
Construcció de perfils d'energia potencial per a reaccions orgàniques pericícliques i electrocícliques.

Ricard M. Barba Obón

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Anyone who is not shocked by quantum theory has not understood it.

Niels Bohr

This work couldn’t have been completed without the essential help of a group of people. I would like to give special thanks to them.

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1. **SUMMARY**

The primary goal of this study is to build potential surfaces of reactions, having a special focus into pericyclic reactions.

Two different reactions will be studied computationally: the ring-opening of ciclobutene to cis-butadiene and the reduction of ethene to ethane by diimide.

The same methodology will be used in both studies. First step is to regard the reactants and products of the reaction that are associated to a minima of the potential energy surface. The next step consists in searching over the potential surface in order to find a stationary point of first order saddle point character. This stationary point corresponds to a transition state.

Finally, the reaction path is computed. The reaction path is a continuous curve on the potential energy surface joining the minima associated to the reactants and products through the transition state. A curve representing a reaction path curve ascends monotonically from reactants to the transition state and descends monotonically from the transition state to the products. It is taken as a reaction path curve the Intrinsic Reaction Coordinate proposed by Fukui (1).

At first stance, the electronic energy is computed at the Hartree-Fock level (RHF). The RHF model assumes that the system can be described well by a single Slater determinant as electronic wave function.

The Born-Oppenheimer approximation is taken into account throughout the study. This assumes that nuclei are static towards the electrons (whose speeds are way greater), so the positions of the nuclei are parameters not variables of the wave function. In this way the nuclei interact with electrons as they were a cloud, and not individual particles.
When the potential surface and the different stationary points are defined, energetic considerations will be taken, in terms of energy activation of reactions.

Finally, but not included on this work since results have not been obtained yet, a brief study of tunnel effect will be considered on the two transferred hydrogen atoms in the reduction reaction. Hydrogen atoms are small particles compared with other atoms and can show this kind of quantum behavior.

**Keywords:** Computational studies, pericyclic reactions, electrocyclic reactions, group transfer reactions, cyclobutene, butadiene, ethene, diimide.
2. Resum

L'objectiu principal d'aquest estudi és construir superfícies de potencial de reaccions, centrant-se especialment en reaccions perícícliques.

Dos reaccions diferents seràn estudiades computacionalment: la obertura de l'anell del ciclobutè a cis-butadiè i la reducció d'etè a età per diimida.

La mateixa metodologia es farà servir a tots dos estudis. El primer pas és considerar els reactius i productes associats als estats mínims de la reacció. El següent és buscar per la superfície de potencial intentant trobar un punt estacionari o un punt de sella de primer ordre. Aquest punt correspon a un estat de transició.

Finalment, el camí de reacció es computa. El camí de reacció és una corba contínua a la superfície d'energia potencial que uneix els mínims associats a reactius i productes a través de l'estat de transició. Una corba representant un camí de reacció ascendeix monòtonament de reactius a estat de transició i desceix monòtonament d'estat de transició a productes. Es fa servir com a camí de reacció la coordenada de reacció intrínseca proposada per Fukui (1).

En primer lloc, la energia electrònica es calcularà a nivell Hartree-Fock (RHF). El model RHF assumeix que tot sistema té una funció d'ona que pot ésser aproximada a un únic determinant de Slater, és a dir, a una única configuració electrònica.

Es tindrà també en compte l'aproximació de Born-Oppenheimer durant l'estudi. Aquesta assumeix que els nuclis són èstatics envers els electrons (que tenen unes velocitats molt més elevades), així les posicions dels nuclis són paràmetres i no variables de la funció d'ona. D'aquesta manera els nuclis interaccionen amb els electrons com si fòssin un núvol i no partícules individuals.
Quan la superfície de potencial i els diferents punts estacionaris estiguin ben definits, es duràn a terme consideracions energètiques, en termes d'energies d'activació.

Finalment, es mencionarà breument un estudi sobre l'efecte túnel en els dos àtoms d'hidrogens transferits en la reacció de reducció. Els àtoms d'hidrogen són partícules petites en relació amb altres àtoms i poden mostrar aquest tipus de comportament.

