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Mayer's chemical energy component analysis as a tool to identify the factors determining the shapes of potential surfaces of chemical reactions

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Energy partitioning is a way to convert the information obtained in numerical quantum chemistry to chemically interpretable, qualitative or semiquantitative information. Such methods may be useful in studying how interactions develop in chemical reactions. In this work we test how one can gain meaningful new information about a chemically reactive system using the mono- and diatomic energy terms calculated with two energy-partitioning schemes developed by István Mayer: the chemical energy component analysis, CECA, and the scheme named E2. In our test reactions a H-atom is transferred from an HR molecule to a methyl radical, CH_3 + H′R → CH_3H′ + R, with R = H, CH_3, $C(CH_3)_3$ and OH. The diatomic energy component associated with the forming bond is zero in the reactant limit and gradually becomes attractive when one moves on the minimum energy path toward the product limit; that of the breaking bond simultaneously changes from attractive to zero. Their sum displays a maximum which appears to be a contributor to the potential barrier. The dominant term in the increase/decrease of the diatomic energy components is exchange, which characterizes the strength of covalent interactions. Its change indicates that the build-up of one covalent interaction does not completely cover the energy needed to break the other. Energy component analysis identified a continuous repulsion between the atoms from/to which the H-atom is transferred, which is also a major contributor to the potential barrier. The origin of this interaction is the repulsion involving overlap densities. Overlap repulsion is also the main contributor to the steric repulsion involving the spectator atoms. Energy component analysis performed on wave functions calculated with different basis sets yields the same semiquantitative information. The CECA method is a promising source of information for studying the change of the nature of interactions during chemical reactions, and can help identify general rules. The diatomic energy components derived with the E2 scheme are close in magnitude to bond dissociation energies and change smoothly with molecular geometry, but they cannot be decomposed into contributions like overlap and exchange.

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Introduction

When the Born–Oppenheimer approximation applies, the kinetics and dynamics of elementary chemical reactions are determined by the topography, the shape of a single potential energy surface (PES).[1] Numerous qualitative rules have accumulated on the correlation of various features of the PES and the dynamics of reactions, the most widely known being the Polanyi rules[2] and their extension.[3] While the advanced methods of *ab initio* quantum chemistry enable us to calculate essentially accurate potential energies at individual molecular geometries, the actual shape of a PES can only be explored by systematic mapping and eventually by fitting the entire potential energy–molecular geometry function. While the PES calculated this way can serve as solid ground for reaction dynamics calculations, from the *ab initio* formalism essentially nothing can be learnt about general qualitative features such as the change of the shape of the PES in a series of reactions, except by calculating the PES for each individual system. Derivation of general rules requires the calculation of numerous systems and an analysis similar to evaluation of experimental data.

In the search for the factors governing the shape of potential energy surfaces, valuable information can be provided by methods designed to extract qualitative or semiquantitative information from *ab initio* wave functions. In the latter field, continuous efforts have been made to translate the information

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obtained in quantum chemistry, which is based on the physicist's picture of a molecule: an ensemble of electrons and atomic nuclei, to the chemist's picture, a set of atoms connected by bonds. For example, a method was developed by Mayer[4] to extract bond order and valence indices from *ab initio* wave functions. Calculation of Mayer's *ab initio* bond order indices,[5–7] along the minimum energy paths (MEPs) of simple atom-transfer reactions showed how the bonds develop and at what stage they are at the potential barrier and that the sum of the bond orders is *approximately* unity.[8,9] Calculation of bond orders also allowed identification of concerted but asynchronous reactions.[10,11]

Another direction to extract chemically useful information from *ab initio* calculations is energy partitioning, pursued since as early as 1967.[12] The idea is that the terms constituting the total energy in an *ab initio* calculation are arranged into atomic and diatomic contributions according to various principles. The problem is similar to population analysis where charge is to be assigned to atoms. An enjoyable overview of the arising "philosophical" aspects can be found in ref. 13. In semiempirical methods based on the neglect of differential overlap, the molecular energy can be exactly written as a sum of mono- and diatomic contributions.[14] However, in routine *ab initio* methods based on atomic orbital basis sets where an atom can be considered to be represented by the orbitals centred on it ("Hilbert-space analysis"), the decomposition is not straightforward, because 3- and 4-center integrals appear in the Hamiltonian. (Note that when atoms are identified by the regions around their nuclei in the physical 3D space, such as in Bader's Quantum Theory of Atoms in Molecules theory (QTAIM)[15] or the fuzzy-atom approach,[16–18] partitioning the *ab initio* molecular energy into one- and diatomic terms is natural and accurate.[19–21]) Since atoms do not appear in the Schrödinger equation of a molecule, there is no unique way to assign energy contributions to atoms, bonds *etc.* As a result, many different methods have been developed for this purpose (see ref. 22 and references therein), each having its own advantages and disadvantages.

A promising energy partitioning scheme called chemical energy component analysis (CECA) was proposed by Mayer[6,7,23–26] to assign energy contributions to atoms and atom pairs. This *a posteriori* scheme relies on the Hartree–Fock energy expression, because the independent-particle model is quite transparent for chemists and offers the possibility of organizing its terms into intraatomic and atom-atom blocks. Although accurate energies can only be obtained by supplementing the Hartree–Fock level of theory by calculating the correlation energy, the decomposition of the latter is not straightforward. In addition, Mayer observed that decomposition of correlation energy seems not to carry significant new chemical insight as compared to what one can get from the HF calculation.[24] The CECA method follows the principles of Mayer's chemical Hamiltonian approach.[27] Namely, the energy contributions expressed in terms of the atomic orbitals in the basis set are decomposed into atomic and diatomic terms by projecting the integrals involving the basis functions onto the subspaces consisting of orbitals centred on the atoms and on atom pairs. It can be shown that the CECA scheme is consistent with Mulliken population analysis and the definition of the Mayer bond order.[24,28,29] It is also valuable that the diatomic energy contributions can be further decomposed into terms coming from different physical interactions,[30,31] namely, exchange, electrostatic and overlap contributions.

The purpose of this paper is to explore how one can utilize the changes of these contributions in a chemically reacting system to gain some useful information that helps one to characterize reactions. In this work we focus on simple atom-transfer reactions and calculate the energy contributions along the MEP of the

$$CH_3 + H'R \rightarrow CH_3H' + R$$

reactions with R = H, CH_3, $C(CH_3)_3$ and OH (reactions (R1), (R2), (R3) and (R4), respectively) and analyse the behaviour of the mono- and diatomic energy components as well as that of the different physical diatomic contributions and compare it with that of bond orders.

We also investigate how much the results depend on the basis set used in the calculations. It must be emphasized that we are after qualitative features, to which practising applied quantum chemists who use methods such as any form of population analysis or QTAIM are accustomed: the numbers one gets are meaningful only for comparative purposes, because we are interested in properties that are not expectation values of operators whose calculation is well defined in quantum mechanics.

