the
abdus salam
international centre for theoretical physics

united nations
educational, scientific
and cultural
organization

international atomic
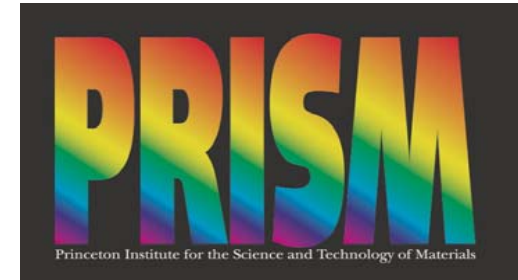energy agency

ICTP 40th Anniversary

_____

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

_____

Introduction to Nanoscale Simulations - Part II

Roberto CAR
Princeton Univ., Princeton Materials Institute
08540-5211 Princeton, U.S.A.

_____

These are preliminary lecture notes, intended only for distribution to participants.

Electronic Structure Theory: Methods and Applications

Roberto Car

Princeton University

Summary

- Density Functional Theory

- First Principles Molecular Dynamics

- Potential Energy Surfaces and Reaction Pathways

- Coarse Graining in Space and Time

Structural Relaxation by simultaneous relaxation of electronic and atomic coordinates

$$M\ddot{R}_I = -\frac{\partial E\big[\{R\},\{\psi\}\big]}{\partial R_I} - \gamma_a M\dot{R}_I$$

$$\mu\ddot{\psi}_n = -\frac{\delta E\big[\{R\},\{\psi\}\big]}{\delta \psi_n^*} - \gamma_e \mu\dot{\psi}_n + \sum_m \Lambda_{nm}\psi_m$$

First-Principles Molecular Dynamics

Molecular Dynamics (MD) is powerful statistical mechanical technique based on numerical integration of classical trajectories

$$M_I \ddot{R}_I = -\frac{\partial \Phi}{\partial R_I} \qquad \left\langle G(\{R\}) \right\rangle = \frac{1}{T} \int_0^T dt \, G(\{R(t)\})$$

First-Principles MD combines MD with DFT, using a DFT potential energy surface to generate atomic trajectories.

It relies on the BO separation of nuclear and electronic dynamics, assuming classical mechanics for the former.

BO Potential Energy Surface:

$$\Phi\left(\{R\}\right) = Min_{\{\psi\}} E_{V(\{R\})}\left[\{\psi\}\right] + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J}{\left|R_I - R_J\right|}$$

Performing a new functional minimization at each time step is expensive. Car and Parrinello (*Phys Rev Lett* **55**, 2471 (85)) proposed to use instead:

$$\tilde{\Phi}\left[\{\psi\};\{R\}\right] = E_{V(\{R\})}\left[\{\psi\}\right] + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J}{\left|R_I - R_J\right|}$$

Minimization is achieved dynamically in the CP equations by separation of the time scales of electronic and nuclear motion.

This is significantly more efficient.

CP equations:

$$M_I \ddot{R}_I = -\frac{\partial \tilde{\Phi}\left[\{R\},\{\psi\}\right]}{\partial R_I}$$

$$\mu \ddot{\psi}_n = -\frac{\delta \tilde{\Phi}\left[\{R\},\{\psi\}\right]}{\delta \psi_n^*} + \sum_m \Lambda_{nm} \psi_m$$

With appropriate choice of μ and initial conditions the electrons

are faster than nuclear motion, and on the time scale of the latter:

$\overline{\tilde{\Phi}} \approx \Phi$ CP dynamics is a good approximation of BO dynamics.

In this approach the fictitious non-interacting electrons of DFT become
fictitious classical dynamical fields.

An example: Interface chemistry of Mg and Alq$_3$

From S. Meloni, A. Palma, J. Schwartz, A. Kahn, and R. C., *J. Am. Chem. Soc.* **2003**, 125, 7808-7809

How does a Mg atom interact with an Alq$_3$ thin film?