**Paraules clau:** Estudis computacionals, reaccions perícícliches, reaccions electrocícliches, reaccions de transferència de grup, ciclobutè, butadiè, etè, diimida.
3. INTRODUCTION

Quantum Chemistry is a useful tool to predict geometries, electronic distribution, energies, vibrational frequencies and other properties of molecules. These are usually a good complement to experimental data, but they play a more important role in the design of new molecules or materials, saving time, money and resources.

There are two approximations used in molecular orbital theory: *ab initio* and semi-empirical. The first one is based only in quantum mechanics and physical constants, but the latter use empirical parameters. The studies held in this project are essentially *ab-initio* methods where the wave function approximation RHF, UHF and MCSCF are used.

The studies will be focus on pericyclic reactions. These kind of organic reactions usually involve an electronic rearrangement (that is to say, a bonding rearrangement) in a concerted mechanism. The name has been chosen because of the cyclic nature of the transition state of these reactions. Text books often distinguish three types of pericyclic reactions: electrocyclic, cycloaddition and sigmatropic, but actually chelotropic, dyotropic and group transfer reactions are also considered pericyclic. (1)

All calculation experiments will be computed on GAMESS software package (2).

Finally, a post-computation treatment will be performed, using data provided by the calculation: analysis of geometries, electronic distributions and orbital disposition; scheme of the potential surface of the reactions and energetic considerations, including the zero-point energy and the electron correlation.
4. **Objectives**

- Build energy profiles using computation techniques as the main tool for obtaining results.
- Deepen into the knowledge of pericyclic reactions and obtain a closer look of this kind of unique reactions.
- Use of simple computation methods, such as RHF and understanding the kind of information and limitations of each one.
- Obtain a criterion when reading or observing about energy profiles and pericyclic reactions.
5. Ring opening of Cyclobutene

It is well known that the cyclobutene thermally rearranges a ring-opening to butadiene and vice versa. This reaction is classified as pericyclic of the type electrocyclic.

Geometry optimizations and exploration of the potential energy surface were performed with the RHF wave function. The 6-31G(d) basis set \(^{(3)}\) was used for all atoms. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or first order saddle points and to obtain zero-point energy (ZPE) and thermal energy corrections at 273.15 K. Single-point energies were calculated with MP2/DZV basis set \(^{(4)}\), which is generally considered to be more accurate for energetics.

More specifically, in the first step the geometry of reactants and products (cyclobutene and cis-butadiene here) is introduced in the form of Z-matrix and optimize this geometry (under the RUNTYP:OPTIMIZE). The optimized geometry and energy of each stationary point is obtained, including the orbital description of the electronic distribution. But it’s necessary to ensure if the points are real minimums of the potential surface. For this issue, normal vibration modes are calculated (under the RUNTYP:HESSIAN), if all proper values of the vibration vector are positive (that is to say, the second derivative of the wave function is positive), it will mean that point is located on one of the potential surface minimums.
5.1. cis-Butadiene

First thing to notice is that the optimized geometry for cis-butadiene is, in fact, a gauche conformation with no symmetry elements, which corresponds to a C\textsubscript{2} point group.\(^{(1)}\)

Normal vibration mode analysis shows that this particular geometry is the one corresponding to a stationary point character minimum of the potential surface. All eigenvalues of the hessian matrix are positive definite.

The most characteristic geometry parameters of this molecule are the C1-C4 distance (2.49 Å), the two double bonds, namely, C1-C2 and C3-C4 (1.33 Å) and the C1-C2-C3-C4 dihedral angle (35.35 degrees). Atom numbering is shown in every figure as compounds are mentioned.

![Gauche-butadiene showing a stretching normal mode.](image)

A proper review of electronic distribution and orbital structure will be taken later, in order to compare them to those of the transition state (if there is one).

Images are obtained with the graphic design software GAMESS-MacmolPlt by Bode\(^{(5)}\).
5.2. **Cyclobutene**

The results reveal a planar structure with a $C_2$ axis and two planes (one horizontal and one vertical) as elements of symmetry, so the molecule belongs to a $C_{2v}$ point group. \(^{(1)}\)

Again normal vibration mode analysis demonstrates that this stationary point is really a minimum in the potential surface.

The most characteristic parameters of this molecule are the C1-C2 single bond (1.57 Å), the C3-C4 double bond (1.33 Å) and the C1-C4 dihedral angle (0.00 degrees).

