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Materials Research Express



PAPER

Molecular dissociation in presence of a catalyst: II. The bond breaking role of the transition from virtual to localized states

RECEIVED
12 May 2016

REVISED
26 July 2016

ACCEPTED FOR PUBLICATION
28 July 2016

PUBLISHED
12 August 2016

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Keywords: atoms, molecules, transition

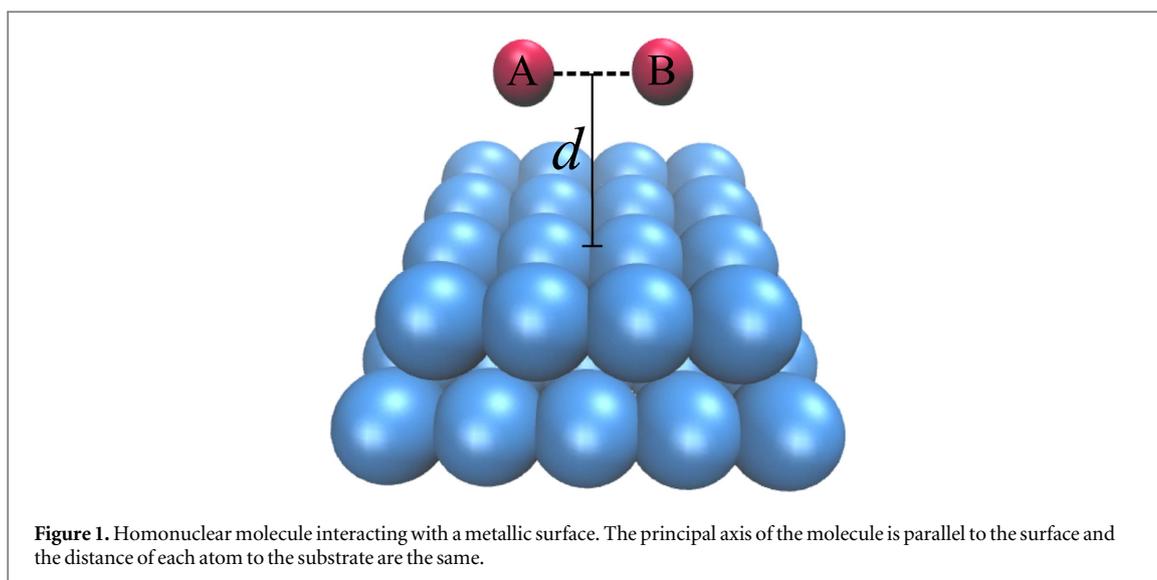
Abstract

We address a molecular dissociation mechanism that is known to occur when a H₂ molecule approaches a catalyst with its *molecular axis parallel to the surface*. It is found that molecular dissociation is a form of quantum dynamical phase transition associated to an analytic discontinuity of quite unusual nature: the molecule is destabilized by the transition from non-physical virtual states into actual localized states. Current description complements our recent results for a molecule approaching the catalyst with its *molecular axis perpendicular to the surface* (Ruderman *et al* 2015 *J. Phys.: Condens. Matter* **27** 315501). Also, such a description can be seen as a further successful implementation of a non-Hermitian Hamiltonian in a well defined model.

1. Introduction

How do molecules form? This has been recognized as one of the ten unsolved mysteries of chemistry, enumerated in 2013 for the year of chemistry celebration [2]. Indeed, when two identical atoms meet a new entity, the dimer, may emerge. The reciprocal is also true: as a dimer approaches a catalyst's surface, it may break down. But when and how does this break down precisely happen? What distinguishes these two different quantum objects, i.e. the molecule and the two independent atoms? It is natural to think that as some control parameter moves, e.g. an inter-atomic distance, a sort of discontinuity or phase transition should happen. While a quantum calculation can be set up to simulate such a reaction, the calculations of an increasingly realistic system quickly begin to overwhelm even the most powerful computer. Indeed, DFT calculations hint a change in chemical bonds as the molecule-catalyst interaction increases when the molecule approaches to the surface [3], but this is confronted with the fact that in a finite system no actual discontinuities can happen. A key for the molecule formation/dissociation mystery could be found in Anderson's inspiring paper 'More is Different' [4]. There, Anderson recalled that the inversion oscillations in ammonia-like molecules suffer a sort of transition into a non-oscillating mode as the masses are increased. Much as in a classical oscillator transition to an over-damped regime, the crucial ingredient that enables a dynamical phase transition is the infinite nature of the environment which induces dissipative friction while preventing the occurrence of Poincaré's recurrences. These concepts were formalized in the context of the Rabi oscillations in a quantum system: a spin dimer immersed in an environment of spins. This was solved in the thermodynamic limit of infinitely many spins which provide the crucial continuum spectrum [5, 6]. In this case, the finite Rabi frequency undergoes a transition into a non-oscillatory mode as the interaction with the environment increases [7–9]. This mathematical analytic discontinuity was termed quantum dynamical phase transition (QDPT) [10].

While the application of these ideas to molecular dissociation/formation is not completely straightforward, in a previous paper we succeeded in describing H₂ molecule formation/dissociation in the presence of a catalyst as a QDPT [1]. This description was achieved using a variant of the model introduced by Newns for hydrogen adsorption in a metallic surface [11]. However, our analysis was restricted to the case when the *molecular axis is perpendicular to the catalyst surface*. In [1] the infinitely many catalyst orbitals provided for an environment



whose influence had to be treated beyond linear response. Indeed, the interactions among the crystal states and the dimer orbitals dramatically perturb each other and they have to be obtained through a self-consistent Dyson equation. In particular, the substrate induces imaginary corrections to the molecular energies, accounting for their finite lifetime. These complex energies, much as those obtained from the Fermi Golden Rule, are eigenvalues of a non-Hermitian effective Hamiltonian. They account for resonances in the electron's scattering probability as well as on the local density of states (LDoS) [12]. Our main result was that *inside* the d band two resonances are formed and that their energy difference present an analytical discontinuity as a function of the molecule–substrate interaction strength [13–15]. Thus, the *molecular dissociation/formation* was identified as the non-analytic *collapse/splitting of these resonances*.

