	1.2466	0.9686	1.0934	1.205
$O + NH_3 \rightarrow OH + NH_2$	1.167	1.2172	0.9686	1.0132	1.203
$O + NH \rightarrow OH + N$	1.3535	1.1246	0.9686	1.0352	1.237
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	1.3266	1.3266	1.0903	1.0903	1.217
$CH_3 + CH_3OH \rightarrow CH_4 + CH_3O$	1.2517	1.2320	1.0903	0.9593	1.212
$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH$	1.3796	1.3011	1.0903	1.0959	1.226
$CH_3 + NH_3 \rightarrow CH_4 + NH_2$	1.2753	1.2829	1.0903	1.0132	1.216
$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3522	1.3155	1.0903	1.0934	1.222
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	1.3819	1.8740	1.0903	1.529	1.227
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3855	1.8686	1.0903	1.5288	1.242
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	1.3947	1.8440	1.0903	1.5306	1.236
$H + CH_3CH_2CN \rightarrow CH_4 + CH_2CN$	1.3596	1.8593	1.0903	1.5356	1.226
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	1.3736	1.8674	1.0903	1.5277	1.238
$H + CH_3OH \rightarrow CH_4 + OH$	1.3528	1.7136	1.0903	1.420	1.222

6-311 + + G(d,p) calculations is 0.031 Å. By comparison, the average difference between r_B^t and r_F^t predicted from the MP2/6-31g* calculations and those predicted by the CCSD(T)/6-311 + + G(d,p) calculations is 0.031 Å. Our statistics are small since we have so few CCSD(T)/6-311 + + G(d,p) calculations, but it is interesting that in the cases shown the errors in geometries predicted via Eqs. (11) and (12) are comparable to the errors in the geometries predicted from MP2/6-31G* calculations.

Overall, the agreement between model and calculation was unexpectedly good, especially considering the approximate nature of the model.

Discussion

The results here show that we can get a reasonable approximation to the transition state positions using Eqs. (5), (11), and (12) using the parameters in Table 6. The agreement between model and calculation is amazingly good. The errors in the approximations are comparable to those of MP2/6-31G(d) calculations and the geometries can be obtained with readily available information: heats of reaction and equilibrium bond lengths in the reactants and products.

We believe that is an important result. After all, one of the hardest parts of an ab initio calculation of a transition state geometry is to find a way to guess initial transition state geometries. Now we have a way to do so.

In order to illustrate the method, we have considered the series of reactions in Table 7. In each case we looked up the equilibrium bond lengths in the CRC handbook [30], obtained heat of reaction data from the NIST webbook [29], and then substituted into Eqs. (5), (11), and (12) to calculate r_B^t and r_F^t. We also considered using Benson's approximation to calculate r_B^t and r_F^t, and picked "typical" bond lengths. The table shows the time it took Gaussian 98 version A.7 to converge to the MP2/aug-cc-pVDZ transition state geometry as a function of the method used to start the calculation.

The results are startling. For example, the first time we ran the algorithm, it took Gaussian 98 351 s to find the transition state for the reaction $H + HF \rightarrow H_2 + F$ starting with the bond lengths given by Eqs. (5), (11), and (12). There was some unexpected behavior, because Gaussian moved away from the transition state during the first step. Nevertheless, the algorithm converged. Interestingly, if we restarted the algorithm using force constants from the previous calculation, the calculation converged in 268 s.

We then tried doing the calculations starting with Benson's approximation for r_B^t and r_F^t and identical values for all other parameters. Gaussian iterated as before, but after 350 s it found a point on the potential energy surface with two complex frequencies, and then the algorithm stopped. The algorithm never found a saddle point.

Table 4. A comparison of r_B^t and r_F^t calculated at the MP2/6-311 + + g(d,p) level to those calculated from Eqs. (11) and (12) with $C_A = 1.0$, $C_{BM} = 1.23$, and $E_A^0 = 10$ kcal/mol for the hydrogen transfer reactions and $C_A = 1.0$, $C_{BM} = 1.25$, and $E_A^0 = 40$ kcal/mol for the methyl transfer reactions. In the table, the heats of reaction were estimated via the G2 method