![Cyclobutene molecule](image)

Fig 2. Cyclobutene showing a stretching normal mode.
It has been observed the frontier orbitals: HOMO and LUMO molecular orbitals and the set of orbitals $\sigma$ bonding, $\pi$ bonding, $\sigma$ anti bonding and $\pi$ anti-bonding; to make sure the structure was correct.

Fig 3. Cyclobutene HOMO

Fig 3. Cyclobutene LUMO
5.3. SEARCHING FOR THE TRANSITION STATE

Finding transition states for chemical reactions is at least more difficult that finding minima. For some reactions, a single coordinate can be found that dominates the transformation from reactants to products. An approximate reaction path can be calculated by stepping along the dominant coordinate and minimizing with respect to all n-1 remaining coordinates. The maximum along such a path should be quite close to the transition structure and an optimization method will converge quickly to the first order saddle point. In the present case we take as the dominant coordinate the C1-C2 bond distance of cyclobutene. The rest of coordinates are optimized along the path. The molecular geometry of the curve with highest energy was taken as a starting point for the final optimization to locate the transition state. This calculation was carried out using the keyword RUNTYP=SADPOINT. The final structure is reported in Figure 3. The analysis of the vibrational frequencies shows an imaginary frequency. Clearly, this is the transition state, a stationary point on the potential energy surface, which is a minimum in all directions except in the transition vector direction, which is the eigenvector of the Hessian matrix with negative eigenvalue.

Fig 3. Transition state of the ring opening reaction.
The most important geometry parameters at the located transition state are C1-C2 bond distance of 2.05 Å, the C3-C4 double bond (1.33 Å) and the C1-C2-C3-C4 dihedral angle (0.02 degrees).

But, as we refer to electrocyclic reactions, we should remember that they can evolve by two types of mechanism: conrotatory or disrotatory. The two methylene groups may rotate in the same direction (conrotatory) or in opposite direction (disrotatory) as the bond breaks and the molecule adopts the gauche conformation.

The transition state (TS) found is then corresponded to a conrotatory or a disrotatory process? According with WoodWard and Hoffmann rules, the TS must conserve the original orbital symmetry of reactants, in terms of avoiding orbital crossing: orbital geometry could change from one orbital to another, but it should never mix geometries of occupied and virtual orbitals. If Woodward and Hoffmann rules are fulfilled, is a permitted transition and the reaction goes on a conrotatory mechanism, other way is a forbidden reaction that goes on a disrotatory one. (6)

Butadiene molecule is formed by two electron non-bonding pairs and four sp\(_2\) carbon atoms, that is to say, four pi orbitals. The butadiene system can virtually be broke down to two ethene combinations and so the four pi molecular orbitals can be described as a combination of the ethenes pi orbitals as well.

These are the possible combinations in butadiene in order of increasing energy:

\[
\begin{align*}
\pi_1 &= \pi_{\text{ethene}_1} + \pi_{\text{ethene}_2} \\
\pi_2 &= \pi_{\text{ethene}_1} - \pi_{\text{ethene}_2} \\
\pi_3 &= \pi^*_{\text{ethene}_1} + \pi^*_{\text{ethene}_2} \\
\pi_4 &= \pi^*_{\text{ethene}_1} - \pi^*_{\text{ethene}_2}
\end{align*}
\]

*Marked in red the occupied ones and in blue the virtual.
During the transformation to the TS, they combine to form two sigma bonds and two pi bonds (both with bonding and anti-bonding set).

Now the analysis of orbital geometry and his conservation during the reaction:

![Fig 4. \( \pi_1 \) butadiene orbital.](image)

There is no symmetry, since the complete spin around the C\(_2\) axis will lead to an inversion of the lob signs.

![Fig 5. \( \pi_2 \) butadiene orbital.](image)
Here, on the other hand, a complete spin around the C$_2$ axis leads to the exactly same lob signs as can be seen in Figure 5. So, a C$_2$ geometry exists.

Using the same criteria, the rest of orbital geometries are assigned in both chemical species. $\pi_3$ orbital show no symmetry.

Figure 7 shows a new orbital with a C$_2$ axis.
Fig 8. $\sigma$ bonding transition state orbital with a $C_2$ axis.

