



# A quantum informational approach for dissecting chemical reactions



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## ABSTRACT

We present a conceptionally different approach to dissect bond-formation processes in metal-driven catalysis using concepts from quantum information theory. Our method uses the entanglement and correlation among molecular orbitals to analyze changes in electronic structure that accompany chemical processes. As a proof-of-principle example, the evolution of nickel–ethene bond-formation is dissected, which allows us to monitor the interplay of back-bonding and  $\pi$ -donation along the reaction coordinate. Furthermore, the reaction pathway of nickel–ethene complexation is analyzed using quantum chemistry methods, revealing the presence of a transition state. Our study supports the crucial role of metal-to-ligand back-donation in the bond-forming process of nickel–ethene.

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## 1. Introduction

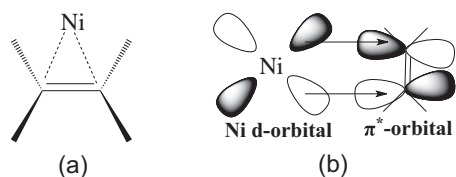
Nickel–ethene complexes have long been of interest in the field of organometallic chemistry. They have been used as localized models to study the chemisorption of ethene onto the surface of transition metals [1–4]. The formation of a metal–olefin bond is made possible through the process of back-donation, in which nickel  $d$ -orbitals push electrons into the  $\pi^*$ -orbitals of ethene (see Figure 1b). This transfer of electrons destabilizes the carbon–carbon double bond, allowing the complex to be used as a homogeneous catalyst for thermally forbidden processes, specifically [2 + 2] cycloaddition reactions which yield cyclobutane derivatives [5,6].

The back-bonding phenomenon is commonly understood using molecular orbital diagrams, where filled metal  $d$ -orbitals interact with empty ligand  $\pi^*$ -orbitals. This donation of electrons from metal to ligand causes a flow of electron density towards the ligands. Molecular orbital theory, however, restricts the understanding of back-donation to a rather simplified and solely qualitative picture, hampering a detailed analysis of metal–ligand bond-formation processes and the specific role of back-bonding therein. To obtain a trustworthy qualitative picture, one first must perform accurate computational studies, and then post-process the complicated information encoded in the correlated wavefunction in a way that facilitates chemical interpretation. Popular analysis

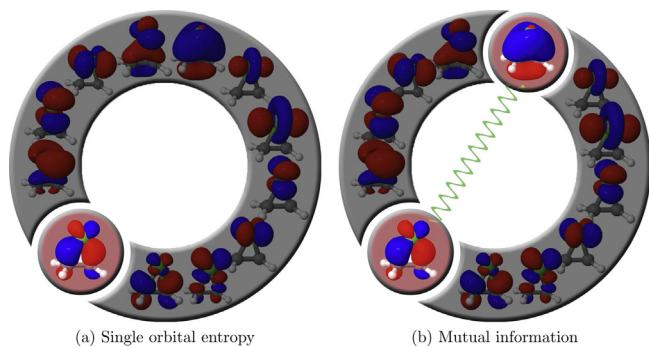
tools in quantum chemistry are, for instance, population analysis, spin and electron density distributions, and local spins. We have recently developed a new approach, where concepts from quantum information theory are used to provide insight into molecular electronic structure and the changes in electronic structure that accompany chemical processes. Specifically, the quantum entanglement of, and between, orbitals [7] can be used to extract bond orders [8,9], dissect weak interactions [10], and analyze orbital interactions [11,12]. Importantly, this approach can be reliably applied whenever the electronic wavefunction can be accurately determined, even when the simple picture of interacting orbitals completely fails. The entanglement between molecular orbitals is quantified using two entropic measures: the single orbital entropy and orbital-pair mutual information [13–15]. Both entanglement measures quantify the correlation of individual orbitals or pairs of orbitals embedded in an orbital space (for instance, the active space in *ab initio* calculations). Orbital entanglement can thus be considered as an alternative to molecular orbital theory, providing quantitative assessment of orbital interactions. A schematic representation of the single orbital entropy and mutual information is shown in Figure 2. Specifically, the single orbital entropy measures how strongly an orbital (encircled in Figure 2a) is entangled with the remaining orbitals (layered in grey in Figure 2a). The single orbital entropy is large for orbitals with unpaired electrons (free radicals, open-shell states) and orbitals participating in chemical bonding [8,9]. The mutual information quantifies the communication between orbital pairs (indicated by the green line in Figure 2b). These correlations include both classical and quantum origin. Examples for strongly correlated orbital pairs are  $\pi$ - and

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**Figure 1.** (a) Lewis structures of nickel–ethene. (b) Schematic representation of back-donation.



**Figure 2.** Schematic representation of orbital entanglement. The orbitals in question are highlighted in red. The single orbital entropy and mutual information are evaluated using the von Neumann entropy. The mutual information is indicated as the green line in (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\pi^*$ -orbitals and metal  $d$ -orbitals. Specifically, if two reactants approach each other, molecular orbitals that are involved in the bond formation process become strongly entangled. An orbital entanglement analysis is, thus, ideal to study molecular reactions because it allows us to identify and monitor the most important orbital interactions along the reaction coordinate. By analyzing the mutual information and single orbital entropy diagrams, we are able to decide which orbital interactions form first and at which points of the dissociation pathway orbitals start communicating with each other.