Tris-(8-hydroxy-quinoline)aluminum (Alq$_3$) is widely used in organic light emitting diodes (OLEDs)

According to DFT calculations an Mg atom forms a weakly bound charge transfer complex with an isolated Alq$_3$ molecule

…However, this is inconsistent with recent XPS experiments (*large* core level shifts – Ni(1s) towards *lower* BE, O(1s) toward *higher* BE)

Mg-Alq$_3$: structures from first-principles electronic structure calculations: (a) isolated molecule, (b) crystalline Alq$_3$ environment
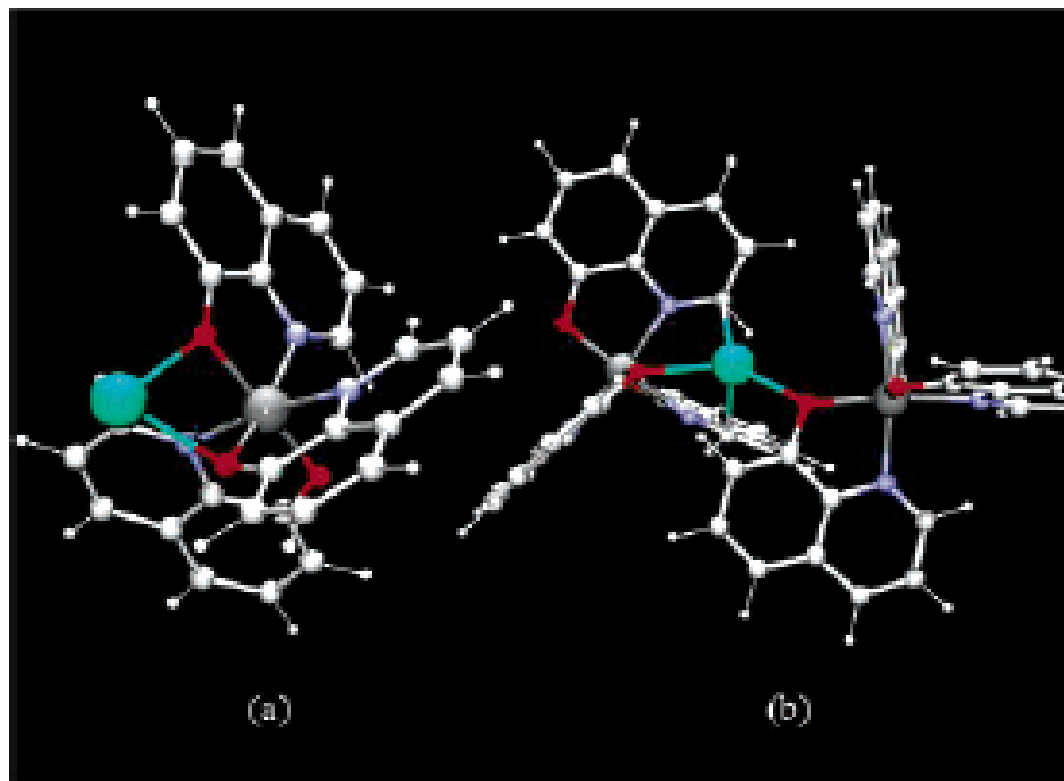
Figure 1. Mg−Alq$_3$ (meridianal) complex: (a) gas phase, (b) solid (crystalline) phase. Atoms are represented by balls: Mg is green, C is gray, N is blue, Al is dark gray, and H is white.
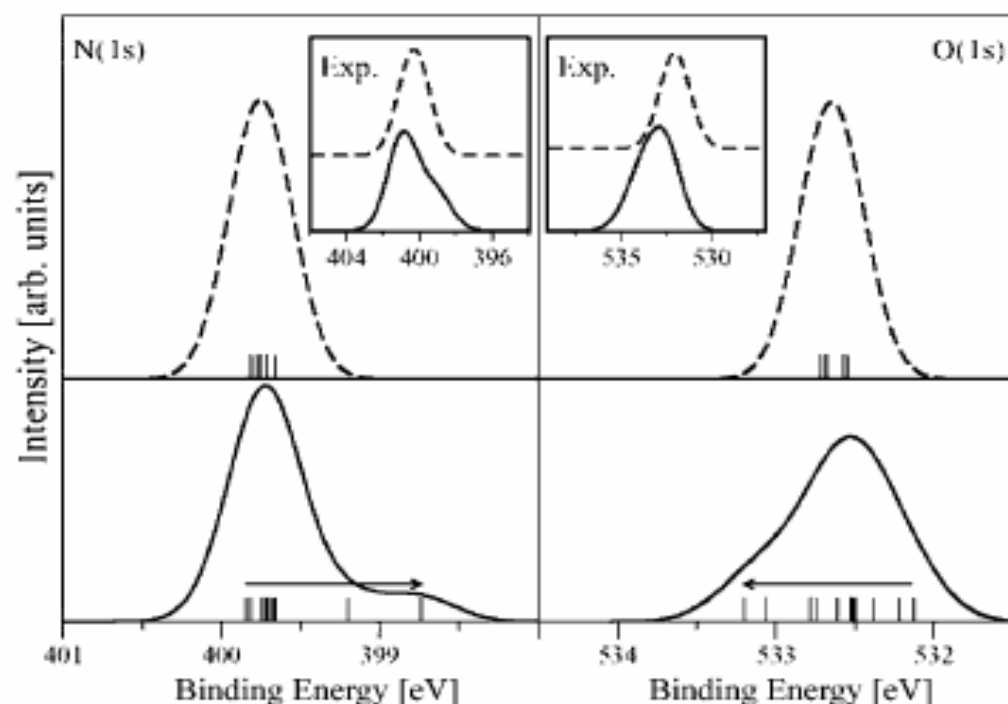
Figure 2. Calculated O(1s) and N(1s) core level shifts in pure Alq₃ (dashed line, upper diagram) and Mg−Alq₃ (continuous line, lower diagram). The calculated BEs (vertical bars) are convoluted with a Gaussian function to obtain the spectra. XPS data from ref 3 are reported in the inset (dashed line, spectra of a pure Alq₃ film; continuous line, spectra after deposition of 4 Å of Mg). In this figure, the absolute energy scale (which is arbitrary in our calculation) has been chosen to closely correspond to experiment.

