

UNIVERSITÀ DEGLI STUDI DI MILANO

Procedura di selezione per la chiamata a professore di I fascia da ricoprire ai sensi dell'art. 18, comma 1, della Legge n. 240/2010 per il settore concorsuale 03/A2 - MODELLI E METODOLOGIE PER LE SCIENZE CHIMICHE (settore scientifico-disciplinare CHIM/02 - CHIMICA FISICA) presso il Dipartimento di Chimica, (avviso bando pubblicato sulla G.U. n.59 del 26/07/2022) - Codice concorso 5024

Rocco Martinazzo

CURRICULUM VITAE

INFORMAZIONI PERSONALI

COGNOME	MARTINAZZO
NOME	ROCCO
DATA DI NASCITA	02/11/1973

TITOLI

TITOLO DI STUDIO

Laurea in Chimica, 110/110 *con lode*

"Application of the Spin-Coupled Valence Bond theory to the calculation of astrophysically relevant ion-molecule interaction potentials"

Marzo 1998, Università degli Studi, Milano, Italia. Relatore: Mario Raimondi

TITOLO DI DOTTORATO DI RICERCA O EQUIVALENTI, CONSEGUITO IN ITALIA O ALL'ESTERO

Dottorato in Scienze Chimiche

"The LiH₂⁺ system: interaction forces and quantum dynamics"

Gennaio 2002, Università degli Studi, Milano, Italia. Relatore: Ermanno Gianinetti

ESPERIENZA LAVORATIVA

2019 Visiting scientist, Weizmann Institute of Science, Rehovot (Israele).
2015 – Professore Associato, Dipartimento di Chimica, Università degli Studi di Milano,
2012 - 2015 Ricercatore, Dipartimento di Chimica, Università degli Studi di Milano, Milano.
2013 Visiting scientist, Laboratoire Collisions Agrégats Réactivité, Tolosa (Francia).
2004 - 2012 Ricercatore, Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano
2005 - 2006 Visiting scientist, Universität Potsdam, Potsdam (Germania).
2001 - 2003 Assegnista di Ricerca, Dipartimento di Chimica, Università degli Studi di Milano
2000 - 2002 Visiting student, Università La Sapienza, Roma.

ATTIVITÀ DIDATTICA

INSEGNAMENTI E MODULI PER CORSI DI LAUREA

2015– **Chimica Fisica B** (Corso di Laurea in Scienze Chimiche, LM-54), 48 h frontali, 6 CFU
L'insegnamento fornisce una esposizione sistematica dei concetti fondamentali dello stato solido della materia e una solida base per la comprensione della vasta e variegata fenomenologia corrispondente (proprietà strutturali, termiche, ottiche e di trasporto). Oltre agli argomenti di base trattati estesamente (modelli di Drude e Drude-Sommerfeld, teorema di Bloch, struttura a bande, teoria semiclassica della dinamica elettronica e trasporto diffusivo, fononi) vengono accennati argomenti moderni di carattere più avanzato (trasporto mesoscopico non-locale, giunzioni molecolari, isolanti topologici). Ampio spazio viene dato alla struttura a bande e alle sue caratteristiche chiave, illustrate nel dettaglio con modelli *tight-binding* attraverso l'uso di semplici script Python.
Affluenza: 15-20 studenti per anno.

- 2015— Chimica Fisica III** (Corso di Laurea in Chimica, L-27), 48 h frontali, 6 CFU
Il corso completa la preparazione di base della Chimica Fisica, fornendo una sistematica e dettagliata interpretazione microscopica della termodinamica e dello stato solido della materia, ed una breve esposizione della teoria cinetica dei gas e della sua applicazione ai fenomeni di trasporto e alla cinetica chimica. La teoria della termodinamica statistica è esposta sistematicamente e corredata da un ampio numero di applicazioni ed esercizi a problemi di interesse chimico. Lo stato solido è introdotto a livello semi-elementare, e particolare enfasi è data alle tecniche di indagine sperimentale (XRD, STM, AFM) e alle applicazioni pratiche (es. fotovoltaico, illuminazione LED).
Affluenza: 80-100 studenti per anno.
- 2007— Chimica Teorica - Modulo A** (Corso di Laurea in Scienze Chimiche, LM-54), 3 CFU
L'insegnamento intende portare lo studente a familiarizzare con i metodi quantomeccanici applicati alla struttura della materia, con particolare riferimento alla dinamica quantistica. Una ampia introduzione agli spazi di Hilbert e operatori lineari agenti su di essi è seguita dall'esposizione sistematica dell'evoluzione degli stati quantistici, sia di sistemi isolati che in interazione con l'ambiente. Particolare attenzione è rivolta alla teoria della risposta lineare e ai metodi di soluzione dell'equazione di Schrödinger dipendente dal tempo per sistemi di grandi dimensioni.
Affluenza: 5-10 studenti.
- 2011** Insegnamento su invito: **"The role of phonons"** in *"Dynamics of molecule-surface reactions"*
Master Degree in Chemistry, Leiden (Paesi Bassi), 8 h
- 2011-2014 Chimica Fisica A - Laboratorio** (Corso di Laurea in Scienze Chimiche)
2009-2014 Chimica Quantistica - Modulo B (Corso di Laurea in Chimica)
2008-2014 Assistenza al corso Chimica-Fisica II - Laboratorio (Corso di Laurea in Chimica)
2008-2009 Assistenza al corso Chimica Fisica A - Laboratorio (Corso di Laurea in Scienze Chimiche)
2006-2007 Assistenza al corso Chimica-Fisica I - Laboratorio (Corso di Laurea in Chimica)

INSEGNAMENTI E MODULI PER SCUOLE DI DOTTORATO

- 2022— HPC@Unimi: INDACO for molecules and solids** (Corsi di Dottorato in Chimica ed in Fisica), 5 h
Corso avanzato di teoria e metodi di struttura elettronica per molecole e solidi. Nel modulo in questione vengono fornite le basi dei metodi a funzione d'onda e della teoria del funzionale densità, e la loro applicazione a tipici problemi di interesse chimico, attraverso il software package Gaussian.
Affluenza: 10 studenti
- 2020— Literature Search in Chemistry** (Corso di Dottorato in Scienze Chimiche), 3 h
Il corso fornisce una visione critica della letteratura scientifica e del processo di pubblicazione, con particolare attenzione alla "bibliometria" e ai processi di valutazione ad essa collegati. Gli studenti affrontano ricerche bibliografiche di settore (Chimica-Fisica nel presente modulo) e analizzano criticamente ricerca e risultati in seminari pubblici.
Affluenza: 5-10 studenti
- 2016-2020 Literature Search in Chemistry** (Corso di Dottorato in Scienze Chimiche), 9 h
2011,2009 Chemistry at surfaces (Corso di Dottorato in Scienze Chimiche), 9 h
2007,2005 Chemical Dynamics (Corso di Dottorato in Scienze Chimiche), 9 h

ATTIVITÀ DI DIDATTICA INTEGRATIVA E DI SERVIZIO AGLI STUDENTI

ATTIVITÀ DI RELATORE DI ELABORATI DI LAUREA, DI TESI DI LAUREA MAGISTRALE E DI TESI DI DOTTORATO¹

"Curvature in carbon π -conjugated systems: a theoretical and computational study", Mirko Leccese, Corso di Dottorato in Scienze Chimiche, AA 2021/2022. Relatore: **Rocco Martinazzo**.

"Reaction rate constants in condensed phase: A numerically exact quantum study", Ambra Sibilla, Corso di Dottorato in Scienze Chimiche, AA 2019/2020. Relatore: **Rocco Martinazzo**.

"Quantum chemical dynamics in complex environments", Paolo Lazzaroni, AA 2019/2020, Corso di Laurea Magistrale in Chimica. Relatore: **Rocco Martinazzo**.

"A different story of π bonds", Marco Cappelletti, AA 2019/2020, Corso di Laurea Magistrale in Chimica. Relatore: **Rocco Martinazzo**.

"Effetto isotopico", Davide Mauri, AA 2019/2020, Corso di Laurea in Chimica. Relatore: **Rocco Martinazzo**.

"Selettività di spin nel trasporto elettronico attraverso molecole chirali", Andrea Fortis, AA 2019/2020, Corso di Laurea in Chimica. Relatore: **Rocco Martinazzo**.

¹ Se non indicato diversamente i lavori di Tesi si intendono svolti presso l'Università degli Studi di Milano.

"Modeling quantum dynamics in complex environments", Samuele Spreafico, AA 2018/2019, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**.

"Kinetic and process models for the upgrading of bioethanol and carbon dioxide", Antonio Tripodi, Corso di **Dottorato in Scienze Chimiche**, AA 2018/2019. Relatore: **Rocco Martinazzo**. Correlatore: Ilenia Rossetti.

" π -coordination, hyperconjugation and anomalous delocalization in carbon sp^2 systems: a theoretical investigation", Mirko Leccese, AA 2017/2018, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**.

"Fully quantum dynamical studies of Eley-Rideal H_2 recombination on graphite", Marta Pasquini, Corso di **Dottorato in Scienze Chimiche**, AA 2016/2017. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"A numerically exact quantum approach to compute rate constants for reactions in condensed phase", Ambra Sibilla, AA 2016/2017, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Silicon nanoribbons: a first-principles investigation", Nicholas Francia, AA 2016/2017, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Oligotiofeni ciclici intrinsecamente chirali: studio ab initio delle loro proprietà enantioselettive", Samuele Spreafico, Corso di **Laurea in Chimica**, AA 2016/2017. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Electronic, optical and mechanical properties of π -conjugated carbon and silicon rings: a first-principles investigation", Francesca Menescardi, AA 2015/2016, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Atomic-scale defects and charged impurities in two-dimensional Dirac materials", Michele Pizzochero, Corso di **Laurea Magistrale in Chimica**, AA 2014/2015. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Hydrogen adsorption on curved graphene sheets", Mattia Peluchetti, Corso di **Laurea Magistrale in Chimica**, AA 2014/2015. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Tunneling elettronico attraverso nanostrutture: un approccio a matrici di trasferimento", Ambra Sibilla, Corso di **Laurea in Chimica**, AA 2014/2015. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Point defects on graphene: a theoretical study", Simone Pellegrini, Corso di **Laurea Magistrale in Chimica**, AA 2013/2014. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Point defects in graphene: challenges and opportunities", Marina Casartelli, Corso di **Dottorato in Scienze Chimiche**, AA 2013/2014. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Quantum study of the isotope effect in the Eley-Rideal H_2 formation on graphite at vanishing energies", Marta Pasquini, Corso di **Laurea Magistrale in Chimica**, AA 2013/2014. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Chimica degli idrocarburi nel mezzo interstellare: studio first-principles dello ione CH_3^+ e dei suoi prodotti di dissociazione", Nicholas Francia, Corso di **Laurea in Chimica**, AA 2013/2014. Relatore: **Rocco Martinazzo**. Correlatore: Matteo Bonfanti.

"Studio first-principles dell'idrogenazione multipla in grafene", Mattia Peluchetti, Corso di **Laurea in Chimica**, AA 2012/2013. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Studio quantistico dell'adsorbimento di idrogeno atomico su grafene epitassiale", Michele Pizzochero, Corso di **Laurea in Chimica**, AA 2011/2012. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Electronic and transport properties of carbon chains", Paolo Bonardi, Corso di **Laurea Magistrale in Chimica**, AA 2011/2012. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Studio quantistico dell'effetto isotopico nella ricombinazione Eley-Rideal dell'idrogeno su grafite", Marta Pasquini, Corso di **Laurea in Chimica**, AA 2011/2012. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Il chemisorbimento di idrogeno su grafene difettuale", Simone Pellegrini, Corso di **Laurea in Chimica**, AA 2011/2012. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

"Wavepacket approaches to dissipative quantum dynamics", Fausto Martelli, Corso di **Dottorato in Scienze Chimiche**, AA 2010/2011. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini.

“Ab initio Molecular Dynamics of reacting D₂ on Cu(111): rotational alignment at finite surface temperature”, Francesco Nattino, AA 2010/2011, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**. Correlatori: Geert-Jan Kroes, Gian Franco Tantardini.

“Kinetic Monte Carlo modeling of H₂ formation on graphitic surfaces”, Elena Gavardi, AA 2008/2009, Corso di **Laurea Magistrale in Chimica**. Relatore: **Rocco Martinazzo**. Correlatore: Herma M. Cuppen.

“Sul comportamento limite per $T \rightarrow 0$ delle costanti cinetiche di associazione radiativa”, Fausto Martelli, Corso di **Laurea Magistrale in Chimica**, AA 2005/2006. Relatore: **Rocco Martinazzo**. Correlatore: Gian Franco Tantardini

ATTIVITÀ DI TUTORATO DEGLI STUDENTI DI CORSI DI LAUREA E DI LAUREA MAGISTRALE E DI TUTORATO DI DOTTORANDI DI RICERCA

“Risonanza, aromaticità e delocalizzazione elettronica secondo la teoria del legame di valenza”, Matteo Piras, Corso di **Laurea in Chimica (Università di Pavia)**, AA 2020/2021. Relatore: Matteo Cococcioni. Correlatore: **Rocco Martinazzo**.

“Graphene edges: structure, electronics and reactivity”, Davide Migliorini, Corso di **Laurea Magistrale in Chimica**, AA 2013/2014. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Reaction at surfaces: beyond the static surface approach in quantum dynamics”, Matteo Bonfanti, Corso di **Dottorato in Scienze Chimiche**, AA 2011/2012. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Idrogenazione di nanoribbon grafenici”, Davide Migliorini, Corso di **Laurea in Chimica**, AA 2011/2012. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Proprietà elettroniche di nanostrutture di carbonio monodimensionali”, Paolo Bonardi, Corso di **Laurea in Chimica**, AA 2009/2010. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Adsorption, clustering and reaction of hydrogen atoms on graphene”, Simone Casolo, Corso di **Dottorato in Scienze Chimiche**, AA 2008/2009. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Excited state properties from imaginary time correlation functions”, Giulia Semeghini, AA 2008/2009, Corso di **Laurea in Fisica**. Relatore: Davide Emilio Galli. Correlatore: **Rocco Martinazzo**.

“Studio teorico della dinamica di rilassamento vibrazionale di adsorbati su superfici”, Marco Pitalieri, AA 2008/2009, Corso di **Laurea Magistrale in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Studio della relazione tra hydrogen affinity e proprietà magnetiche negli idrocarburi policiclici aromatici”, Matteo Bonfanti, AA 2007/2008, Corso di **Laurea Magistrale in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Studio first principles di superfici grafite funzionalizzate per l’hydrogen storage”, Angelo Giussani, AA 2007/2008, Corso di **Laurea Magistrale in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Tunneling diffusion di idrogeno atomico su superficie di grafite”, Elena Gavardi, AA 2006/2007, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Studi modello della dinamica non adiabatica dello ione CH₂⁺”, Ahmed Muhamed Orlando, AA 2006/2007, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Fisisorbimento di idrogeno su grafite e diffusione per effetto tunneling”, Valentina Villa, AA 2005/2006, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Applicazione della dinamica quasi-classica allo studio di reazioni ioniche coinvolgenti litio e idrogeno”, William Giuliano, AA 2005/2006, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Studio quantistico della formazione Eley-Rideal di idrogeno su grafite nel regime delle collisioni cold”, Simone Casolo, AA 2005/2006, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Studio quantistico della dinamica di reazione C⁺+H₂ col metodo del pacchetto d’onda”, Manuel Montenegro, AA 2003/2004, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**

“Calcolo teorico delle sezioni d’urto di associazione radiativa. Applicazione a sistemi di interesse astrofisico”, Simone Casolo, AA 2003/2004, Corso di **Laurea in Chimica**. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**

“Dinamica Eley-Rideal e Hot-Atom nella formazione di H₂ su Ni(100)”, Stefania Assoni, Corso di Laurea in Chimica (VO), AA 2002/2003. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

“Il mistero del CH⁺ nel mezzo interstellare: studio ab initio dello ione CH₂⁺”, Pierfrancesco Di Benedetto, Corso di Laurea in Chimica (VO), AA 2002/2003. Relatore: Gian Franco Tantardini. Correlatore: **Rocco Martinazzo**.

ATTIVITÀ DI RICERCA SCIENTIFICA

Al confine tra la Chimica e la Fisica l'attività di ricerca di Rocco Martinazzo è concentrata sullo sviluppo di teorie e metodi computazionali e sulla loro applicazione allo studio della struttura e della dinamica (quantistica) di sistemi molecolari. Di particolare interesse sono i problemi in fase condensata ed all'interfaccia solido-gas, con un *focus* su nanostrutture a base di Carbonio, Dinamica quantistica in ambienti complessi e Teoria del legame chimico. Campi di applicazione comprendono Nanotecnologie, Scienza delle Superfici e Catalisi, Elettronica Molecolare, Astrochimica. I principali mezzi di indagine utilizzati sono le leggi fondamentali che governano la materia a livello microscopico, le loro simmetrie e le loro proprietà geometriche e topologiche.

Rocco Martinazzo ha pubblicato ca. 90 articoli *peer-reviewed* in riviste internazionali, 5 *conference proceedings* e 13 contributi in volumi, ottenendo 2,287 citazioni (1,976 escludendo le auto-citazioni) ed un *h-index* di 28 (fonte: Scopus). Le pubblicazioni includono riviste considerate *top-rank* in chimica e fisica, quali ad esempio *Advanced Optical Materials*, *ACS Catalysis*, *ACS Nano*, *Carbon*, *Chemistry: a European journal*, *Journal of Chemical Theory and Computation*, *Monthly Notices of the Royal Astronomical Society*, *Physics Reports*, *Physical Review Letters*, *Proceedings of the National Academy of Sciences (US)*.

10 PUBBLICAZIONI SCIENTIFICHE SELEZIONATE

1. **Quantum dynamics with electronic friction**, *Physical Review Letters*, 128(20): 206002. 5 2022, R. Martinazzo* and I. Burghardt.
Significance. *Reactions in condensed phases may depart significantly from the standard (adiabatic) model of chemical dynamics since the presence of dense manifolds of electronic states leads to severe deviations from the Born-Oppenheimer approximation. At metal surfaces (of relevance, for instance, for catalytic processes) energy is usually dissipated in the form of low-energy electronic excitations (electron-hole pair formation). Electronic friction describes a regime where non-adiabaticity is of limited extent and can be subsumed in a frictional force that the electrons exert on the moving nuclei, in addition to the usual Born-Oppenheimer forces. This and the companion paper (PRA 105, 052215, 2022) settle a critical issue in the field by devising a novel framework (and a viable approach) to account for electronic friction in a fully quantum setting of the combined electron-nuclear system.*
2. **Lower bounds to eigenvalues of the Schrödinger equation by solution of a 90-y challenge**, *Proc. Natl. Acad. Sci.*, 117, 16181 (2020), R. Martinazzo* and E. Pollak*.
Significance. *In quantum theory accurate upper bounds to eigenvalues of Hermitian operators have been known and used since a celebrated theorem due to Ritz. The search for complementary lower bounds - which would bound the error in the computed eigenvalues - started in the early days of quantum mechanics but little progress had been reported since then and the lower bounds remained long much looser than the complementary Ritz bounds. This work represents a step forward to settle this issue and introduces rigorous lower bounds whose accuracy is similar to that of the upper bounds. Subsequent works extended and applied the method to Coulombic systems (ACS Physical Chemistry Au, 2: 23 (2021), Journal of Chemical Theory and Computation, 17: 1535 (2021)).*
3. **Local-In-Time Error in variational quantum dynamics**, *Physical Review Letters*, 124, 150601 (2020), R. Martinazzo* and I. Burghardt.
Significance. *This work sets the foundations of the theory of error control in variational quantum dynamics. It forms the basis for natural (and rigorous) spawning and pruning algorithms that aim to optimize the overall computational cost of a quantum dynamical simulation. Such adaptive schemes are a crucial requirement for devising and applying on-the-fly quantum dynamical methods to molecular and condensed-phase problems. Besides the numerical applications, the work also highlights a hitherto unexplored geometric structure of the variational principle and its physical consequences. It impacts on our ability to simulate quantum systems on both classical and quantum computers.*
4. **Sticking of atomic hydrogen on graphene**, *J. of Physics: Cond. Matter*, 30, 283002 (2018), M. Bonfanti and S. Achilli and R. Martinazzo*.
Significance. *This invited topical review summarizes the experimental and theoretical efforts done in the previous decade that aimed at understanding graphene hydrogenation at a microscopic level. The emphasis was put on the interplay between the adatom structures, their formation dynamics, and the electric, magnetic and chemical properties of the carbon sheet. The topics covered by the article range from the diluted regime where adatoms are quasi-isolated on a free-standing graphene sheet to the high coverage conditions on both free-standing and supported graphene where complex (sometimes ordered) structures form.*
5. **Quantum dynamics of hydrogen atoms on graphene: II Sticking**, *J. Chem. Phys.*, 124, 124704 (2015), M. Bonfanti, B. Jackson, K. H. Hughes, I. Burghardt and R. Martinazzo*.