Computational details

Mayer proposed several energy partitioning schemes. Here we consider the original CECA scheme[23] and the scheme named E2.[24,32] Without repeating the quite extensive derivations presented in, for example, ref. 7 and 23–25, we briefly mention only that both schemes are designed for Hilbert-space analysis and use projection operators corresponding to individual atoms to arrange the terms in the Hartree–Fock energy expression into mono- and diatomic contributions. The E2 scheme is one of the "exact" ones derived systematically based on atomic projection operators,[33] in which the energy components exactly sum up to the total energy of the molecule:

$$E = \sum_{A} E_A + \sum_{A<B} E_{AB} \quad (1)$$

(hence '*E*' in the name E2). In the CECA scheme the decomposition is approximate, because the three- and four-centre integrals are replaced by their one- and two-centre parts by projecting out the non-diatomic contributions, but the deviation from the accurate total energy is generally minor and can be neglected without loss of chemical information. (Tests have shown that the neglected terms are not systematic and they do not change the conclusions presented below.) The main difference between the two schemes is that the kinetic energy is considered intra-atomic in CECA and partly diatomic in the exact E2 scheme. Formally, in the CECA scheme all kinetic energy terms are assigned to the monoatomic components,

while in E2 those coming from orbitals on different atoms are moved to the diatomic energy components, a consequence of which is that the diatomic energy contributions are less attractive in the latter (remember that the kinetic energy is always positive). We also calculated the exchange and overlap contributions to the diatomic terms available in CECA,[30,31] which will be shown to be informative.

Mayer made his codes freely available[34] (see also ref. 35 and 36), which allows one to perform energy component analysis starting from the formatted checkpoint files provided by the Gaussian suite of programs. For generating the latter, in the present work we used the Gaussian 09 version. In our test system, reaction (R1) is qualitatively correctly described by single-determinant wave functions, and the *ab initio* calculations were performed at the unrestricted Hartree–Fock level. The balanced 6-31G** basis set was used in the majority of calculations. We tested also the 6-311++G** and the STO-3G basis sets. Unfortunately, Mayer's code was set up to handle basis sets containing only s, p and d orbitals and it is not possible to use basis sets which contain f, g, *etc.* orbitals. For this reason, we were not able to investigate more sophisticated basis sets. We also tested the minimal STO-3G basis set because it proved to provide very reasonable results in the studies of the behaviour of bond order and valence indices in chemically reacting systems.[8–10,37]

The detailed protocol used in the generation of energy partitioning data is described in the SI.

Results and discussion

Qualitative picture: bond orders along the MEP

In our test reaction, a H–H bond is broken and a C–H bond is formed. The reaction is slightly exoergic because the forming C–H bond is somewhat stronger than the H–H bond. The change of chemical state of atoms in reactions can be well characterized by Mayer's bond order and valence indices. To set the scene, we plotted in Fig. 1 the bond order indices for the breaking of H′–H″ and the forming of C–H′ bonds against the reaction coordinate, the distance along the MEP. In addition, the free-valence index (the part of the atom's valence that is not involved in bonds) is also shown for the carbon and the H″ atoms. These atoms were selected because the C-atom is initially a radical centre in the reactant CH_3 radical and builds a new bond in the reaction, while the H″ atom is involved in complementary changes. The bond order and valence indices in stable compounds are rarely as close to unity as those obtained at the UHF/6-31G** level for the C–H bond in methane (0.978) and in the methyl radical (0.962) and the H–H bond in the H_2 molecule. According to our experience, in more complicated molecules one can generally find bond order indices deviating from the formal integer bond orders by as much as 0.2 or even more. Yet, the variation of the bond orders as a function of important parameters, such as the position along the minimum energy path or in a series of reactions is informative.

As expected, one can see in Fig. 1 that the bond order of the breaking H′–H″ bond smoothly decreases from close to unity to

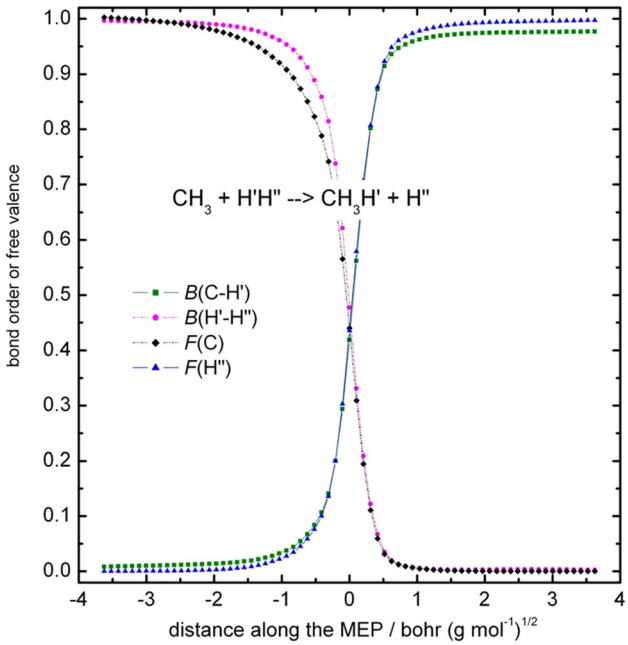

Fig. 1 Bond orders of the breaking and forming bonds and the free valences of the terminal atoms along the minimum energy path of reaction (R1) calculated at the UHF/6-31G** level.

essentially zero while that of the forming C–H′ bond changes in the opposite way. The bond orders approximately complement each other: their sum is close to unity along the MEP (bond order is approximately "conserved"). The change of the free-valence indices is in agreement with that of the bond orders: at the beginning of the reaction, the free valence of the carbon atom is essentially unity and decreases to zero, while the H-atom donor H″ atom initially involved in a single bond becomes free. Remarkable is how close the bond-order and free-valence curves run.

Diatomic energy components of the total energy

There is no physical basis that dictates how to separate the total energy of a molecule into mono- and diatomic components. While chemical intuition does not tell you what to think about the monoatomic contributions, the diatomic ones in chemical reactions can certainly be expected to reflect the bond rupture and formation. In Fig. 2 the contributions from the C–H′, H′–H″ and C–H″ atom pairs (which occasionally will be referred to as "bonds") are shown along the MEP for reaction (R1), together with the total-energy profile (the analogous figures for reactions (R2)–(R4) are very similar, see Fig. S1–S3 in the SI). The contribution of the breaking H′–H″ bond is attractive in the reactant limit and converges to zero when the bond breaks. The C–H′ energy component changes from zero to a level that is somewhat lower than the initial H′–H″ component. There are several notable features in the figure. First, the magnitude of the energy components is rather large in the reactant and product limits: for the reactant H_2 molecule it is about $-0.5\ E_h$, more than 300 kcal mol^{-1}; that for the C–H′ bond in the product is an additional 93mE_h, 58 kcal mol^{-1} lower. Compared with the

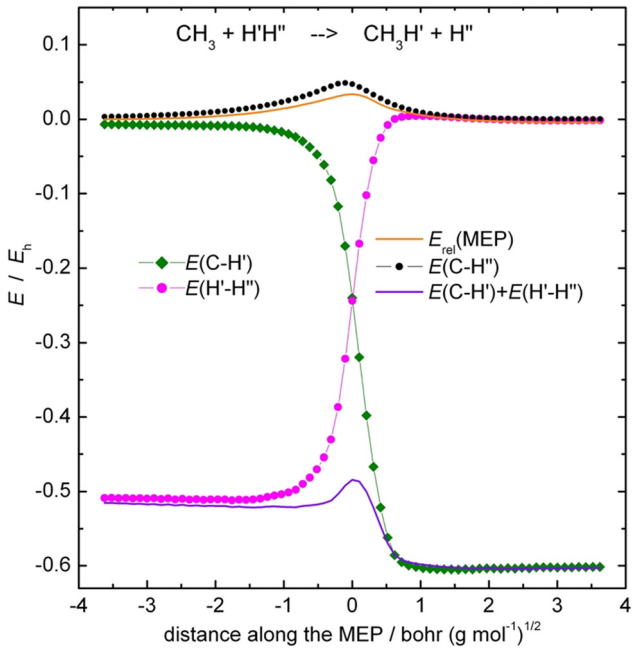

Fig. 2 Diatomic energy contributions of atom pairs involved in reaction (R1) as a function of the position along the minimum energy path, obtained with the CECA method from the UHF/6-31G** wave function.

