Density-Functional Based Determination of the CH$_3$-CH$_4$ Hydrogen Exchange Reaction Barrier

Mark R. Pederson
Complex Systems Theory Branch
Naval Research Laboratory, Washington D.C. 20375
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Due to the overbinding that is inherent in existing local approximations to the density-functional formalism, certain reaction energies have not been accessible. Since the generalized gradient approximation significantly decreases the overbinding, prospects for density-functional-based reaction dynamics are promising. Results on the generalized-gradient based determination of the CH$_3$-CH$_4$ hydrogen exchange reaction are presented. Including all Born-Oppenheimer effects an energy barrier of 9.5 kcal/Mole is found which is a very significant improvement over the local-density approximation.

I. INTRODUCTION

Over the past two or three decades quantum-mechanical methods based on the Hohenberg-Kohn density-functional theory have steadily evolved in scope, complexity, numerical precision and intrinsic accuracy. A representative albeit incomplete list of some of the successes related to gaussian-orbital density-functional applications include the accurate prediction of molecular geometries and the accurate determination of molecular vibrational frequencies. Specifically, in Ref. [1], the local density approximation (LDA) was used to accurately calculate geometries of H$_2$, C$_2$, C$_2$H, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_6$H$_6$, CH$_3$C$_2$H and CH$_4$ and in Ref. [2], Andzelm et al showed that the LDA would lead to accurate geometries and vibrational modes for approximately ten other well characterized molecules in the same size regime. Handy et al performed exceedingly careful calculations on the benzene molecule and showed that density-functional based frequencies within a local approximation are particularly encouraging since they are more accurate than the MP2 frequencies. More recently independent calculations by Quong, Pederson and Feldman and Wang, Ho and Wang have shown that the local-density-approximation reproduces the experimentally observed vibrational energies of the C$_{60}$ molecule to approximately 15-30 cm$^{-1}$.

Another interesting success of the density-functional theory that is relevant to this paper is the work by Salahub et al and more recently Pederson et al and Handy et al on the methylene molecule. While the local-density-approximation underestimates the singlet-triplet energy splitting, it leads to the correct ordering and accurately describes the linear-bent energy barrier of 5.3 kcal/mole. Another example of an energy barrier that is accurately determined within the LDA is the eclipsed-staggered energy barrier of 2.8 kcal/mole in ethane. These barriers are qualitatively similar since the bondlengths and connectivities are essentially unperturbed during the distortion. However, in a reaction where bonds are broken and reformed, the overbinding in LDA may seriously limit the accuracy of the reaction surface. For example, using a highly converged basis set, consisting of a total of 65 even-tempered gaussian functions on each carbon and hydrogen atom, we have found that atomization energies of nine hydrocarbon molecules are overestimated by approximately 0.7 eV per bond within the local density approximation. Since a typical reaction energy is approximately 0.5-1.0 eV, the need for better accuracy is readily apparent. Recently, Perdew and Wang and Becke have developed the generalized gradient approximation (GGA) which has led to vast improvements in describing the bonding associated with light atoms (at least). For example, using geometries and densities from the local-density-approximation, we find the average error in GGA bond energies to be 0.1 eV for the hydrocarbon molecules discussed in the first paragraph. These energies have been compared by properly accounting for effects due to zero-point energies. Also, Salahub et al and Handy et al have shown that the methylene singlet-triplet energy splitting is accurately determined with gradient corrected energy functionals. Due to the improvements realized from the generalized gradient approximation, the possibility for obtaining reaction energies within a density-functional framework appears fruitful and some researchers have begun looking at reactions within the generalized gradient approximation. For example, Hammer et al have studied the polarization and charge transfer that occurs during H$_2$ dissociation on the aluminum (110) surface.

Since the ability to calculate reaction surfaces quickly, precisely and with chemical accuracy are prerequisite to a first-principles understanding of reactive processes and catalysis, and since the density-functional formulation is intrinsically faster than conventional quantum-chemistry schemes, this point is investigated here. The density-functional based calculations presented here are numeri-
ically precise, converged with respect to basis set, and include relaxation of the core electrons. In this letter results on the well-understood hydrogen exchange reaction that occurs between a methyl [CH₃] radical and methane [CH₄] molecule are discussed. The experimental barrier is well characterized and is known to be about 14 kcal/mole. [16] This reaction barrier has been studied within several quantum-chemical techniques by several researchers as well. [7]-[9]