- Significance.** This work is the first fully converged quantum study of hydrogen atom sticking to graphene. It was shown that sticking is determined by a competition between barrier-crossing and energy transfer to the surface, which ensures a very fast energy relaxation and leads to an unexpectedly high sticking probability, as later confirmed by carefully conducted scattering experiments (H. Jang et al., *Science* 364: 379 (2019)). The work also shows that a satisfactory description of the dynamics can be achieved with a simple impulsive model of a classical particle scattering off a quantum surface, thereby highlighting the importance of a quantum description of the graphene surface.
6. **Structure and stability of hydrogenated carbon atom vacancies in graphene**, *Carbon*, 77, 165 (2014), M. Casartelli, S. Casolo, G.F. Tantardini and R. Martinazzo*.
Significance. This work reports on a detailed investigation of the hydrogenation of carbon atom vacancies in graphene and its effects on the substrate properties. Comparison with transmission electron microscopy, scanning tunneling microscopy and muon-spin-resonance experiments showed that vacancies in graphene can be hydrogenated to various degree under ordinary conditions. The work settled puzzling issues concerning the value of the magnetic moment of a carbon atom vacancy in graphene.
 7. **Insights into hydrogen formation in space from ab initio molecular dynamics**, *Proc. Natl. Acad. Sci.*, 110, 6674 (2013), S. Casolo, G.F. Tantardini and R. Martinazzo*.
Significance. This work reports on an ab initio molecular dynamics study of the (Eley-Rideal) recombination of hydrogen atoms on graphitic substrates. It was shown that the reaction dominates at interstellar medium conditions and alone may explain astronomical observations if the possibility of facile sticking at special sites (edges, point defects, etc.) of the surface of the dust grains is taken into account. See also *Phys. Org.*, "[Of grains and graphite: Simulating interstellar hydrogen formation](#)".
 8. **Universal Markovian reduction of Brownian particle dynamics**, *J. Chem. Phys. (Communication)*, 134, 011101 (2011), R. Martinazzo*, B. Vacchini, K. H. Hughes, and I. Burghardt.
Significance. This work reports, for the first time, an explicit construction of a Markovian embedding in a key physical problem, that of a Brownian particle obeying the generalized (classical or quantum) Langevin equation. It sparked the birth of the "reaction coordinate method", a useful tool that since then has found use in disparate disciplines like quantum thermodynamics, molecular electronics and the theory of orthogonal polynomials.
 9. **Symmetry-induced band gap opening in graphene superlattices**, *Phys. Rev. B* 81, 245420 (2010), R. Martinazzo*, S. Casolo, G.F. Tantardini.
Significance. In this work it was shown by symmetry arguments and electronic-structure calculations that, contrary to widespread belief, it is possible to open a band gap in graphene without breaking its symmetry. The proposed structures, honeycomb superlattices of unitary defects, were shown to have new Dirac cones right close to the gapped region, and optimal gap size with respect to their length scale. The unexpected presence of low-energy flat bands resembles the situation of twisted-bilayer graphene, where such bands have been recently found to host a variety of exotic many-body phases, from superconducting to topological-Mott-insulating ones. Paper selected for the "Virtual Journal of Nanoscale Science & Technology".
 10. **Understanding adsorption of hydrogen atoms on graphene**, *J. Chem. Phys.*, 130, 054704 (2009), S. Casolo, O. M. Lovvik, R. Martinazzo* and G. F. Tantardini.
Significance. This work reports on a detailed investigation of the binding and barrier energies for sequential sticking of hydrogen atoms on graphene. The results were rationalized in light of Pauling's Resonating Valence Bond theory of chemical bond and used to explain the formation of hydrogen dimer and cluster structures that had been long observed in graphene. Paper selected for the "Virtual Journal of Nanoscale Science & Technology".

PUBBLICAZIONI SCIENTIFICHE SU RIVISTE PEER-REVIEWED

2022 (8)

- [Signatures of coherent vibronic exciton dynamics and conformational control in two-dimensional electronic spectroscopy of conjugated polymers.](#) Brey, D.; Binder, R.; Martinazzo, R.; and Burghardt*, I. *Faraday Discussions*. 2022.
Abstract. Two-dimensional electronic spectroscopy (2DES) signals for homo-oligomer J-aggregates are computed, with a focus on the role of structural change induced by low-frequency torsional modes along with quasi-stationary trapping effects induced by high-frequency polaronic modes. To this end, a model system is derived from an ab initio parametrized site-based Hamiltonian for oligothiophenes [Binder et al., *Phys. Rev. Lett.*, 2018, 120, 227401]. To obtain a compact representation, we introduce a collective lattice mode whose vibronic coupling depends nonlinearly on the exciton density. As a result, an N-site model with a single polaronic mode and a single torsional mode is obtained. Further, a quantum-classical treatment is employed where the torsional mode is treated within a mean-field Ehrenfest-Langevin approximation. 2DES spectra are computed using the Equation-of-Motion Phase-Matching Approach (EOM-PMA) within a wavefunction description. It is seen that the spectra combine vibronic fine structure due to the polaronic mode and a dynamic Stokes shift due to torsional relaxation. The signatures of coherent effects and adiabatic evolution in the 2DES spectra are discussed.
- [Modelling ultrafast dynamics at a conical intersection with regularized diabatic states: An approach based on multiplicative neural networks.](#) Błasiak, B.; Brey, D.; Koch, W.; Martinazzo, R.; and Burghardt*, I. *Chemical Physics*, 560: 111542. 2022.

Abstract. Neural-network (NN) potentials are employed in conjunction with the Multiconfiguration Time-Dependent Hartree (MCTDH) method in order to simulate an ultrafast photoinduced cis-trans type isomerization process induced by a conical intersection. To this end, NN potentials are fitted to a diabatic potential of regularized diabatic states type [Köppel et al., *J. Chem. Phys.* 115, 2377 (2001)], which entirely relies on adiabatic potential information. Multiplicative NNs are employed which match the sum-of-products form of the multiconfigurational MCTDH wavefunction. Good agreement with the reference dynamics is obtained for simulations of the highly correlated dynamics with up to 13 degrees of freedom. This study contributes to developing NN methodologies suitable for photochemical dynamics at complex excited-state topologies.

- [Dissipative tunneling rates through the incorporation of first-principles electronic friction in instanton rate theory. I. Theory.](#) Litman*, Y.; Pócs, E., S.; Box, C., L.; **Martinazzo, R.**; Maurer, R., J.; and Rossi*, M. *The Journal of Chemical Physics*, 156(19): 194106. 2022.

Abstract. Reactions involving adsorbates on metallic surfaces and impurities in bulk metals are ubiquitous in a wide range of technological applications. The theoretical modeling of such reactions presents a formidable challenge for theory because nuclear quantum effects (NQE) can play a prominent role and the coupling of the atomic motion with the electrons in the metal gives rise to important non-adiabatic effects (NAEs) that alter atomic dynamics. In this work, we derive a theoretical framework that captures both NQEs and NAEs and, due to its high efficiency, can be applied to first-principles calculations of reaction rates in high-dimensional realistic systems. More specifically, we develop a method that we coin ring polymer instanton with explicit friction (RPI-EF), starting from the ring polymer instanton formalism applied to a system-bath model. We derive general equations that incorporate the spatial and frequency dependence of the friction tensor and then combine this method with the ab initio electronic friction formalism for the calculation of thermal reaction rates. We show that the connection between RPI-EF and the form of the electronic friction tensor presented in this work does not require any further approximations, and it is expected to be valid as long as the approximations of both underlying theories remain valid.

- [Dissipative tunneling rates through the incorporation of first-principles electronic friction in instanton rate theory. II. Benchmarks and applications.](#) Litman*, Y.; Pócs, E., S.; Box, C., L.; **Martinazzo, R.**; Maurer, R., J.; and Rossi*, M. *The Journal of Chemical Physics*, 156(19): 194107. 2022.

Abstract. In Paper I [Litman et al., *J. Chem. Phys.* (in press) (2022)], we presented the ring-polymer instanton with explicit friction (RPI-EF) method and showed how it can be connected to the ab initio electronic friction formalism. This framework allows for the calculation of tunneling reaction rates that incorporate the quantum nature of the nuclei and certain types of non-adiabatic effects (NAEs) present in metals. In this paper, we analyze the performance of RPI-EF on model potentials and apply it to realistic systems. For a 1D double-well model, we benchmark the method against numerically exact results obtained from multi-layer multi-configuration time-dependent Hartree calculations. We demonstrate that RPI-EF is accurate for medium and high friction strengths and less accurate for extremely low friction values. We also show quantitatively how the inclusion of NAEs lowers the crossover temperature into the deep tunneling regime, reduces the tunneling rates, and, in certain regimes, steers the quantum dynamics by modifying the tunneling pathways. As a showcase of the efficiency of this method, we present a study of hydrogen and deuterium hopping between neighboring interstitial sites in selected bulk metals. The results show that multidimensional vibrational coupling and nuclear quantum effects have a larger impact than NAEs on the tunneling rates of diffusion in metals. Together with Paper I [Litman et al., *J. Chem. Phys.* (in press) (2022)], these results advance the calculations of dissipative tunneling rates from first principles.

- [Quantum algorithms for grid-based variational time evolution.](#) Ollitrault, P., J.; Jandura, S.; Miessen, A.; Burghardt, I.; **Martinazzo, R.**; Tacchino, F.; and Tavernelli*, I., arXiv:2203.02521, 2022. DOI <https://doi.org/10.48550/arXiv.2203.02521>

Abstract. The simulation of quantum dynamics calls for quantum algorithms working in first quantized grid encodings. Here, we propose a variational quantum algorithm for performing quantum dynamics in first quantization. In addition to the usual reduction in circuit depth conferred by variational approaches, this algorithm also enjoys several advantages compared to previously proposed ones. For instance, variational approaches suffer from the need for a large number of measurements. However, the grid encoding of first quantized Hamiltonians only requires measuring in position and momentum bases, irrespective of the system size. Their combination with variational approaches is therefore particularly attractive. Moreover, heuristic variational forms can be employed to overcome the limitation of the hard decomposition of Trotterized first quantized Hamiltonians into quantum gates. We apply this quantum algorithm to the dynamics of several systems in one and two dimensions. Our simulations exhibit the previously observed numerical instabilities of variational time propagation approaches. We show how they can be significantly attenuated through subspace diagonalization at a cost of an additional $O(MN^2)$ 2-qubit gates where M is the number of dimensions and N is the total number of grid points.

- [Quantum Dynamics with Electronic Friction.](#) **Martinazzo*, R.**; and Burghardt, I. *Physical Review Letters*, 128(20): 206002. 2022.

Abstract. A theory of electronic friction is developed using the exact factorization of the electronic-nuclear wave function. No assumption is made regarding the electronic bath, which can be made of independent or interacting electrons, and the nuclei are treated quantumly. The ensuing equation of motion for the nuclear wave function is a nonlinear Schrödinger equation including a friction term. The resulting friction kernel agrees with a previously derived mixed quantum-classical result by Dou et al., [*Phys. Rev. Lett.* 119, 046001 (2017)], except for a pseudomagnetic contribution in the latter that is here removed. More specifically, it is shown that the electron dynamics generally washes out the gauge fields appearing in the adiabatic dynamics. However, these are fully re-established in the typical situation where the electrons respond rapidly on the slow time scale of the nuclear dynamics (Markov limit). Hence, we predict Berry's phase effects to be observable also in the presence of electronic friction. Application to a model vibrational relaxation problem proves that the proposed approach represents a viable way to account for electronic friction in a fully quantum setting for the nuclear dynamics.

- [Quantum theory of electronic friction.](#) **Martinazzo*, R.**; and Burghardt, I. *Physical Review A*, 105(5): 052215. 2022.

Abstract. Electronic friction is an important energy loss channel for atoms and molecules scattering off, reacting, or simply vibrating at metallic surfaces. It is usually well described by mixed classical-quantum approaches where the nuclei evolve classically according to Langevin-type equations of motion, and Born-Oppenheimer forces and friction kernels are obtained from first-principles electronic structure calculations. However, classical dynamics falls short when light atoms are involved, which is also the situation where electronic friction becomes the dominant dissipation channel and its role in the dynamics can be unambiguously assessed. Furthermore, the interplay between electronic friction and nuclear quantum effects in molecular processes at surfaces is largely unknown; in fact, it is not even clear how to include electronic friction in a quantum setting. Here we fill this gap by developing a fully quantum theory of electronic friction at $T=0$ K. The electronic bath is considered to be entirely general and can be made of interacting electrons, potentially in a strongly correlated state. The

derived friction kernel agrees with a recently obtained mixed quantum-classical result [Dou, Miao, and Subotnik, *Phys. Rev. Lett.* **119**, 046001 (2017)], except for a pseudomagnetic contribution in the latter that is removed here. The ensuing equation of motion for the nuclear wave function is a nonlinear Schrödinger equation with a frictional vector potential that depends on the past wave function behavior. The equation becomes local-in-time in the typical situation where the electrons respond rapidly on the slow timescale of the nuclear dynamics (Markov limit) and generalizes previously known Schrödinger-Langevin equations to coordinate-dependent, tensorial friction kernels.

- [Adsorption of Polycyclic Aromatic Hydrocarbons and C₆₀ onto Forsterite: C-H Bond Activation by the Schottky Vacancy.](#) Campisi*, D.; Lamberts, T.; Dzade, N., Y.; Martinazzo, R.; Kate, I., L., t.; and Tielens, A., G., G., M. *ACS Earth and Space Chemistry*. 2022.

Abstract. Understanding how to catalytically break the C-H bond of aromatic molecules, such as polycyclic aromatic hydrocarbons (PAHs), is currently a big challenge and a subject of study in catalysis, astrochemistry, and planetary science. In the latter, the study of the breakdown reaction of PAHs on mineral surfaces is important to understand if PAHs are linked to prebiotic molecules in regions of star and planet formation. In this work, we employed a periodic density functional theory along with Grimme's D4 (DFT-D4) approach for studying the adsorption of a sample of PAHs (naphthalene, anthracene, fluoranthene, pyrene, coronene, and benzocoronene) and fullerene on the [010] forsterite surface and its defective surfaces (Fe-doped and Ni-doped surfaces and a MgO-Schottky vacancy) for their implications in catalysis and astrochemistry. On the basis of structural and binding energy analysis, large PAHs and fullerene present stronger adsorption on the pristine, Fe-doped, and Ni-doped forsterite surfaces than small PAHs. On a MgO-Schottky vacancy, parallel adsorption of the PAH leads to the chemisorption process (C-Si and/or C-O bonds), whereas perpendicular orientation of the PAH leads to the catalytic breaking of the aromatic C-H bond via a barrierless reaction. Spin density and charge analysis show that C-H dissociation is promoted by electron donation from the vacancy to the PAH. As a result of the undercoordinated Si and O atoms, the vacancy acts as a Frustrated Lewis Pair (FLP) catalyst. Therefore, a MgO-Schottky vacancy [010] forsterite surface proved to have potential catalytic activity for the activation of C-H bond in aromatic molecules.

2021 (8)

- [Interaction of Aromatic Molecules with Forsterite: Accuracy of the Periodic DFT-D4 Method.](#) Campisi*, D.; Lamberts, T.; Dzade, N., Y.; Martinazzo, R.; Ten Kate, I., L.; and Tielens, A., G. *Journal of Physical Chemistry A*, 125(13): 2770-2781. 2021.

Abstract. Density functional theory (DFT) has provided deep atomic-level insights into the adsorption behavior of aromatic molecules on solid surfaces. However, modeling the surface phenomena of large molecules on mineral surfaces with accurate plane wave methods (PW) can be orders of magnitude more computationally expensive than localized atomic orbitals (LCAO) methods. In the present work, we propose a less costly approach based on the DFT-D4 method (PBE-D4), using LCAO, to study the interactions of aromatic molecules with the 010 forsterite (Mg₂SiO₄) surface for their relevance in astrochemistry. We studied the interaction of benzene with the pristine 010 forsterite surface and with transition-metal cations (Fe²⁺ and Ni²⁺) using PBE-D4 and a vdW-inclusive density functional (Dion, Rydberg, Schröder, Langreth, and Lundqvist (DRSLL)) with LCAO methods. PBE-D4 shows good agreement with coupled-cluster methods (CCSD(T)) for the binding energy trend of cation complexes and with PW methods for the binding energy of benzene on the forsterite surface with a difference of about 0.03 eV. The basis set superposition error (BSSE) correction is shown to be essential to ensure a correct estimation of the binding energies even when large basis sets are employed for single-point calculations of the optimized structures with smaller basis sets. We also studied the interaction of naphthalene and benzocoronene on pristine and transition-metal-doped 010 forsterite surfaces as a test case for PBE-D4. Yielding results that are in good agreement with the plane wave methods with a difference of about 0.02-0.17 eV, the PBE-D4 method is demonstrated to be effective in unraveling the binding structures and the energetic trends of aromatic molecules on pristine and transition-metal-doped forsterite mineral surfaces. Furthermore, PBE-D4 results are in good agreement with its predecessor PBE-D3(BJ) and with the vdW-inclusive density functionals, as long as transition metals are not involved. Hence, PBE-D4/CP-DZP has been proven to be a robust theory level to study the interaction of aromatic molecules on mineral surfaces.

- [Lower Bounds for Coulombic Systems.](#) Pollak*, E.; and Martinazzo*, R. *Journal of Chemical Theory and Computation*, 17(3): 1535-1547. 2021.

Abstract. As of the writing of this paper, lower bounds are not a staple of quantum chemistry computations and for good reason. All previous attempts at applying lower bound theory to Coulombic systems led to lower bounds whose quality was inferior to the Ritz upper bounds so that their added value was minimal. Even our recent improvements upon Temple's lower bound theory were limited to Lanczos basis sets and these are not available to atoms and molecules due to the Coulomb singularity. In the present paper, we overcome these problems by deriving a rather simple eigenvalue equation whose roots, under appropriate conditions, give lower bounds which are competitive with the Ritz upper bounds. The input for the theory is the Ritz eigenvalues and their variances; there is no need to compute the full matrix of the squared Hamiltonian. Along the way, we present a Cauchy-Schwartz inequality which underlies many aspects of lower bound theory. We also show that within the matrix Hamiltonian theory used here, the methods of Lehmann and our recent self-consistent lower bound theory (J. Chem. Phys. 2020, 115, 244110) are identical. Examples include implementation to the hydrogen and helium atoms.

- [Comment on "Regularizing the MCTDH equations of motion through an optimal choice on-the-fly \(i.e., spawning\) of unoccupied single-particle functions" \[D. Mendive-Tapia, H.-D. Meyer, J. Chem. Phys. 153, 234114 \(2020\)\].](#) Martinazzo*, R.; and Burghardt*, I., arXiv:2102.12117, 2021.

Abstract. The purpose of the present Comment is to point out the connection between an approach to spawning and regularization that was recently introduced by D. Mendive-Tapia and H.-D. Meyer [J. Chem. Phys. 153, 234114 (2020)] in the context of the Multiconfiguration Time-Dependent Hartree (MCTDH) method, and earlier work where adaptive variational quantum propagation based on the Local-in-Time Error (LITE) was introduced [R. Martinazzo and I. Burghardt, Phys. Rev. Lett. 124, 150601 (2020); arXiv:1907.00841 [quant-ph] (2019)]. Furthermore, we show that the LITE represents a gauge-invariant distance which provides a natural, physically sound tool for adaptive quantum dynamics.