The formation of an organometallic complex explains the results
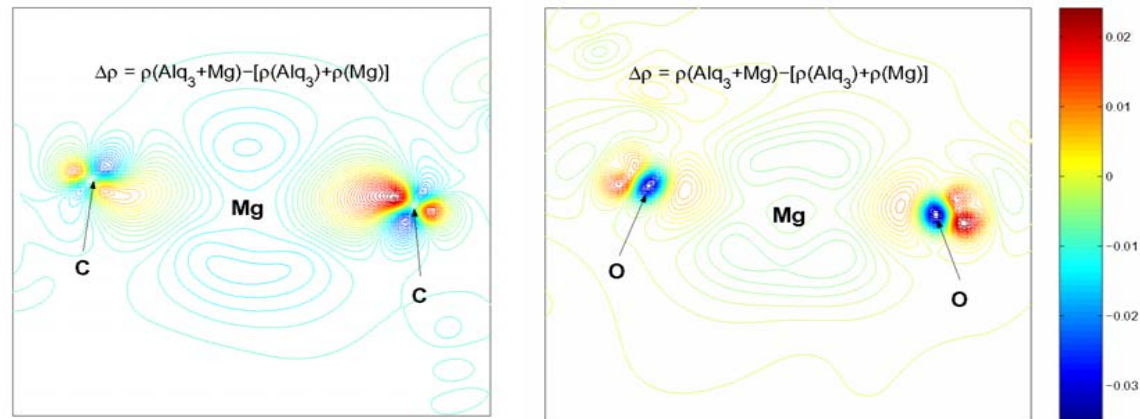
- MD at finite temperature helped to identify the new structure

- An isolated molecule is not sufficient to model a thin film environment (even though molecules in the film interact weakly among themselves via Van der Waals forces)

Phase diagrams from first-principles

An example showing:

• molecular dynamics allows us to compute thermodynamical properties

• the effect of the energy functional on the predicted properties

melting transition

Melting transitions can be studied by FPMD, transition temperatures and other thermodynamic properties (enthalpies, entropies etc.) can be *predicted* from FPMD calculations.