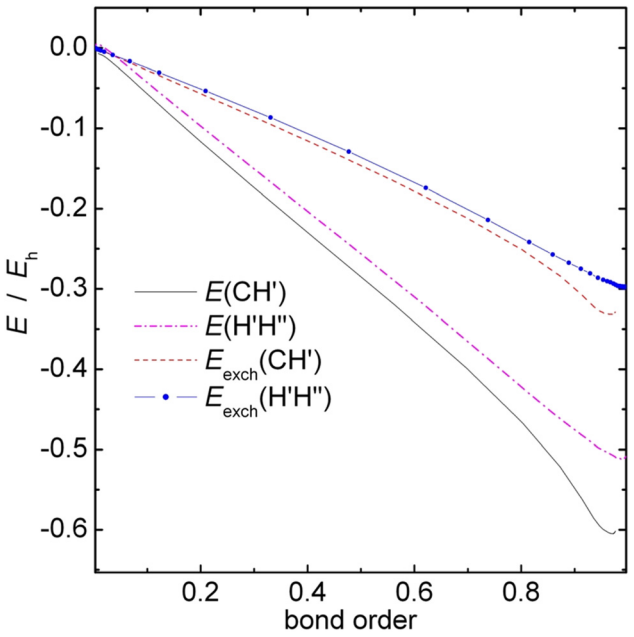

Fig. 3 Correlation between the diatomic energy contributions and the bond orders of the breaking and forming bonds along the minimum energy path of reaction (R1) obtained from the UHF/6-31G** wave function with the CECA method (lower two curves) and the corresponding exchange contributions (upper two curves).

corresponding bond dissociation energies, in absolute value both energy components are about three times larger. Such a deviation is huge for a seasoned quantum chemist, yet the shape of the diatomic energy component plots is qualitatively correct: the C–H′ bond, being a bit stronger, should have a larger limiting bonding contribution. The total electronic energy difference between the reactants and products is $-4.1\mathrm{m}E_\mathrm{h}$ = -2.6 kcal mol^{-1}, quite close to the experimental -0.6 kcal mol^{-1}, so the 58 kcal mol^{-1} difference between the H′–H″ and C–H′ diatomic energy components is really exaggerated. The discrepancy between dissociation energies and diatomic energy components was observed by Mayer[24,25] and prompted him to search for other schemes such as E2. Note also that the diatomic energy components constitute a minor part of the total energy of the system, which is in the order of $40E_\mathrm{h}$ for reaction (R1) and much larger for (R2)–(R4). Considering this comparison, the CECA diatomic components can be considered to be almost "on the chemical scale". At this point we do not intend to comment on this issue because our purpose now is to see not the magnitude of the CECA energy components but whether their changes can help one understand various factors related to chemical reactions.

In Fig. 2 one can also see that the shape of the C–H′ and H′–H″ energy-contribution curves is very similar to those of the bond order changes seen in Fig. 1. This suggests a strong correlation between the bond order of a bond and the corresponding diatomic energy contribution. Fig. 3 shows the C–H′ and H′–H″ energy components as a function of the corresponding bond order: the correlation is surprisingly close to linear. (The analogous curves we obtained with the other two basis sets are very close to those in Fig. 3.) This reminds one of the bond-energy–bond-order (BEBO) method[38–40] designed by Johnston and co-workers, which is used to calculate potential energy curves along the MEP for atom-transfer reactions of the

$$\mathrm{A + BC \rightarrow AB + C}$$

type. The central quantity in the method is the "chemists' bond order" proposed by Pauling and co-workers,[41–43] which is an exponential function of the extension of the bond with respect to the single bond:

$$n_\mathrm{XY} = \exp(-(R_\mathrm{XY} - R_\mathrm{XY,s})/0.28\ \text{Å})$$

where $R_\mathrm{XY,s}$ is the length of the single X–Y bond and R_XY is the bond length at the given point along the MEP. The correlation was found to hold also for Mayer bond orders.[26,44]

In the BEBO method, the coordinates of the MEP in terms of the lengths R_XY of the breaking and forming bonds were obtained from the conservation of bond order,

$$n_\mathrm{AB} + n_\mathrm{BC} = 1$$

The energy at a point along the MEP was also obtained from the bond order: the contribution of the (partial) breaking or forming bond was assumed to be a bond-order-dependent fraction of the bond (dissociation) energy of the corresponding single bond, $E_\mathrm{XY,s}$:

$$E_\mathrm{XY} = n_\mathrm{XY}^p E_\mathrm{XY,s}.$$

The calculated bond energy–bond order correlation shown in Fig. 3 suggests that the exponent p in the power function (originally handled as an empirical parameter) could be close to unity.

One can make some further interesting observations concerning Fig. 2. For reaction (R1) the changes of the diatomic contributions of the breaking and forming bonds along the MEP do not exactly compensate each other. In Fig. 2 we also plotted their sum (violet line), the change of which is not monotonic. Instead, it passes a maximum when both bonds are about halfway between the reactant and product limits, very close to the location of the potential maximum along the MEP. This seems to be one of the factors responsible for the appearance of the potential maximum along the MEP (and the saddle point on the full-dimensional PES). However, there are many other contributions to the total energy that can also influence the shape of the PES. Remarkable is the diatomic component associated with the ''end-atoms'', the carbon and the H″ atom, which is a pure repulsive interaction, shown in Fig. 2 as black diamonds. The repulsion is negligible when the two atoms are far from each other but is appreciable when they are the closest to each other, which coincides with the location of the potential maximum. It is remarkable that the bond order index of the remote C–H″ ''bond'' is pretty large, almost 0.05 at the top of the potential barrier. Bond orders of this magnitude are generally interpreted as a temporal formation of a weak bond. However, the C–H″ diatomic energy component is repulsive, which means that the bond order index cannot distinguish weak attraction from weak repulsion. This points at the advantage of energy partitioning with respect to bond orders: it does differentiate the attractive from repulsive interactions.

Interestingly, in the BEBO method a repulsive end-atom interaction was also included as a contributor to the total energy. It was assumed to arise because in the simplest bonding picture the spins of the electrons located on the two end-atoms should be parallel, and for this reason, the phenomenon was called ''triplet repulsion''. The repulsion between the end-atoms is expected to be the largest near the saddle point where the distance between them is the smallest. The C–H″ diatomic chemical energy component in Fig. 2 could be the *ab initio* manifestation of this repulsion. We return to its physical origin later.