In this paper, we address another reaction mechanism, that known to occur when a H_2 molecule approaches a catalyst with its *molecular axis parallel to the surface*. It is found that molecular dissociation is also a phase transition associated to an analytic discontinuity, but now of a different and unusual nature: the molecule is destabilized by the transition of non-physical virtual states into actual localized states. While in the rest of the article we will be dealing with a similar model and the same tools introduced in our previous work [1], the different geometry will provide a substantially new perspective into the molecular dissociation/formation problem.

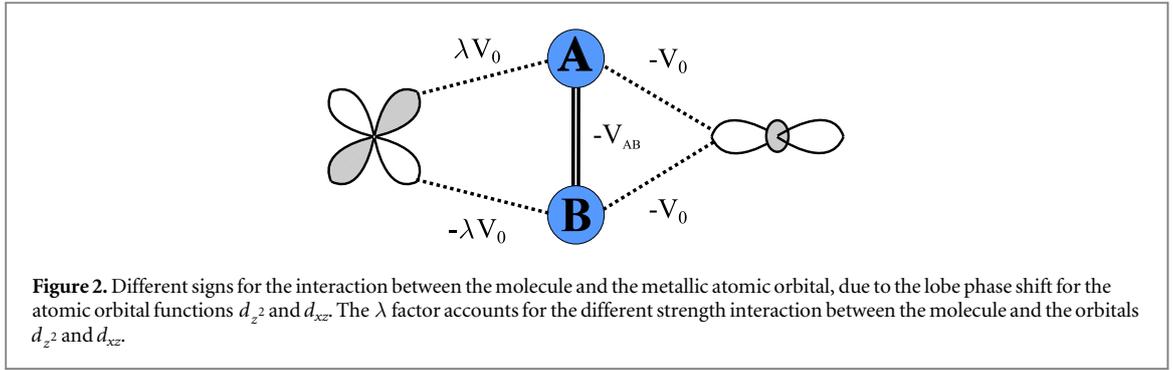
2. The model

Given a homonuclear molecule AB and a metal electrode with a half filled d band, two independent geometries arise to describe the interaction. The particular configuration of a molecule approaching with its axis *perpendicular* to the metal surface, was previously investigated in [1]. A new problem arises when the axis along the molecule lies *parallel* to the surface. In this configuration the distances between a given atom belonging to the metal surface and both atoms forming the molecule remain equal, i.e. $d_A = d_B = d$ (see figure 1). Therefore, both atoms interact identically with the metal, resulting in a completely different Hamiltonian respect to the perpendicular case, and hence yielding yet another mechanism for the dissociation.

To set up the model Hamiltonian for the interaction between the molecule and the metal, we write the molecule's Hamiltonian as:

$$\hat{H}_{\text{mol}} = E_A |A\rangle\langle A| + E_B |B\rangle\langle B| - V_{AB}(|A\rangle\langle B| + |B\rangle\langle A|).$$

The atomic energies E_A and E_B are identical and their degeneracy is broken by the mixing element $-V_{AB}$ that leads to the bonding and antibonding states, i.e. the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. In this orientation, the molecule can only have substantial overlap with the metal d_{z^2} and d_{xz} orbitals of the underlying metallic atom. Therefore, z is considered to be perpendicular to the surface and x is chosen parallel to the molecular axis. Both orbitals interact with the target molecule in different ways [16], as depicted in figure 2. On one side, the overlap of the d_{z^2} with the atomic orbitals A and B have the same the sign and magnitude, resulting in a Hamiltonian coupling element $-V_0$. On the other side, the molecule also interacts with the d_{xz} orbital of the metal. In this case, while having equal strengths a different sign appears for each atomic orbital. Taking these considerations into account, there are two



concurrent mechanisms for molecule-metal interaction:

$$\hat{V}_{\text{int}} = V_0(|A\rangle\langle d_{z^2}| + |B\rangle\langle d_{z^2}|) + \lambda V_0(-|A\rangle\langle d_{xz}| + |B\rangle\langle d_{xz}|),$$

where $|d_{z^2}\rangle$ and $|d_{xz}\rangle$ are the metallic orbitals that interact with the molecule. Furthermore, we have included a λ factor to account for the difference among the interaction strengths with the two d orbitals.

In figure 2 we represent explicitly two, assumed independent, sets of metallic d orbitals associated with each symmetry of the surface orbitals (i.e. $|d_{z^2}\rangle$ and $|d_{xz}\rangle$). Therefore, the relevant part of the metal Hamiltonian can be represented using a narrow band model. This approximation was first proposed by News [11], who stated that the projection of the d band LDoS over the specific orbital (either d_{z^2} or d_{xz}) could be schematized as a semielliptical energy band that strongly interacts with the molecule [17]. This picture is validated by appealing to a Lanczos's transformation [1, 18, 19] to obtain this simple electronic structure for the d band. The basic procedure is visualized in figure 3 for a two dimensional metal represented as two distinct collections of orthonormal d orbitals. By choosing one of the interacting metallic orbitals as a reference, the intermetallic interactions provide (through the Lanczos's procedure) for combination of atomic d orbitals consistent with the initial symmetry. Typically, these are progressively included according to their distance to the initial orbital. These 'collective' substrate orbitals are naturally arranged in the Hilbert space in order to evidence the tridiagonal nature of the Hamiltonian in the new basis. By means of this procedure, the general three-dimensional geometry of a catalyst is reduced to an effective linear chain. The same reasoning applies for both symmetries. Then, we can write the metal d_{z^2} Hamiltonian as:

$$\hat{H}_{\text{met}}^{z^2} = \sum_{n=1}^{\infty} E_n^{z^2} |n\rangle\langle n| - \sum_{n=1}^{\infty} V_{n,n+1}^{z^2} (|n\rangle\langle n+1| + |n+1\rangle\langle n|), \quad (1)$$

where $|n\rangle$ and $E_n^{z^2}$ are the n th collective metal orbital obtained by the Lanczos's transformation and the energy corresponding to that orbital, respectively. For the sake of simplicity, all the hopping elements $V_{n,n+1}^{z^2}$ are considered to be equal to V . This is consistent with the fast convergence of the hopping elements, first addressed by Haydock *et al* [19]. A similar Hamiltonian $\hat{H}_{\text{met}}^{xz}$ is obtained for the xy symmetry. Thus

$$\hat{H}_{\text{met}} = \hat{H}_{\text{met}}^{z^2} + \hat{H}_{\text{met}}^{xz}.$$

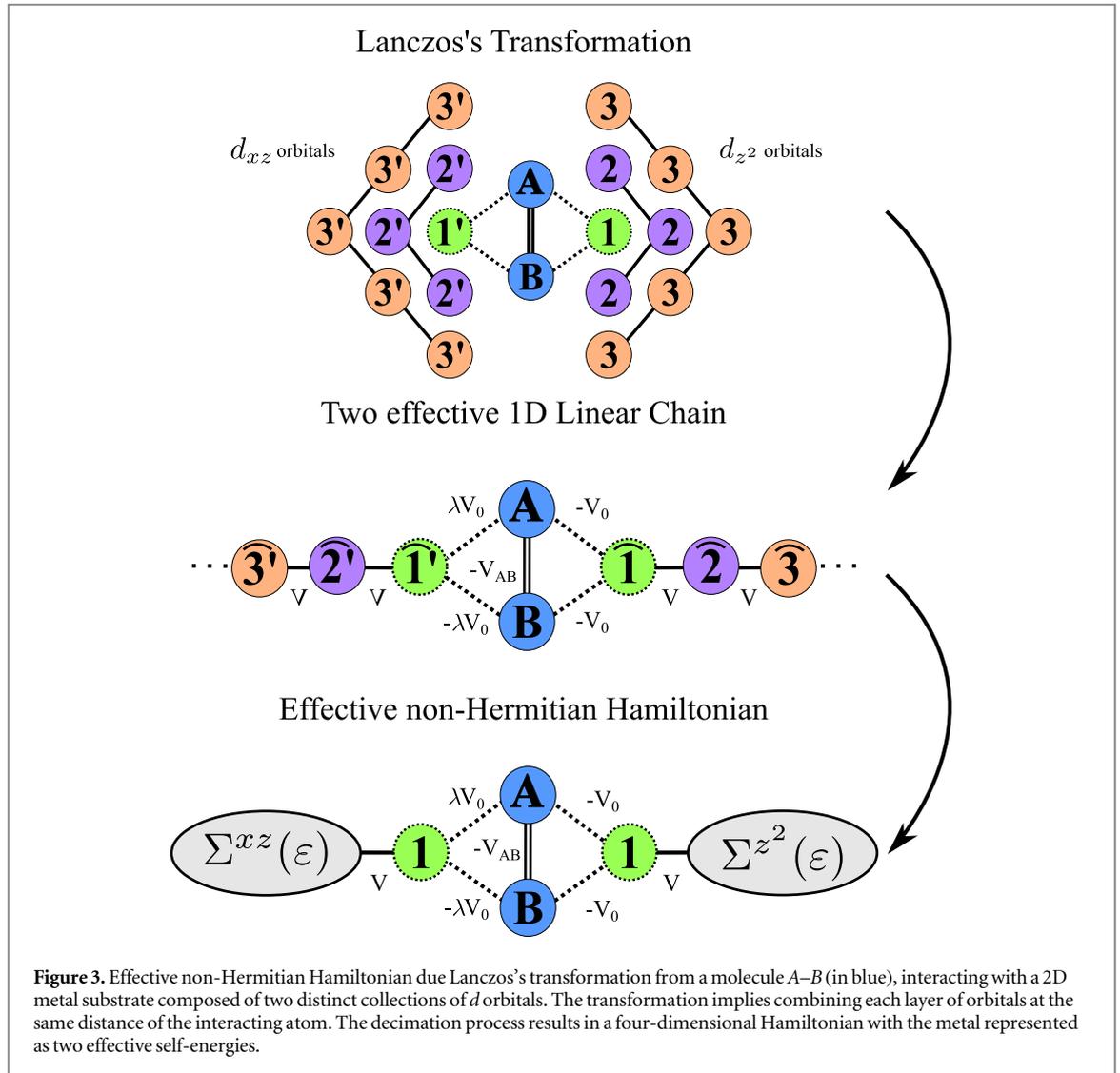
In order to obtain an optimal configuration for our discussion on the dissociation process [20, 21], we make the d band to be centered around the Fermi energy E by making $E_A = E_B = E_n = E$. Then, the bonding and antibonding molecular states, i.e. HOMO and LUMO, fall outside the band as $2|V_{AB}| > 4|V|$ [22]. This choice is consistent with the standard knowledge of the Marcus–Hush theory for optimal conditions of electron transfer and molecular dissociation. In this work, we used $V_{AB}/V = 2.5$ which is typical for H_2 .