About 10 years ago (O. Sugino and R.C., *PRL* 1995) we showed how this can be done using thermodynamic integration techniques: the results for the melting temperature were somehow disappointing:

T_m = 1,350 K (LDA) vs T_m = 1,685 K (expt)

LDA<GGA<Meta-GGA

F/eV ~~ T/K

lda=1379 K

meta = 1675K

pbe=1518K
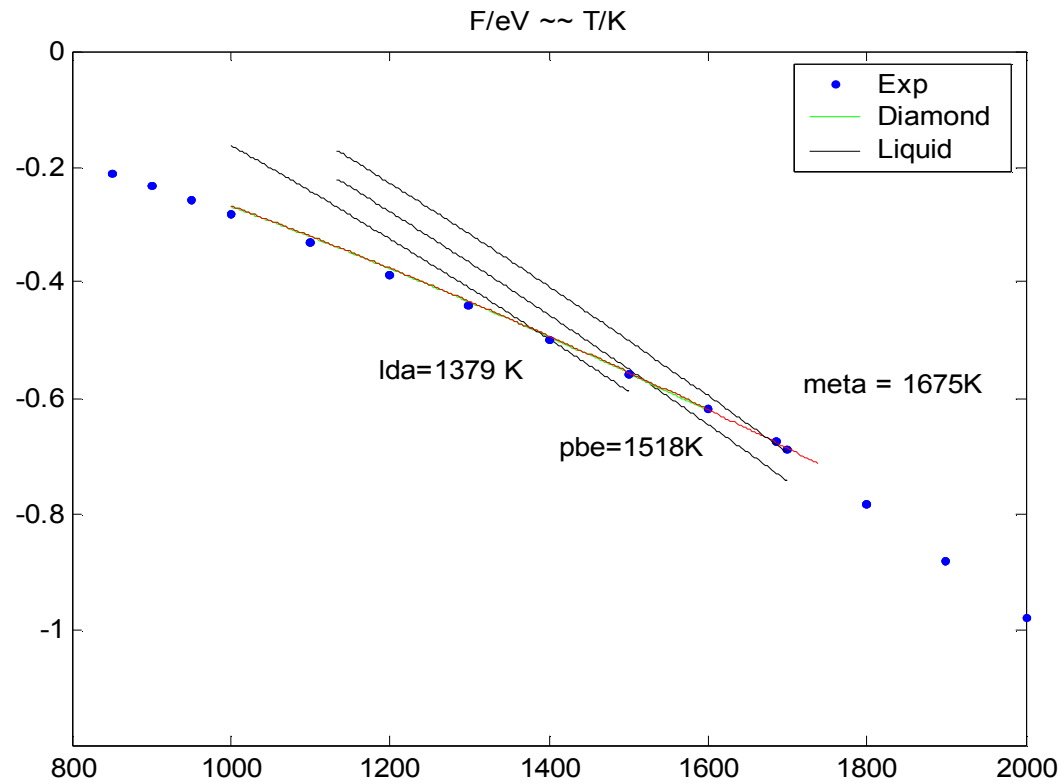
(from X. Wang, S.Scandolo, and R.C., unpublished (2004))

META-GGA

Tao Perdew Staroverov, Scuseria: TPSS functional (*PRL* 2003)

$$\varepsilon_{XC}^{TPSS}(\rho, \nabla\rho, \tau) \quad \text{where} \quad \tau(r) = \frac{1}{2}\sum_{n}\left|\nabla\psi_n(r)\right|^2$$

Reaction Pathways

FPMD simulations are currently limited to time scales of tens of ps

Most chemical reactions are activated processes that occur on longer time scales and are not accessible in direct FPMD simulations (and would not be accessible even in classical MD simulations).

Identifying **reaction pathways** is central to the study of chemical reactions. Here we show that the **string method** for reaction pathways (W. E and collaborators *(PRB* **66**, 052301 (2002))) is ideal to combine with FPMD

String Method (at T=0)

A Minimum Energy Path $\varphi(\alpha)$ connecting two end points

satisfies $\left(\nabla V[\varphi]\right)^{\perp} = 0$

A longitudinal constraint, requiring only *uniform* stretching, is imposed by Lagrange multipliers:
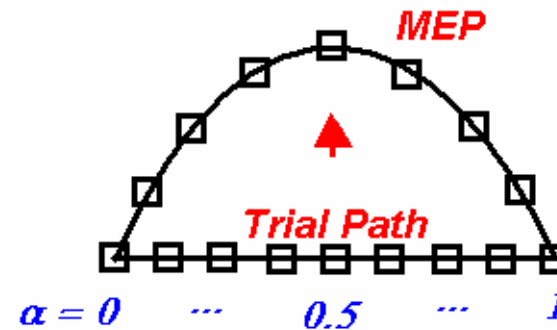
$$\left[\nabla V(\varphi(\alpha))\right]^{\perp} - \lambda(\alpha)\hat{\tau}(\alpha) = 0$$