Many books on the subject of reaction dynamics exist [21] and a recent discussion of how to calculate reaction dynamics from a reactive surface is due to Truhlar and Gordon [22]. Here, the interest is in determining how accurate a density-functional based reaction surface may be and assessing the merits of the generalized gradient approximation as compared to the local density approximation. With respect to algorithmic issues, even in the favorable case where intuition identifies a small set (M) of active nuclear coordinates participating in a chemical reaction, the quantum-mechanical determination of the pathway over a reaction barrier requires approximately L^M (with L=5-10) times as many electronic-structure calculations than are required to determine the energy of an N-atom system. Since scaling with system size is already a problem for density-functional electronic-structure-based geometrical optimizations and ab initio quantum-chemical methods, the need for intrinsic speed, chemical intuition and novel algorithmic approaches to such problems is clear. The relative speed and more favorable scaling associated with density-functional based techniques is very attractive for these studies.

II. COMPUTATIONAL AND THEORETICAL DETAILS

To perform the calculations discussed here, the all-electron, full-potential gaussian-orbital cluster code [23,24] has been used. As discussed in Ref. [22], the potential is calculated analytically on a variational integration mesh which allows for the calculation of the electronic structure, total energies and Pulay-Corrected Hellmann-Feynman [24,26] forces with any desired numerical precision. More recently, we have incorporated the calculation of vibrational modes into the cluster codes. This is accomplished by calculating the Hellmann-Feynman-Pulay forces at the equilibrium geometry and neighboring points and using a finite-differencing algorithm. Except where explicitly stated, moderately large contracted gaussian-orbital basis sets, with gaussian decay parameters of Huzinaga [27], have been used. On each carbon atom, I have used ten bare gaussians (α=0.1146 to 4232.61) [27] to construct a basis set of 3 s-type (1 of which have an r^2 prefactor), 1×3=3 p-type, and 1×5=5 d-type functions. On each hydrogen atom, I have used six bare gaussians [27] to construct a basis set of 3 s-type (1 of which have an r^2 prefactor), 1×3=3 p-type, and 1×5=5 d-type functions. This amounts to a total of 133 single or contracted gaussian orbitals on the seven atom complex. This basis set has been developed over many years of local-density-based simulations on hydrocarbon molecules, diamond, fullerene molecules and tubules and is accurate. [10] As described in detail below, we have further tested the precision of these results by using a huge basis set of a total of 404 even-tempered gaussian functions distributed over the complex, and by using this basis we determined that the basis set discrepancies are exceedingly small. The geometrical optimizations that were required for these calculations utilized the conjugate-gradient algorithm and the simulations proceeded until the forces were less than 0.01 eV/Å. All the results discussed here have been performed with the spin-polarized density functionals.

III. RESULTS AND DISCUSSION

Pictured in Fig. 1 is a schematic diagram on how the hydrogen exchange reaction proceeds. As discussed in the figure caption, the reaction proceeds from configuration A to configuration C by allowing the hydrogen atoms to relax as the two carbon atoms come close together. The intrabond hydrogen overcomes a small barrier at the transition state (Configuration B) and then relaxes downhill to configuration C.