The main features of the system, i.e. energy spectrum and relevant eigenvalues properties, could be obtained using a decimation procedure [23, 24].

This formulation deploys an infinite order perturbation theory for the interaction \hat{V}_{int} to dress the molecular Hamiltonian \hat{H}_{mol} into an effective molecular Hamiltonian that accounts for the presence of the catalyst, and yields a complex correction, Σ , to the molecular bonding and antibonding energies. This is sketched in the bottom panel of figure 3. This precisely defined procedure resorts to the Green's function matrix associated with the total Hamiltonian $\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{met}} + \hat{V}_{\text{int}}$,

$$\mathbb{G}(\varepsilon) = (\varepsilon\mathbb{I} - \mathbb{H})^{-1}. \quad (2)$$

Traditionally, $\mathbb{G}(\varepsilon)$ has been used to evaluate the different LDOS and localization properties of electrons in solids [25]. By now, it has become a standard tool in molecular electronics, where it provides scattering probabilities [24] needed to evaluate coherent and decoherent quantum conductances [24, 26]. Here, we are going to profit from the fact that the poles of the Green's function are the eigenvalues of the system. At this point,



a brief introduction to the decimation technique is convenient for the sake of clarity. Let us first consider the molecular Hamiltonian without the presence of the metal:

$$\mathbb{H}_{\text{mol}} = \begin{bmatrix} E_A & -V_{AB} \\ -V_{AB} & E_B \end{bmatrix}. \quad (3)$$

Then, the Green's function matrix adopts the form:

$$\mathbb{G}_{\text{mol}} = \frac{1}{(\varepsilon - E_A)(\varepsilon - E_B) - |V_{AB}|^2} \begin{bmatrix} \varepsilon - E_B & V_{AB} \\ V_{AB} & \varepsilon - E_A \end{bmatrix}. \quad (4)$$

The Green's function for atom A, the first diagonal element of \mathbb{G}_{mol} , can be written as

$$G_{\text{mol}}^{AA} = (\varepsilon - E_A - \Sigma_A)^{-1}.$$

Therefore, the energy of atom A is modified by the presence of the atom B through the self-energy

$$\Sigma_A = |V_{AB}|^2 / (\varepsilon - E_B).$$

This decimation procedure can be extended to the full semi-infinite chain that describes the components of the d band that couple with the HOMO and LUMO according to their symmetry. The procedure consists on 'dressing' the successive 'Lanczos's orbitals' with the corresponding self-energies to account for the interaction with the neighbor atom at the right. In a finite system of $N + 2$ orbitals, Σ_A is written in terms of $N + 1$ levels of a continued fraction until one reaches the last level. To simplify the study of the spectral density, the energies of the system can be renormalized by introducing an imaginary small quantity $-i\eta$, thus $E \rightarrow E - i\eta$. This energy correction can be seen as a weak environmental interaction, a role that could be assigned to the sp band states [26]. Thus, in the thermodynamic limit of a semi-infinite chain ($N \rightarrow \infty$), the self-energy correction due to the metal becomes:

$$\Sigma(\varepsilon) = \frac{|V|^2}{\varepsilon - (E - i\eta) - \Sigma(\varepsilon)} = \Delta(\varepsilon) - i\Gamma(\varepsilon), \quad (5)$$

by setting $E = 0$ in the whole system (i.e. setting down the Fermi level as the energy reference) the analysis is further simplified. Equation (5) has two solutions with different signs. The solution with physical meaning provides a retarded response and results:

$$\Sigma(\varepsilon) = \frac{\varepsilon + i\eta}{2} - \text{sgn}(\varepsilon) \times \left(\sqrt{\frac{r+x}{2}} + i \times \text{sgn}(y) \times \sqrt{\frac{r-x}{2}} \right), \quad (6)$$

with $x = \frac{\varepsilon^2 - \eta^2}{2} - V^2$, $y = \frac{\varepsilon\eta}{2}$ and $r = \sqrt{x^2 + y^2}$.

Then, the restriction to the first four orbitals of the total Hamiltonian can be written in a simple way:

$$\mathbb{H} = \begin{bmatrix} \Sigma^{z^2}(\varepsilon) & -V_0 & -V_0 & 0 \\ -V_0 & -i\eta & -V_{AB} & +\lambda V_0 \\ -V_0 & -V_{AB} & -i\eta & -\lambda V_0 \\ 0 & +\lambda V_0 & -\lambda V_0 & \Sigma^{xz}(\varepsilon) \end{bmatrix}. \quad (7)$$

Now, a basis change can be made to a molecular *bonding* and *antibonding* representation. Equation (8) shows the Hamiltonian in the new basis. Notice that, the bonding state (second diagonal element) does not interact with $\Sigma^{xz}(\varepsilon)$ (fourth diagonal element) and the antibonding state (third diagonal element) does not interact with $\Sigma^{z^2}(\varepsilon)$ (first diagonal element):

$$\widetilde{\mathbb{H}}' = \widetilde{\mathbb{H}}_+ \otimes \widetilde{\mathbb{H}}_- = \begin{bmatrix} \Sigma^{z^2}(\varepsilon) & -\sqrt{2}V_0 & 0 & 0 \\ -\sqrt{2}V_0 & -V_{AB} - i\eta & 0 & 0 \\ 0 & 0 & V_{AB} - i\eta & \sqrt{2}\lambda V_0 \\ 0 & 0 & \sqrt{2}\lambda V_0 & \Sigma^{xz}(\varepsilon) \end{bmatrix}. \quad (8)$$