It is informative to compare the changes in the different H–H as well as the C–H diatomic energy components which are shown in Fig. 4 and 5, respectively. Among the H–H interactions, in the reaction only the H′–H″ energy component achieves a large magnitude (visible in Fig. 2); the components associated with the (non-chemical) interactions involving the spectator H atoms are much smaller. Fig. 4 is zoomed-in on these energy components. The spectator H atoms (distinguished as H from H′ and H″) display appreciable repulsion (E(H–H)) between each other all the way along the MEP. The change between the reactant and product limits is small, and the direction of change depends on the basis set.

When the H″ atom is very far from the spectator H atoms of the methyl group (which happens both at the reactant and the product limit), the H–H″ energy contributions are negligible. When they get temporarily close, CECA shows some weak attraction between them, not exceeding 2.3 mE_h. More interesting is the interaction of the H′ atom involved in the reaction

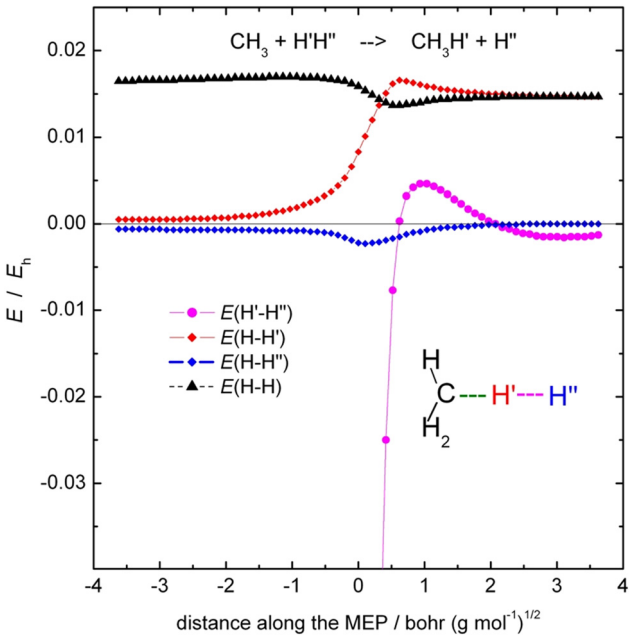

Fig. 4 The diatomic CECA energy components corresponding to the hydrogen–hydrogen atom pairs along the MEP of reaction (R1) obtained at the UHF/6-31G** level.

with the H atoms of the methyl group: at the reactant limit the associated energy component is zero because the H′ atom is far. During the reaction the H–H′ and the H–H″ energy curves bifurcate and the H–H′ energy component increases and, as expected, merges the E(H–H) curve at the product limit (where the H′ atom is equivalent to the other three methyl H atoms).

We discuss the behaviour of the diatomic contributions for the example of the somewhat more complicated reaction (R3), for which the diatomic energy components corresponding to all carbon–hydrogen as well as carbon–carbon atom pairs in the reaction centre are plotted in Fig. 5. Here well visible is the temporary repulsion between the two ''end''-atoms, C and C′ analogous to that seen in Fig. 2 for reaction (R1). The C atom of the reactant methyl and C″ atoms in the *t*-Bu group also slightly repel each other. The C′–C″ interaction in the C′(C″H$_3$)$_3$ group becomes stronger in the radical than in iso-butane. Similarly, the C–H interaction is stronger in the CH_3 radical than in the CH_4 molecule. Remarkable is that the end-points of the C–H interaction lines for reactions (R1)–(R3) almost perfectly coincide, indicating remarkable transferability. The analogue of Fig. 5 for reaction (R1) is shown as Fig. S4 of the SI.

Monoatomic CECA energy components

The majority of the total energy of the CH_3–H–R systems comes from the monoatomic terms, among which the overwhelming contribution is that of the carbon or oxygen atoms. Since the magnitude of the monoatomic terms is very different, it seems reasonable to shift them to a common scale by subtracting from them the energy of the respective free atom. This difference is just the energy that is needed to move the free atom into

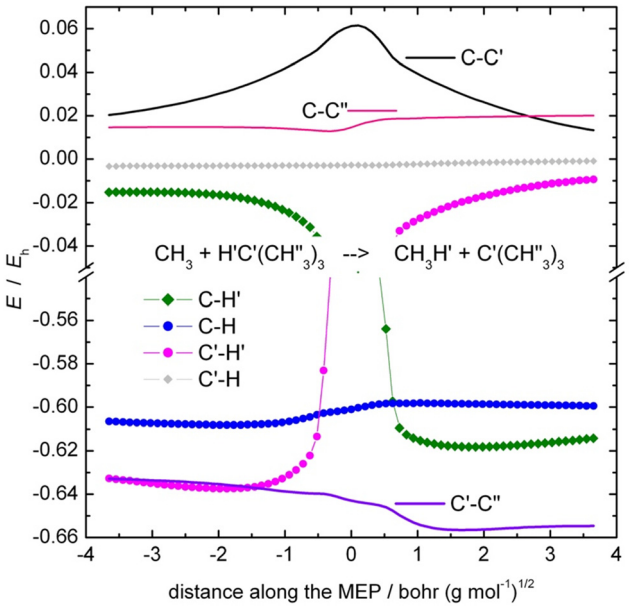

Fig. 5 The diatomic CECA energy components corresponding to the carbon–hydrogen and carbon–carbon atom pairs along the MEP of reaction (R3) obtained at the UHF/6-31G** level.

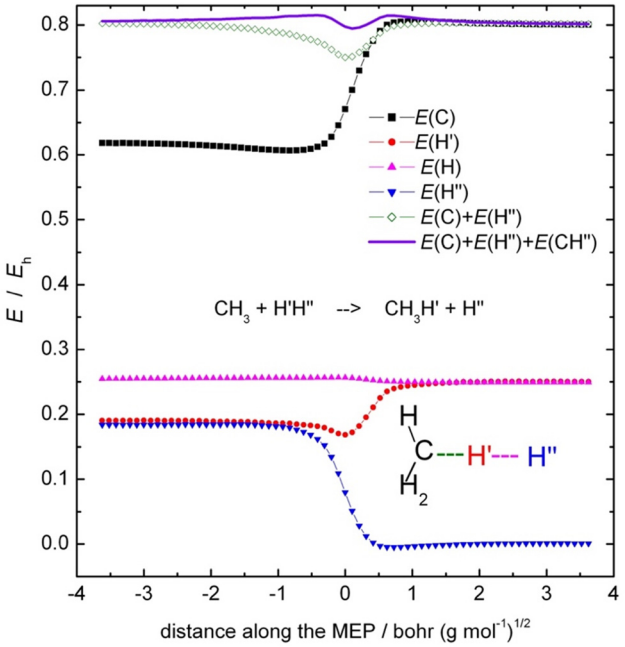

Fig. 6 The "crude" promotion energy, defined here as the monoatomic CECA energy component relative to the energy of the respective free atoms for the four nonidentical atoms along the MEP of reaction (R1), obtained at the UHF/6-31G** level. See the text for details.

the state in the molecule (here on the way from reactants to products), *i.e.* a "crude"† promotion energy.[45] We calculated the reference energy of the free atoms with the UHF Hamiltonian, which was used throughout the calculations.‡ The promotion energies for the four non-equivalent atoms in reaction (R1) are plotted in Fig. 6 and those for reaction (R3) are shown in Fig. S5 in the SI. In agreement with the concept of promotion energy, they are positive: the calculated monoatomic energy components are less negative than the energy of the respective free atom.