Pictured in the lower panel of Fig. 2 is the energy surface, as calculated within the local-density-approximation (LDA). The minimum energy as a function of C-C separation is shown in Fig. 2. This corresponds to the energy of the seven-atom complex as it travels along the lowest energy reaction path in Fig. 2. As argued qualitatively above, the LDA hydrogen-exchange reaction energy is significantly suppressed due to the tendency to overestimate bond strengths. The final result is that LDA leads to a classical energy barrier of approximately 0.7 kcal/mole which is a factor of 20 smaller than experiment. The reactive surface has also been determined within the framework of the generalized gradient approximation of Perdew et al. [11,12] Using the techniques discussed in Ref. [11] the GGA reactive surface has been determined and is shown in the upper panel of Fig. 2. The minimum LDA and GGA energies as a function of the C-C separation (i.e. all hydrogenic degrees of freedom are relaxed) are compared in Fig. 2. Comparison of the reactive surfaces and pathways show that the LDA and GGA lead to qualitatively different results. Most importantly, the GGA leads to a classical reaction barrier of 8.7 kcal/mole which is reasonably close to the experimentally known barrier of 14 kcal/mole. [16] Also evident is that the LDA predicts a significantly more compact reactive complex. Within LDA, the lowest geometry of the CH₄-CH₃ complex is bound by 2.8 kcal/mole and has a
C-C separation of approximately 3.27 Å. In contrast, within GGA, the lowest geometry is only bound by 0.7 kcal/mole and has a C-C separation of approximately 4.1 Å. It is difficult to determine from experiment, whether the LDA or GGA result is more accurate for this complex. However, in this regime, the interactions are not expected to be too different from the CH4-CH4 Van der Waals interactions which are well understood. For methane-methane interactions, the carbon atoms are separated by 4.28 Å and are bound by 0.3 kcal/mole. For energies of this size, the effects of zero-point motion must be taken into account to accurately determine the enthalpy (rather than energy) of formation. To determine the effects due to zero-point motion, the vibrational frequencies of isolated CH3 and CH4 molecules and of the bound CH3-CH4 complex have been calculated. For methane, two triply degenerate vibrational modes of 1231 and 3082 cm\(^{-1}\), a doubly degenerate mode at 1473 cm\(^{-1}\) and a nondegenerate mode at 2961 cm\(^{-1}\) are found. These agree favorably with the experimental modes of 1306, 3020, 1526 and 2914 cm\(^{-1}\) respectively. For the methyl-radical the vibrational modes within LDA are found to be 537, 3037 (nondegenerate), 1345, and 3158 (doubly degenerate) cm\(^{-1}\). By subtracting the zero-point energies of both the bound and isolated systems the enthalpy of formation for the CH3-CH4 complex is found to be closer to 0.4 kcal/mole. The fact that the zero-point energy is larger for the complex than for the isolated modes can be qualitatively explained by noting that for the isolated molecules there are a total of twelve zero-energy modes. However, when the two systems complex, only six zero-energy modes survive and six additional positive energy modes emerge. Assuming that the original non-zero modes do not significantly soften, an overall increase of the zero-point motion results.

Based on experience gained in many calculations on hydrocarbon molecules, diamond and fullerene-based systems, the energetics obtained with the original basis set are expected to be very accurate. To further address this point, I have used a huge set of gaussians to ensure the accuracy of these calculations. On each carbon atom I have placed eleven even-tempered s-gaussians with \(\alpha=0.1\) to 5000, nine even-tempered p-type gaussian sets with \(\alpha=0.1\) to 574.349, and four even-tempered d-type cartesian gaussian sets with \(\alpha=0.1\) to 2.56857. On each hydrogen atom I have placed seven even-tempered s-type gaussians with \(\alpha=0.08\) to 138.889, five even-tempered p-type gaussian sets with \(\alpha=0.08\) to 11.556, and three even-tempered d-type gaussian sets with \(\alpha=0.08\) to 0.9615. Since the cartesian polynomials in front of d-type gaussians can also lead to a spherical function of the form \(r^2\exp(-\alpha r^2)\), there are actually 15 and 10 spherical functions on each carbon and hydrogen respectively. Taking account of the degeneracies of the p and d sets this leads to 404 gaussians in the basis set. The calculation of the energy along the reaction path with this basis has been repeated and the changes are indeed small with the GGA and LDA barriers increasing by 0.6 kcal/mole. It is noted that this does not suggest that a larger basis necessarily increases the barrier and is probably more indicative of the maximum change expected. For energy scales this small, one should also consider that a small change in transition state geometry could partially offset this small increase. Regardless, the results of this paragraph show that the basis set used in these calculations is sufficiently accurate to quantitatively determine the improvements that are realized when a gradient-corrected functional is used in place of a local functional.

As is well known, the simulation of a reaction requires the calculation of a classical reaction surface and the additional ability to treat the nuclei quantum-mechanically. Methods for such simulations include path-integral techniques or the techniques discussed in Ref. [21]. Here the interest is in qualitatively determining the scale of the nuclear quantum mechanical effects and in assessing the intrinsic numerical precision that is possible. The vibrational modes have been calculated at the density-functional-based transition state which is realized by separating the two C-C atoms by 2.677 Å, placing a H atom midway between the two carbon atoms and then tying off each of the C atoms by 3 hydrogens with C-H bond distances of 1.103 Å (configuration B in Fig. 4). Our geometry is in good agreement with the geometry of Musgrave et al. who find a C-C separation of 2.72 Å and a C-H separation of 1.089 Å. It is well known that at this transition state one expects six zero-energy modes, fourteen positive frequencies and one imaginary frequency. If the translational and rotational degrees of freedom are projected out of the hessian matrix prior to diagonalization, the imaginary and low-energy modes are found to be at 883i, 52, 280, 282, 507, 643 and 646 cm\(^{-1}\). If the rotational and translational degrees of freedom are not explicitly removed prior to diagonalization, the zero point motion of the complex changes by only 0.12 kcal/mole but the results from the more accurate projected treatment of the hessian matrix are used here.