This is easily solved by *Damped Molecular Dynamics* using the *SHAKE* procedure for the Lagrange multipliers

Damped Molecular Dynamics of a String

$$\ddot{\varphi}(\alpha;t) = -\left[\nabla V(\varphi(\alpha;t))\right]^{\perp} - \gamma\dot{\varphi}(\alpha;t) + \lambda(\alpha;t)\hat{\tau}(\alpha;t)$$

In this way an initial trial path is locally optimized to get a MEP

This is closely related to the **NEB** method by H. Jonsson and co.: the latter can be seen as a string method in which a constraint is imposed by a penalty function (rather than a Lagrange multiplier)

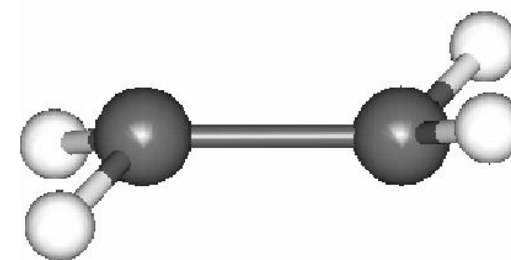# First Principles String Molecular Dynamics

$$M\ddot{R}_I^\alpha = -\left[\frac{\partial E\left[\{R^\alpha\},\{\psi^\alpha\}\right]}{\partial R_I^\alpha}\right]^\perp - \gamma_I M\dot{R}_I^\alpha + \lambda(\alpha)\hat{\tau}(\alpha)$$

$$\mu\ddot{\psi}_n^\alpha = -\frac{\delta E\left[\{R^\alpha\},\{\psi^\alpha\}\right]}{\delta(\psi_n^\alpha)^*} - \gamma_e \mu\dot{\psi}_n^\alpha + \sum_m \Lambda_{nm}^\alpha \psi_m^\alpha$$

(From Y. Kanai, A. Tilocca, A. Selloni and R.C., *JPC* (to appear 2004)

Hydrogenation of disilene (Si_2H_4) to disilane (Si_2H_6)

► Unlike planar C_2H_4, calculations and recent experiments suggest trans-bent C_{2h} symmetry for Si_2H_4.