- [Comparison of an Improved Self-consistent Lower Bound Theory with Lehmann's Method for Low-lying Eigenvalues.](#) Ronto, M.; Pollak*, E.; and Martinazzo, R. *ResearchSquare*, 2021. DOI: <https://doi.org/10.21203/rs.3.rs-492850/v1>

Abstract. Ritz eigenvalues only provide upper bounds for the energy levels, while obtaining lower bounds requires at least the calculation of the variances associated with these eigenvalues. The well-known Weinstein and Temple lower bounds based on the eigenvalues and variances converge very slowly and their quality is considerably worse than that of the Ritz upper bounds. Lehmann presented a method that in principle optimizes Temple's lower bounds with significantly improved results. We have recently formulated a Self-Consistent Lower Bound Theory

(SCLBT), which improves upon Temple's results. In this paper, we further improve the SCLBT and compare its quality with Lehmann's theory. The Lánczos algorithm for constructing the Hamiltonian matrix simplifies Lehmann's theory and is essential for the SCLBT method. Using two lattice Hamiltonians, we compared the improved SCLBT (iSCLBT) with its previous implementation as well as with Lehmann's lower bound theory. The novel iSCLBT exhibits a significant improvement over the previous version. Both Lehmann's theory and the SCLBT variants provide significantly better lower bounds than those obtained from Weinstein's and Temple's methods. Compared to each other, the Lehmann and iSCLBT theories exhibit similar performance in terms of the quality and convergence of the lower bounds. By increasing the number of states included in the calculations, the lower bounds are tighter and their quality becomes comparable with that of the Ritz upper bounds. Both methods are suitable for providing lower bounds for low-lying excited states as well. Compared to Lehmann's theory, one of the advantages of the iSCLBT method is that it does not necessarily require the Weinstein lower bound for its initial input, but Ritz eigenvalue estimates can also be used. Especially owing to this property the iSCLBT method sometimes exhibits improved convergence compared to that of Lehmann's lower bounds

- [The Different Story of \$\pi\$ Bonds](#). Cappelletti, M.; Leccese, M.; Cococcioni, M.; Proserpio, D., M.; and Martinazzo*, R. *Molecules* 2021, Vol. 26, Page 3805, 26(13): 3805. 2021.

Abstract. We revisit "classical" issues in multiply bonded systems between main groups elements, namely the structural distortions that may occur at the multiple bonds and that lead, e.g., to trans-bent and bond-length alternated structures. The focus is on the role that orbital hybridization and electron correlation play in this context, here analyzed with the help of simple models for σ - and π -bonds, numerically exact solutions of Hubbard Hamiltonians and first principles (density functional theory) investigations of an extended set of systems.

- [Quantum Dynamics with Electronic Friction](#). Martinazzo*, R.; and Burghardt, I., arXiv:2108.02622, 2021. DOI: <https://doi.org/10.48550/arXiv.2108.02622>

Abstract. A theory of electronic friction is developed using the exact factorization of the electron-nuclear wavefunction. No assumption is made regarding the electronic bath, which can be made of independent or interacting electrons, and the nuclei are treated quantumly. The ensuing equation of motion for the nuclear wavefunction is a non-linear Schrödinger equation including a friction term. The resulting friction kernel agrees with a previously derived mixed quantum-classical result by Dou, Miao & Subotnik (Phys. Rev. Lett. 119, 046001 (2017)), except for a pseudo-magnetic contribution in the latter that is here removed. More specifically, it is shown that the electron dynamics generally washes out the gauge fields appearing in the adiabatic dynamics. However, at $T=0$ K, the pseudo-magnetic force is fully re-established in the typical situation where the electrons respond rapidly on the slow time-scale of the nuclear dynamics (Markov limit). Hence, we predict Berry's phase effects to be observable also in the presence of electronic friction, and non-trivial geometric phases should be attainable for molecules on metallic magnetic surfaces.

- [Comparison of an improved self-consistent lower bound theory with Lehmann's method for low-lying eigenvalues](#). Ronto, M.; Pollak*, E.; and Martinazzo, R. *Scientific Reports* 2021 11:1, 11(1): 1-14. 2021.

Abstract. Ritz eigenvalues only provide upper bounds for the energy levels, while obtaining lower bounds requires at least the calculation of the variances associated with these eigenvalues. The well-known Weinstein and Temple lower bounds based on the eigenvalues and variances converge very slowly and their quality is considerably worse than that of the Ritz upper bounds. Lehmann presented a method that in principle optimizes Temple's lower bounds with significantly improved results. We have recently formulated a Self-Consistent Lower Bound Theory (SCLBT), which improves upon Temple's results. In this paper, we further improve the SCLBT and compare its quality with Lehmann's theory. The Lánczos algorithm for constructing the Hamiltonian matrix simplifies Lehmann's theory and is essential for the SCLBT method. Using two lattice Hamiltonians, we compared the improved SCLBT (iSCLBT) with its previous implementation as well as with Lehmann's lower bound theory. The novel iSCLBT exhibits a significant improvement over the previous version. Both Lehmann's theory and the SCLBT variants provide significantly better lower bounds than those obtained from Weinstein's and Temple's methods. Compared to each other, the Lehmann and iSCLBT theories exhibit similar performance in terms of the quality and convergence of the lower bounds. By increasing the number of states included in the calculations, the lower bounds are tighter and their quality becomes comparable with that of the Ritz upper bounds. Both methods are suitable for providing lower bounds for low-lying excited states as well. Compared to Lehmann's theory, one of the advantages of the iSCLBT method is that it does not necessarily require the Weinstein lower bound for its initial input, but Ritz eigenvalue estimates can also be used. Especially owing to this property the iSCLBT method sometimes exhibits improved convergence compared to that of Lehmann's lower bounds.

- [Lower Bounds for Nonrelativistic Atomic Energies](#). Ireland, R., T.; Jeszenszki, P.; Mátyus*, E.; Martinazzo*, R.; Ronto, M.; and Pollak*, E. *ACS Physical Chemistry Au*, 2(1): 23-37. 2021.

Abstract. A recently developed lower bound theory for Coulombic problems (E. Pollak, R. Martinazzo, J. Chem. Theory Comput. 2021, 17, 1535) is further developed and applied to the highly accurate calculation of the ground-state energy of two- (He, Li⁺, and H⁺) and three- (Li) electron atoms. The method has been implemented with explicitly correlated many-particle basis sets of Gaussian type, on the basis of the highly accurate (Ritz) upper bounds they can provide with relatively small numbers of functions. The use of explicitly correlated Gaussians is developed further for computing the variances, and the necessary modifications are here discussed. The computed lower bounds are of submilli-Hartree (parts per million relative) precision and for Li represent the best lower bounds ever obtained. Although not yet as accurate as the corresponding (Ritz) upper bounds, the computed bounds are orders of magnitude tighter than those obtained with other lower bound methods, thereby demonstrating that the proposed method is viable for lower bound calculations in quantum chemistry applications. Among several aspects, the optimization of the wave function is shown to play a key role for both the optimal solution of the lower bound problem and the internal check of the theory.

2020 (5)

- [Local-in-Time Error in Variational Quantum Dynamics](#). Martinazzo*, R.; and Burghardt, I. *Physical Review Letters*, 124(15): 150601. 2020.

Abstract. The McLachlan "minimum-distance" principle for optimizing approximate solutions of the time-dependent Schrödinger equation is revisited, with a focus on the local-in-time error accompanying the variational solutions. Simple, exact expressions are provided for this error, which are then evaluated in illustrative cases, notably the widely used mean-field approach and the adiabatic quantum molecular dynamics. Based on these findings, we demonstrate the rigorous formulation of an adaptive scheme that resizes on the fly the underlying variational manifold and, hence, optimizes the overall computational cost of a quantum dynamical simulation. Such adaptive schemes are a crucial requirement for devising and applying direct quantum dynamical methods to molecular and condensed-phase problems.

- [Lower bounds to eigenvalues of the Schrödinger equation by solution of a 90-y challenge.](#) Martinazzo*, R.; and Pollak*, E. *Proceedings of the National Academy of Sciences of the United States of America*, 117(28): 16181-16186. 2020.

Abstract. The Ritz upper bound to eigenvalues of Hermitian operators is essential for many applications in science. It is a staple of quantum chemistry and physics computations. The lower bound devised by Temple in 1928 [G. Temple, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 119, 276-293 (1928)] is not, since it converges too slowly. The need for a good lower-bound theorem and algorithm cannot be overstated, since an upper bound alone is not sufficient for determining differences between eigenvalues such as tunneling splittings and spectral features. In this paper, after 90 y, we derive a generalization and improvement of Temple's lower bound. Numerical examples based on implementation of the Lanczos tridiagonalization are provided for nontrivial lattice model Hamiltonians, exemplifying convergence over a range of 13 orders of magnitude. This lower bound is typically at least one order of magnitude better than Temple's result. Its rate of convergence is comparable to that of the Ritz upper bound. It is not limited to ground states. These results complement Ritz's upper bound and may turn the computation of lower bounds into a staple of eigenvalue and spectral problems in physics and chemistry.

- [Self-consistent theory of lower bounds for eigenvalues.](#) Pollak*, E.; and Martinazzo, R. *The Journal of Chemical Physics*, 152(24): 244110. 2020.

Abstract. A rigorous practically applicable theory is presented for obtaining lower bounds to eigenvalues of Hermitian operators, whether the ground state or excited states. Algorithms are presented for computing "residual energies" whose magnitude is essential for the computation of the eigenvalues. Their practical application is possible due to the usage of the Lanczos method for creating a tridiagonal representation of the operator under study. The theory is self-consistent, in the sense that a lower bound for one state may be used to improve the lower bounds for others, and this is then used self-consistently until convergence. The theory is exemplified for a toy model of a quartic oscillator, where with only five states the relative error in the lower bound for the ground state is reduced to $6 \cdot 10^{-6}$, which is the same as the relative error of the least upper bound obtained with the same basis functions. The lower bound method presented in this paper suggests that lower bounds may become a staple of eigenvalue computations.

- [Benzodithienyl Silanes for Organic Electronics: AIE Solid-State Blue Emitters and High Triplet Energy Charge-Transport Materials.](#) Bossi, A.; Arnaboldi, S.; Castellano, C.; Martinazzo, R.; and Cauteruccio*, S. *Advanced Optical Materials*, 8(22): 2001018. 2020.

Abstract. A novel class of benzo[1,2-b:4,3-b']dithienyl (BDT) silanes 1-3 in which a tetrahedral silicon atom connects two BDT units is developed as high triplet energy 3D-host. The photophysical and electrochemical properties of these structures are investigated, demonstrating that the peculiar features of the constituting BDT units are preserved in the corresponding silanes. All compounds display deep UV absorption ($E_g = 4.10$ - 3.52 eV) and fluorescent emission (300-400 nm for 1 and 2, and 350-450 nm for 3). Phosphorescence is observed at low temperature and the respective T1 states set at 2.65, 2.59, and 2.25 eV. Emission efficiency in solution is as high as 0.18 in 3. Compound 1 crystallizes in two monoclinic structures without relevant intra-inter-molecular contacts; both display similar and intriguing aggregation induced emission-like deep blue emission (390-397 nm) with quantum yield up to 13%. A blue and a green emissive organic light emitting diode devices are realized using silane 1 as semiconductive host material. The perfect sensitization of the green Ir(ppy)3 emitter results in a device which nicely compares, in terms of efficiency, with a standard one. The blue FIrpic emitter is instead only partially sensitized on account of the too closed triplets.

- [Superhydrogenation of pentacene: the reactivity of zigzag-edges.](#) Campisi*, D.; Simonsen, F., D., S.; Thrower, J., D.; Jaganathan, R.; Hornekær, L.; Martinazzo, R.; and Tielens*, A., G. *Physical Chemistry Chemical Physics*, 22(3): 1557-1565. 2020.

Abstract. Investigating the hydrogenation of carbonaceous materials is of interest in a wide range of research areas including electronic device development, hydrogen storage, and, in particular, astrocatalytic formation of molecular hydrogen in the universe. Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in space, locking up close to 15% of the elementary carbon. We have used thermal desorption measurements to study the hydrogenation sequence of pentacene from adding one additional H to the fully hydrogenated pentacene species. The experiments reveal that hydrogenated species with an even number of excess H atoms are highly preferred over hydrogenated species with an odd number of H atoms. In addition, the experiments show that specific hydrogenation states of pentacene with 2, 4, 6, 10, 16 and 22 extra H atoms are preferred over other even numbers. We have investigated the structural stability and activation energy barriers for the superhydrogenation of pentacene using Density Functional Theory. The results reveal a preferential hydrogenation pattern set by the activation energy barriers of the hydrogenation steps. Based on these studies, we formulate simple concepts governing the hydrogenation that apply equally well for different PAHs.

2019 (5)

- [Dual-Route Hydrogenation of the Graphene/Ni Interface.](#) Lizzit, D.; Trioni, M., I.; Bignardi, L.; Lacovig, P.; Lizzit*, S.; Martinazzo, R.; and Larciprete*, R. *ACS Nano*, 13(2): 1828-1838. 2019.

Abstract. Nanostructured architectures based on graphene/metal interfaces might be efficiently exploited in hydrogen storage due to the attractive capability to provide adsorption sites both at the top side of graphene and at the metal substrate after intercalation. We combined in situ high-resolution X-ray photoelectron spectroscopy and scanning tunneling microscopy with theoretical calculations to determine the arrangement of hydrogen atoms at the graphene/Ni(111) interface at room temperature. Our results show that at low coverage H atoms predominantly adsorb as monomers and that chemisorption saturates when $\sim 25\%$ of the surface is hydrogenated. In parallel, with a much lower rate, H atoms intercalate below graphene and bind to Ni surface sites. Intercalation progressively destabilizes the C-H bonds and triggers the release of the hydrogen chemisorbed on graphene. Valence band and near-edge absorption spectroscopy demonstrate that the graphene layer is fully lifted when the Ni surface is saturated with H. Thermal programmed desorption was used to determine the stability of the hydrogenated interface. Whereas the H atoms chemisorbed on graphene remain unperturbed over a wide temperature range, the intercalated phase abruptly desorbs 50-100 K above room temperature.

- [To bend or not to bend, the dilemma of multiple bonds.](#) Pizzochero, M.; Bonfanti, M.; and Martinazzo*, R. *Physical Chemistry Chemical Physics*, 21(48): 26342-26350. 2019. Selected as "2019 Hot PCCP Article".

Abstract. Beyond the second row of the periodic table, the nature of the multiple bonds between the elements of the main groups remains yet elusive, and "non-classical" bonding schemes are often invoked for their description. Here, focusing on group 14, we have performed an

accurate modeling of the Si-Si and C-C double bonds, including electron correlation effects. We have shown that SiSi bonds are “classical” and closely resemble CC ones, being similarly subjected to a sort of tug of war in which the σ bond favors distortion and the π bond opposes it. The essential difference between Si and C boils down to the sizes of their valence shells, which determine the π -bending stiffness. In carbon, such a stiffness is large because, upon bending, the atomic s orbitals interfere destructively with the p ones. In silicon, the s shell is smaller than the p one, the bending stiffness is reduced and the π bonds typically succumb, distort, and weaken. Electron correlation plays a major role in this context, since π bonds are far from their molecular orbital limit. Hence, we have further shown that upon weakening the effective repulsion between π electrons one may remove any structural instability, strengthen the π bonds and turn Si into a closer relative of C than it used to be.

- [Kinetic model for the ammoxidation of ethanol to acetonitrile](#). Tripodi, A.; Ripamonti, D.; Martinazzo, R.; Folco, F.; Tabanelli, T.; Cavani, F.; and Rossetti, I. *Chemical Engineering Science*, 207: 862-875. 2019.

Abstract. A comprehensive kinetic study, based on V-based catalysts (Vanadium Pyro-Phosphate, VPP, VOx/TiO₂ and VOx/ZrO₂), was modeled to retrieve the surface reaction mechanism and kinetic parameters for the ammoxidation of ethanol to acetonitrile. In all the cases, the catalysts showed a moderate to good acetonitrile selectivity, that in turn resulted correlated primarily to the reaction temperature, while the byproducts distribution was more influenced by the thermodynamic stability of the reacting mixture. A large and comprehensive collection of data on ammoxidation of C₂ substrates for acetonitrile production was analysed and 5 groups of experiments on VOx-based catalysts (operating in the temperature range 250-450 °C) were selected. The base reactant was ethanol and ammonia and oxygen were fed in optimal ratios of 1:3-1:4 mol/mol. A kinetic model was then derived applying the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach to accepted catalytic oxidation mechanisms: for every catalytic material, eight to ten reactions with rates described by the Arrhenius formula were employed. Fixing the reaction orders according to the mechanistic assumption and adjusting only the kinetic and adsorption parameters, the calculated molar fractions of ethanol, ammonia, acetonitrile and ethylene resulted in good agreement with the extensive collection of experimental data available.

- [Identification of stable configurations in the superhydrogenation sequence of polycyclic aromatic hydrocarbon molecules](#). Jensen, P., A.; Leccese, M.; Simonsen, F., D.; Skov, A., W.; Bonfanti, M.; Thrower, J., D.; Martinazzo, R.; and Hornekær*, L. *Monthly Notices of the Royal Astronomical Society*, 486(4): 5492-5498. 2019.

Abstract. Superhydrogenated polycyclic aromatic hydrocarbon (PAH) molecules have been demonstrated to act as catalysts for molecular hydrogen formation under interstellar conditions. Here we present combined thermal desorption mass spectrometry measurements and density functional theory calculations that reveal the most stable configurations in the superhydrogenation sequence of the PAH molecule coronene (C₂₄H₁₂). Specifically, the experiments demonstrate the presence of stable configurations of superhydrogenated coronene at specific hydrogenation levels of 2, 10, 14, 18, and 24 extra hydrogen atoms. Density functional theory calculations of binding energies and barrier heights explain why these configurations are particularly stable and provide new insights into the superhydrogenation process of PAH molecules under interstellar conditions. Furthermore, an experimental cross-section for the first hydrogen atom addition to the neutral coronene molecule of $\sigma_{\text{add}} = 2.7 \pm 2.7 \cdot 0.9 \times 10^{-22} \text{ m}^2$ is derived from the experimental hydrogenation data-

- [Vibronic coupling models for donor-acceptor aggregates using an effective-mode scheme: Application to mixed Frenkel and charge-transfer excitons in oligothiophene aggregates](#). Popp, W.; Polkehn, M.; Hughes, K., H.; Martinazzo, R.; and Burghardt*, I. *The Journal of Chemical Physics*, 150(24): 244114. 2019.

Abstract. A reduced-dimensional effective-mode representation is developed in order to efficiently describe excited-state dynamics of multichromophoric donor-acceptor aggregates within a linear vibronic coupling model. Specifically, we consider systems where vibrational modes pertaining to a given molecular fragment couple both to local excitations of Frenkel type and delocalized states of charge transfer exciton type. A hierarchical chain representation is constructed which is suitable to describe correlated fluctuations, leading to a set of correlated spectral densities. An application is shown for a first-principles parameterized model of an oligothiophene H-type aggregate whose properties are modified due to the presence of charge transfer excitons. Within a pentamer model comprising 13 electronic states and 195 normal modes, good convergence of the effective-mode representation of the spectral densities is achieved at the eighth order of the hierarchy with 104 modes, and a qualitatively correct picture is obtained at the sixth order with 78 modes.