Reaction	r_F^t, Å (MP2/6-311 + + G(d,p))	r_B^t, Å (MP2/6-311 + + G(d,p))	r_F^t, Å (equ 12)	r_B^t, Å (equ 11)	ΔU_r, kcal/mol (G2)
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	0.8884	1.3836	0.9274	1.3256	−3.66
$H + CH_3CH_2CH_3 \rightarrow H_2 + CH_2CH_2CH_3$	0.8861	1.3896	0.9230	1.3306	−2.83
$H + CH_3CH_2NH_2 \rightarrow H_2 + CH_2CH_2NH_2$	0.8877	1.3906	0.9239	1.3313	−2.99
$H + CH_3CH_2CN \rightarrow H_2 + CH_2CH_2CN$	0.8781	1.3999	0.8818	1.3702	5.00
$H + CH_3CH_2CF_3 \rightarrow H_2 + CH_2CH_2CF_3$	0.8802	1.3945	0.9178	1.3335	−1.84
$H + CH_3OH \rightarrow H_2 + CH_2OH$	0.9608	1.3441	0.9812	1.2749	−13.86
$H + CH_3OH \rightarrow H_2 + CH_3O$	0.8411	1.2657	0.9112	1.1768	−0.64
$H + CH_4 \rightarrow H_2 + CH_3$	0.8737	1.4055	0.9098	1.3393	−0.33
$H + CH_3CH_2OH \rightarrow H_2 + CH_2CH_2OH$	0.8927	1.4103	0.9199	1.3336	−2.23
$H + NH_3 \rightarrow H_2 + NH_2$	0.8593	1.3289	0.8983	1.2561	1.95
$H + H_2O \rightarrow H_2 + OH$	0.8125	1.3319	0.8410	1.2585	13.68
$H + HF \rightarrow H_2 + F$	0.7749	1.3962	0.7383	1.3236	41.23
$OH + CH_4 \rightarrow H_2O + CH_3$ (Forces converged but not geometry)	1.3207	1.1908	1.2651	1.2674	−12.45
$OH + CH_3CH_3 \rightarrow H_2O + CH_2CH_3$	1.3067	1.2088	1.2942	1.2421	−17.34
$OH + NH_3 \rightarrow H_2O + NH_2$	1.3108	1.1086	1.2582	1.1794	−11.73
$OH + CH_3 \rightarrow H_2O + CH_2$	1.2939	1.1869	1.2403	1.2789	−8.31
$OH + CH_2 \rightarrow H_2O + CH$	1.2406	1.2067	1.3086	1.2096	−19.92
$O + CH_4 \rightarrow OH + CH_3$	1.2408	1.2679	1.1675	1.3649	4.03
$O + CH_3CH_3 \rightarrow OH + CH_2CH_3$	1.2371	1.2466	1.1965	1.3398	−0.86
$O + NH_3 \rightarrow OH + NH_2$	1.167	1.2172	1.1643	1.2733	4.75
$O + NH \rightarrow OH + N$	1.3535	1.1246	1.3484	1.1163	−27.26
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	1.3266	1.3266	1.3411	1.3411	0
$CH_3 + CH_3OH \rightarrow CH_4 + CH_3O$	1.2517	1.2320	1.3333	1.1877	1.31
$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH$	1.3796	1.3011	1.3892	1.2999	−7.65
$CH_3 + NH_3 \rightarrow CH_4 + NH_2$	1.2753	1.2829	1.3367	1.2506	0.72
$CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3522	1.3155	1.3718	1.3142	−4.89
$H + CH_3CH_3 \rightarrow CH_4 + CH_3$	1.3819	1.8740	1.3729	1.8489	−16.89
$H + CH_3CH_2CH_3 \rightarrow CH_4 + CH_2CH_3$	1.3855	1.8686	1.3729	1.8486	−16.93
$H + CH_3CH_2NH_2 \rightarrow CH_4 + CH_2NH_2$	1.3947	1.8440	1.3856	1.8381	−23.62
$H + CH_3CH_2CN \rightarrow CH_4 + CH_2CN$	1.3596	1.8593	1.3676	1.8623	−14.05
$H + CH_3CH_2CF_3 \rightarrow CH_4 + CH_2CF_3$	1.3736	1.8674	1.3627	1.87575	−11.47
$H + CH_3OH \rightarrow CH_4 + OH$	1.3528	1.7136	1.3637	1.7264	−12.54