Among the monoatomic energy components, those corresponding to the two end-atoms change the most along the MEP. The promotion energy of the carbon atom increases from a lower level in the methyl radical to the about 0.2 E_h higher level in methane, suggesting it needs to be promoted further. Simultaneously, the bond the carbon atom is involved in strengthens, the C–H′ diatomic component changes from zero to about ~ -0.6 E_h, virtually covering the extra promotion energy of the carbon. Similar compensatory changes involve the H″ atom: its monoatomic component decreases from about -0.3 E_h in H_2 to the value of about -0.5 E_h of the free hydrogen atom (the respective promotion energies being ~ 0.2 and 0 E_h) as it gets "de-promoted" and the energy "released" can be considered to contribute to that needed to "break" the H′–H″ bond whose (diatomic) energy component changes from the binding -0.5 E_h toward zero.§ The monoatomic contributions (and the promotion energies) from the spectator atoms were found to be essentially constant.

Fig. 6 also shows the sum of the E(C) and E(H″) monoatomic energy components to demonstrate how much they compensate each other. In contrast to the shape of the E(C–H′) + E(C–H″) line in Fig. 2, here one can see a minimum (green diamonds) in the neighbourhood of the saddle point. To estimate the overall contribution of the three atoms involved in the reaction by adding the component of the H′ atom, one obtains a curve (violet solid line) that seems to mirror that of the E(C–H′) + E(C–H″) line. These conclusions also hold for reactions (R2)–(R4). This suggests that the monoatomic terms do not induce the formation of the potential barrier, instead, they reduce the height of the barrier observed on the sum of the key diatomic terms. This can be seen if one plots the sum of all diatomic contributions together with the sum of all monoatomic ones, as well as the sum of all mono- and diatomic energy components (see Fig. 7). This means that according to CECA, the barrier is mostly formed because (1) the diatomic contributions from the forming and breaking bonds do not compensate each

† Note that Mayer invested serious effort into defining the promotion energy, and showed that the precise calculation of the promotion energy should reflect the distortion of the (effective) atomic orbitals upon bond formation, but it should not include the bonding, charge transfer and delocalization effects. Since the monoatomic energy components do include the latter, the difference of the monoatomic terms and the energy of the free atom corresponds to a crude promotion energy which we refer to simply as "promotion energy."

‡ Mayer used the ROHF Hamiltonian when he studied promotion in closed-shell molecules. In our case the UHF/6-31G** energy of the C-atom is 3.7 mE_h lower than what the ROHF/6-31G** calculation provides (the deviation is hardly visible when the promotion energy is plotted).

§ A technical note: for H″ at the product limit very small negative promotion energies can be observed whose magnitude is in the mE_h range. We think that this can be considered as "white noise", just as occasional negative bond orders observed in other systems.

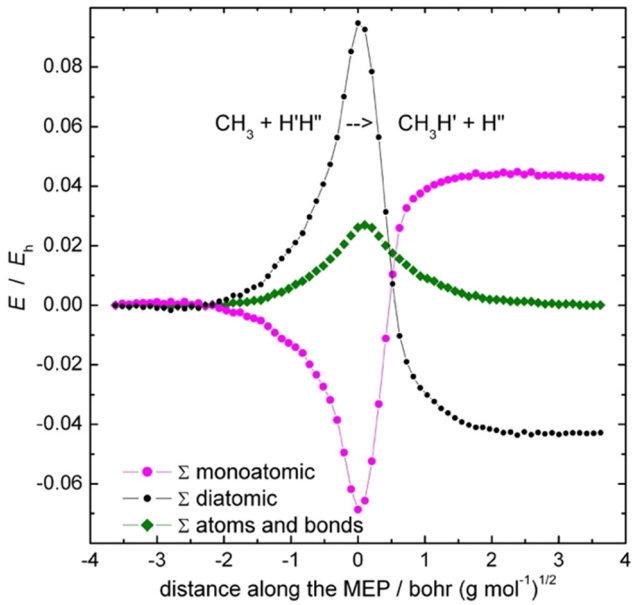

Fig. 7 The change of the sum of all monoatomic, the sum of all diatomic, and the sum of all contributions along the MEP of reaction (R1) calculated with the CECA scheme from the UHF/6-31G** wave functions. All curves are shifted to a common origin.

other so that their sum displays a maximum, (2) the repulsion between the end-atoms reinforces this effect and (3) the monoatomic terms counteract somewhat.

Basis set dependence

All the features discussed so far can be observed with the two other basis sets we studied. The details of the dependence of various contributions on the location along the MEP are sometimes different, but the overall picture is the same in each case. In Fig. S6a–c available in the SI, all monoatomic and the major diatomic contributions for reaction (R1) are plotted for the STO-3G, 6-31G** and 6-311++G** basis sets. The energy curves obtained with the two split-valence basis sets look very similar, while those calculated with the STO-3G basis set seem to display somewhat less structure. The minimal basis was found to be very useful in the calculation of bond order and valence indices; the STO-3G and 6-31G** indices generally agree very well. The observation that energy partitioning using STO-3G seems to be less informative is a new piece of information and further experience is needed to see how general this is.

Exchange, overlap and electrostatic contributions to the diatomic energy components

Further insight can be gained about the factors influencing the shape of the potential energy surfaces of reactions by investigating the contributions with different physical origins. According to Hamza and Mayer,[30,31,46] diatomic electrostatic, exchange and overlap terms can be separated from the Hartree–Fock expression of the total energy of a molecule, rewritten in atomic and diatomic terms. In the first, the nucleus–electron and the electron distribution–electron distribution Coulomb terms are collected. The exchange contributions come from the exchange part of the Hartree–Fock energy expression, which is related to the ''Fermi hole'', summarizing the effects arising because the electronic wave function must be antisymmetric with respect to interchanging any two electrons. The exchange terms are closely related to bond order indices and both to electron sharing between atoms, and if they are large, the interaction between the two atoms has a significant covalent part. The exchange contribution is expected to be attractive, because it is closely related to the correlation of the fluctuation of charge densities on the atoms involved in the bond.[47] The fluctuation in this context is to be meant in a statistical sense, referring to the statistical interpretation of the wave function. When the correlation of fluctuations (the measure of which is the bond order index[47]) is large, then the charge depletion on one atom is associated with charge abundance on the other, which gives rise to attraction. This picture is accurate in diatomic molecules, but when an atom is in a polyatomic molecule, then the charge density fluctuation on it cannot be unequivocally decomposed into terms associated with the atoms it is bonded to, which is probably the origin of the generally negligibly small positive exchange contributions occasionally found between remote atoms.

The ''overlap'' contributions contain energy integrals involving pairs of atomic orbitals centred on different atoms. The ''overlap densities'' contracted to atoms are generally relatively large and positive when the two atoms are covalently bonded and negative when they are not (because their ''shells'' are ''closed'', *i.e.*, saturated). In the former case, the diatomic overlap contributions are relatively large attractive terms, while in the latter case they are positive due to ''overlap repulsion'', representing some kind of steric repulsion.

The exchange, overlap and electrostatic contributions obtained for the minimum energy path of reaction (R1) are collected in Fig. 8a for the carbon–hydrogen, and in Fig. 8b for the hydrogen–hydrogen energy components. Comparison with Fig. 2 shows that the exchange contribution to the strongest interactions, the C–H′, H′–H″ and the spectator C–H bonds accounts for about one half of the corresponding CECA energy components.