Fig 9. $\pi$ bonding transition state orbital with no symmetry.
Marked in red the occupied ones and in blue the virtual. During the transformation to the TS, they combine to form two sigma bonds and two pi bonds (both with bonding and anti-bonding set).

Now the analysis of orbital geometry and his conservation during the reaction:

Fig 10. $\pi$ antibonding transition state orbital with a $C_2$ axis.

Fig 11. $\sigma$ antibonding transition state orbital with no symmetry.
During the transformation to the TS, they combine to form two sigma bonds and two pi bonds (both with bonding and antibonding set).

As it can be seen, no crosslinking is observed during the transformation to the TS, so it's a conrotatory process.

Woodward and Hofdmann rules are kind of mnemonic rules for this issues and are demonstrated to work very precisely, but with the help of the nowadays software, it is possible to literally see the conrotatory motion.

As far as the TS had been confirmed, a path connecting reactants, products and TS really exists and could be confirmed too. It is possible to follow the reaction path from the TS downhill to reactants and products (backward or forward), making many little steps (making a constant and monotone change of C1-C2 bond distance). Each step has a geometry attached, which can be registered and shown by software MacMolPlt. (7)

It is very important to note that the path founded doesn't have to be the minimum energy path (MEP). The MEP is a path connecting reactants and products but localized in a valley of the potential surface and further studies may be taken to confirm our path as MEP. This is not carried out in this work due to time and complexity reasons. (8)
Another detail for confirming the conrotatory motion is the Dewar-Zimmermann rules \(^{(9)}\), which say every TS whose structure is analogous to an aromatic structure is a permitted reaction mode.

Otherwise, an antiaromatic-like TS structure will result in a forbidden reaction mode. The concept of aromaticity is different depending on the system: it always has to be planar and cyclic, but the number of delocalized electrons which causes one behaviour or another is depending on the orbital overlapping of the system. An even number of overlaps lead to a Hückel system which is aromatic with \(4n + 2\) delocalized electrons and antiaromaric with \(4n\); an odd number of overlaps, however, are proper of Moebius systems which aromaticity electron rules are exactly the inverse. \(^{(9)}\)

Since conrotatory motion leads to a Moebius system and there are two pairs of delocalized electrons in the TS structure (a structure closer to gauche-butadiene rather than cyclobutene), it satisfies the needs of an aromatic system \((4n)\), so it's a permitted transition.

![Fig 13. TS obtained with conrotatory motion. Aromatic structure.](image)
5.4. THE DISROTATORY PROCESS

Once the reaction path of the conrotatory process has been located the next task is to find the possible reaction path associated to the disrotatory one.

In order to locate the disrotatory path on the potential energy surface, some additional constraints need to be added in the calculation otherwise will converge to the conrotatory region. Now, it is not only the C1-C2 bond distance the only crucial parameter in the course of the reaction. If methylenes are allowed to rotate freely, they will converge into the conrotatory motion that leads to the aromatic-like TS. So, it seems that if the angle between C1-C2 is held to 0,0 degree (limiting the two atoms to be in the same plane) maybe somehow the methylenes will be forced to rotate in different directions, leading to cis-butadiene (which lately can evolve into gauche-butadiene, more stable). With these restrictions, the molecular geometry turns from $C_{2v}$ to $C_{s}$ point group symmetry, being the symmetry proposed by the Woodward-Hoffmann rules for the disrotatory process.
With these restrictions and the optimization process, a stationary point was found; however, the frequency analysis showed that this point is a second order saddle point. A transition vector with negative eigenvalue is related with the disrotatory motion whereas the other one is related with the conrotatory motion implying a $C_s$ symmetry breaking. At this point is important to consider that the wave function used in this calculation was the UHF. The reason is the following.

In RHF the same molecular orbital is used for both possible spin states of an electron ($\alpha$ and $\beta$), so it exists the concept of doubly occupied orbitals, a concept widely used in inorganic and organic chemistry. But it’s important to remark that it’s only an answer valid for the RHF approximation, which gives very useful results for classical chemistry. However, the quantum reality is far away from this RHF answer and is absolutely invalid for systems that need more than a single Slater determinant to be described properly. The disrotatory process of this ring-opening falls in this group.