2018 (5)

- [Magnetic Moments and Electron Transport through Chromium-Based Antiferromagnetic Nanojunctions](#). Bragato, M.; Achilli, S.; Cragnoni, F.; Ceresoli, D.; Martinazzo, R.; Soave, R. and Trioni*, M. *Materials*, 11: 2030. 2018

Abstract. We report the electronic, magnetic and transport properties of a prototypical antiferromagnetic (AFM) spintronic device. We chose Cr as the active layer because it is the only room-temperature AFM elemental metal. We sandwiched Cr between two non-magnetic metals (Pt or Au) with large spin-orbit coupling. We also inserted a buffer layer of insulating MgO to mimic the structure and finite resistivity of a real device. We found that, while spin-orbit has a negligible effect on the current flowing through the device, the MgO layer plays a crucial role. Its effect is to decouple the Cr magnetic moment from Pt (or Au) and to develop an overall spin magnetization. We have also calculated the spin-polarized ballistic conductance of the device within the Büttiker-Landauer framework, and we have found that for small applied bias our Pt/Cr/MgO/Pt device presents a spin polarization of the current amounting to $\approx 25\%$.

- [Multi-configurational Ehrenfest simulations of ultrafast nonadiabatic dynamics in a charge-transfer complex](#). Ma, T.; Bonfanti*, M.; Eisenbrandt, P.; Martinazzo, R. and Burghardt*, I. *The Journal of Chemical Physics*, 149: 244107. 2018.

Abstract. Multi-configurational Ehrenfest (MCE) approaches, which are intended to remedy the lack of correlations in the standard mean-field Ehrenfest method, have been proposed as coherent-state based ansätze for quantum propagation [D. V. Shalashilin, *J. Chem. Phys.* **130**, 244101 (2009)] and also as the classical limit of the variational Gaussian-based multiconfiguration time dependent Hartree (G-MCTDH) method [S. Römer and I. Burghardt, *Mol. Phys.* **111**, 3618 (2013)]. In the present paper, we establish the formal connection between these schemes and assess the performance of MCE for a coherent-state representation of the classical-limit subsystem. As a representative model system, we address the ultrafast, coherent charge transfer dynamics in an oligothiophene-fullerene donor-acceptor complex described by a two-state linear vibronic coupling model. MCE calculations are compared with reference calculations performed with the MCTDH method, for 10-40 vibrational modes. Beyond a dimensionality of 10 modes, it is shown that the correct representation of electronic coherence depends crucially on the sampling of initially unoccupied Gaussians.

- [Full quantum dynamical investigation of the Eley-Rideal reaction forming H₂ on a movable graphitic substrate at T = 0 K.](#) Pasquini, M.; Bonfanti, M.; and **Martinazzo***, R. *Physical Chemistry Chemical Physics*, 20(2): 977-988. 2018.

Abstract. The dynamics of the Eley-Rideal abstraction reaction of hydrogen atoms on a movable graphitic surface is investigated for the first time in a numerically exact fully quantum setting. A system-bath strategy was applied where the two recombining H atoms and a substrate C atom form a relevant subsystem, while the rest of the lattice takes the form of an independent oscillator bath. High-dimensional wavepacket simulations were performed in the collision energy range 0.2-1.0 eV with the help of the multi-layer multi-configuration time-dependent Hartree method, focusing on the collinear reaction on a zero-temperature surface. Results show that the dynamics is close to a sudden limit in which the reaction is much faster than the substrate motion. Unpuckering of the surface is fast (some tens of fs) but starts only after the formation of H₂ is completed, thereby determining a considerable substrate heating (~0.8 eV per reactive event). Energy partitioning in the product molecule favors translational over vibrational energy, and H₂ molecules are vibrationally hot (~1.5 eV) though to a lesser extent than previously predicted.

- [Comment on "theoretical study of the dynamics of atomic hydrogen adsorbed on graphene multilayers".](#) Bonfanti, M.; and **Martinazzo***, R. *Physical Review B*, 97(11): 117401. 2018.

Abstract. It is shown that the theoretical prediction of a transient magnetization in bilayer and multilayer graphene (M. Moaied, *Phys. Rev. B* 91, 155419 (2015) PRBMD01098-012110.1103/PhysRevB.91.155419) relies on an incorrect physical scenario for adsorption, namely, one in which H atoms adsorb barrierless on graphitic substrates and form a random adsorption pattern of monomers. Rather, according to experimental evidence, H atom sticking is an activated process, and adsorption is under kinetic control, largely ruled by a preferential sticking mechanism that leads to stable, nonmagnetic dimers at all but the smallest coverages (<0.004). Theory and experiments are reconciled by reconsidering the hydrogen atom adsorption energetics with the help of van der Waals-inclusive density functional calculations that properly account for the basis set superposition error. It is shown that today van der Waals-density functional theory predicts a shallow physisorption well that nicely agrees with available experimental data and suggests that the hydrogen atom adsorption barrier in graphene is 180 meV high, within ~5 meV accuracy.

- [Sticking of atomic hydrogen on graphene.](#) Bonfanti, M.; Achilli, S.; and **Martinazzo***, R. *Journal of Physics: Condensed Matter*, 30(28): 283002. 2018.

Abstract. Recent years have witnessed an ever growing interest in the interactions between hydrogen atoms and a graphene sheet. Largely motivated by the possibility of modulating the electric, optical and magnetic properties of graphene, a huge number of studies have appeared recently that added to and enlarged earlier investigations on graphite and other carbon materials. In this review we give a glimpse of the many facets of this adsorption process, as they emerged from these studies. The focus is on those issues that have been addressed in detail, under carefully controlled conditions, with an emphasis on the interplay between the adatom structures, their formation dynamics and the electric, magnetic and chemical properties of the carbon sheet.

2017 (2)

- [Process Simulation for the Design and Scale Up of Heterogeneous Catalytic Process: Kinetic Modelling Issues.](#) Tripodi, A.; Compagnoni, M.; **Martinazzo, R.**; Ramis, G.; and Rossetti*, I. *Catalysts* 2017, Vol. 7, Page 159, 7(5): 159. 2017.

Abstract. Process simulation represents an important tool for plant design and optimization, either applied to well established or to newly developed processes. Suitable thermodynamic packages should be selected in order to properly describe the behavior of reactors and unit operations and to precisely define phase equilibria. Moreover, a detailed and representative kinetic scheme should be available to predict correctly the dependence of the process on its main variables. This review points out some models and methods for kinetic analysis specifically applied to the simulation of catalytic processes, as a basis for process design and optimization. Attention is paid also to microkinetic modelling and to the methods based on first principles, to elucidate mechanisms and independently calculate thermodynamic and kinetic parameters. Different case studies support the discussion. At first, we have selected two basic examples from the industrial chemistry practice, e.g., ammonia and methanol synthesis, which may be described through a relatively simple reaction pathway and the relative available kinetic scheme. Then, a more complex reaction network is deeply discussed to define the conversion of bioethanol into syngas/hydrogen or into building blocks, such as ethylene. In this case, lumped kinetic schemes completely fail the description of process behavior. Thus, in this case, more detailed—e.g., microkinetic—schemes should be available to implement into the simulator. However, the correct definition of all the kinetic data when complex microkinetic mechanisms are used, often leads to unreliable, highly correlated parameters. In such cases, greater effort to independently estimate some relevant kinetic/thermodynamic data through Density Functional Theory (DFT)/ab initio methods may be helpful to improve process description.

- [A family of solution-processable macrocyclic and open-chain oligothiophenes with atropisomeric scaffolds: structural and electronic features for potential energy applications.](#) Quartapelle Procopio, E.; Benincori, T.; Appoloni, G.; Mussini, P., R.; Arnaboldi, S.; Carbonera, C.; Cirilli, R.; Cominetti, A.; Longo, L.; **Martinazzo, R.**; Panigati, M.; and Po'*, R. *New Journal of Chemistry*, 41(18): 10009-10019. 2017.

Abstract. FeCl₃ oxidation of the racemate of C₂ symmetric, inherently chiral, sexithiophene monomer 1 (2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bithianaphthene) affords a mixture of cyclic oligomers, from the prevailing dimer to traces of the pentamer. The oligomers are constituted by mixtures of stereoisomers which are two for dimer 2, four for trimer 3 and six for tetramer 4. Cyclooligomers 2 and 3 could be separated by chromatography, while 4 was synthesized by ring closure of open chain dimer 2a, prepared in turn by controlled coupling of the anion of racemic 1. The optical properties of open-chain stereoisomer 2a and tetramer 4 have been compared with those of 2 and 3 respectively. The macrocyclic oligomers have been tested as donor materials in bulk heterojunction solar cell prototypes both as a crude mixture resulting from oxidation of 1 and as a single oligomer. Theoretical calculations support the photophysical properties of these new materials.

2016 (7)

- [Classical and quantum dynamics at surfaces: Basic concepts from simple models.](#) Bonfanti, M.; and **Martinazzo***, R. *International Journal of Quantum Chemistry*, 116(21): 1575-1602. 2016.

Abstract. Elementary processes involving atomic and molecular species at surfaces are reviewed. The emphasis is on simple classical and quantum models that help to single out unifying dynamical themes and to identify the basic physical mechanisms that underlie the rich variety of phenomena of surface chemistry. Starting from an elementary description of the energy transfer between a gas-phase species and a surface—

for both classical and quantum lattices—the key processes establishing the formation of an adsorbed phase (sticking, diffusion and vibrational relaxation) are discussed. This is instrumental for introducing the simplest chemical transformations involving adsorbed species and/or scattering of gas-phase molecules: Langmuir-Hinshelwood, Hot-Atom, and Eley-Rideal reactions forming complex molecules from elementary constituents, and dissociative chemisorption of molecules into smaller fragments. Applications are also provided illustrating the ideas developed along the way at work in real-world gas-surface problems.

- [Quantum dynamical investigation of the isotope effect in H₂ formation on graphite at cold collision energies.](#) Pasquini, M.; Bonfanti, M.; and **Martinazzo***, R. *Physical Chemistry Chemical Physics*, 18(9): 6607-6617. 2016.

Abstract. The Eley-Rideal abstraction of hydrogen atoms on graphitic surfaces at cold collision energies was investigated using a time-dependent wave packet method within the rigid-flat surface approximation, with a focus on hydrogen-deuterium isotopic substitutions. It is found that the marked isotope effect of collinear collisions disappears when the full dimensionality of the problem is taken into account, thereby suggesting that abstraction is less direct than commonly believed and proceeds through glancing rather than head-on collisions. In contrast, a clear isotope effect is observed for “hot-atom” formation, which appears to be strongly favored for heavy projectiles because of their higher density of physisorbed states. Overall, the dynamics is essentially classical and reasonably well described by quasi-classical trajectory methods at all but the lowest energies (≤ 10 meV). A comparison of the results obtained in the (substrate) adiabatic and diabatic limits suggests that the reaction is only marginally affected by the lattice dynamics, but highlights the importance of including energy dissipation processes in order to accurately describe the internal excitation of the product molecules.

- [Hydrogen on silicene: like or unlike graphene?](#) Pizzochero, M.; Bonfanti, M.; and **Martinazzo***, R. *Physical Chemistry Chemical Physics*, 18(23): 15654-15666. 2016.

Abstract. Hydrogenation of free-standing silicene, the two-dimensional allotrope of silicon, is investigated in detail using first-principles methods and compared with the adsorption of H atoms on graphene. Similarly to graphene, chemisorption of a single H atom on silicene induces the formation of a semilocalized state around the adatom, a sharp peak in the density of states at the Fermi level which acts as a strong resonant scatterer for charge carriers. This state hosts an unpaired electron, the itinerant electron of the resonating valence bond picture which primarily resides on the “majority” sublattice and biases the reactivity towards specific lattice positions. Contrary to graphene, sticking of hydrogen atoms is barrierless, on both the pristine and the hydrogenated surface. As a consequence, hydrogen adsorption on silicene is expected to proceed randomly under typical laboratory conditions, and preferential binding to form balanced dimers (or clusters) only occurs when thermodynamic equilibrium conditions prevail. The absence of clustering can be experimentally confirmed using scanning tunneling microscopy techniques since simulated imaging shows that the investigated structures provide distinguishable features that should allow their easy identification, if present on the surface. Overall, our findings can be rationalized by the fact that in silicene π bonds are weaker and the lattice is softer than in graphene and suggest that in silicene adatoms may severely limit carrier mobility.

- [Hydrogen Recombination and Dimer Formation on Graphite from Ab Initio Molecular Dynamics Simulations.](#) Casolo, S.; Tantardini, G., F.; and **Martinazzo***, R. *Journal of Physical Chemistry A*, 120(27): 5032-5040. 2016.

Abstract. We studied Eley-Rideal molecular hydrogen formation on graphite using ab initio molecular dynamics, in the energy range relevant for the chemistry of the interstellar medium and for terrestrial experiments employing cold plasma (0.02-1 eV). We found substantial projectile steering effects that prevent dimer formation at low energies, thereby ruling out any catalytic synthetic pathways that form hydrogen molecules. Ortho and para dimers do form efficiently thanks to preferential sticking, but only at energies that are too high to be relevant for the chemistry of the interstellar medium. Computed reaction cross sections and ro-vibrational product populations are in good agreement with available experimental data and capable of generating adsorbate configurations similar to those observed with scanning tunneling microscopy techniques.

- [Note: Caldeira-Leggett model describes dynamics of hydrogen atoms on graphene.](#) Gottwald, F.; Bonfanti, M.; **Martinazzo***, R.; Ivanov*, S., D.; and Kühn, O. *The Journal of Chemical Physics*, 145(12): 126101. 2016.

- [Exploiting the Photonic Crystal Properties of TiO₂ Nanotube Arrays to Enhance Photocatalytic Hydrogen Production.](#) Chiarello*, G., L.; Zuliani, A.; Ceresoli, D.; **Martinazzo**, R.; and Selli, E. *ACS Catalysis*, 6(2): 1345-1353. 2016.

Abstract. Two series of self-assembled TiO₂ nanotube (NT) arrays were grown by electrochemical anodization on a metallic titanium substrate with different anodization times and applied potentials in HF-containing ethylene glycol electrolyte solutions and postcalcined at 450°C. The obtained thin films were characterized by FESEM, XRD, and UV-vis-NIR DRS analyses and tested as photoanodes in incident photon to current efficiency (IPCE) measurements and in a two-compartment photoelectrochemical cell (PEC) for separate H₂ and O₂ production. The photocatalytic performance of the NT arrays significantly increased with an increase in the potential applied during anodization (i.e., with increasing the NT inner diameter) and the incident angle of the light. IPCE measurements revealed that such unexpected behavior is due to a red shift of the activity threshold that allows harvesting and converting a larger portion of the solar spectrum. This phenomenon is ascribed to the parallel shift of the photonic band gap position originated by the intrinsic photonic crystal properties and demonstrates the important role played by ordered hierarchical structures in improving the photocatalytic performance of NT arrays by confining and manipulating light.

- [Inherently Chiral Spider-Like Oligothiophenes.](#) Sannicolò, F.; Mussini*, P., R.; Benincori*, T.; **Martinazzo***, R.; Arnaboldi, S.; Appoloni, G.; Panigati, M.; Quartapelle Procopio, E.; Marino, V.; Cirilli, R.; Casolo, S.; Kutner, W.; Noworyta, K.; Pietrzyk-Le, A.; Iskierko, Z.; and Bartold, K. *Chemistry - A European Journal*, 22(31): 10839-10847. 2016. Hot Paper, selected for Journal Cover.

Abstract. The racemate of an inherently chiral “spider-like” octathiophene monomer T83, in which chirality is generated by torsion in its backbone, was synthesized. The racemate was resolved into configurationally stable antipodes by HPLC on a chiral stationary phase. Electrooxidation of the enantiomers resulted in materials displaying high enantioselective recognition ability towards the antipodes of some chiral probes. Moreover, the T83racemate demonstrated great aptitude to stimulate formation of 3D rigid architectures if used as a cross-linking monomer for molecular imprinting. This feature was exploited to devise a molecularly imprinted polymer-based chemosensor selective for a thymine-adenine oligonucleotide.

- [Electron transport in carbon wires in contact with Ag electrodes: a detailed first principles investigation.](#) Bonardi, P.; Achilli, S.; Tantardini, G., F.; and **Martinazzo***, R. *Physical Chemistry Chemical Physics*, 17(28): 18413-18425. 2015.

Abstract. The structure and electronic properties of carbon atom chains C_n in contact with Ag electrodes are investigated in detail with first principles means. The ideal Ag(100) surface is used as a model for binding, and electron transport through the chains is studied as a function of their length, applied bias voltage, presence of capping atoms (Si, S) and adsorption site. It is found that the metal-molecule bond largely influences electronic coupling to the leads. Without capping atoms the quality of the electric contact improves when increasing the carbon atom coordination number to the metal (1, 2 and 4 for adsorption on a top, bridge and hollow position, respectively) and this finding translates almost unchanged in more realistic tip-like contacts which present one, two or four metal atoms at the contact. Current-voltage characteristics show Ohmic behaviour over a wide range of bias voltages and the resulting conductances change only weakly when increasing the wire length. The effect of a capping species is typically drastic, and either largely reduces (S) or largely increases (Si) the coupling of the wire to the electrodes. Comparison of our findings with recent experimental results highlights the limits of the adopted approach, which can be traced back to the known gap problem of density-functional-theory.

- [Vibrational relaxation and decoherence in structured environments: a numerical investigation.](#) Bonfanti*, M.; Hughes, K., H.; Burghardt, I.; and **Martinazzo***, R. *Annalen der Physik*, 527(9-10): 556-569. 2015.

Abstract. Vibrational relaxation is a key issue in chemical reaction dynamics in condensed phase and at the gas-surface interface, where the environment is typically highly structured and cannot be expressed in terms of a simple friction coefficient. Rather, full knowledge of the coupling of the molecular oscillator to the environment is required, as typically subsumed in the spectral density of the environmental coupling. Here, we focus on harmonic Brownian motion and investigate the effectiveness of classical, canonical position autocorrelation functions to compute the spectral density of the coupling needed to describe vibrational relaxation in complex environments. Classical dynamics is performed on model systems, and several effects are investigated in detail, notably the presence of anharmonicity, the role of a high-frequency "Debye" cutoff in the environment and the influence of the detailed structure of the latter. The spectral densities are then used in standard independent oscillator Hamiltonian models which are numerically solved at $T = 0$ K to investigate quantum relaxation and decoherence.

- [Quantum dynamics of hydrogen atoms on graphene. I. System-bath modeling.](#) Bonfanti*, M.; Jackson, B.; Hughes, K., H.; Burghardt, I.; and **Martinazzo***, R. *The Journal of Chemical Physics*, 143(12): 124703. 2015.

Abstract. An accurate system-bath model to investigate the quantum dynamics of hydrogen atoms chemisorbed on graphene is presented. The system comprises a hydrogen atom and the carbon atom from graphene that forms the covalent bond, and it is described by a previously developed 4D potential energy surface based on density functional theory *ab initio* data. The bath describes the rest of the carbon lattice and is obtained from an empirical force field through inversion of a classical equilibrium correlation function describing the hydrogen motion. By construction, model building easily accommodates improvements coming from the use of higher level electronic structure theory for the system. Further, it is well suited to a determination of the system-environment coupling by means of *ab initio* molecular dynamics. This paper details the system-bath modeling and shows its application to the quantum dynamics of vibrational relaxation of a chemisorbed hydrogen atom, which is here investigated at $T = 0$ K with the help of the multi-configuration time-dependent Hartree method. Paper II deals with the sticking dynamics.

- [Quantum dynamics of hydrogen atoms on graphene. II. Sticking.](#) Bonfanti*, M.; Jackson, B.; Hughes, K., H.; Burghardt, I.; and **Martinazzo***, R. *The Journal of Chemical Physics*, 143(12): 124704. 2015.

Abstract. Following our recent system-bath modeling of the interaction between a hydrogen atom and a graphene surface [Bonfanti et al., *J. Chem. Phys.* **143**, 124703 (2015)], we present the results of converged quantum scattering calculations on the activated sticking dynamics. The focus of this study is the collinear scattering on a surface at zero temperature, which is treated with high-dimensional wavepacket propagations with the multi-configuration time-dependent Hartree method. At low collision energies, barrier-crossing dominates the sticking and any projectile that overcomes the barrier gets trapped in the chemisorption well. However, at high collision energies, energy transfer to the surface is a limiting factor, and fast H atoms hardly dissipate their excess energy and stick on the surface. As a consequence, the sticking coefficient is maximum (~ 0.65) at an energy which is about one and half larger than the barrier height. Comparison of the results with classical and quasi-classical calculations shows that quantum fluctuations of the lattice play a primary role in the dynamics. A simple impulsive model describing the collision of a classical projectile with a quantum surface is developed which reproduces the quantum results remarkably well for all but the lowest energies, thereby capturing the essential physics of the activated sticking dynamics investigated.