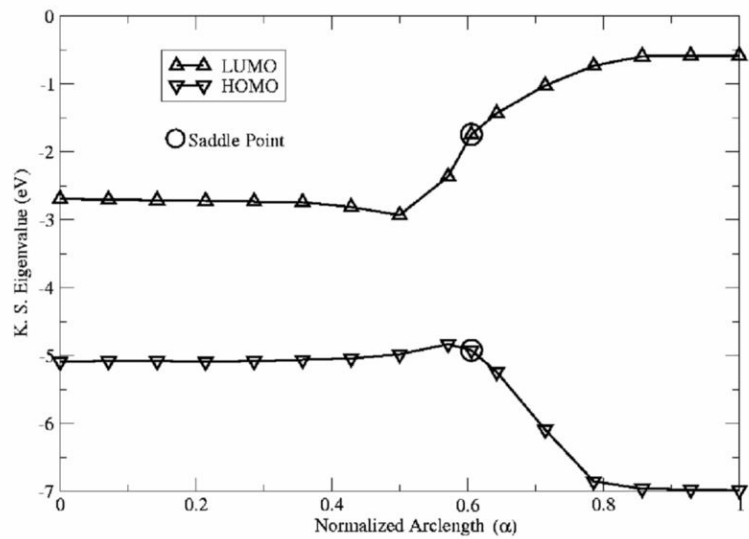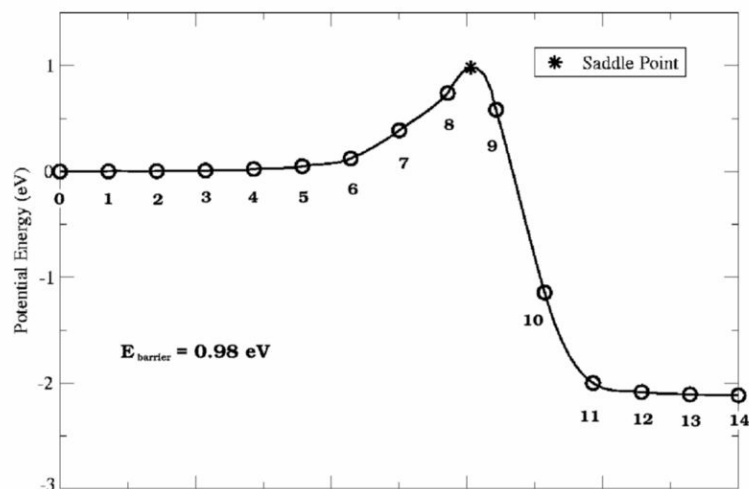

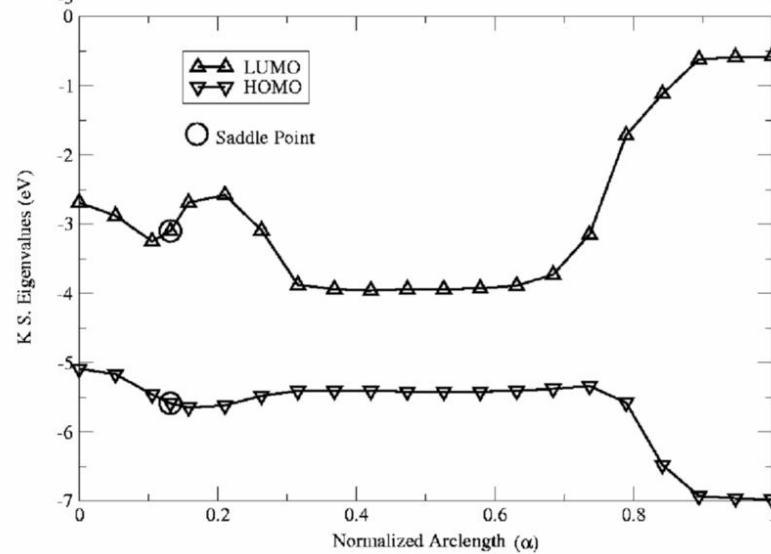► Two possible hydrogenation pathways.

(A) 1,2 Addition

$$H_2 \, SiSi \, H_2 + H_2 \; \rightarrow \; Si_2H_6$$

(B) 1,1 Addition

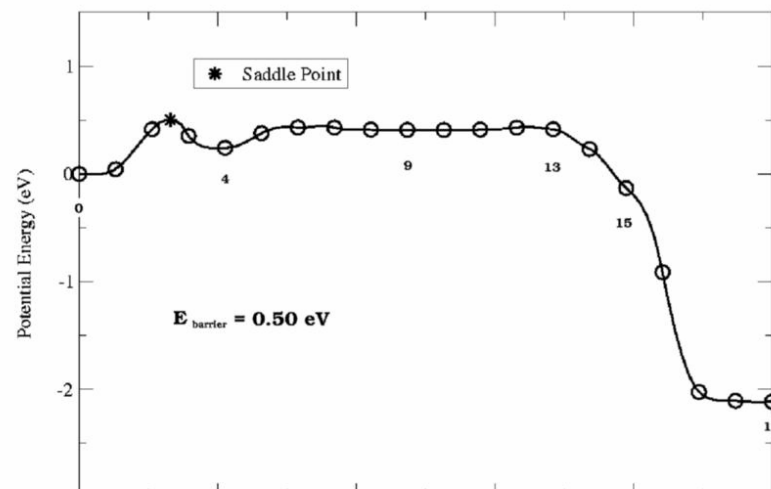$$H_2 \, SiSi \, H_2 + H_2 \; \rightarrow \; H_3SiSiH + H_2 \; \rightarrow \; Si_2H_6$$
$$\text{(intermediate)}$$