In Fig. 9 the exchange contributions for the breaking and forming bonds are shown in the style of Fig. 2 for reaction (R1) (and in Fig. S7 for reaction (R3)). They change in a way very similar to the corresponding diatomic CECA contributions. Their sum also displays a barrier whose size is the same as that of the CECA diatomic barrier. This suggests that one of the main contributors to the appearance of the potential barrier is that the variation of the exchange contributions corresponding to the breaking and forming bonds do not exactly balance each other, as if the degree of covalency were smaller in the region of the potential barrier.

One can see in Fig. 8 that the overlapping contributions are roughly 50% less than the exchange, and the electrostatic ones are about one fourth of the corresponding exchange contributions. Similar observations have been made concerning reactions (R2)–(R4). The bottom panel in Fig. 8b shows the interactions between the non-bonded hydrogen atoms. Although these interactions are weak, one can still see that the energy

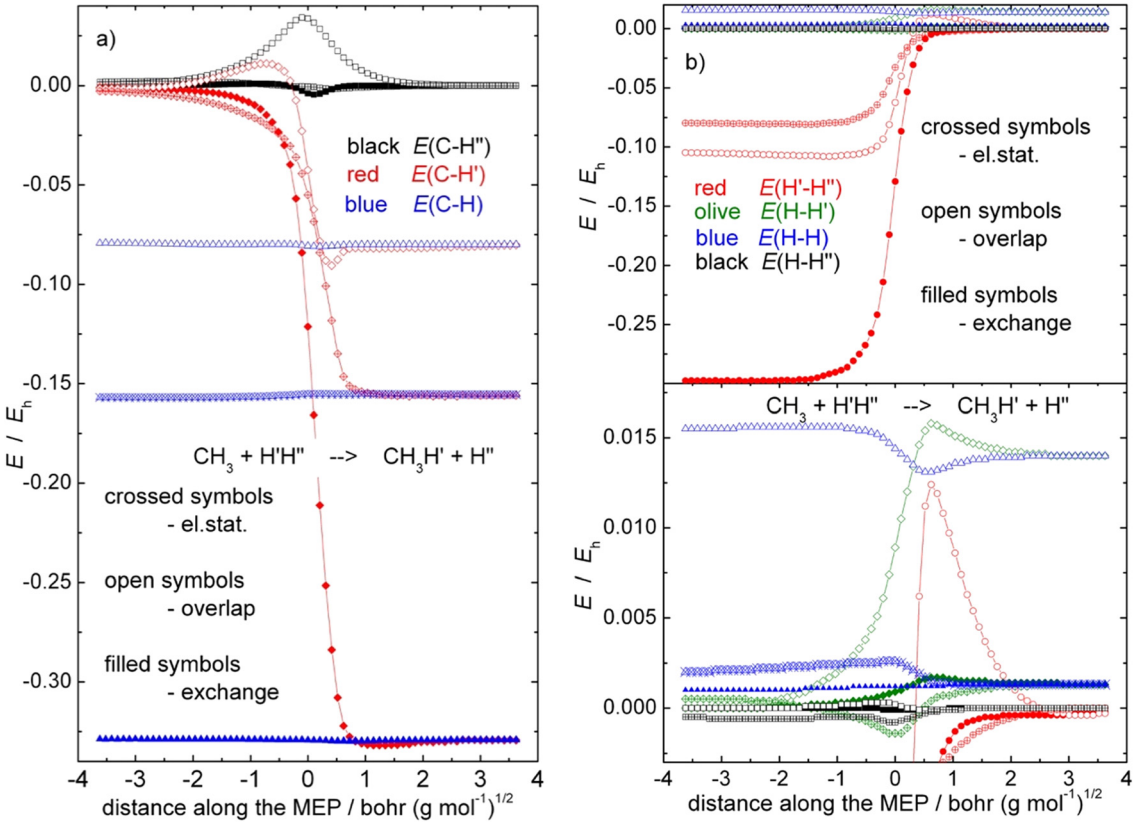

Fig. 8 The CECA exchange- (closed symbols), overlap- (open symbols) and electrostatic (crossed symbols) contributions to the diatomic energy components corresponding to the carbon–hydrogen (a) and the hydrogen–hydrogen (b) atom pairs in reaction (R1) obtained from the UHF/6-31G** wave functions. The bottom panel in Fig. 8b is zoomed-in on the 0–15 mE_h region.

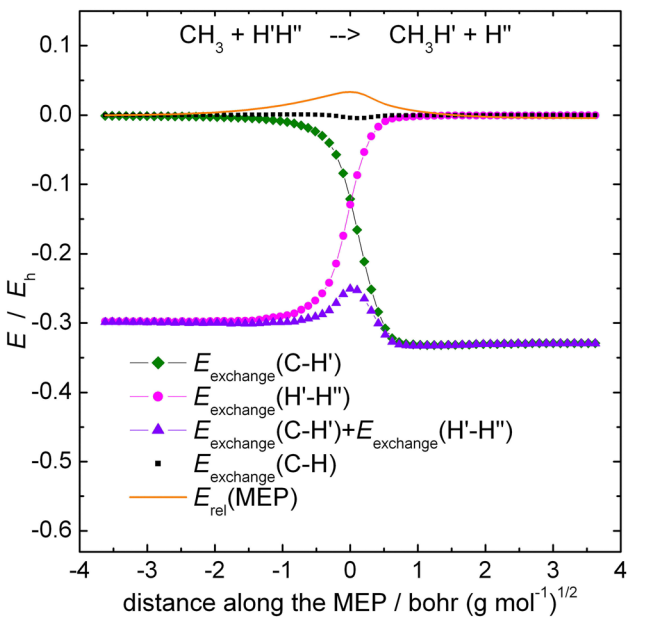

Fig. 9 The change of the diatomic exchange contributions of the breaking and forming bonds and their sum along the MEP of reaction (R1), calculated at the UHF/6-31G** level. The energy scale is kept the same as in Fig. 2.

components properly characterize the way the interactions change along the MEP. In particular, one can see that the H–H spectator–spectator interaction is essentially pure overlap repulsion. In general, overlap repulsion occurs between non-bonded atoms and seem to constitute the energetic origin of steric repulsion in organic molecules. This is manifested in the relatively large H–H overlap terms. The repulsion between the spectator and the reactive H′ atom is negligible at the reactant limit when the H′ atom is far from the methyl radical, but in the reaction it increases to match that between the other H–H pairs in the product methane.