- [Hydrogen adsorption on nitrogen and boron doped graphene.](#) Pizzochero, M.; Leenaerts*, O.; Partoens, B.; **Martinazzo***, R.; and Peeters, F., M. *Journal of Physics: Condensed Matter*, 27(42): 425502. 2015.

Abstract. Hydrogen adsorption on boron and nitrogen doped graphene is investigated in detail by means of first-principles calculations. A comprehensive study is performed of the structural, electronic, and magnetic properties of chemisorbed hydrogen atoms and atom pairs near the dopant sites. The main effect of the substitutional atoms is charge doping which is found to greatly affect the adsorption process by increasing the binding energy at the sites closest to the substitutional species. It is also found that doping does not induce magnetism despite the odd number of electrons per atom introduced by the foreign species, and that it quenches the paramagnetic response of chemisorbed H atoms on graphene. Overall, the effects are similar for B and N doping, with only minor differences in the adsorption energetics due to different sizes of the dopant atoms and the accompanying lattice distortions.

2014 (6)

- [Structure and stability of hydrogenated carbon atom vacancies in graphene.](#) Casartelli, M.; Casolo, S.; Tantardini, G., F.; and **Martinazzo***, R. *Carbon*, 77: 165-174. 2014.

Abstract. Adsorption of hydrogen atoms to a carbon atom vacancy in graphene is investigated by means of periodic first principles calculations, up to the fully hydrogenated state where six H atoms chemically bind to the vacancy. Addition of a single H atom is highly exothermic and barrierless, and binding energies remain substantial for further hydrogenation, with a preference towards structures with the least number of geminal pairs. Thermodynamic analysis shows that defective graphene is extremely sensitive to hydrogenation, with the triply hydrogenated anti-structure prevailing at room temperature and for a wide range of H_2 partial pressures, from ~ 1 bar down to $< 10^{-20}$ bar. This structure has one unpaired electron and provides a spin-half local magnetic moment contribution to graphene paramagnetism. Comparison of our results

with recent transmission electron microscopy, scanning tunneling microscopy and muon-spin-resonance experiments suggest that carbon atom vacancies may actually be hydrogenated to various degrees under varying conditions.

- [Non-Markovian reduced dynamics of ultrafast charge transfer at an oligothiophene-fullerene heterojunction.](#) Hughes*, K., H.; Cahier, B.; Martinazzo, R.; Tamura, H.; and Burghardt, I. *Chemical Physics*, 442: 111-118. 2014.

Abstract. We extend our recent quantum dynamical study of the exciton dissociation and charge transfer at an oligothiophene-fullerene heterojunction interface (Tamura et al., 2012) [6] by investigating the process using the non-perturbative hierarchical equations of motion (HEOM) approach. Based upon an effective mode reconstruction of the spectral density the effect of temperature on the charge transfer is studied using reduced density matrices. It was found that the temperature had little effect on the charge transfer and a coherent dynamics persists over the first few tens of femtoseconds, indicating that the primary charge transfer step proceeds by an activationless pathway.

- [Structural and optical properties of inherently chiral polythiophenes: A combined CD-electrochemistry, circularly polarized luminescence, and TD-DFT investigation.](#) Longhi*, G.; Abbate, S.; Mazzeo, G.; Castiglioni, E.; Mussini, P.; Benincori, T.; Martinazzo, R.; and Sannicolò, F. *Journal of Physical Chemistry C*, 118(29): 16019-16027. 2014.

Abstract. Circular dichroism (CD) and ultraviolet absorption (UV) spectra of films obtained by electrochemical polymerization of inherently chiral 2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bithianaphthene (T4-BT2) are taken during electrochemical polarization cycles. Besides the bisignate CD features in the near UV range recorded at zero potential, new features in the visible-near-infrared range are observed under increased applied potential. Results are interpreted with the help of static and time-dependent (TD) density functional theory (DFT) calculations, which shed light on the structural and electronic properties of neutral and charged oligomers (from monomers to tetramers) and reproduce UV and CD spectra satisfactorily. Furthermore, properties of the excited state of T4-BT2 monomers in solution are enlightened by combining circularly polarized luminescence (CPL) measurements with TD-DFT calculations.

- [Hydrogen-dimer lines and electron waveguides in graphene.](#) Achilli, S.; Tantardini, G., F.; and Martinazzo*, R. *Physical Chemistry Chemical Physics*, 16(33): 17610-17616. 2014.

Abstract. The electronic and transport properties of graphene ribbons sandwiched between hydrogen dimer lines, of the kind recently realized by Nilsson et al., *Carbon*, 2012, 50, 2052, are investigated with the help of first principles methods. It is found that such lines of hydrogen atoms block conduction between neighboring channels and effectively allow the confinement of graphene charge carriers, thereby opening the possibility of imprinting nano-circuits in graphene by controlled hydrogenation.

- [Adiabatic potential energy surfaces for the low-energy collisional dynamics of C⁺\(²P\) ions with H₂ molecules.](#) Bonfanti, M.; Tantardini, G., F.; and Martinazzo*, R. *Journal of Physical Chemistry A*, 118(33): 6595-6603. 2014.

Abstract. The low-energy electronic states of the CH₂⁺ molecular ion are investigated with multireference configuration interaction calculations based on complete active space self-consistent field reference wave functions using a large C(6s5p4d3f)/H(8s6p3d1f) basis set. The focus is on the three lowest-lying states describing formation and destruction of the astrophysically relevant methylidene cation CH⁺. Both processes are discussed in light of the topology of the relevant potential energy surfaces and their intersections.

- [Inherently Chiral Macrocyclic Oligothiophenes: Easily Accessible Electrosensitive Cavities with Outstanding Enantioselection Performances.](#) Sannicolò*, F.; Mussini, P., R.; Benincori, T.; Cirilli, R.; Abbate, S.; Arnaboldi, S.; Casolo, S.; Castiglioni, E.; Longhi, G.; Martinazzo, R.; Panigati, M.; Pappini, M.; Procopio, E., Q.; and Rizzo, S. *Chemistry - A European Journal*, 20(47): 15298-15302. 2014. Selected for Journal Cover.

Abstract. Linear conjugated oligothiophenes of variable length and different substitution pattern are ubiquitous in technologically advanced optoelectronic devices, though limitations in application derive from insolubility, scarce processability and chain-end effects. This study describes an easy access to chiral cyclic oligothiophenes constituted by 12 and 18 fully conjugated thiophene units. Chemical oxidation of an "inherently chiral" sexithiophene monomer, synthesized in two steps from commercially available materials, induces the formation of an elliptical dimer and a triangular trimer endowed with electrosensitive cavities of different tunable sizes. Combination of chirality with electroactivity makes these molecules unique in the current oligothiophenes literature. These macrocycles, which are stable and soluble in most organic solvents, show outstanding chiroptical properties, high circularly polarized luminescence effects and an exceptional enantioselective ability.

2013 (2)

- [Spin coupling around a carbon atom vacancy in graphene.](#) Casartelli, M.; Casolo, S.; Tantardini, G., F.; and Martinazzo*, R. *Physical Review B - Condensed Matter and Materials Physics*, 88(19): 195424. 2013.

Abstract. We investigate the details of the electronic structure in the neighborhoods of a carbon atom vacancy in graphene by employing magnetization-constrained density-functional theory on periodic slabs, and spin-exact, multireference, second-order perturbation theory on a finite cluster. The picture that emerges is that of two local magnetic moments (one π -like and one σ -like) decoupled from the π band and coupled to each other. We find that the ground state is a triplet with a planar equilibrium geometry where an apical C atom opposes a pentagonal ring. This state lies ~ 0.2 eV lower in energy than the open-shell singlet with one spin flipped, which is a bistable system with two equivalent equilibrium lattice configurations (for the apical C atom above or below the lattice plane) and a barrier ~ 0.1 eV high separating them. Accordingly, a bare carbon atom vacancy is predicted to be a spin-1 paramagnetic species, but spin-1/2 paramagnetism can be accommodated if binding to foreign species, ripples, coupling to a substrate, or doping are taken into account.

- [Insights into H₂ formation in space from ab initio molecular dynamics.](#) Casolo, S.; Tantardini, G., F.; and Martinazzo*, R. *Proceedings of the National Academy of Sciences of the United States of America*, 110(17): 6674-6677. 2013.

Abstract. Hydrogen formation is a key process for the physics and the chemistry of interstellar clouds. Molecular hydrogen is believed to form on the carbonaceous surface of dust grains, and several mechanisms have been invoked to explain its abundance in different regions of space, from cold interstellar clouds to warm photon-dominated regions. Here, we investigate direct (Eley-Rideal) recombination including lattice dynamics, surface corrugation, and competing H-dimers formation by means of ab initio molecular dynamics. We find that Eley-Rideal reaction

dominates at energies relevant for the interstellar medium and alone may explain observations if the possibility of facile sticking at special sites (edges, point defects, etc.) on the surface of the dust grains is taken into account.

2012 (4)

- [Non-Markovian reduced dynamics based upon a hierarchical effective-mode representation.](#) Burghardt*, I.; Martinazzo, R.; and Hughes, K., H. *The Journal of Chemical Physics*, 137(14): 144107. 2012.

Abstract. A reduced dynamics representation is introduced which is tailored to a hierarchical, Mori-chain type representation of a bath of harmonic oscillators which are linearly coupled to a subsystem. We consider a spin-boson system where a single effective mode is constructed so as to absorb all system-environment interactions, while the residual bath modes are coupled bilinearly to the primary mode and among each other. Using a cumulant expansion of the memory kernel, correlation functions for the primary mode are obtained, which can be suitably approximated by truncated chains representing the primary-residual mode interactions. A series of reduced-dimensional bath correlation functions is thus obtained, which can be expressed as Fourier-Laplace transforms of spectral densities that are given in truncated continued-fraction form. For a master equation which is second order in the system-bath coupling, the memory kernel is re-expressed in terms of local-in-time equations involving auxiliary densities and auxiliary operators

- [Quantum dynamics of ultrafast charge transfer at an oligothiophene-fullerene heterojunction.](#) Tamura, H.; Martinazzo, R.; Ruckebauer, M.; and Burghardt*, I. *The Journal of Chemical Physics*, 137(22): 22A540. 2012. Selected as "Research Highlight" from the "The Journal of Chemical Physics".

Abstract. Following up on our recent study of ultrafast charge separation at oligothiophene-fullerene interfaces [H. Tamura, I. Burghardt, and M. Tsukada, *J. Phys. Chem. C* 115, 10205 (2011)], we present here a detailed quantum dynamical perspective on the charge transfer process. To this end, electron-phonon coupling is included non-perturbatively, by an explicit quantum dynamical treatment using the multi-configuration time-dependent Hartree (MCTDH) method. Based upon a distribution of electron-phonon couplings determined from electronic structure studies, a spectral density is constructed and employed to parametrize a linear vibronic coupling Hamiltonian. The diabatic coupling is found to depend noticeably on the inter-fragment distance, whose effect on the dynamics is here investigated. MCTDH calculations of the nonadiabatic transfer dynamics are carried out for the two most relevant electronic states and 60 phonon modes. The electron transfer process is found to be ultrafast and mediated by electronic coherence, resulting in characteristic oscillatory features during a period of about 100 fs.

- [Compact MCTDH wave functions for high-dimensional system-bath quantum dynamics.](#) Bonfanti, M.; Tantardini, G., F.; Hughes, K., H.; Martinazzo*, R.; and Burghardt*, I. *Journal of Physical Chemistry A*, 116(46): 11406-11413. 2012.

Abstract. We employ a simple multiconfiguration time-dependent Hartree (MCTDH) ansatz tailored to an effective-mode transformation of environmental variables that brings the bath into a linear chain form. In this form, important (primary) degrees of freedom can be easily identified and treated at a high correlation level, whereas secondary modes are left uncorrelated. The resulting approach scales linearly with the bath dimensions and allows us to easily access recurrence times much longer than usually possible, at a very small computational cost. Test calculations for model atom-surface problems show that the system dynamics is correctly reproduced in the relevant time window, and quantitative agreement is attained for energy relaxation and sticking, particularly in non-Markovian environments. These results pave the way for tackling realistic system-bath quantum dynamical problems on the picosecond scale

- [Reduced and exact quantum dynamics of the vibrational relaxation of a molecular system interacting with a finite-dimensional bath.](#) Bouakline, F.; Lüder, F.; Martinazzo, R.; and Saalfrank*, P. *Journal of Physical Chemistry A*, 116(46): 11118-11127. 2012.

Abstract. We investigate the vibrational relaxation of a Morse oscillator, nonlinearly coupled to a finite-dimensional bath of harmonic oscillators at zero temperature, using two different approaches: Reduced dynamics with the help of the Lindblad formalism of reduced density matrix theory in combination with Fermi's Golden Rule, and exact dynamics (within the chosen model) with the multiconfiguration time-dependent Hartree (MCTDH) method. Two different models have been constructed, the situation where the bath spectrum is exactly resonant with the anharmonic oscillator transition frequencies, and the case for which the subsystem is slightly off-resonant with the environment. At short times, reduced dynamics calculations describe the relaxation process qualitatively well but fail to reproduce recurrences observed with MCTDH for longer times. Lifetimes of all the vibrational levels of the Morse oscillator have been calculated, and both Lindblad and MCTDH results show the same dependence of the lifetimes on the initial vibrational state quantum number. A prediction, which should be generic for adsorbate systems is a striking, sharp increase of lifetimes of the subsystem vibrational levels close to the dissociation limit. This is contradictory with harmonic/linear extrapolation laws, which predict a monotonic decrease of the lifetime with initial vibrational quantum number.

2011 (7)

- [A few simple rules governing hydrogenation of graphene dots.](#) Bonfanti, M.; Casolo, S.; Tantardini, G., F.; Ponti, A.; and Martinazzo*, R. *The Journal of Chemical Physics*, 135(16): 164701. 2011.

We investigated binding of hydrogen atoms to small polycyclic aromatic hydrocarbons (PAHs)—i.e., graphene dots with hydrogen-terminated edges—using density functional theory and correlated wavefunction techniques. We considered a number of PAHs with three to seven hexagonal rings and computed binding energies for most of the symmetry unique sites, along with the minimum energy paths for significant cases. The chosen PAHs are small enough to not present radical character at their edges, yet show a clear preference for adsorption at the edge sites which can be attributed to electronic effects. We show how the results, as obtained at different levels of theory, can be rationalized in detail with the help of a few simple concepts derivable from a tight-binding model of the π electrons

- [Unraveling a Brownian particle's memory with effective mode chains.](#) Martinazzo*, R.; Hughes, K., H.; and Burghardt, I. *Physical Review E*, 84(3): 030102. 2011.

Abstract. Memory effects in quantum dynamical processes involving structured environments are presently difficult, if not impossible, to investigate using standard approaches. Progress can be made by transforming the environmental variables to a suitable chain representation which effectively performs a Markovian embedding of the dynamics. Here, we show that this effective-mode chain representation provides a unique way of unraveling the memory kernel $\kappa(t)$ as a function of time. Truncated or Markov-closed chains with n effective modes exactly

reproduce $\kappa(t)$ to the 4th order in time, up to an irrelevant constant of order $\kappa(0)/n$. These favorable convergence properties pave the way for efficient quantum simulations of fast (non-Markovian) processes by reduced dynamical models.

- [Surface models and reaction barrier in Eley-Rideal formation of \$H_2\$ on graphitic surfaces](#). Bonfanti, M.; Casolo, S.; Tantardini, G., F.; and Martinazzo*, R. *Physical Chemistry Chemical Physics*, 13(37): 16680-16688. 2011.

Abstract. The exothermic, collinearly-dominated Eley-Rideal hydrogen formation on graphite is studied with electronic structure and quantum dynamical means. In particular, the focus is on the importance of the model used to describe the graphitic substrate, in light of the marked discrepancies present in available literature results. To this end, the collinear reaction is considered and the potential energy surface is computed for a number of different graphitic surface models using Density Functional Theory (DFT) for different dynamical regimes. Quantum dynamics is performed with wavepacket techniques down to the cold collision energies relevant for the chemistry of the interstellar medium. Results show that the reactivity at moderate-to-high collision energies sensitively depends on the shape of the PES in the entrance channel, which in turn is related to the adopted surface model. At low energies we rule out the presence of any barrier to reaction, thereby highlighting the importance of quantum reflection in limiting the reaction efficiency.

- [Band engineering in graphene with superlattices of substitutional defects](#). Casolo*, S.; Martinazzo*, R.; and Tantardini, G., F. *Journal of Physical Chemistry C*, 115(8): 3250-3256. 2011.

Abstract. We investigate graphene superlattices of nitrogen and boron substitutional defects. Using symmetry arguments and electronic structure calculations we show how such superlattices can be used to modify graphene band structure. Specifically, depending on the superlattice symmetry, the structures considered here can either preserve the Dirac cones (D6h superlattices) or open a band gap (D3h). Relevant band parameters (carrier effective masses, group velocities, and gaps, when present) are found to depend on the superlattice constant n as $1/np$ where p is in the range 1-2, depending on the case considered. Overall, the results presented here show how one can tune the graphene band structure to a great extent by modifying a few superlattice parameters.

- [Benchmark calculations for dissipative dynamics of a system coupled to an anharmonic bath with the multiconfiguration time-dependent Hartree method](#). López-López, S.; Martinazzo, R.; and Nest*, M. *The Journal of Chemical Physics*, 134(9): 094102. 2011.

Abstract. In this paper, we present benchmark results for dissipative dynamics of a harmonic oscillator coupled to an anharmonic bath of Morse oscillators. The microscopic Hamiltonian has been chosen so that the anharmonicity can be adjusted as a free parameter, and its effect can be isolated. This leads to a temperature dependent spectral density of the bath, which is studied for ohmic and lorentzian cases. Also, we compare numerically exact multiconfiguration time-dependent Hartree results with approximate solutions using continuous configuration time-dependent self-consistent field and local coherent state approximation.

- [Communication: Universal Markovian reduction of Brownian particle dynamics](#). Martinazzo*, R.; Vacchini, B.; Hughes, K., H.; and Burghardt, I. *The Journal of Chemical Physics*, 134(1): 011101. 2011.

Abstract. Non-Markovian processes can often be turned Markovian by enlarging the set of variables. Here we show, by an explicit construction, how this can be done for the dynamics of a Brownian particle obeying the generalized Langevin equation. Given an arbitrary bath spectral density J_0 , we introduce an orthogonal transformation of the bath variables into effective modes, leading stepwise to a semi-infinite chain with nearest-neighbor interactions. The transformation is uniquely determined by J_0 and defines a sequence $\{J_n\}_{n \in \mathbb{N}}$ of residual spectral densities describing the interaction of the terminal chain mode, at each step, with the remaining bath. We derive a simple one-term recurrence relation for this sequence and show that its limit is the quasi-Ohmic expression provided by the Rubin model of dissipation. Numerical calculations show that, irrespective of the details of J_0 , convergence is fast enough to be useful in practice for an effective Ohmic reduction of the dissipative dynamics.

- [Generalized CC-TDSCF and LCSA: The system-energy representation](#). López-López, S.; Nest, M.; and Martinazzo*, R. *The Journal of Chemical Physics*, 134(1): 014102. 2011.

Abstract. Typical (sub)system-bath quantum dynamical problems are often investigated by means of (approximate) reduced equations of motion. Wavepacket approaches to the dynamics of the whole system have gained momentum in recent years and there is hope that properly designed approximations to the wavefunction will allow one to correctly describe the subsystem evolution. The continuous-configuration time-dependent self-consistent field (CC-TDSCF) and local coherent-state approximation (LCSA) methods, for instance, use a simple Hartree product of bath single-particle functions for each discrete variable representation (DVR) state introduced in the Hilbert space of the subsystem. Here we focus on the above two methods and replace the DVR states with the eigenstates of the subsystem Hamiltonian, i.e., we adopt an energy-local representation for the sub-system. We find that stable and semiquantitative results are obtained for a number of dissipative problems, at the same (small) computational cost of the original methods. Furthermore, we find that both methods give very similar results, thus suggesting that coherent-states are well suited to describe (local) bath states. As a whole, present results highlight the importance of the system basis-set in the selected-multiconfiguration expansion of the wavefunction. They suggest that accurate and yet computationally cheap methods may be simply obtained from CC-TDSCF/LCSA by letting the subsystem states be variationally optimized.