In UHF, a different molecular orbital is used for each electron set, distinguishing between $\alpha$-set and $\beta$-set orbitals. This doesn't mean that the method include two different Slater determinants, it a single one with coupled equations, for each set. More than one electronic configuration will be seen further. But with the inclusion of UHF, the concept of double occupation is already obsolete, making way to the single occupation. (8)

Then, with all the preparations completed, a new search over the potential surface is overcome (obviously, in a different region), making the same type of monotone and constant change in the C1-C2 bond distance and optimizing the geometry at every point. But then, and abrupt change in the energy profile appeared leading to a discontinuous energy profile.

This unusual behaviour was caused by a bad mix of the orbital sets at every step of the potential surface search, in a manner which didn’t allow the calculus to proceed correctly by UHF and falling again into RHF answer. The error was fixed with the order MIX=.TRUE. and then it was possible to select a point near to the maxima in order to look for the TS over there.

But once again, the TS couldn’t be reached and UHF method wasn’t giving any serious error. At this point, a more powerful method was needed.
Next step in calculus capability is Density Functional Theory (DFT), but it was decided to attack the problem with a more powerful method, the Multi-Configurational-Self-Consistent-Field (MCSCF) method, which uses configuration determinants to approximate the exact electronic wave function. It is recommended and very reliable when all other methods have failed or are unable to give a correct answer.\(^{(8)}\)(\(^{(10)}\))

Finally, the TS is reached at a C1-C2 bond distance of 2.94 Å, but in fact it's not at all a TS but a secondary order stationary point, having two normal modes with negative proper values, feat that leads to two imaginary frequencies: one corresponding to the reaction coordinate as happened with the conrotatory process and the other corresponding to the disrotatory motion itself.

So, it doesn't exist a reaction path connecting reactants with products, because a path needs a TS to interconnect them and this is not the case, at least at the ground state. Perhaps a TS can be found at the first excited state, or the second, or beyond. This correlates with the idea transferred in organic chemistry texts books: that disrotatory mechanisms are allowed under photochemical (excited) conditions.

Following this reasoning, an IRC cannot be calculated neither, as there is no path to follow.
The disrotatory process doesn't satisfy the Woodward-Hoffmann rules like the conrotatory process did, as have been mentioned in the section Searching for the transition state. That is because the correlation symmetry of the orbitals is mixed between occupied and virtual, producing a crossing.

Fig 16. Correlation diagram for the disrotatory mechanism.

And referring to Dewar-Zimmerman rules, during the disrotatory motion a Hückel system would be formed, which is anti-aromatic like, because the number of electrons delocalized is 4n.

Fig 17. 2nd order stationary point anti-aromatic like obtained during disrotatory process.
So, the disrotatory process is forbidden indeed, there is a very few small probability for the reaction to evolve that way. The major part of the molecules will go under the conrotatory mechanism.

5.5. Energetic Considerations

With all the previous results it is now possible to draw an energy profile of the reaction, and calculate the activation energies of the processes.

<table>
<thead>
<tr>
<th>Energies</th>
<th>Breakdown</th>
<th>Value (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ae_1$</td>
<td>$E_{\text{conrotTS}} - E_{\text{g-butadiene}}$</td>
<td>47.5</td>
</tr>
<tr>
<td>$Ae_2$</td>
<td>$E_{\text{conrotTS}} - E_{\text{cyclobutene}}$</td>
<td>30.5</td>
</tr>
<tr>
<td>Reaction energy</td>
<td>$E_{\text{cyclobutene}} - E_{\text{g-butadiene}}$</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Tab 1. The computed reaction and activation energies of the cyclobutene ring opening.

It can be seen that the more favourable process is the ring-opening rather than the closing, as the energetic barrier that is needed to overpass is lower.

No activation energies of the disrotatory mechanism are calculated, because there is no path connecting reactants, products and a TS at this ground state (remember it was a 2\textsuperscript{nd} order stationary point). It can be said there is a difference of 58.9 Kcal/mol between the stationary point and gauche-butadiene and 41.9 Kcal/mol with cyclobutene. As expected, the energetic difference is higher than for the conrotatory way, as it's a forbidden transition.
Fig 18. Ring-opening energy profile showing activation energies and the 2nd order disrotatory stationary point.
6. HYDROGENATION OF ETHENE BY DIIMIDE

The second reaction studied is the two hydrogen transfer between diimide and ethene to give ethane and nitrogen molecule. Since the particles transferred are actually protons, it's possible to observe tunnel effect during the reaction. \(^{(11)}\) This effect will not be considered in the present, nevertheless is important when rate constants should evaluate.