An interesting observation can be made in Fig. 8a concerning the C–H″ interaction: the repulsion between the end-atoms seen in Fig. 2 is essentially pure overlap repulsion, similar to that between the H-atoms in CH_3 and CH_4. The same can be seen in Fig. S1–S3 for reactions (R2)–(R4). Since this term is one of the major contributors to the formation of the potential barrier, it seemed worthwhile exploring whether this repulsion is related to the spin densities on the end-atoms. To this end we repeated the energy partitioning for the negatively charged closed-shell CH_3–H–H ion at the geometries along the MEP of the uncharged open-shell system. According to the atomic charges, the Hartree–Fock description corresponds to the

$$CH_3^- + H_2 \rightarrow CH_4 + H^-$$

proton-transfer reaction. The carbon and the H″ atom are both negatively charged all along the MEP of reaction (R1). Obviously, the importance of the electrostatic terms grows significantly with the introduction of the extra electron (see Fig. S8a–c). Because of the slow decay of Coulombic forces with distance, the energy contributions decrease much slower from the barrier towards the reactant/product limits. The most remarkable difference between the uncharged and anionic systems concerns the interaction between the C and H″ atoms that are both partially negatively charged: the electrostatic contribution increases by three orders of magnitude to around 100 mE_h at the maximum. At the same time, the change of the exchange contribution remains small, about 10 mE_h. The overlap contribution remains repulsive and increases, but only by about 50% with respect to the uncharged system (at the peak from about 35 to about 52 mE_h). It is not surprising that due to the appearance of the negative charge, electrostatic end-atom repulsion becomes huge, but it is remarkable that the overlap contribution is increased only slightly. If it were associated with the triplet repulsion as assumed in the 1960s, in the closed-shell anionic system it should disappear. More probable is the origin of the repulsion, both in the presence and in the absence of the extra electron, is the regular overlap repulsion between not chemically bonded but closely-spaced atoms.

One can conclude that among the factors responsible for the appearance of the potential barrier, the most important is that the bond rupture and formation do not balance each other exactly, which is reflected in the changes of the exchange contributions. The other important contribution is the overlap repulsion between the end-atoms which is large when the latter are close.

In Fig. 3 we plotted the bond-order dependence of the exchange contributions for comparison. Similar to the CECA energy contributions, the correlation is quite close to linear. This is in a sense not surprising, since the bond order formulas can be derived with the same abstract formalism from the exchange density as the diatomic exchange component from the Hartree–Fock energy formula.[24]

Comparison with the E2 energy partitioning scheme

Mayer proposed two exact energy decomposition schemes. We explored the behaviour of the energy partitioning according to the E2 scheme, which can also be performed by the APOST-4 code available online.[34] Mayer demonstrated several times that the advantage of this scheme is that it produces diatomic energy components that are closer to bond energies at equilibrium geometries. However, he found that, against the expectation, they tend to increase when a bond is stretched.[24,25] This might prevent it from providing meaningful information for reactions where the lengths of bonds change extensively.

The energy partitioning results obtained along the MEP of reaction (R1) with the E2 and CECA schemes from the same UHF/6-31G** wave function are compared in Fig. 10a–c. The analogous results obtained for reaction (R3) are shown in Fig. S9. The most conspicuous in the plots is that the general shape of the diatomic energy component curves is the same with both methods, the C–H′ component decreases from zero, and simultaneously the H′–H″ term increases along the MEP, which is reassuring. On the other hand, the relative magnitudes of the mono- and diatomic energy components are completely different. With CECA one gets about three times more attractive diatomic terms than with E2 (Fig. 10a) but, with one exception, less negative monoatomic terms. This is in agreement with Mayer's observations.

In contrast to CECA, the E2 diatomic energies almost exactly match the H′–H″ and C–H′ bond dissociation energies. The reduction of the magnitude of the diatomic terms occurring when one switches from CECA to E2 is necessarily compensated by the increase of the absolute value of the monoatomic terms. For example, the carbon monoatomic term in the reactant limit is −37.0626 E_h with CECA and −37.6559 E_h with E2, while the respective numbers in the product limit are −36.8802 E_h and −37.6890 E_h, the E2 values being more than 0.5 mE_h more negative. The crude promotion energy for the C atom obtained with the E2 scheme (with the UHF/6-31G** energy of a free carbon atom, −37.6809 E_h) is negative, −8.1 mE_h in the product limit, the same as the RHF/6-31G** result for CH_4. Note that the E2 crude promotion energy for the O-atom in water and the N-atom in ammonia is also negative at the RHF/6-31G** level. Even though the crude promotion energy is contaminated by terms beyond the mere distortion of the orbitals when an atom enters into the state in the molecule, consistently negative crude promotion energies may indicate that the monoatomic term derived according to the E2 scheme is too negative.

The raw CECA and E2 monoatomic terms are compared in Fig. 10b. With the exception of the H″ atom in the product limit (where it must converge to the free hydrogen-atom), the E2 monoatomic energy components are more negative by 0.2 to 0.3 mE_h than what CECA produces, thus the monoatomic energy changes roughly compensate for the reduction of the magnitude of the diatomic terms. The hydrogen monoatomic terms calculated with E2 are very close to each other, and do not seem to follow any recognizable tendency. In addition, the inset in Fig. 10b shows that in the strong interaction region some wiggles can be seen (see also the diatomic terms in Fig. 10a), but we found no obvious reason why the changes should not be smooth in this region.

In Fig. 10c the sums of all diatomic terms, of all monoatomic terms and of all energy components obtained with the CECA as well as the E2 scheme are plotted. The overall result of the regrouping of kinetic energy from the atomic to the diatomic components is that the summed monoatomic and the summed diatomic terms change places and characters. The sum of the diatomic terms obtained with CECA is very attractive and display a maximum, which is dominated by the incomplete balance of the components corresponding to the breaking and forming bonds, capped by the C–H″ repulsion. The summed CECA monoatomic terms are much less attractive and pass through a minimum at the saddle point of the PES. The opposite is obtained with the E2 scheme, where the monoatomic terms are more negative (they are even below the CECA diatomic contributions) and have a maximum and *vice versa*.