2010 (2)

- [Effective spectral densities for system-environment dynamics at conical intersections: \$S_2\$ - \$S_1\$ conical intersection in pyrazine](#). Martinazzo, R.; Hughes, K., H.; Martelli, F.; and Burghardt*, I. *Chemical Physics*, 377(1-3): 21-29. 2010.

Abstract. A recently developed effective-mode representation is employed to characterize the influence of a multi-dimensional environment on the S_2 - S_1 conical intersection in pyrazine, taken as a paradigm case of high-dimensional dynamics at a conical intersection. We consider a simplified model by which four modes are strongly coupled to the electronic subsystem while a number of weakly coupled tuning modes, inducing energy gap fluctuations, are sampled from a spectral density. The latter is approximated by a series of simplified spectral densities which can be cast into a continued-fraction form, as previously demonstrated in Hughes et al. (K.H. Hughes, C.D. Christ, I. Burghardt, *J. Chem. Phys.* 131 (2009) 124108). In the time domain, the hierarchy of spectral densities translates to truncated effective-mode chains with a Markovian or quasi-Markovian (Rubin type) closure. A sequential deconvolution procedure is employed to generate this chain representation. The implications for the ultrafast dynamics and its representation in terms of reduced-dimensional models are discussed.

- [Symmetry-induced band-gap opening in graphene superlattices.](#) Martinazzo*, R.; Casolo, S.; and Tantardini, G., F. *Physical Review B - Condensed Matter and Materials Physics*, 81(24): 245420. 2010. Selected for the "Virtual Journal of Nanoscale Science & Technology".

Abstract. We study $n \times n$ honeycomb superlattices of defects in graphene. The considered defects are missing pz orbitals and can be realized by either introducing C atom vacancies or chemically binding simple atomic species at the given sites. Using symmetry arguments and electronic-structure calculations we show that it is possible to open a band gap without breaking graphene point symmetry. This has the advantage that new Dirac cones appear right close to the gapped region. We find that the induced gaps have an approximate square-root dependence on the defect concentration $x = 1/n^2$ and compare favorably with those found in nanoribbons at the same length scale.

2009 (2)

- [Understanding adsorption of hydrogen atoms on graphene.](#) Casolo, S.; Løvvik, O.; Martinazzo*, R.; and Tantardini, G. *Journal of Chemical Physics*, 130(5): 054704. 2009. Selected for the "Virtual Journal of Nanoscale Science & Technology".

Abstract. Eley - Rideal formation of hydrogen molecules on graphite, as well as competing collision induced processes, are investigated quantum dynamically at typical interstellar cloud conditions, focusing in particular on gasphase temperatures below 100 K, where much of the chemistry of the so-called diffuse clouds takes place on the surface of bare carbonaceous dust grains. Collisions of gas-phase hydrogen atoms with both chemisorbed and physisorbed species are considered using available potential energy surfaces (Sha et al., *J. Chem. Phys.* 2002 116, 7158), and state-to-state, energy-resolved cross sections are computed for a number of initial vibrational states of the hydrogen atoms bound to the surface. Results show that (i) product molecules are internally hot in both cases, with vibrational distributions sharply peaked around few (one or two) vibrational levels, and (ii) cross sections for chemisorbed species are $2-3 \times$ smaller than those for physisorbed ones. In particular, we find that H₂ formation cross sections out of chemically bound species decrease steadily when the temperature drops below ~ 1000 K, and this is likely due to a quantum reflection phenomenon. This suggests that such Eley-Rideal reaction is all but efficient in the relevant gas-phase temperature range, even when gas-phase H atoms happen to chemisorb barrierless to the surface as observed, e.g., for forming so-called para dimers. Comparison with results from classical trajectory calculations highlights the need of a quantum description of the dynamics in the astrophysically relevant energy range, whereas preliminary results of an extensive first-principles investigation of the reaction energetics reveal the importance of the adopted substrate model.

- [Quantum dynamics of the Eley-Rideal hydrogen formation reaction on graphite at typical interstellar cloud conditions.](#) Casolo, S.; Martinazzo*, R.; Bonfanti, M.; and Tantardini, G. *Journal of Physical Chemistry A*, 113(52): 14545. 2009.

Abstract. Eley - Rideal formation of hydrogen molecules on graphite, as well as competing collision induced processes, are investigated quantum dynamically at typical interstellar cloud conditions, focusing in particular on gasphase temperatures below 100 K, where much of the chemistry of the so-called diffuse clouds takes place on the surface of bare carbonaceous dust grains. Collisions of gas-phase hydrogen atoms with both chemisorbed and physisorbed species are considered using available potential energy surfaces (Sha et al., *J. Chem. Phys.* 2002 116, 7158), and state-to-state, energy-resolved cross sections are computed for a number of initial vibrational states of the hydrogen atoms bound to the surface. Results show that (i) product molecules are internally hot in both cases, with vibrational distributions sharply peaked around few (one or two) vibrational levels, and (ii) cross sections for chemisorbed species are $2-3 \times$ smaller than those for physisorbed ones. In particular, we find that H₂ formation cross sections out of chemically bound species decrease steadily when the temperature drops below ~ 1000 K, and this is likely due to a quantum reflection phenomenon. This suggests that such Eley-Rideal reaction is all but efficient in the relevant gas-phase temperature range, even when gas-phase H atoms happen to chemisorb barrierless to the surface as observed, e.g., for forming so-called para dimers. Comparison with results from classical trajectory calculations highlights the need of a quantum description of the dynamics in the astrophysically relevant energy range, whereas preliminary results of an extensive first-principles investigation of the reaction energetics reveal the importance of the adopted substrate model.

2008 (1)

- [Quasi-classical trajectory study of the adiabatic reactions occurring on the two lowest-lying electronic states of the LiH₂⁺ system.](#) Pino*, I.; Martinazzo, R.; and Tantardini, G. *Physical Chemistry Chemical Physics*, 10(36): 5545. 2008.

Abstract. Quasi-classical trajectory calculations have been performed on the adiabatically allowed reactions taking place on the two lowest-lying electronic states of the LiH₂⁺ system, using the ab initio potential energy surfaces of Martinazzo et al. (*J. Chem. Phys.*, 2003, 119, 11 241). These reactions comprise: (i) the exoergic H₂ and H₂⁺ formation occurring through LiH⁺ + H and LiH + H collisions in the ground and in the first electronically excited state, respectively; (ii) the endoergic (ground state) LiH + dissociation induced by collisions with H atoms; and (iii) the endoergic (excited state) Li + H₂⁺ \rightarrow LiH + H reaction. The topic is of relevance for a better understanding of the lithium chemistry in the early universe. Thermal rate constants for the above reactions have been computed in the temperature range 10-5000 K and found in reasonably good agreement with estimates based on the capture model.

2007 (2)

- [Physisorption and diffusion of hydrogen atoms on graphite from correlated calculations on the H-coronene model system.](#) Bonfanti, M.; Martinazzo, R.; Tantardini, G.; and Ponti*, A. *Journal of Physical Chemistry C*, 111(16): 5825. 2007.

Abstract. Correlated, counterpoise corrected wave function calculations on the hydrogen-coronene system are used to investigate the energy landscape and the dynamic behavior of hydrogen atoms physisorbed on graphite. The adopted MP2 correlation level, employing the aug-cc-pVDZ basis set augmented with bond functions, has been selected after extensive investigation on the smaller hydrogen-benzene system. The computed physisorption energy (39.7 meV) is in excellent agreement with the existing experimental value of (39.2 ± 0.5) meV for a graphite single layer (Ghio, E.; Mattera, L.; Salvo, C.; Tommasini, F.; Valbusa, U. *J. Chem. Phys.* 1980, 73, 557) and makes one confident of the computed barriers to diffusion. A simple, analytical expression of the corrugated potential energy surface fitted to the calculated energy values is then used in 3D quantum dynamical calculations of the tunneling contribution to the diffusion coefficient. Results show that hydrogen atoms physisorbed on graphite are highly mobile on the surface even at $T = 0$ K. This suggests that hydrogen formation in cold, interstellar clouds can indeed occur down to very low temperatures through recombination of hydrogen atoms previously physisorbed on the surface of dust grains.

- [Chemistry at surfaces: From ab initio structures to quantum dynamics](#). Lanzani, G.; Martinazzo*, R.; Materzanini, G.; Pino, I.; and Tantardini, G. *Theoretical Chemistry Accounts*, 117(5-6): 805. 2007.

Abstract. Recent years have witnessed an ever growing interest in theoretically studying chemical processes at surfaces. Apart from the interest in catalysis, electrochemistry, hydrogen economy, green chemistry, atmospheric and interstellar chemistry, theoretical understanding of the molecule-surface chemical bonding and of the microscopic dynamics of adsorption and reaction of adsorbates are of fundamental importance for modeling known processes, understanding new experimental data, predicting new phenomena, controlling reaction pathways. In this work, we review the efforts we have made in the last few years in this exciting field. We first consider the energetics and the structural properties of some adsorbates on metal surfaces, as deduced by converged, first-principles, plane-wave calculations within the slab-supercell approach. These studies comprise water adsorption on Ru(0001), a subject of very intense debate in the past few years, and oxygen adsorption on aluminum, the prototypical example of metal passivation. Next, we address dynamical processes at surfaces with classical and quantum methods. Here the main interest is in hydrogen dynamics on metallic and semi-metallic surfaces, because of its importance for hydrogen storage and interstellar chemistry. Hydrogen sticking is studied with classical and quasi-classical means, with particular emphasis on the relaxation of hot-atoms following dissociative chemisorption. Hot atoms dynamics on metal surfaces is investigated in the reverse, hydrogen recombination process and compared to Eley-Rideal dynamics. Finally, Eley-Rideal, collision-induced desorption, and adsorbate-induced trapping are studied quantum mechanically on a graphite surface, and unexpected quantum effects are observed.

2006 (3)

- [Quantum study of Eley-Rideal reaction and collision induced desorption of hydrogen atoms on a graphite surface. I. H-chemisorbed case](#). Martinazzo*, R.; and Tantardini, G. *Journal of Chemical Physics*, 124(12): 124702. 2006.

Abstract. Collision induced (CI) processes involving hydrogen atoms on a graphite surface are studied quantum mechanically within the rigid, flat surface approximation, using a time-dependent wave packet method. The Eley-Rideal (ER) reaction and collision induced desorption (CID) cross sections are obtained with the help of two propagations which use different sets of coordinates, a "product" and a "reagent" set. Several adsorbate-substrate initial states of the target H atom in the chemisorption well are considered, and CI processes are studied over a wide range of projectile energy. Results show that (i) the Eley-Rideal reaction is the major reactive outcome and (ii) CID cross sections do not exceed 4 Å² and present dynamic thresholds for low values of the target vibrational quantum number. ER cross sections show oscillations at high energies which cannot be reproduced by classical and quasiclassical trajectory calculations. They are related to the vibrational excitation of the reaction products, which is a rather steep decreasing function of the collision energy. This behavior causes a selective population of the low-lying vibrational states and allows the quantization of the product molecular states to manifest itself in a collisional observable. A peak structure in the CID cross section is also observed and is assigned to the selective population of metastable states of the transient molecular hydrogen.

- [Quantum study of Eley-Rideal reaction and collision induced desorption of hydrogen atoms on a graphite surface. II. H-physisorbed case](#). Martinazzo*, R.; and Tantardini, G. *Journal of Chemical Physics*, 124(12): 124703. 2006.

Abstract. Following previous investigation of collision induced (CI) processes involving hydrogen atoms chemisorbed on graphite [R. Martinazzo and G. F. Tantardini, *J. Chem. Phys.* 124, 124702 (2006)], the case in which the target hydrogen atom is initially physisorbed on the surface is considered here. Several adsorbate-substrate initial states of the target H atom in the physisorption well are considered, and CI processes are studied for projectile energies up to 1 eV. Results show that (i) Eley-Rideal cross sections at low collision energies may be larger than those found in the H-chemisorbed case but they rapidly decrease as the collision energy increases; (ii) product hydrogen molecules are vibrationally very excited; (iii) collision induced desorption cross sections rapidly increase, reaching saturation values greater than 10 Å²; (iv) trapping of the incident atoms is found to be as efficient as the Eley-Rideal reaction at low energies and remains sizable (3-4 Å²) at high energies. The latter adsorbate-induced trapping results mainly in formation of metastable hot hydrogen atoms, i.e., atoms with an excess energy channeled in the motion parallel to the surface. These atoms might contribute in explaining hydrogen formation on graphite.

- [A local coherent-state approximation to system-bath quantum dynamics](#). Martinazzo*, R.; Nest, M.; Saalfrank, P.; and Tantardini, G. *Journal of Chemical Physics*, 125(19): 194102. 2006.

Abstract. A novel quantum method to deal with typical system-bath dynamical problems is introduced. Subsystem discrete variable representation and bath coherent-state sets are used to write down a multiconfigurational expansion of the wave function of the whole system. With the help of the Dirac-Frenkel variational principle, simple equations of motion-a kind of Schrödinger-Langevin equation for the subsystem coupled to (pseudo) classical equations for the bath-are derived. True dissipative dynamics at all times is obtained by coupling the bath to a secondary, classical Ohmic bath, which is modeled by adding a friction coefficient in the derived pseudoclassical bath equations. The resulting equations are then solved for a number of model problems, ranging from tunneling to vibrational relaxation dynamics. Comparison of the results with those of exact, multiconfiguration time-dependent Hartree calculations in systems with up to 80 bath oscillators shows that the proposed method can be very accurate and might be of help in studying realistic problems with very large baths. To this end, its linear scaling behavior with respect to the number of bath degrees of freedom is shown in practice with model calculations using tens of thousands of bath oscillators.

2005 (2)

- [Testing wave packet dynamics in computing radiative association cross sections](#). Martinazzo*, R.; and Tantardini, G. *Journal of Chemical Physics*, 122(9): 094109. 2005.

Abstract. A time-dependent wave packet method is used to compute cross sections for radiative recombination reactions using the $\text{Li}(^2S) + \text{H}^+ \rightarrow \text{LiH}^+ (X^2\Sigma^+) + \gamma$ as a test case. Cross sections are calculated through standard time-to-energy mapping of the time-dependent transition moment and a useful method is introduced to deal with the low collision energy regime. Results are in quantitative agreement over the whole energy range 10⁻⁴-5 eV with previous time-independent results for the same system [I. Baccarelli, L. Andric, T. Grodzanov, and R. McCarroll, *J. Chem. Phys.* 117, 3013 (2002)], thereby suggesting that the method can be of help in computing radiative association cross sections for more complicated systems.

- [Quantum effects in an exoergic, barrierless reaction at high collision energies](#). Martinazzo*, R.; and Tantardini, G. *Journal of Physical Chemistry A*, 109(42): 9379. 2005.

Abstract. The exoergic Eley-Rideal hydrogen recombination on graphite surfaces is known to produce vibrationally hot product molecules. Realistic quantum scattering calculations at normal incidence over a wide range of collision energies show that the degree of vibrational excitation of the reaction product is a steep decreasing function of the collision energy. This results in selective population of the lower-lying

vibrational levels and gives rise to an oscillating structure in the total reaction cross-sections at high energies, which cannot be reproduced by classical and quasi-classical trajectory calculations. An analogous quantum structure appears in the total collision-induced desorption cross-sections and is assigned to selective population of the metastable states of the transient molecular hydrogen.

2004 (2)

- [Hot-atom versus Eley-Rideal dynamics in hydrogen recombination on Ni\(100\). I. The single-adsorbate case.](#) Martinazzo, R.; Assoni, S.; Marinoni, G.; and Tantardini*, G. *Journal of Chemical Physics*, 120(18): 8761. 2004.

Abstract. The scattering of a projectile hydrogen atom off a target hydrogen atom adsorbed on the Ni(100) surface was studied. Both the rigid and the moving surface cases were considered and the results were compared over a wide range of collision energies and for different aiming cells. Particular attention was paid to the process of energy transfer while studying the collision system in the presence of an explicit thermal bath. The problems associated with the use of PBCs were approximately solved by breaking the dynamics into two steps.

- [Potential energy surface, bound states, and rotational inelastic cross sections of the He-CH₄ system: A theoretical investigation.](#) Calderoni, G.; Cargnoni*, F.; Martinazzo, R.; and Raimondi, M. *Journal of Chemical Physics*, 121(17): 8261. 2004.

Abstract. We determined two potential energy surfaces (PES) for the He-CH₄ system by means of MP4 and Valence Bond (VB) calculations. The MP4 potential is similar to the one commonly adopted for this system [U. Buck, K. H. Kohl, A. Kolhase, M. Faubel, and U. Staemmler, *Mol. Phys.* 55, 1255 (1985)], while the VB PES is slightly more attractive. To evaluate the reliability of these potentials, we investigated the scattering properties by performing close coupling calculations, and concluded that: (i) the available experimental data do not permit the ranking among the PES considered; (ii) some theoretical predictions differ considerably from the experimental data, and these discrepancies cannot entirely be ascribed to the inaccuracy of the ab initio calculations; (iii) the scattering properties at low energy might discriminate between the MP4 and VB potentials

2003 (4)

- [The gas-phase lithium chemistry in the early universe: Elementary processes, interaction forces and quantum dynamics.](#) Bodo, E.; Gianturco*, F.; and Martinazzo, R. *Physics Reports*, 384(3): 85. 2003.

Abstract. In this work we review the efforts made in the last 10 years to understand the neutral and ionic chemistry of LiH. The relevance of most of the studies on this subject is due to the possible importance of the LiH molecules and relative ions in the primordial universe chemistry. Although it is still not clear what could be the role of LiH in the early universe chemistry, since experimentally important data are indeed still missing and its relevance may be limited by the small abundance of Li molecular species that is thought to exist at the recombination era, it is already important from a fundamental point of view to gather the various results obtained up to now since, in our opinion, they are already able to shed light on a large portion of the gas-phase chemistry of LiH and of its positive ion. Most of the results that will be summarized here are theoretical and computational, intending to provide the present state of our knowledge on the relevant potential energy surfaces and dynamical processes which ensue from their features.

- [A modified variable-phase algorithm for multichannel scattering with long-range potentials.](#) Martinazzo, R.; Bodo, E.; and Gianturco*, F. *Computer Physics Communications*, 151(2): 187. 2003.

Abstract. A new Variable-Phase (VP) algorithm for solving the close coupled equations of inelastic scattering in atom-molecule collisions driven by a strong long range potential is presented. The proposed method allows for a rigorous, gradual reduction of the number of closed channels during the outward propagation of the solution of the VP equations. In this way it allows a considerable saving of CPU time when dealing with strong, long-range potentials. A further saving of computational time is achieved by the use of a zero order effective potential in the reference problem which avoids the calculation of the computationally expensive Bessel functions. The K matrix version of the VP equations are solved with a standard Runge-Kutta integrator with adaptive step size. The low-energy, rotational excitation process in the LiH-H⁺ system is used to test the resulting algorithm and we show that the present method once applied to long-range interactions, can be orders of magnitude faster than the widely used, adaptive-step size LogDerivative/Airy propagator while keeping the same level of accuracy.

- [Accurate potential energy surfaces for the study of lithium-hydrogen ionic reactions.](#) Martinazzo, R.; Tantardini*, G.; Bodo, E.; and Gianturco, F. *Journal of Chemical Physics*, 119(21): 11241. 2003.