Potential Energy Profile along MEP
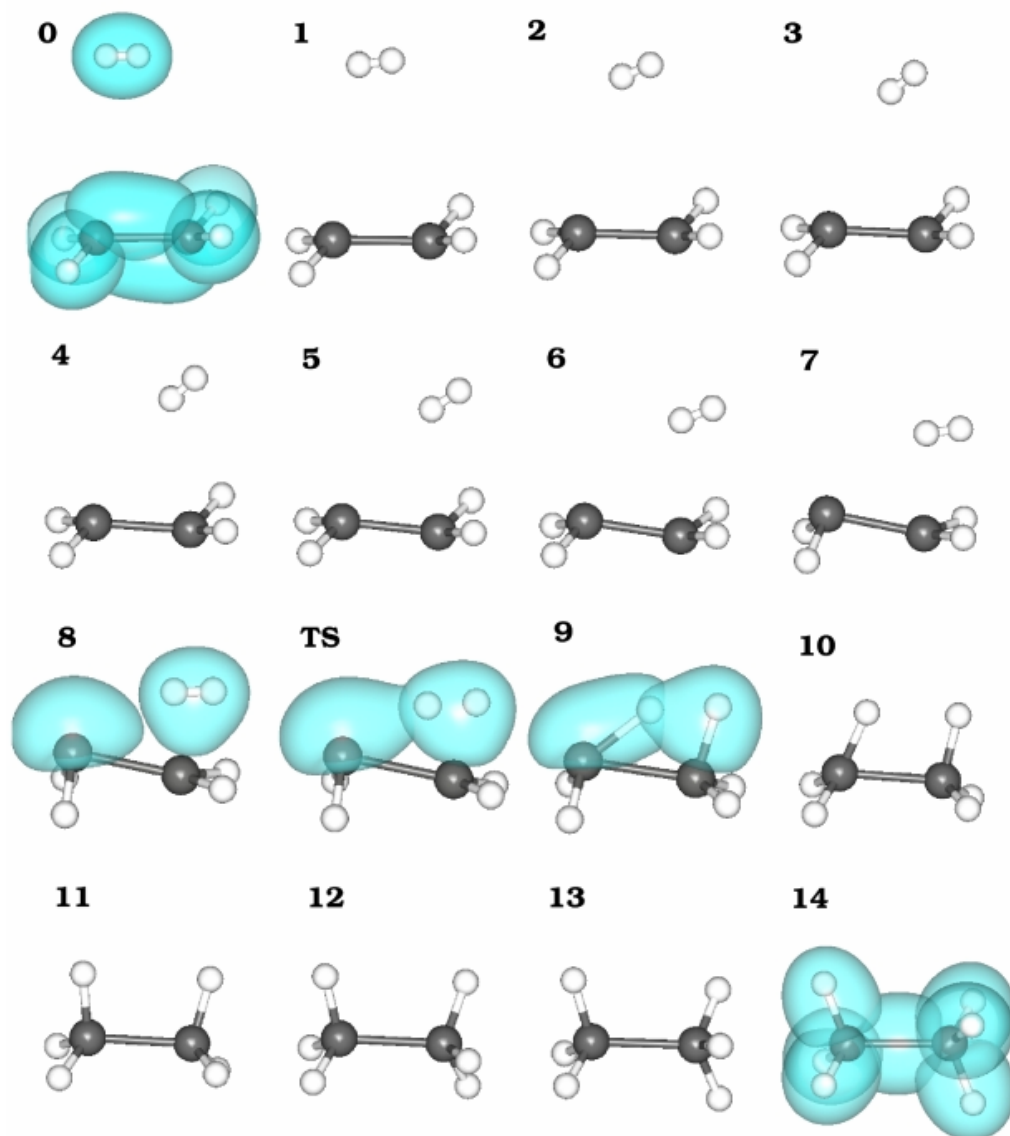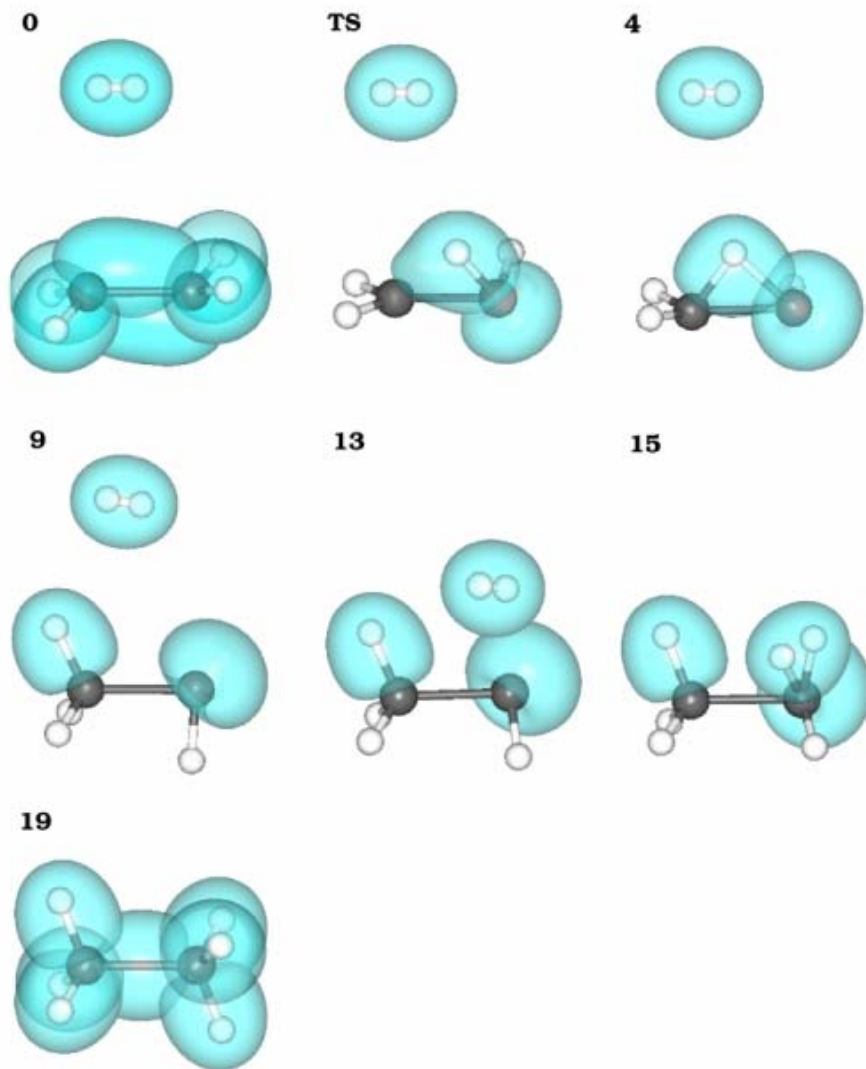
1,2 Addition