Therefore, the system is naturally detached in two portions in which the Green's function matrices can be solved independently. For the bonding subspace, i.e. the bonding molecular orbital interacting with $\Sigma^{z^2}(\varepsilon)$, the Green's function takes the form:

$$\mathbb{G}_+ = \frac{1}{(\varepsilon - V_{AB} + i\eta)(\varepsilon - \Sigma^{z^2}(\varepsilon)) - 2V_0^2} \begin{bmatrix} \varepsilon + V_{AB} + i\eta & -\sqrt{2}V_0 \\ -\sqrt{2}V_0 & \varepsilon - \Sigma^{z^2}(\varepsilon) \end{bmatrix}, \quad (9)$$

while, for the antibonding molecular orbital interacting with $\Sigma^{xz}(\varepsilon)$, there is a subspace where

$$\mathbb{G}_- = \frac{1}{(\varepsilon + V_{AB} + i\eta)(\varepsilon - \Sigma^{xz}(\varepsilon)) - 2(\lambda V_0)^2} \begin{bmatrix} \varepsilon - \Sigma^{xz}(\varepsilon) & \sqrt{2}\lambda V_0 \\ \sqrt{2}\lambda V_0 & \varepsilon - V_{AB} + i\eta \end{bmatrix}. \quad (10)$$

For the rest of the article λ will be set $\lambda \sim 1$ and $\Sigma^{xz} = \Sigma^{z^2}$. The eigenenergies and resonances of the system are obtained by finding the poles of equations (9) and (10). This is achieved solving the equations:

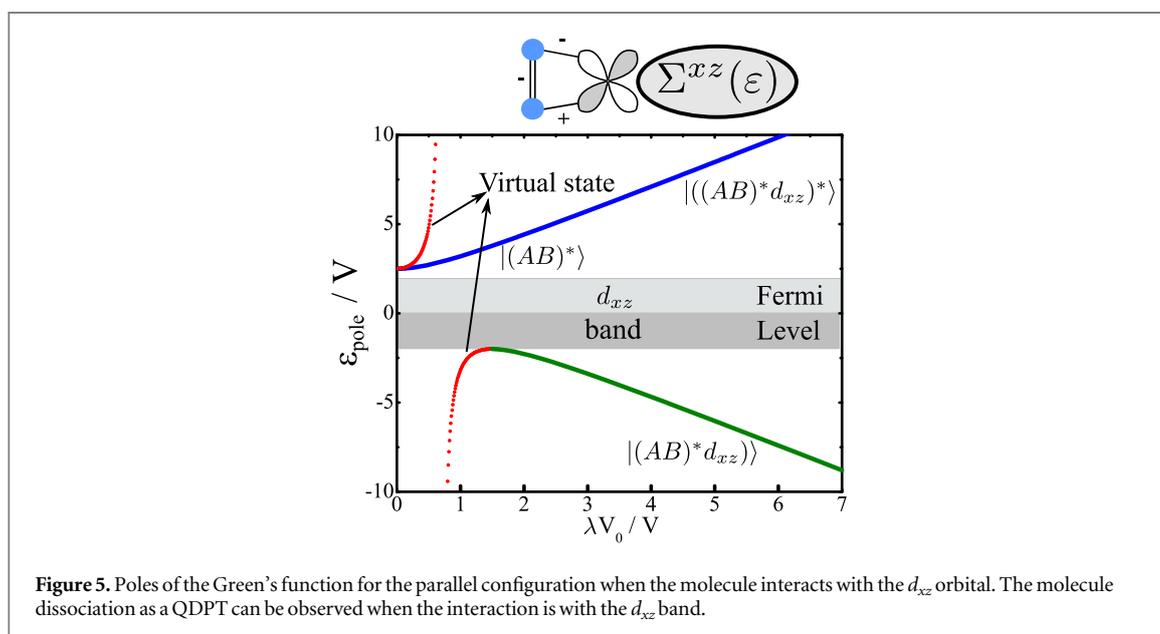
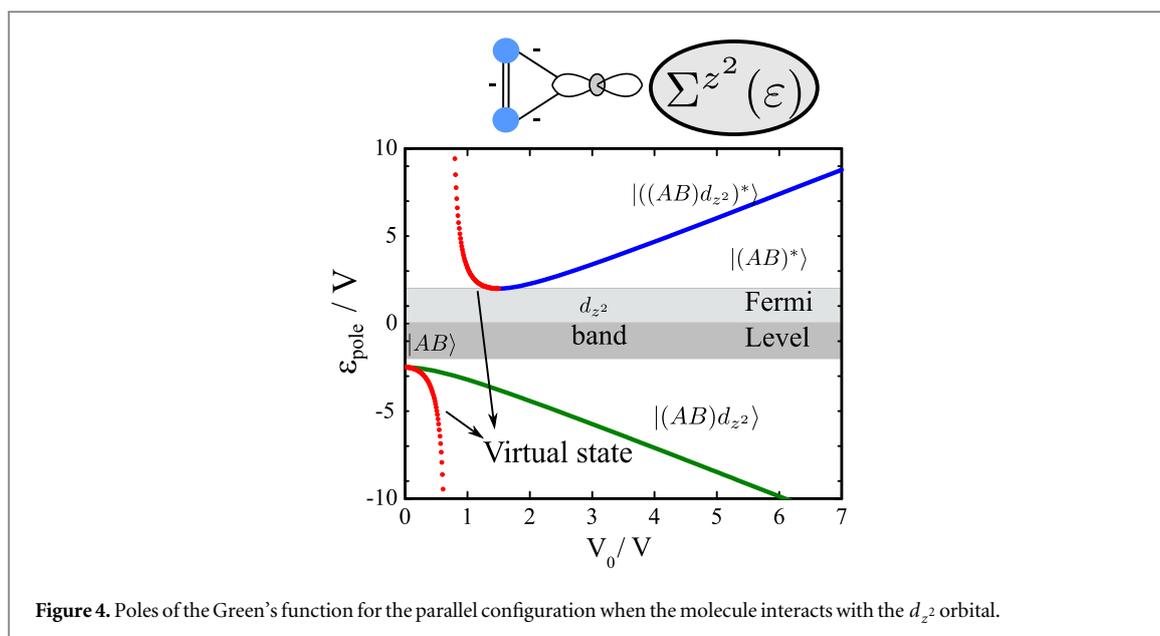
$$\varepsilon - V_{AB} - 2\alpha\Sigma(\varepsilon) = 0, \quad (11)$$