Abstract. Three-dimensional potential energy surfaces (PESs) have been computed, and numerically fitted, for the two lowest electronic states of the LiH₂⁺ system, which are of importance for the astrophysically relevant LiH⁺+H→Li⁺+H₂ and LiH+H⁺→Li+H₂ exoergic reactions. We extend the recently computed 11000 multi reference valence bond ab initio energy values [Martinazzo et al., *Chem. Phys.* 287, 335 (2003)] with 600 multireference configuration interaction calculations with complete active self-consistent field reference functions and a large Li(12s10p4d1f)/H(8s6p3d1f) basis set. We have fitted the full set of energy values with a modified Aguado-Paniagua ansatz that correctly takes into account in this ionic system the important long-range contributions to the potential. Calibration calculations on the three-body potential term and the use of essentially exact results for the two-body contributions allow us to estimate the overall accuracy of the analytic PESs to be within that required for accurate quantum scattering calculations. The above reactions can be treated adiabatically because of the large energy gap separating the two electronic states. The relevant potential energy surfaces have a very different shape. On the one hand, the ground-state PES shows a simple structure, with a downhill route to the products and a shallow well at the C_{2v} geometry which lies 0.286 eV below the Li⁺+H₂ asymptote. On the other hand, the first excited state is characterized by one deep, dipole-charge well which lies 1.315 eV below the LiH+H⁺ asymptote, one charge-induced dipole well 0.586 eV below the Li+H+H₂ asymptote, and a saddle point between them which lies 0.227 eV below the LiH+H⁺ asymptote. A conical intersection with the second excited state has been found but not yet studied in detail, since we deemed it to be of no direct relevance for the above reactions.

- [Three-dimensional reactive surfaces for the LiH₂⁺ system: An analysis of accurate ab initio results.](#) Martinazzo, R.; Bodo*, E.; Gianturco*, F.; and Raimondi, M. *Chemical Physics*, 287(3): 335. 2003.

Abstract. Calculations for the reactive potential energy surfaces, which are relevant for examining the low-energy channels connected with the LiH₂⁺ three atom ionic system, are carried out using a multireference valence bond (MRVB) approach. More than 11000 points have been computed over the grid of the three relevant coordinates (two bond distances and the enclosed angle) and the lowest three electronic states

have been followed over the spatial configuration of the above coordinates. Several aspects of the reactive behavior could be gleaned from an analysis of the computed surfaces and various features of the reactive outcomes are extracted from that analysis

2002 (1)

- [Photoexcitation of \$\text{LiH}_2^+\$ from selected initial states: A time-dependent model.](#) Satta, M.; Bodo, E.; Martinazzo, R.; and Gianturco*, F. *Journal of Chemical Physics*, 117(1): 177. 2002.

Abstract. A quantum time-dependent treatment was employed to model the photoexcitation of LiH_2^+ . The study was carried out by monitoring the fragmentation probabilities, the final vibrational distributions of the molecular fragments, and the angular evolution of the wave functions of the complex on the excited electronic surface. The comparison between different initial conditions shed light on the microscopic mechanism of the energy redistribution, with reference to the angular coordinate providing efficient energy channeling during the evolution.

2001 (5)

- [Reactive behavior of the \$\[\text{LiH}_2\]^+\$ system II. Collision-induced dissociation and collinear reaction dynamics of \$\text{LiH}^+ + \text{H}\$ from quantum time dependent calculations.](#) Bodo, E.; Gianturco*, F.; and Martinazzo, R. *Journal of Physical Chemistry A*, 105(49): 10986. 2001.

Abstract. The time-dependent approach to reactive scattering is applied to the study of the collinear collisions for the $\text{LiH}^+ + \text{H}$ system. The reaction $\text{LiH}^+ + \text{H} \rightarrow \text{H}_2 + \text{Li}^+$ is adiabatically confined to the ground electronic state of the LiH_2^+ system and is highly exoergic (~ 4.2 eV). However, despite the strong energetic gain, the present calculations show that the reactive component is only a negligible outcome of the encounters while the simple inelastic scattering process and the collision-induced dissociation dominate the dynamics. The binding energy of the $\text{LiH} + \text{reagent molecule}$ is so weak that the threshold of the triatomic dissociation channels becomes open at a collision energy of only a few tenths of an electronvolt. The total dissociation probabilities are obtained via an accurate computation of all the possible bound-to-bound transition probabilities (reactive and nonreactive) using the quantum time-dependent approach described herein.

- [Reactive behavior of the \$\[\text{LiH}_2\]^+\$ system I. Evaluation of the lower-lying electronic potentials for the collinear geometries.](#) Bodo, E.; Gianturco*, F.; Martinazzo, R.; and Raimondi, M. *Journal of Physical Chemistry A*, 105(49): 10994. 2001.

Abstract. The reactive behavior of the $[\text{LiH}_2]^+$ system is investigated by computing the potential energy surfaces (PES) for the collinear geometries. The three lowest-lying PESs have been obtained using a multireference valence bond approach and subsequently have been fitted with modified Laguerre functions. The results appear to exclude any significant nonadiabatic interaction between the first two electronic states and already suggest differences in the dynamical behavior of the title system when moving on each of these potential energy surfaces. Thus, at least within a collinear approach, a direct reactive dynamics should be expected for the ground-state reaction of $\text{LiH}^+ + \text{H} \rightarrow \text{Li}^+ + \text{H}_2$, while the formation of a temporary complex is suggested to occur for the partners interacting via the electronically excited PES pertaining to $\text{LiH} + \text{H}^+ \rightarrow \text{Li} + \text{H}_2^+$.

- [Possible reaction paths in the \$\text{LiH}_2^+\$ chemistry: A computational analysis of the interaction forces.](#) Bodo, E.; Gianturco*, F.; Martinazzo, R.; and Raimondi, M. *Chemical Physics*, 271(3): 309. 2001.

Abstract. The present study addresses the problem of establishing from fully ab initio quantum methods some quantitative features of the chemical interactions which play an important role in the ionic lithium chemistry of astrophysical relevance. In particular, the $\text{LiH} + 2 + \text{energetics}$ is examined by looking at the various possible chemical channels producing LiH , LiH^+ , H_2 and H_2^+ . An accurate evaluation of the relative energy landscapes as the complex breaks up into its asymptotic partners is presented for the first time. It allows us to clearly select those reactive pathways which can be excluded when setting up a kinetic modeling of the lithium chemistry network in early universe processes.

- [Computed orientational anisotropy and vibrational couplings for the \$\text{LiH} + \text{H}\$ interaction potential.](#) Bodo, E.; Gianturco*, F.; Martinazzo, R.; and Raimondi, M. *European Physical Journal D*, 15(3): 321. 2001.

Abstract. The interaction between LiH and H has been calculated using a Coupled Cluster approach in view of examining the strength of the coupling between the impinging atom and the rovibrational LiH states in low energy collision regimes. The potential energy surface was thus obtained by considering not only the angular anisotropy but also the dependence of the interaction energy on the vibrational motion of the LiH molecule, hence producing the strength of the vibrational coupling. The main objective is that of gaining a realistic description of the interaction in the sub-reactive region. The results of our calculations show here that this interaction should be used in conjunction with that of the reactive configurational space because of the strong coupling between the non-reactive and the reactive channels in the present system makes the full reactive scattering calculations a more reliable way to obtain realistic cross-sections also for inelastic relaxation and excitation processes.

- [A multireference valence bond approach to electronic excited states.](#) Martinazzo, R.; Famulari, A.; Raimondi, M.; Bodo, E.; and Gianturco*, F. *Journal of Chemical Physics*, 115(7): 2917. 2001.

Abstract. A multireference valence bond approach based on orthogonality conditions to ground state spin coupled (SC) orbitals was applied for the treatment of electronic excited states. Optimization of excited spin coupled wave functions was used to introduce correlation corrections in the excited state. The optimization was achieved using simple orthogonality constraints on the spin coupled orbitals.

2000 (3)

- [Applications of a variational coupled-electron pair approach to the calculation of intermolecular interaction in the framework of the VB theory: study of the van der Waals complex \$\text{He-CH}_4\$.](#) Specchio, R.; Famulari, A.; Martinazzo, R.; and Raimondi, M. *Journal of Chemical Physics*, 113(16): 6724. 2000.

Abstract. The potential surfaces of the He-CH_4 complex was studied by means of a general molecular orbital-valence bond (MO-VB) ab initio approach. Correlation contributions were determined using a very compact multistructure VB wave function. Further, a scheme for the intermediation generation of two virtual orbitals was devised.

- [Testing van der Waals interactions with quantum dynamics: Repulsive anisotropy and well depth in the LiH+He system.](#) Bodo, E.; Gianturco*, F.; **Martinazzo, R.**; Paesani, F.; and Raimondi, M. *Journal of Chemical Physics*, 113(24): 11071. 2000.

Abstract. The rigid rotor surface for the LiH-He interaction was studied numerically. The study showed that the well depth and anisotropy of the new surface differ from the valence bond calculations. The performance of potential energy surfaces to generate quantum observables is examined. The two surfaces show small differences in their short-range repulsive anisotropy. They show larger differences in their well depths. The different behavior of their wells in supporting van der Waals bound states was examined.

- [Spatial energetics of protonated LiH: Lower-lying potential energy surfaces from valence bond calculations.](#) Bodo, E.; Gianturco*, F.; **Martinazzo, R.**; Forni, A.; Famulari, A.; and Raimondi, M. *Journal of Physical Chemistry A*, 104(51): 11972. 2000.

Abstract. The detailed features of the interaction forces within the LiH_2^+ triatomic system are calculated using the spin-coupled valence bond (SCVB) method in terms of the three Jacobi coordinates of the LiH (LiH^+) and H^+/H fragments within a broad range of relative orientations and of internuclear distances. The specific features of the systems and of their asymptotic molecular fragments are examined with the view of estimating from them the collisional probabilities for producing rovibrationally excited partners with detectable radiative behavior. The possibility of having a charge-transfer process within the two electronic states of the LiH_2^+ ion is also analyzed and discussed. The calculations suggest, albeit still qualitatively, that a direct charge-transfer reaction between $\text{LiH} + \text{H}^+ \rightarrow \text{LiH}^+ + \text{H}$ is unlikely to take place during bimolecular collisions in a low-density medium.

CONTRIBUTI IN VOLUMI

- Atomic-Scale Defects and Impurities in Graphene.
R. Martinazzo

In: (a cura di): M. Aliofkhazraei; N. Ali; W.I. Milne; C.S. Ozkan; S. Mitura; J.L. Gervasoni, *Graphene Science Handbook: Nanostructure and Atomic Arrangement*. CRC Press, ISBN: 9781466591370, p. 21-37, (2016).

- Ultrafast Energy and Charge Transfer in Functional Molecular Nanoscale Aggregates.
H. Tamura, K. H. Hughes, **R. Martinazzo**, J. Wahl, R. Binder, I. Burghardt

In: (a cura di): S. Haacke; I. Burghardt, *Ultrafast Dynamics at the Nanoscale: Biomolecules and Supramolecular Assemblies*. CRC Press, ISBN: 9789814745338, p. 407-435, (2016).

- Unitary Approaches to Dissipative Quantum Dynamics.
M. Bonfanti, **R. Martinazzo**

In: (a cura di): P. Bracken, *Research Advances in Quantum Dynamics*. InTech, ISBN: 9789535124856, doi: 10.5772/62686, p. 165-194, (2016).

- Hydrogen recombination on graphitic surfaces.
R. Martinazzo, S. Casolo, L. H. Hornekaer

In: (a cura di): R. Diez Muiño; H.F. Busnengo, *Dynamics of gas-surface interactions: Atomic-level understanding of scattering processes at surfaces (Vol. 50)*. Springer, Heidelberg. ISBN: 9783642329548, doi: 10.1007/978-3-642-32955-5_7, p. 157-177, (2013).

- Hierarchical Effective-Mode Approach for Extended Molecular Systems.
R. Martinazzo, K. H. Hughes, I. Burghardt

In: (a cura di): P.E.E. Hoggan; E.J.J. Brändas; J. Maruani; P. Piecuch and G. Delgado-Barrio, *Advances in the Theory of Quantum Systems in Chemistry and Physics (Vol. 22)*. Springer, ISBN: 978-94-007-2075-6, doi: 10.1007/978-94-007-2076-3_15, p. 269-283, (2012).

- Conical intersections coupled to an environment.
Burghardt, K. H. Hughes, **R. Martinazzo**, H. Tamura, E. Gindersperger, H. Koeppe, L. S. Cederbaum

In: (a cura di): W. Domcke; D. R. Yarkony and H. Köppel, *Conical Intersections: Theory, Computation and Experiment*. World Scientific, ISBN: 9789814313452, p. 301-346, (2011).

- The effect of atomic-scale defects and dopants on graphene electronic structure.
R. Martinazzo, S. Casolo, G.F. Tantardini

In: (a cura di): S. Mikhailov,

Physics and Applications of Graphene - Theory.
InTech, ISBN: 9789533071527, doi: 10.5772/14118, p. 45-70, (2011).

- Local-coherent state approximation to system-bath quantum dynamics.
R. Martinazzo, I. Burghardt, F. Martelli, M. Nest

In: (a cura di): D. Shalashilin; M.P. de Miranda,
Multidimensional quantum mechanics with trajectories.
Collaborative Computational Project on Molecular Quantum Dynamics, ISBN: 978-0-9545289-8-0, p. 133-144, (2009).

- The G-MCTDH method: related system-bath dynamics using Gaussian wavepackets.
Burghardt, **R. Martinazzo**, F. Martelli, G. Worth

In: (a cura di): D. Shalashilin; M.P. de Miranda,
Multidimensional Quantum Mechanics with Trajectories
Collaborative Computational Project on Molecular Quantum Dynamics, ISBN: 978-0-9545289-8-0, p. 124-132, (2009).

- Simulating chemical processes from scratch: classical and quantum molecular dynamics.
R. Martinazzo, I. Pino, S. Casolo, G. F. Tantardini

In: (a cura di): *Research activities on high performance computing clusters at CILEA 2006.*
CILEA - Consorzio Interuniversitario Lombardo per l'Elaborazione Automatica, Segrate: CILEA, ISBN: 978-88-88971-12-4,
p. 87-104, (2007).

- System-bath quantum dynamics of vibrational excitation and relaxation of adsorbates.
P. Saalfrank, I. Andrianov, S. Beyvers, Y. Ohtsuki, **R. Martinazzo**

In: (a cura di): K.H. Hughes,
Dynamics of open quantum systems.
ISBN: 978-0-9545289-6-6, p. 74-79, (2006).

- Two exothermic reactions in the Lithium Chemistry Network.
E. Bodo, **R. Martinazzo**, F. A. Gianturco

In: (a cura di): A. Miani; J. Tennyson; T. van Mourik,
High accuracy potentials for quantum dynamics.
Warrington: Daresbury Laboratory, ISBN: 0-9545289-0-5, p. 43-47, (2003).

- Recent developments of the SCVB method.
M. Sironi, M. Raimondi, **R. Martinazzo**, F. A. Gianturco, D. L. Cooper

In: (a cura di): D.L. Cooper,
Valence Bond Theory. vol. 10,
Elsevier, ISBN: 0-444-50889-9, p. 261-342, (2002).

ALTRE PUBBLICAZIONI

- [Cover Picture: Inherently Chiral Spider-Like Oligothiophenes \(Chem. Eur. J. 31/2016\).](#) Sannicolò, F.; Mussini, P., R.; Benincori, T.; **Martinazzo, R.**; Arnaboldi, S.; Appoloni, G.; Panigati, M.; Quartapelle Procopio, E.; Marino, V.; Cirilli, R.; Casolo, S.; Kutner, W.; Noworyta, K.; Pietrzyk-Le, A.; Iskierko, Z.; and Bartold, K. *Chemistry - A European Journal*, 22(31): 10681-10681. 7 2016.

Abstract. The racemate of an inherently chiral "spider-like" octathiophene monomer T83, in which chirality is generated by torsion in its backbone, was synthesized. In the cover image, the (S)-T83 has woven a highly selective chiral web in which enantiomeric insects (l- and d-DOPA, R- and S-FcA) are differently entrapped. More information can be found in the Full Paper by P. R. Mussini, T. Benincori, R. Martinazzo et al. on page 10839. Image credit to Rocco Martinazzo.

- [Cover Image \(Int. J. of Quantum Chemistry, Vol. 116, Issue 21\).](#) **Martinazzo, R.**; Bonfanti, M., 2016, DOI: 10.1002/qua.25192.

Abstract. On page 1575, Matteo Bonfanti and Rocco Martinazzo examine reactions at surfaces under a magnifying glass. Fruitful combination of theory, modelling, and simulations provides a powerful tool to understand the dynamics of atoms and molecules at the gas-solid interface. This is pictured on the cover with a simple illustration of two prototypical recombination processes, the Eley-Rideal (left) and the Langmuir-Hinshelwood (right) reactions. Image credit goes to Matteo Bonfanti.

- [Cover Picture: Inherently Chiral Macrocyclic Oligothiophenes: Easily Accessible Electrosensitive Cavities with Outstanding Enantioselection Performances \(Chem. Eur. J. 47/2014\)](#) Sannicolò, F.; Mussini, P., R.; Benincori, T.; Cirilli, R.; Abbate, S.; Arnaboldi, S.; Casolo S.; Castiglioni, E.; Longhi, G.; **Martinazzo, R.**; Panigati, M.; Pappini, M.; Quartapelle Procopio, E.; Rizzo, S. *Chemistry - A European Journal*, 22(31): 10681-10681. 7 2016.

Abstract. When new topologically appealing molecules are formed, fantasy-assisted cogitation tries to associate their shapes to objects of everyday life: knots, cylinders, pretzels, baskets, ladders, etc. Chirality adds a touch of intelligence to these molecules, which gain the ability to recognize enantiomorphic species. In their Communication on page 15298 ff., F. Sannicolò et al. describe some inherently chiral elliptical and triangular oligothiophene macrocycles which they associate with the pictograms of some more or less mysterious crop circles. Photograph courtesy of Mr. Steve Alexander, www.temporarytemples.co.uk. Image credit to Rocco Martinazzo.

- [A new wide band gap form of hydrogenated graphene](#). Casolo*, S.; Tantardini, G.; and Martinazzo, R., [GraphITA2011](#), Carbon Nanostructure Book Series, Springer, 2012, DOI: 10.1007/978-3-642-20644-3_5.

Abstract. We propose a new form of partially hydrogenated graphene in which hydrogen atoms lay in para position to each other, forming a honeycomb-shaped superlattice. This arrangement is shown to be favored by progressive preferential sticking events, while its particular lattice symmetry guarantees the presence of a wide band gap. With the help of first principles DFT and many-body calculations we find this structure to be an insulator, similarly to graphene.

- [The effect of atomic-scale defects on graphene electronic structure](#). Martinazzo*, R.; Casolo, S.; and Tantardini, G., [GraphITA2011](#), Carbon Nanostructure Book Series, Springer, 2012, DOI: 10.1007/978-3-642-20644-3_16

Abstract. Graphene, being one-atom thick, is extremely sensitive to the presence of adsorbed atoms and molecules and, more generally, to defects such as vacancies, holes and/or substitutional dopants. This feature, apart from being directly usable in molecular sensor devices, can also be employed to tune graphene electronic properties. Here we focus on those basic features of atomic-scale defects that can be useful for material design. Starting with isolated p z defects, we analyse the electronic structure of the defective substrate and how it determines the chemical reactivity towards adsorption (chemisorption) of atomic/molecular species. This is shown to produce non-random arrangement of adatoms on the surfaces. Then, we consider the reverse problem, that is how to use defects to engineer graphene electronic properties. In particular, we show that arranging defects to form honeycomb-shaped superlattices (what we may call "supergraphenes") a sizeable gap opens in the band structure and new Dirac cones are created right close to the gap region. These possible structures might find important technological applications in the development of graphene-based logic transistors.

- Nano-technology, theoretical chemistry and computational chemistry. Tantardini, G.; Martinazzo, R.; and Casolo, S. *Mondo Digitale*, 9(3). 2010.