Proceeding as in the previous study, we look for the stationary points of character minimum, associated to the reactants and products. For this reason the stationary point is located and the Hessian matrix is calculated and diagonalized to confirm its minimum character. The resulting molecular geometries are given in Fig.19 and Fig. 20.

![Fig 19. Reactants: diimide and ethene](image)
Fig 20. Products: molecular nitrogen and ethane.

The $C_{2v}$ point group symmetry will be maintained during the course of the reaction.
6.1. Searching again for a transition state

The initial guess molecular geometry was restricted to preserve the C$_{2v}$ point group symmetry during the optimization to locate the transition state.

The located stationary point is that reported in Fig. 21. The analysis of the diagonalized Hessian matrix confirmed the transition state nature of this stationary point.

Fig 21. The geometry structure of the TS for the hydrogenation of ethane by diimide. The transition vector is also shown.

From the located TS the Intrinsic Reaction Coordinate (IRC) reaction path calculation was done to ensure that the TS joins the two minimums, ethane-diimide and ethane-nitrogen molecule. In Fig. 22 the energy profile following the IRC is shown.
Fig 22. Representation of the energy profile according to the Intrinsic Reaction Coordinate reaction path of the concerted hydrogenation of ethane by diimide.
6.2. Activation Energies

Finally, the reaction and activation energies are computed as the energy profile has been drawn. The values are reported in Table 2.

<table>
<thead>
<tr>
<th>Energies</th>
<th>Breakdown</th>
<th>Value (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ae_1$</td>
<td>$E_{TS structure} - E_{Ethene+Diimide}$</td>
<td>28.5</td>
</tr>
<tr>
<td>$Ae_2$</td>
<td>$E_{TS structure} - E_{Ethane+Nitrogen}$</td>
<td>114.4</td>
</tr>
<tr>
<td>Reaction energy</td>
<td>$E_{Ethene+Diimide} - E_{Ethane+Nitrogen}$</td>
<td>85.9</td>
</tr>
</tbody>
</table>

Table 2. The computed reaction and activation energies of the hydrogenation of ethene by diimide.

As can be seen, the products given by hydrogenation are much more stable than their double bond versions and so the energetic barrier to give that species is much lower.

Additionally, a comparison study can be done. In previous works, it has been observed those kind of hydrogenation reaction are faster with the presence of heteroatoms instead of between entirely carbon substances. \(^{(12)}\)

Exactly the same procedure has been followed in order to obtain optimized structures, TS and reaction path of a hydrogenation reaction between two ethene molecules to give ethane and ethyne.

After successful results an analogous energy profile can be built along with the activation energies of the process, and can be compared with the hydrogenation involving N atoms.
Table 3. The computed reaction and activation energies of the hydrogenation of ethene by another ethene.

<table>
<thead>
<tr>
<th>Energies</th>
<th>Breakdown</th>
<th>Value (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ae_3$</td>
<td>$E_{TSstructure} - E_{Ethane+Ethyne}$</td>
<td>73.0</td>
</tr>
<tr>
<td>$Ae_4$</td>
<td>$E_{TSstructure} - E_{Ethene+Ethene}$</td>
<td>87.6</td>
</tr>
<tr>
<td>Reaction energy 2</td>
<td>$E_{Ethane+Ethyne} - E_{Ethene+Ethene}$</td>
<td>14.6</td>
</tr>
</tbody>
</table>

It is more difficult for this reaction to reach the transition state, as its activation energies are higher than for the ethene/diimine system. This will lead to lower reaction rates too, as was observed in other works and commented before.

The reason after this behavior is inherently related to N atoms whose electronegativity is enough different with carbon and hydrogen to generate light charge densities which accelerate the transfer of the two hydrogen atoms. The reaction will be even faster if hydrogen peroxide is one of the reactants. \(^{(12)}\)
7. **Final Considerations**

The RHF method, or even so the MCSCF method does not give the exact solution of the Schrödinger equation describing the wave function. This type of wave function only reports the so-called strong electron correlation. With the inclusion of the weak or dynamical electron correlation one can reach the “exact energy” of the system. The reason why this important detail was not calculated before it is that RHF and MCSCF are standard methods but not for the dynamic one, where perturbational based methods are needed.