$$\varepsilon + V_{AB} - 2\alpha\Sigma(\varepsilon) = 0, \quad (12)$$

with $\alpha = (V_0/V)^2$. The roots of equation (11) accounts for the poles of the Green's function associated to the bonding state interacting with the d_{z^2} band while equation (12) for the poles of the antibonding state interacting with the d_{xz} band. We should point that to evaluate the roots of equations (11) and (12) one has first to get rid of the square root by transforming them into quartic polynomial equations.

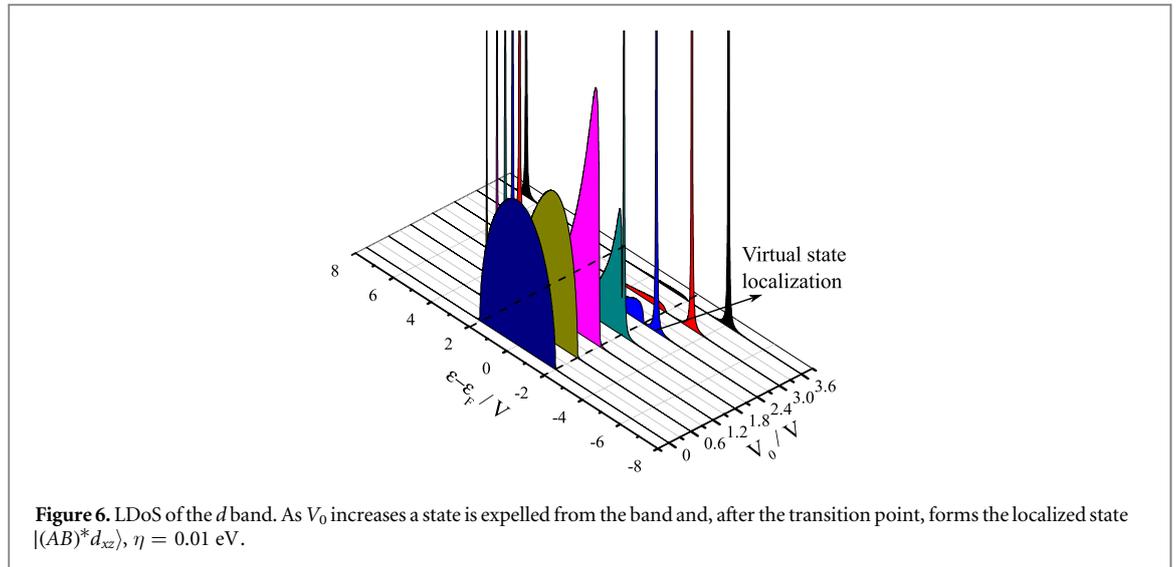
3. Molecular dissociation

A first hint for molecular dissociation arises from analyzing the molecular bonding orbital that interacts with the d band through the d_{z^2} orbital, figure 4. In this case, equation (11) provides two poles which are below the d band at the molecular bonding energy $\varepsilon = -V_{AB}$. One is a physical localized pole (green on-line) bottom line in figure 4 which corresponds to the bonding state $|AB\rangle$. As the interaction increases, $|AB\rangle$ evolves to a bonding combination between the bonding state of the molecule and the metal, i.e. $|(AB)d_{z^2}\rangle$, becoming more localized and its energy lying well below the Fermi level. The other pole corresponds to a non-physical virtual state which, as the interaction increases, escapes to negative energies and reappears at positive values (red on-line) dots in figure 4. As the non-physical pole gets closer to the d band, it finally meets the band-edge and suffers a transition into a physical localized state. This is an antibonding combination between the molecular bonding state and the metal $|(AB)d_{z^2}\rangle^*$ (blue line). In this scenario, bound weakening occurs because occupying the $|(AB)d_{z^2}\rangle$ state



implies a diminishing occupation of the bonding $|AB\rangle$ from 100% into a final 50%. Indeed, the molecular bonding state now has 50% participation in the unoccupied $|((AB)d_{z^2})^*\rangle$ localized orbital that emerged from the upper top of the d band.

The previous discussion has a precise equivalence in the analysis of the states that evolve from the molecular antibonding state. However, the same formulation has now completely different meaning. The molecular antibonding state interacts with the d band through the d_{xz} surface orbital. The poles resulting from equation (12), are shown in figure 5. At the antibonding energy $\varepsilon = V_{AB}$, two poles appear. A physical localized state, related to the molecular antibonding state $|((AB)^*)\rangle$ (blue line in figure 5), whose energy increases as V_0 increases and becomes an antibonding combination between the molecular antibonding state and the metal site $|((AB)^*d_{xz})^*\rangle$. The other pole at $\varepsilon = V_{AB}$ is a virtual state [27, 28] (red dots in figure 5) which diverges as V_0 increases and appears again from $-\infty$ until its energy touches the d band. At this critical value, the virtual state suffers a transition and becomes a localized state (green line in figure 5) which is a bonding combination between the molecular antibonding state and the metal band $|((AB)^*d_{xz})\rangle$. Therefore, molecular dissociation can be interpreted as occurring at the precise value when the virtual pole touches the d band and becomes the localized, and occupied, state $|((AB)^*d_{xz})\rangle$. Thus, molecular dissociation occurs at a non-analytical point of the physical observables, e.g. total energies. At this point the molecular electrons have a transition from an increasingly occupied bonding state that participates of the delocalized band into a localized combination between the d



states and antibonding molecular orbital. This is a form of QDPT which, to the best of our knowledge, has not been identified before in the context of molecular dissociation.