► Lone pair electrons are formed at one end of Si-Si bond before the TS.

► Si-Si bond order is effectively reduced before the TS.

MLWF (Marzari-Vanderbilt Transformation) [5, 6]

1,1 Addition

► Structures 4 (SiH_2-H-SiH) and 9 (SiH_3SiH) are local energy minimas.

► Lone pair electrons are formed at one end of Si-Si bond.

► Activation barrier is in an isomerization process.

MLWF (Marzari-Vanderbilt Transformation) [5, 6]

Influence of xc functional : PBE (GGA) vs. TPSS[2] (meta-GGA)

▶ DFT-GGA underestimates the barriers for these reactions [3,4].

▶ Barriers as well as reaction energies improve using meta-GGA (TPSS).

▶ Preliminary results are promising and call for further studies to assess the performance of the meta-GGA (TPSS) functional.

* Excluding ZPE and entropy contributions

Reaction Energy (eV)

	$H_2+Si(100)$	$H_2 + Si_2H_4$
PBE	1.94	2.11
TPSS	2.18	2.37
B3LYP /aug-cc-pVQZ [7]	–	2.25
QMC (estimate) [4*]	2.40 ± 0.15	–

Reaction Barriers (eV)

	$H_2+Si(100)$		$H_2+Si_2H_4$	
	Intra	Inter	1,2	1,1
PBE	0.40	0.24	0.98	0.50
TPSS	0.56	0.40	1.27	0.67
B3LYP /aug-cc-pVQZ [7]	–	–	1.31	0.60
QMC (estimate) [4*]	0.66 ± 0.15	0.54 ± 0.09	–	–