A new energy of every stationary point can be calculated introducing the order MPLVL=2 and using DZV basis set (owned by GAMESS). The resulting energy incorporates an important contribution of dynamical electron correlation, being the final energy value much more closer to the exact energy solution of the Schrödinger equation.

Since the 2\textsuperscript{nd} order stationary point associated to the disrotatoty process of cyclobutene ring opening does not have physical importance we do not report the correction energy.

In Table 4 and Table 5 we report the correlation energies corrections for the cyclobutene ring opening and the hydrogenation of ethane by diimide, respectively.
<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>HF energy</th>
<th>Exact energy</th>
<th>Correlation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g )-butadiene</td>
<td>-539.6</td>
<td>-551.7</td>
<td>-12.1</td>
</tr>
<tr>
<td>Cyclobutene</td>
<td>-522.6</td>
<td>-532.1</td>
<td>-9.5</td>
</tr>
<tr>
<td>Conrotatory TS</td>
<td>-492.1</td>
<td>-501.0</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

Tab 4. Correlation energy corrections of ring-opening reaction.

* All energies are given in Kcal/mol.

Activation energies have suffered very little change (\( A_e_1 = 114.4 \) Kcal/mol before vs 111.9 Kcal/mol after and \( A_e_2 = 28.5 \) Kcal/mol before vs 31.9 after).

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>HF energy</th>
<th>Exact energy</th>
<th>Correlation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene + Diimide</td>
<td>-580.1</td>
<td>-597.5</td>
<td>-17.4</td>
</tr>
<tr>
<td>Ethane + Nitrogen</td>
<td>-666.0</td>
<td>-677.5</td>
<td>-11.5</td>
</tr>
<tr>
<td>TS structure</td>
<td>-551.6</td>
<td>-565.6</td>
<td>-14.0</td>
</tr>
</tbody>
</table>

Tab 5. Correlation energy corrections of hydrogenation reaction.

* All energies are given in Kcal/mol.

Those activation energies also have suffered very little variation (\( A_e_1 = 58.9 \) Kcal/mol before vs 62.1 Kcal/mol after and \( A_e_2 = 41.9 \) Kcal/mol before vs 43.0 after).
Zero point energies have been calculated as well, and are shown in Table 5. It is the lowest possible energy that a quantum physical system may have, the ground state.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Zero point energy (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-butadiene</td>
<td>57.8</td>
</tr>
<tr>
<td>Cyclobutene</td>
<td>58.7</td>
</tr>
<tr>
<td>Ethene + Diimide</td>
<td>54.7</td>
</tr>
<tr>
<td>Ethane + Nitrogen</td>
<td>53.9</td>
</tr>
</tbody>
</table>
8. CONCLUSIONS

- The ring opening of cyclobutene disrotatory process is forbidden by Woodward and Hoffmann and Deward Zimmermann rules, so it is much less probable than the conrotatory one.

- Is that so, constraints and more powerful computation methods are needed to find its maximum stationary point of the energy profile.

- At the ground state, the conrotatory process has a transition state, but the disrotatory motion has a second order stationary point instead. This means a reaction path exists only for the conrotatory mechanism. Maybe it exists for the disrotatory one at excited states.

- A group transfer reaction involving hydrogen atoms in hydrocarbon organic compounds is faster if there are heteroatoms included. This is because they cause a charge delocalization which stabilizes the transition structure. As the value of the electronegativity of the heteroatom increases, it also increases the stabilization effect and reaction rate.

- The correlation energy provides the correction to the Schrödinger equation answer provided by HF and post-HF methods to give the exact solution of the non-relativistic Schrödinger equation.
9. References and Notes

7. Gregory A. Natanson, Bruce C. Garret, Thanh N., Truong, Tomi Joseph, Donald G. Truhlar; The Definition of Reaction Coordinates for Reaction Path Dynamics; accepted 22 January 1991.
Building the energy profiles for electrocyclic and pericyclic organic reactions