From our results it becomes evident that the most interesting situation is when the antibonding molecular orbital interacts with the d_{xz} . From equation (10) we get the diagonal Green's function at the d_{xz} metallic orbital:

$$G_{d_{xz}}(\varepsilon) = \frac{1}{\varepsilon + i\eta - \Sigma(\varepsilon) - \frac{2(\lambda V_0)^2}{\varepsilon + i\eta + V_{AB}}}. \quad (13)$$

The LDoS for the d_{xz} band can be obtained from equation (13)

$$N_{d_{xz}}(\varepsilon) = -\frac{1}{\pi} \lim_{\eta \rightarrow 0^+} \text{Im} [G_{d_{xz}}(\varepsilon)], \quad (14)$$

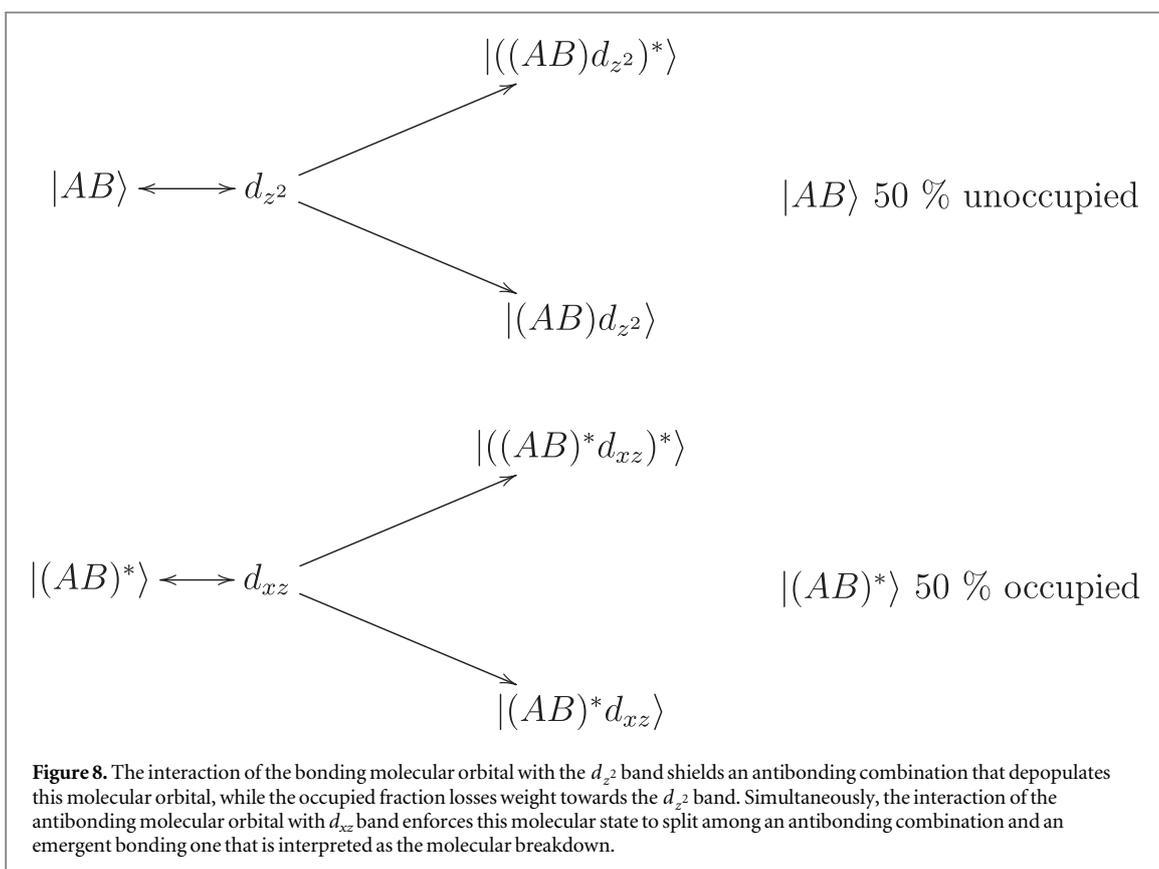
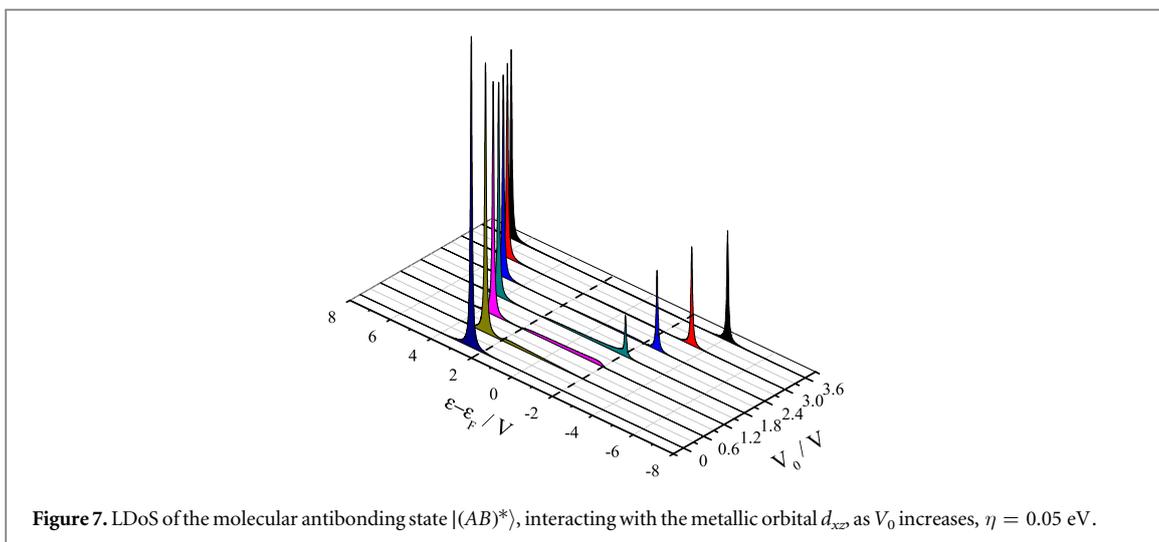
which becomes of great help to reinforce and extend the previous discussion. This LDoS is shown in figure 6 for $\lambda V_0/V$ between 0 and 3.6 for $\lambda = 1$. When $V_0 \sim 0$ the shape of the LDoS corresponds to a non interacting d_{xz} band. As λV_0 increases the d_{xz} band starts to mix with the antibonding state of the dimer. The energy of this antibonding combination $|((AB)^*d_{xz})^*\rangle$, progresses toward increasingly positive values as the interaction grows. Meanwhile, the virtual state approaches the d_{xz} band from negative energies while it produces an 'attraction' that increases the LDoS near the band edge. As the virtual state meets the band a localized state *emerges* from the band edge and gains weight. A similar issue was recently discussed in the context of engineered plasmonic excitations in metallic nanoparticle arrays [28]. There, it was shown analytically that the distorted band is the product among the original semi-elliptic band and a Lorentzian centered in the virtual state. This concentrates a density of states near band edge until it becomes a divergence and a localized state is expelled at a critical interaction strength, shown as a dot in figure 5.