As noted above and pictured in Fig. 4 the GGA energy of formation required to prepare this state is 8.7-9.4 kcal/mole depending on whether the energy is measured with respect to the separated molecules (8.7) or the reactive complex (9.4). Recently, Fan and Ziegler [29,30] have performed similar calculations on the CH3-CH4 hydrogen exchange reaction within local and nonlocal density-functional formalisms. In good accord with the results of this paper, they find a classical barrier of 11.7 kcal/mole with a gradient corrected functional and 1.9 kcal/mole for a local functional. The 1-2 kcal/mole deviation between their results and the results here is significantly smaller than the deviations between different quantum-chemical methods and should therefore be considered as good agreement since
the numerical methods used were quite different. Ziegler and Fan use Slater-type orbitals, the frozen-core approximation, least-square-fits for the solution of Poisson’s equation, Vosko-Wilk-Nusair LDA, Perdew’s nonlocal correlation, Becke’s non-local exchange, and Boerrigter’s numerical integration scheme. In contrast, in this work I use Gaussian-type orbitals, relaxed cores, analytic solution of Poisson’s equation, Perdew-Zunger LDA, the Perdew 91 non-local exchange and correlation, and the numerical variational integration mesh of Pederson and Jackson. The calculations here and those of Ziegler et al. use spin-polarized functionals throughout. Given all the numerical and formal differences, it appears that there is good agreement between the philosophically identical density-functional based methods.

The reaction barrier for the CH$_4$-CH$_3$ hydrogen transfer reaction has been studied with quantum chemical techniques as well and is known to be about 14 kcal/mole experimentally. Several researchers have used various quantum-chemistry algorithms to determine the barrier and have obtained estimates in the range of 17-35 kcal/mole. While many more calculations on other molecular systems are required before drawing definitive conclusions, it appears that the generalized-gradient approximation to the density-functional theory is yielding results that are as accurate as traditional quantum-chemical techniques for this reaction. Further from the point of view of scaling with system size, the density-functional framework is undoubtedly more advantageous. Hybrid methods, which employ fast density-functional methods for pathway determination and more traditional calculations for the final determination of energetics might also be useful.

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FIG. 1. Schematic diagram of reaction pathway followed during the hydrogen exchange reaction. The lowest-energy pathway between configuration A and C is realized by allowing the two carbon atoms to come within 2.677 Å from one another at the transition state (configuration B). The remaining six hydrogen atoms relax to accommodate the environment mandated by the C-C separation and intrabond H location. At the transition state configuration (B), there is one imaginary root and the classical equilibrium geometry is determined by allowing the C-C atoms to separate and the active hydrogen to relax off center.

FIG. 2. The LDA (a) and GGA (b) reaction surfaces. The y-axis corresponds to the separation between the two carbon atoms and the x-axis corresponds to the placement of the active hydrogen atom with respect to the bond center. In contrast to LDA, which predicts a vanishingly small energy barrier, the GGA predicts a classical barrier of 8.7-9.4 kcal/mole depending on whether the energy is measured with respect to isolated or weakly bound reactant states. Also illustrated by the wire-mesh plots is the need to determine the energy, interatomic forces and vibrational modes on a two-dimensional Born-Oppenheimer surface of variable convexity which enhances the computational cost by approximately $10^2$ over a simple geometrical optimization for the same system.

FIG. 3. The minimum energy of the CH$_3$-CH$_4$ complex as a function of the C-C separation. This potential curve was generated by allowing all hydrogenic and electronic degrees of freedom to relax with the constrained C-C separation and was derived by the lowest energy paths between the separated reactant states and the transition state. The geometries are schematically presented at the top of the figure. In comparison to GGA, the LDA predicts a very compact and more strongly bound reactive complex. As is also shown in Fig. 2, the energy of the transition state is significantly improved by the addition of GGA. The horizontal line at the minimum of the GGA potential represents the excess zero-point motion that the complex appropriates upon congregation. Including zero-point effects, the GGA predicts that the complex is bound by approximately 0.4 kcal/mole. The insert shows the energy along the entire reaction path.
Fig. 3 - M. R. Pederson

![Graph showing energy vs. C-C separation in Angstroms for GGA and LSD energies.](image)