As transition metal compounds possess a non-negligible multireference character, they are a remarkable challenge for theoretical investigations. Several Complete-Active-Space Self-Consistent-Field (CASSCF) and Complete-Active-Space Self-Consistent-Field including second-order Perturbation Theory (CASPT2) studies have been conducted on metal–olefin complexes in the past [4,16–19], however, the small active spaces used might not be ideal for an accurate description of transition metals. These limitations are alleviated by the Density Matrix Renormalization Group [20,21] (DMRG) algorithm that allows us to efficiently extend computational studies to large active spaces. The first application of DMRG to transition metal chemistry was presented by Marti *et al.* [22], demonstrating its superiority against conventional multireference approaches (see, for instance, Refs. [23–28,11] for recent examples).

In this Letter, we investigate the reaction pathway of nickel–ethene complexation (see Figure 1a) using quantum chemistry methods and demonstrate that the bond-formation process of nickel–ethene can be resolved by means of orbital entanglement. Specifically, orbital entanglement will allow us to determine exactly when back-donation starts to occur, and at which point of the reaction coordinate the bond between nickel and ethene forms.

## 2. Computational details

### 2.1. Geometry optimization

The structures of the nickel–ethene were optimized using the ADF software package [29–31]. We performed a constrained

geometry optimization, where the bond lengths of the Ni–C dissociating centers were systematically varied while the structure of the ethene subsystem was relaxed. The Ni–C distances were varied from 1.75 Å to 2.75 Å. In all calculations, the TZ2P [32] basis set was used, along with the BP86 exchange–correlation functional [33,34]. Scalar relativistic effects were incorporated through the Zero-th Order Regular Approximation to the Dirac equation.

### 2.2. CASSCF

All CASSCF [35–37] calculations were performed in the DALTON2013 program package [38]. A TZP ANO-RCC basis set was used with the following contractions: H: (8s4p3d1f) → [6s4p3d1f] [39], C: (8s7p4d3f2g) → [4s3p2d1f] [40], Ni: (10s9p8d6f4g2h) → [6s5p3d2f1g] [41]. Scalar relativistic effects were included through the second-order Douglas–Kroll–Hess Hamiltonian [42,43].

The  $\pi$ - and  $\pi^*$ -orbitals of ethene, as well as the  $3d_{z^2}$ -,  $3d_{x^2-y^2}$ -,  $3d_{xy}$ -,  $3d_{xz}$ -,  $3d_{yz}$ -,  $4s$ -,  $4d_{z^2}$ -,  $4d_{x^2-y^2}$ -,  $4d_{xz}$ -, and  $4d_{yz}$ -orbitals of the nickel atom were correlated, resulting in an active space of 12 electrons correlated in 12 orbitals (CAS(12,12)SCF). To analyse the importance of the  $\sigma$ - and  $\sigma^*$ -orbitals of ethene, we performed additional CAS(14,14)SCF calculations (cf. Table S1). In all CASSCF calculations, we have imposed  $C_{2v}$  point group symmetry for the nickel–ethene complex. The CAS(12,12)SCF orbitals are collected in Figure S1 in the Supporting Information [44].

### 2.3. DMRG

The Budapest DMRG program [45] was used to perform the DMRG calculations. As orbital basis, the natural orbitals obtained from the CAS(12,12)SCF calculations as described in the previous subsection were used. The active spaces were extended by including additional occupied and virtual natural orbitals. Eight additional occupied orbitals (3 in  $A_1$ , 2 in  $B_1$ , 1 in  $A_2$  and 2 in  $B_2$ ) and sixteen virtual orbitals (5 in  $A_1$ , 5 in  $B_1$ , 2 in  $A_2$  and 4 in  $B_2$ ) were added to the active space, increasing it to 28 electrons correlated in 36 orbitals (DMRG(28,36)). Furthermore, we made sure that the active spaces contained similar orbitals along the reaction coordinate, *i.e.*, molecular orbitals with similar atomic contributions. To enhance convergence, we optimized the orbital ordering [26]. The initial guess was generated using the dynamically extended-active-space procedure (DEAS) [13]. In all DMRG calculations, the Davidson diagonalization threshold was set to  $10^{-6}$ . The minimum number of block states,  $m$ , was set to 64, while the maximum number was set to 2048. For  $m=2048$ , we applied the dynamic block state selection (DBSS) approach [46,47] with a quantum information loss of  $10^{-5}$ . The convergence of DMRG with respect to  $m$  is summarized in Table S1 of the Supporting Information [44]. We should note that we used different schemes to optimize the orbital ordering and the CAS vector for the DEAS procedure (an ordering scheme as described in Ref. [26] and a black-box Fiedler vector based optimization routine). For all orbital orderings, we obtained similar energies in our large- $m$  DMRG calculations.

### 2.4. UCCSD(T)

The Unrestricted Coupled Cluster Singles Doubles (UCCSD) and the Unrestricted Coupled Cluster Singles Doubles and perturbative Triples (UCCSD(T)) calculations were performed with the MOLPRO2012 [48] software package using the same basis set and relativistic Hamiltonian as in CASSCF. The core orbitals were kept frozen, while all the remaining orbitals were correlated.

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