The previous conclusion is reinforced by the analysis of LDoS at the antibonding orbital. Figure 7 shows how the unoccupied antibonding state $|((AB)^*)\rangle$ loses its weight towards a participation on a linear combination with the d_{xz} band which finally emerges as an *occupied localized state*. This is a crucial contribution to molecular destabilization. As in the first part of this work [1] the new transition can be seen as a successful implementation of a non-Hermitian Hamiltonian [12] in a well defined model.

Notice that figures 6 and 7 also serve to discuss the interaction between the bonding molecular state $|AB\rangle$ and the d_{z^2} band by exchanging the sign of the energy. Thus, in this case, the $|((AB)d_{z^2})^*\rangle$ emerges as an unoccupied localized state above the d_{z^2} band, while $|AB\rangle$ state loses occupation as the $|((AB)d_{z^2})\rangle$ state forms with increasing interaction.

4. Conclusions

As a H_2 molecule approaches a catalyst with its axis parallel to the surface, the interaction creates two independent collective orbitals which are superpositions with different surface d orbitals that are part of their corresponding metallic bands. The molecular bonding state becomes mixed with the d_{z^2} band while the molecular antibonding state interacts with the d_{xz} band. This gives rise to two processes described by the same algebra, but with different physical meanings as their energies are the reverse of each other.



On one side, the mixing of the molecular bonding state produces a decrease of its occupation. While this occurs, the LDoS of the d_{z^2} band is distorted at its upper edge much as if it were ‘attracted’ upwards by the virtual state. Finally, at a critical interaction strength the divergent peak is expelled as a localized state emerging from the upper (i.e. unoccupied) part of the d_{z^2} band. This new *unoccupied* state is an antibonding combination among the surface d_{z^2} orbital and the *bonding* state of the dimer.

On the other side, a fraction of the molecular antibonding state gets increasingly mixed with the d_{xz} metallic band. This produces a decrease of the dimer participation on its unoccupied antibonding combination. Simultaneously, the d_{xz} LDoS is ‘attracted’ towards its lower edge until it finally emerges as an *occupied localized state* build as a bonding combination among the molecular *antibonding* state and the d_{xz} band.

These simultaneous mixing processes, i.e. the depopulation of the molecular bonding state and the occupation of the molecular antibonding state, both schematized in figure 8, are responsible for the dimer destabilization that leads to its breakdown.

While the essence of the molecule dissociation mechanisms are already hinted by the resolution of toy models for the catalyst such as small metallic clusters or even a single metal atom, the criticality of the dissociation transition would not be readily captured. Indeed, as in the first part of this work [1], the quasi-continuum nature of a metallic substrate is crucial to describe dissociation as an analytical discontinuity. In this case, we interpreted dissociation as the emergence of the localized state from the band edges as the interaction strength increases. This is an actual QDPT. Remarkably, the elusive virtual states (i.e. states that are non-physical poles of $|\mathbb{G}(\epsilon)|^2$ [29, 30]) acquire a physical meaning as ‘attractors’ of a distortion of the continuum band creating a LDoS divergence that finally expels a localized state. That is, a non-analytical transition that heralds the molecule dissociation.

Acknowledgments

We acknowledge the financial support from CONICET (PIP 112-201001-00411), SeCyT-UNC, ANPCyT (PICT-2012-2324) and DFG (research network FOR1376). We thank R Bustos-Marín, P Serra and W Schmickler for discussions and references.

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