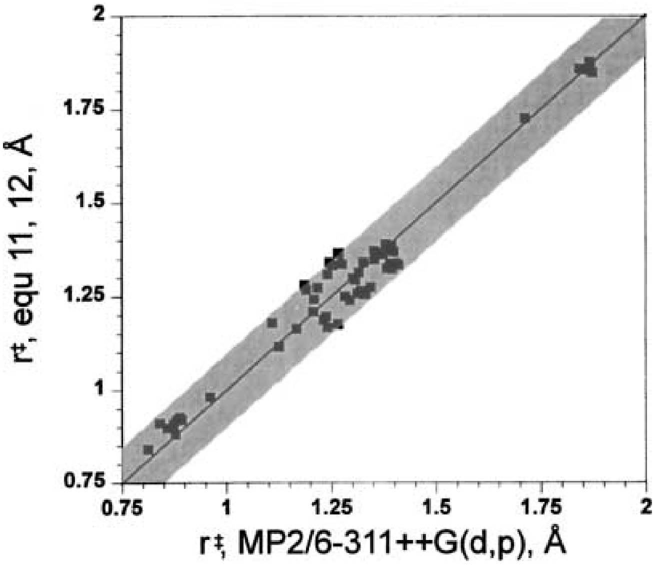

Fig. 3. A comparison of r_B^t and r_F^t for a number of reactions calculated at the MP2/6-311 + +G(d,p) level to those estimated from Eqs. (11) and (12) with $C_A = 1.0$ and $E_A^0 = 10$ kcal/mol for the hydrogen transfer reactions and $C_A = 1$ and $E_A^0 = 40$ kcal/mol for the methyl transfer reactions. The *shaded area* represents a maximum error of 0.1 Å

We reran the case described in the previous paragraph using the noeigentest option in Gaussian. In this case the algorithm did finally converge, but the run took 681 s, about twice as long as the cases where we used Eqs. (5), (11), and (12) to estimate a starting guess.

We also did tests where we picked "typical" HH and HF transition state bond lengths and ran the algorithm. Again, convergence was slow, but the algorithm converged to the correct transition state geometry.

The reaction O + NH → OH + N was simpler. In this case, the starting guess was close to the transition state geometry, but Gaussian moved away from the saddle point in the first step. It took 600 s for Gaussian to converge to the saddle point geometry. Surprisingly, when we restarted the run using the same initial guesses, but read the force fields, the time went down to 134 s. By comparison, if we started with Benson's approximation the algorithm took 800 s.

In the other three cases in the table, Gaussian found the saddle point quickly if we used Eqs. (5), (11), and (12) to estimate transition state geometries. In contrast, the algorithm never found the saddle point when other guesses were used. For example, with the reaction $OH + NH_3 \rightarrow H_2O + NH_2$ Gaussian iterated as before, but after 912 s, it found a point on the potential

Table 5. A comparison of r_B^t and r_F^t calculated at various levels to those calculated from equations 11 and 12 with the parameter values in tables 1 and 3. In the CCSD rows, the bond lengths were calculated with $C_A = 1.0$, $C_{BM} = 1.25$, and $E_A^0 = 10$ kcal/mol