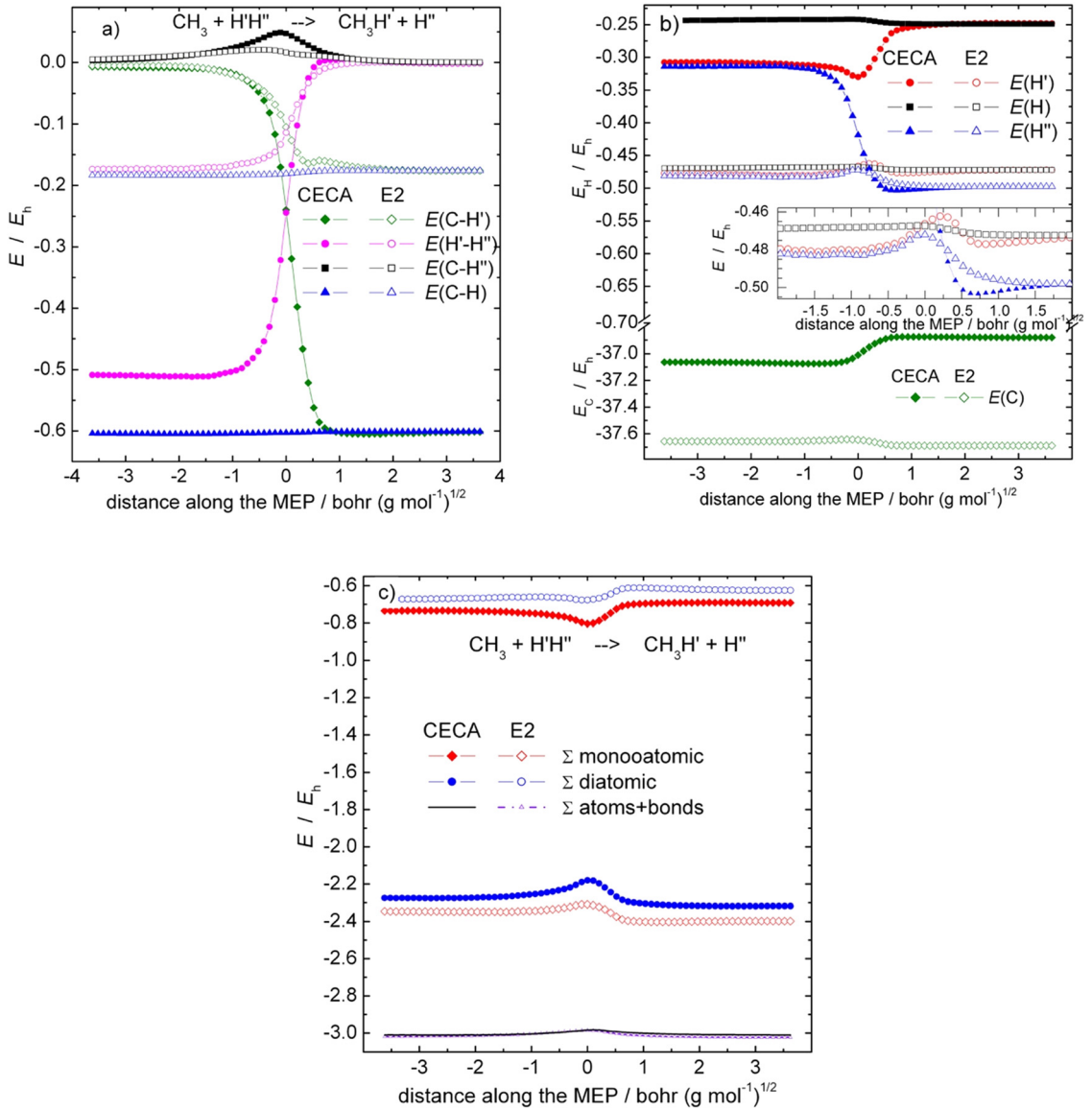

Fig. 10 The (a) diatomic, (b) monoatomic energy components and (c) sum of all monoatomic and of all diatomic energy components as well as the sum of all energy components along the MEP of reaction (R1) derived according to the CECA (closed symbols) and E2 (open symbols) schemes from the UHF/6-31G** wave functions. In panel (b) note the break and scale change on the energy axis.

Virtually, together with moving a part of the kinetic energy from the monoatomic in CECA to diatomic in E2, the barrier is also moved but from the diatomic to the monatomic part. The sum of all terms (the black lines in Fig. 10c) is in both cases the same, except for some deviations arising because the CECA energy sum deviates somewhat from the HF energy, due to the approximations involved in this scheme.

Overall, the E2 scheme seems to provide in absolute value smaller diatomic and larger monoatomic energy components than the CECA method. The behaviour of the E2 diatomic components change along the MEP qualitatively according to the expectation, without any obvious sign of counter-intuitive global behaviour with changing molecular geometries. This contrasts the unreasonable bond length dependence of the E2 diatomic contributions Mayer worried about. The price of having diatomic energy components in E2 that are close to bond dissociation energies is the interchange of the magnitude and shape E2 mono- and diatomic contributions with respect to their CECA counterparts. It is not favourable that the E2 monoatomic energy contributions do not change smoothly in the region of the potential maximum along the MEP, while the curves produced by the CECA method are smooth and one can interpret the directions of their changes. Another weak point of the E2 method is that the diatomic energy contributions cannot be decomposed into terms of different physical origin.

Conclusions

At the end of the 19th century, the temperature dependence of chemical reactions was known to be described by the Arrhenius

equation. Arrhenius surmised that, to be able to react, the reactants need to have energy that surpasses a threshold, which was called the activation energy. The origin of this threshold was obscure. By performing approximate quantum mechanical calculations on the simplest chemical reaction, H + H_2, Eyring and Polányi[48] showed that the energy requirement comes from quantum mechanics: there is a potential energy barrier on the potential energy surface of a reaction that is determined by the geometry-dependent energy eigenvalue of the electronic Schrödinger equation. Nowadays, the calculation of essentially accurate potential energy surfaces is routine, but it produces numbers that do not provide chemical insight. Qualitative pictures are conceptually important, and numerous methods, among them, partitioning a molecule's energy into atomic and diatomic components have been worked out for interpretive purposes.

In this work we evaluated two energy partitioning schemes developed by Mayer, and found that they offer the possibility of getting further, chemically meaningful insight into the origin of the potential barrier in atom-transfer reactions.

We studied four CH_3–H′–R type reactions ((R1)–(R4), see above) from the same class as H + H_2, using Mayer's chemical energy component analysis (CECA) and the E2 scheme. Particular attention was paid to the diatomic energy components that are devoted to describing the strength of the interaction, and the exchange, overlap and electrostatic contributions they can be decomposed into.

According to the CECA method, along the minimum energy path of such reactions the diatomic energy component corresponding to the breaking H′–H, H′–C or H′–O bond is strongly attractive, and along the minimum energy path it gradually tends to zero. Simultaneously, the energy component corresponding to the forming C–H′ bond decreases from zero to the level in the product methane molecule. The changes of these two components are simultaneous but their sum displays a maximum at the position along the minimum energy path where the total energy has its maximum, virtually being one of the major factors responsible for the formation of the potential barrier.

The leading contribution to the diatomic energy terms for covalently bonded atom pairs comes from exchange, which characterizes the degree of electron sharing, and the strength of the covalent bond. The exchange contributions change along the MEP parallel to the overall diatomic component of the corresponding bond. Importantly, their sum displays a maximum around the location of the potential barrier, which proves to be the major contributor to the appearance of the maximum of all diatomic components and of the maximum of the total energy along the MEP. A possible interpretation is that the attraction corresponding to the covalent interactions is reduced when both the forming and breaking bonds are partially broken, virtually, the rupture of one is not completely compensated for by the formation of the other.

Among the other contributions to the diatomic energy components, the electrostatic ones seem to be balanced along the MEP, thus they do not to play a major role in the "formation" of the barrier. More relevant proved to be the diatomic overlap contributions. These describe the repulsive interaction arising from the overlap of atomic orbitals centred on different atoms as well as from two-electron repulsion integrals involving "overlap densities", products of orbitals centred on two different atoms. Such terms arise between not directly bonded atoms, corresponding to what chemists consider as steric repulsion. Particularly important is the overlap repulsion between the atoms between which the H′ atom is transferred. This interaction is the largest when these two "end-atoms" are close, which happens at geometries where the potential barrier is located. This repulsive maximum seems to be another important contributor to the formation of the potential barrier for reactions of this kind. It is worth mentioning that this repulsion is not related to the spin densities on the end-atoms: the maximum remains there after adding an electron to close the open shell.

Evaluation of the E2 energy-partitioning scheme suggests that the diatomic energy components in the reactant and product limits are very close to the bond dissociation energies, and they change reasonably along the MEP, but the price is that the role and magnitude of the monoatomic terms are large.

The interesting insight into the factors the CECA energy decomposition scheme provides on atom-transfer reactions suggests that the method is appropriate for the analysis of factors determining the shapes of potential surfaces of chemical reactions and deserves the attention of people interested in comparing different kinds of reactions and in the classification of reactive systems according to semiquantitative information.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information: (1) calculation protocol; (2) Fig. S1 with the basis set dependence of energy components; (3) Fig. S2 with energy components for the negatively charged CH_3HH system; (4) the energy components for reaction (R1). See DOI: https://doi.org/10.1039/d5cp04854k.

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