Reaction	Calculation	r_F^t, Å ab initio	r_B^t, Å ab initio	$\frac{r_B^t+r_F^t}{r_{B,\text{equ}}+r_{F,\text{equ}}}$	r_F^t, Å (Eq. 12)	r_B^t, Å (Eq. 11)
$H + HF \rightarrow H_2 + F$	MP2/6-31g*	0.7993	1.3219	1.269	0.7672	1.2888
$H + HF \rightarrow H_2 + F$	MP2/6-311 + + g(d,p)	0.7749	1.3962	1.312	0.7383	1.3236
$H + HF \rightarrow H_2 + F$	MP2/aug-cc-pVTZ	0.7746	1.4206	1.323	0.7376	1.4013
$H + HF \rightarrow H_2 + F$	CCSD/6-31g*	0.8120	1.3338	1.277	0.7462	1.4204
$H + HF \rightarrow H_2 + F$	CCSD(T)/ 6-311+ +g(d,p)	0.7745	1.4672	1.355	0.7383	1.3939
$H + HF \rightarrow H_2 + F$	CCSD(T)/aug-cc-pVTZ	0.7734	1.5206	1.379	0.7430	1.4012
$H + H_2O \rightarrow H_2 + OH$	MP2/6-31g*	0.8409	1.2932	1.251	0.8580	1.3090
$H + H_2O \rightarrow H_2 + OH$	MP2/6-311+ +g(d,p)	0.8125	1.3319	1.256	0.8413	1.2470
$H + H_2O \rightarrow H_2 + OH$	CCSD(T)/6-311+ +g(d,p)	0.8280	1.3279	1.259	0.8592	1.2979
$H + CH_4 \rightarrow H_2 + CH_3$	MP2/6-31g*	0.8784	1.4230	1.259	0.9085	1.3391
$H + CH_4 \rightarrow H_2 + CH_3$	MP2/6-311 + + g(d,p)	0.8737	1.4055	1.246	0.9098	1.3393
$H + CH_4 \rightarrow H_2 + CH_3$	CCSD(T)/6-311+ +g(d,p)	0.8955	1.3970	1.250	0.9397	1.3810
$H + NH_3 \rightarrow H_2 + NH_2$	MP2/6-31g*	0.8812	1.3168	1.253	0.9003	1.2576
$H + NH_3 \rightarrow H_2 + NH_2$	MP2/6-311+ +g(d,p)	0.8593	1.3289	1.249	0.8983	1.2561
$H + NH_3 \rightarrow H_2 + NH_2$	CCSD(T)/6-311+ +g(d,p)	0.8895	1.3057	1.250	0.9261	1.7028
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	MP2/6-31g*	0.8920	1.4049	1.255	0.9209	1.3305
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	MP2/6-311+ +g(d,p)	0.8884	1.3836	1.240	0.9274	1.3256
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_3$	CCSD(T)/6-31g*	0.9224	1.3903	1.261	0.9603	1.3652
$H + CH_3CH_3 \rightarrow H_2 + CH_2CH_2$	CCSD(T)/6-311+ +g(d,p)	0.9149	1.3687	1.244	0.9603	1.3710

Table 6. The optimum values of the parameters at various levels of theory

Level	C_{BM}	C_{A}
MP2/6-31G(d)	1.23	0.5 (hydrogen transfer); 1.0 (methyl transfer)
MP2/6-311 + + G(d,p)	1.25	1.0
CCSD(T)/6-311 + + G(d,p)	1.27	1.0

energy surface with two complex frequencies, and then the algorithm stopped. The algorithm never found a saddle point.

We reran the reaction using the noeigentest option in Gaussian. In this case the algorithm continued going, but the reactants separated. We stopped the algorithm after 18,000 s. At that point the algorithm still was not close to the transition state.

In the reactions $O + CO \rightarrow O_2 + C$ and $H + O_2 \rightarrow OH + O$ the algorithm again failed when Benson's approximation was used. One could get the algorithm to converge with the noeigentest option, but it converged to a stable structure, not a saddle point.

Clearly, the approximations here are useful ways to start transition state calculations.

Conclusion

In summary, we have a model that allows one to predict approximate transition state structures from readily available information. The model works extremely well. One can predict transition state geometries to an accuracy which approaches the accuracy of MP2/6-31G* calculations with pencil and paper calculations. We do not know if the model will be widely applicable.

Table 7. The time it takes Gaussian 98 version A.7 to converge to the MP2/aug-cc-pVDZ transition state geometry as a function of the method used to start the calculation. These calculations were done on the Exemplar machine at the national center for supercomputing applications

Method used to generate initial geometry	Eqs. (5), (11), (12)	Eqs. (5), (11), (12)		Benson	"Typical" geometry	"Typical" geometry
Algorithm	Berny + Calcfc	Berny + Readfc	Berny	Berny + noeigentest	Berny	Berny + noeigentest
$H + HF \rightarrow H_2 + F$	351 s	268 s	Failed	629 s	Failed	710 s
$O + NH \rightarrow OH + N$	600 s	134 s	861 s	855 s	901 s	891 s
$OH + NH_3 \rightarrow H_2O + NH_2$	5601 s	1584 s	Failed	Never converged (18000 s limit)	Failed	Never converged (18000 s limit)
$O + CO \rightarrow O_2 + C$	2168 s	636 s	Failed	Never converged (18000 s limit)	Failed	Converged to incorrect geometry (stable COO molecule)
$H + O_2 \rightarrow OH + O$	879 s	195 s	Failed	Converged to incorrect geometry (stable HOO molecule)	SCF convergence failure	Converged to incorrect geometry (stable HOO molecule)

Still, in the cases we have considered so far, the model is able to predict excellent starting geometries for ab initio calculations.

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