ORGANIZZAZIONE, DIREZIONE E COORDINAMENTO DI CENTRI O GRUPPI DI RICERCA NAZIONALI E INTERNAZIONALI O PARTECIPAZIONE AGLI STESSI

- 2019 Eli Pollak's group, Weizmann Institute of Science, Rehovot, Israele.
Visiting scientist.
- 2014— Chemical Dynamics Theory Group, R. Martinazzo, Università degli Studi di Milano, Milano, Italia.
Group Leader
- 2016-2020 EuroPAH, PI dell'unità locale Unimi, Partner organization della network H2020-MSCA-ITN-2016
EU Grant n. 722346
- 2013 Laboratoire Collisions Agrégats Réactivité - Université Paul-Sabatier, Toulouse, Francia
Visiting scientist.
- 2005-2006 Theoretical Chemistry Group, P. Saalfrank, Universität Potsdam, Potsdam, Germania.
Visiting scientist.
- 2002-2014 Chemical Dynamics Theory Group, G.F. Tantardini, Università degli Studi di Milano, Milano, Italia.
Membro senior.
- 2000-2001 Theoretical Chemistry Group, F. A. Gianturco, Università La Sapienza, Roma, Italia.
Studente.
- 1998-2002 Gruppo di ricerca del Prof. M. Raimondi, Università degli Studi di Milano, Milano, Italia.
Studente.

ATTIVITÀ QUALI LA DIREZIONE O LA PARTECIPAZIONE A COMITATI EDITORIALI DI RIVISTE SCIENTIFICHE

- 2022— [Frontiers in Carbon](#). Review Editor for Graphite-ene Section.

TITOLARITÀ DI BREVETTI

- Electro-active macrocyclic oligoarenes and oligoheteroarenes with stereogenic axes, F. Sannicolò et al.
Patent No. WO2015177763A9 (2015)

Abstract. *The present invention relates to electro-active, both achiral and chiral, polyconjugated macrocyclic oligoarene and oligoheteroarene compounds, optionally used as single enantiomers, and derivatives thereof, which are used in the manufacture of devices for the electronics field, the sensors field, the photovoltaics field, the chromatographic separation field or in stereoselective catalysis reactions.*

PREMI E RICONOSCIMENTI NAZIONALI E INTERNAZIONALI

2017 **Abilitazione Scientifica Nazionale a Professore di I Fascia in Chimica Fisica** (Settore Concorsuale 03/A2)

2014 **Abilitazione Scientifica Nazionale a Professore di II Fascia in Chimica Fisica** (Settore Concorsuale 03/A2)

1992 **Medaglia d'Argento** alla XXIVth International Chemistry Olympiads, Pittsburg, United States

1992 **Attestato di Benemerenza**, per meriti dall' Associazione Periti Industriali di Milano, Milano, Italia

FINANZIAMENTI

2018 **NEQRate**, Grant computazionale al centro HPC CINECA, ca. 60,000 € equivalenti.

2017 **ExGas**, Grant Unimi, Piano di sviluppo dell'Ateneo, 7,400 €.

2016-2020 **EuroPAH**, PI dell'unità locale Unimi, Partner organization della network H2020-MSCA-ITN-2016, EU Grant n. 722346. Totale finanziamento: 4,009,452 €.

2014 **LISA-MolrGr**, Grant computazionale al centro HPC CINECA, ca. 80,000 € equivalenti.

2013 **NEXT Mobility Grant**, Laboratoire Collisions Agrégats Réactivité, Université Paul-Sabatier Toulouse, Francia, ca. 8,000 €.

2014 **LISA-IrGraphe**, Grant computazionale al centro HPC CINECA, ca. 62,000 € equivalenti.

2009-2011 **PRIN-2009C28YBF**, membro dell'unità di ricerca Unimi.

2008 **Vinci**, Grant dall'Université Franco-Italienne, supporto alla *co-tutorship* del PhD project di Fausto Martelli. In collaborazione con I. Burghardt dell'École Normale Supérieure, Paris, Francia, ca. 5,000 €.

2006-2008 **PRIN-2006030944**, membro dell'unità di ricerca Unimi

2004-2006 **PRIN-2004034838**, membro dell'unità di ricerca Unimi

2002-2004 **Postdoc fellow**, Dipartimento di Chimica-Fisica ed Elettrochimica, Università degli Studi di Milano,

2001-2002 **Max Planck Society**, supporto finanziario alla visita al gruppo del prof. F. A. Gianturco Dip. di Chimica, Università La Sapienza, Milano, Italia.

1992-1998 **Borsa di studio**, dall'Istituto per il diritto allo Studio Universitario.

FINANZIAMENTI (ALTRO)

2022 **χISS: CHirality-Induced Spin Selectivity**, PRIN, Prot. 2022FL4NZ4, in valutazione. In collaborazione con Matteo Cococcioni (Università di Pavia). Finanziamento richiesto 250,000 €.

2020 **ENDCond**, ERC-2020-SyG, Proposal n. 951373, corresponding author (project PI). Rejected at Step 2. In collaborazione con Irene Burghardt (Goethe University of Frankfurt) e Davide Ceresoli (CNR). Finanziamento richiesto (totale): 6,210,000 €.

PARTECIPAZIONE IN QUALITÀ DI RELATORE A CONGRESSI E CONVEGNI DI INTERESSE INTERNAZIONALE

- 09/2022 **Exact factorization and Bohmian Mechanics**, Bristol, Regno Unito.
Relazione su invito: "*Quantum theory of electronic friction*"
- 06/2022 **MARVEL - First-Principles modelling of Defects in Solids**, ETH Zurich, Svizzera.
Relazione su invito: "*Atomic-scale defects in graphene*"
- 02/2022 **DQML - Dynamics, Quantum Effects and Machine Learning in Materials Science and Computational Chemistry**, Hintertux, Austria.
Relazione su invito: "*Quantum dynamics in condensed phases*".
- 06/2021 **MARVEL - First-Principles modelling of Defects in Solids**, ETH Zurich, Svizzera.
Relazione su invito. Postponed to 2022 due to Covid-19
- 06/2020 **CosmicPAH - Life Cycle of Cosmic PAHs**, Aarhus, Danimarca. Relazione su invito.
Postponed to 2022 due to Covid-19
- 07/2019 **Advanced Electronic Structure Methods in Condensed Matter Physics**, EPFL, Lausanne, Svizzera.
Lezione su invito: "*Quantum dynamics in condensed phase*".
- 03/2019 **EPoLM-4, 4th Workshop on Energetic processing of large molecules**, Madrid, Spagna.
Relazione su invito: "*The interaction of H atoms with coronene: a quantum chemist's perspective*".
- 09/2018 **ETSF, 23rd Workshop on electronic excitations: interdisciplinary views on quantum many-body theory**, Milano, Italia. Relazione su invito: "*Why Silicon is not Carbon?*".
- 07/2015 **13th International workshop on Quantum Reactive Scattering**, Salamanca, Spagna.
Relazione su invito: "*Quantum dynamics of hydrogen atoms on graphene*".
- 10/2014 **16th Workshop on Dynamical Phenomena at Surfaces**, Madrid, Spagna.
Relazione su invito: "*Adsorption, clustering and reactions of hydrogen atoms on graphene*".
- 05/2014 **Quantum and Classical Complexity: From Atoms to Biosystems**, Frankfurt, Germania.
Relazione su invito: "*Effective mode representation of structured environments: towards first principles quantum dynamics of hydrogen atoms on graphene*".
- 11/2013 **Scattering of atoms and molecules from surfaces**, Potsdam, Germania.
Relazione su invito: "*Hydrogen atoms on graphene: structure, energetics and dynamics*".
- 04/2013 **Exploring mechanisms for H₂ formation on very small carbonaceous grains and PAHs of astrophysical interest**, Toulouse, Francia.
Relazione su invito: "*Adsorption and reaction of hydrogen atoms on graphitic substrates*".
- 04/2013 **Rome School on Open Systems and the Quantum-Classical Boundary**, Roma, Italia.
Relazione su invito: "*Effective mode representation of structured environments*".
- 09/2012 **GrpHEL**, Mykonos, Grecia.
Contributo orale: "*Spin-coupling around a carbon atom vacancy in graphene*".
- 09/2011 **Adsorption, Réactivité et Contrôle de l'Hydrogène En interaction avec des Surfaces**, Alenya (Perpignan), Francia.
Relazione su invito: "*Interaction of hydrogen atoms with carbon sp² structures*".
- 09/2011 **Challenges in modelling the reaction chemistry of interstellar dust**, Leiden, Paesi Bassi.
Contributo orale: "*Interaction of hydrogen atoms with carbon sp² structures: adsorption energetics and Eley-Rideal dynamics*".
- 05/2011 **Theoretical Molecular Dynamics with Surfaces and PAHs**, Toulouse, Francia.
Relazione su invito: "*Hydrogen formation on graphitic surfaces: energetics and dynamics of elementary processes*".
- 05/2011 **GraphITA**, Gran Sasso National Laboratories, Assergi (L'Aquila), Italia.
Relazione su invito: "*The effect of atomic-scale defects on graphene electronic structure*"
- 12/2010 **Elementary Reactive Processes at Surfaces**, Bordeaux, Francia.
Relazione su invito: "*Adsorption, clustering and reactions of H atoms on graphene*".

- 09/2010 **ECOSS 27, 27th European Conference on Surface Science**, Groningen, Paesi Bassi.
Contributo orale: "*Symmetry-induced band-gap opening in graphene superlattices*".
- 12/2008 **Winter modeling workshop**, Pisa, Italia.
Relazione su invito: "*Wavepacket approaches to system-bath quantum dynamics*".
- 09/2008 **Multidimensional Quantum Mechanics with Trajectories**, Leeds, Regno Unito.
Relazione su invito: "*Local coherent-state approximation to system-bath quantum dynamics*".
- 07/2008 **ECOSS 25, 25th European Conference on Surface Science**, Liverpool, Regno Unito.
Relazione su invito: "*Theoretical study of hydrogen adsorption and dynamics on graphitic surfaces*".
- 02/2008 **XXXVII Congresso Nazionale della Divisione di Chimica Fisica della SCI**, Camogli (Genova), Italia.
Contributo orale: "*The influence of quantum reflection on the Eley-Rideal hydrogen formation reaction at interstellar cloud conditions*".
- 08/2007 **Elementary Reactive Processes at Surfaces**, Donostia (S. Sebastian), Spagna.
Relazione su invito: "*Quantum studies of Hydrogen dynamics on graphite surfaces*".
- 07/2007 **Mathematical challenges in Quantum Chemistry Problems**, Coventry, Regno Unito.
Relazione su invito: "*The Local Coherent-State Approach to System-Bath Quantum Dynamics and Its Extensions*".
- 06/2007 **The Quantum World in Real Time: Is it accessible?** Safed, Israele.
Relazione su invito: "*The Local Coherent State Approach to System-Bath Quantum Dynamics*".
- 12/2006 **VI Convegno GICC**, S. Servolo (Venezia), Italia.
Contributo orale: "*The Local Coherent State Approach to System-Bath Quantum Dynamics*".
- 09/2006 **XXII Congresso Nazionale della SCI**, Firenze, Italia.
Contributo orale: "*A Local Coherent State Approach to System-Bath Quantum Dynamics*".
- 06/2005 **XXXIV Congresso Nazionale della Divisione di Chimica Fisica della SCI**, Siena, Italia.
Contributo orale: "*Exotic reactions in space and the CH⁺ mystery: ab initio investigation of the CH₂⁺ molecular ion*".

ORGANIZZAZIONE DI CONGRESSI E WORKSHOP

- 08/2022 **ECOSS 35, 35th European Conference on Surface Science**, Luxembourg, Luxembourg.
Program Committee.
- 09/2021 **Challenges in reaction dynamics of gas-surface interactions, Methodological advances in dissipative and non-adiabatic process**, Toulouse, Francia, *Co-organizzatore.*
- 08/2018 **ECOSS 34, 34th European Conference on Surface Science**, Aarhus, Danimarca, *Program Committee.*
- 06/2017 **Challenges in reaction dynamics of gas-surface interactions, Methodological advances in dissipative and non-adiabatic process**, Albi, Francia, *Co-organizzatore.*
- 09/2010 **XXXIX Congresso Nazionale della Divisione di Chimica Fisica della SCI**, Stresa (Verbania), Italia.
Comitato Organizzatore.
- 09/2009 **ECOSS 26, 26th European Conference on Surface Science**, Parma, Italia.
Chairman alla sessione: "Nanoelectronic materials and graphene".

SEMINARI SU INVITO

- 10/2022 **Center for Interstellar Catalysis**, Aarhus, Denmark
"*Hydrogen adsorption and reaction on sp² carbon structures: energetics and dynamics*" (Webinar)
- 07/2021 **Catalan Institute of Nanoscience and Nanotechnology**, Stephen Roche's group, Barcelona, Spagna.
"*Graphene as a quantum pinball*" (Webinar)
- 02/2015 **Goethe-Universität Frankfurt am Main**, Irene Burghardt's group, Frankfurt, Germania
"*Quantum dynamics of hydrogen atoms on graphene*"

- 04/2013 **Université Paul Sabatier, Christine Joblin's group, Toulouse, Francia**
"Interaction of hydrogen atoms with sp^2 carbon atoms"
- 11/2011 **Universiteit Leiden, Leiden, Paesi Bassi. Van Marum Colloquium.**
"Effective mode representation of quantum mechanical energy transfer to surfaces".
- 06/2011 **Aarhus University, Liv Hornekaer's group, Aarhus, Danimarca.**
"Hydrogen formation on graphitic surfaces: energetics and dynamics of elementary processes".
- 02/2011 **Technische Universität München, Mathias Nest's group, Munich, Germania**
"Generalized LCSA dynamics: the energy representation".
- 12/2010 **Universität Potsdam, Peter Saalfrank's group, Potsdam, Germania.**
"Reaction of H atoms on graphene".
- 11/2009 **Universität Duisburg-Essen, Eckart Hasselbrink - Peter Kratzer groups, Duisburg, Germania.**
"Tailoring graphene electronic properties via adsorption of hydrogen atoms".
- 06/2009 **Universität Tübingen, Christian Lubich's group, Tübingen, Germania.**
"Wavepacket approaches to system-bath quantum dynamics".
- 12/2008 **Universität Potsdam, Peter Saalfrank's group, Potsdam, Germania.**
"Understanding adsorption of hydrogen atoms on graphenic substrates".
- 04/2008 **Università di Siena, Carlo Petrongolo's group, Siena, Italia.**
"Carbon chemistry in the interstellar medium and the CH^+ mystery".
- 02/2008 **Universität Potsdam, Peter Saalfrank's group, Potsdam, Germania.**
"System-bath dynamics with the Local Coherent State Approximation".

ATTIVITA' DI REVISIONE

Per riviste internazionali (>100 in totale, in grassetto se > 10)

ACS Appl. Mater. Interfaces — ACS Nano — Carbon — Catalysis Today — Chem. Phys. — Chem. Phys. Lett. — Chirality — Comp. Mat. Sci. — Eur. Phys. J — Int. J. Quantum Chem. — J. Comp. Phys. — J. Mat. Chem. — J. Nanoparticle Res. — J. Photochem. Photobio. A — J. Phys. B: Cond. Matter — J. Phys. Cond D: App. Phys. — J. Phys. Chem. A — J. Phys. Chem. C — J. Phys. Chem. Lett. — **J. Chem. Phys.** — Materials — Mater. Res. Express — Nanotechnology — Nature Comm. — Phys. A — Phys. B — **Phys. Chem. Chem. Phys.** — **Phys. Rev. B** — **Phys. Rev. Lett.** — Phys. Rev. App. — Phys. Rev. Mat. — Phys. Scr. — Phys. Status Solidi — RSC Advances — 2D Materials

Per agenzie di finanziamento (>10 in totale, in grassetto se > 1)

ANR (Francia) — RGC (Hong-Kong) — FMO (Paesi Bassi) — NWO (Paesi Bassi) — ACS Petroleum Research Fund (U.S.) — FWF (Austria) — **CINECA** (Italia) — Fondazione CARIPLO (Italia) — COST Association (esperto esterno) — MIUR-FARE

Tesi di Dottorato (>10 in totale)

Goethe University Frankfurt — University of Barcelona — Politecnico di Milano — Università degli Studi di Milano — Università di Genova — Università La Sapienza

COMMISSIONI DI VALUTAZIONE E SELEZIONE

2022 Commissione di valutazione di Ricercatore a Tempo Determinato RTD/B
 ai fini della chiamata a Professore di Seconda Fascia, Università degli Studi di Milano, Italia

2020 Commissione di valutazione, Master Thesis, Goethe University Frankfurt, Germania

2019 Commissione di valutazione, PhD Thesis, Università degli Studi di Milano, Italia

2019 Commissione di valutazione di Ricercatore a Tempo Determinato RTD/B
 ai fini della chiamata a Professore di Seconda Fascia, Università degli Studi di Milano, Italia

2019 Commissione di valutazione di Ricercatore a Tempo Determinato RTD/B
ai fini della chiamata a Professore di Seconda Fascia, Università degli Studi di Milano, Italia

2018 Commissione di selezione per il reclutamento di un Ricercatore a Tempo Determinato RTD/A
Università di Sassari, Italia

2019 Commissione di valutazione, PhD Thesis, Goethe University Frankfurt, Germania

2018 Commissione di valutazione, PhD Thesis, University of Barcelona, Spagna

2017 Commissione di valutazione, PhD Thesis, Politecnico di Milano, Italia

2014 Commissione di valutazione, Master Thesis, Goethe University Frankfurt, Germania

2008 Commissione di valutazione, PhD Thesis, University of Rome, Italy

PRINCIPALI COLLABORATORI

- **Irene Burghardt**, Institute of Chemistry, Goethe University of Frankfurt, Germania
Quantum dynamics
- **Eli Pollak**, Dept. of Chemical Physics, Weizmann Institute of Science, Israele
Quantum mechanics
- **Ivano Tavernelli**, IBM research, Zurich Research Laboratory, Zurich, Svizzera
Quantum computing
- **Liv Hornaekær**, Dept. of Physics and Astronomy, Aarhus University, Danimarca
Interstellar chemistry
- **Alexander Tielens**, Leiden Observatory, Leiden University, Paesi Bassi
Interstellar chemistry
- **Matteo Cococcioni**, Dip. di Fisica, Università di Pavia, Italia
Chemical Bonding & CISS effect
- **Davide Maria Proserpio**, Dip. di Chimica, Università degli Studi di Milano, Italia
Chemical Bonding

COMPUTER SKILLS

<i>OS</i>	Linux/Unix, MacOS, Windows
<i>programming</i>	Fortran, bash, Python
<i>Job related</i>	Linux (System Administration)
<i>typography</i>	L ^A T _E X, Microsoft Office

ATTIVITÀ GESTIONALI, ORGANIZZATIVE E DI SERVIZIO

INCARICHI DI GESTIONE E AD IMPEGNI ASSUNTI IN ORGANI COLLEGIALI E COMMISSIONI, PRESSO RILEVANTI ENTI PUBBLICI E PRIVATI E ORGANIZZAZIONI SCIENTIFICHE E CULTURALI, OVVERO PRESSO L'ATENEIO O ALTRI ATENEI

2020– **Referente di Dipartimento** nella piattaforma di calcolo scientifico (Unitech INDACO),
Università degli Studi di Milano

2020–2022 **Referente di Dipartimento** nella Biblioteca Scientifica (BICF),
Università degli Studi di Milano

2018– **Referente di Dipartimento** per la Valutazione della Qualità della Ricerca

(insieme a D.M. Proserpio), Università degli Studi di Milano

- 2018— **Membro della Commissione Scientifica** del Dipartimento di Chimica,
Università degli Studi di Milano
- 2017–2019 **Membro della Commissione Didattica**
con funzione di **Referente di settore Chimica Fisica** per i corsi di laurea Chimici
Università degli Studi di Milano
- 2016–2020 **Direttore Scientifico della Biblioteca di Chimica**
Università degli Studi di Milano
- 2015— **Referente di Dipartimento** per I test di ammissione ai corsi di laurea Chimici,
Università degli Studi di Milano
- 2015–2020 **Referente di Ateneo** per il calcolo scientifico al CINECA
Università degli Studi di Milano
- 2013— **Membro del Collegio Docenti del Dottorato in Chimica**
Università degli Studi di Milano
- 2011–2013 **Membro della Commissione Paritetica** del Dipartimento di Chimica
Università degli Studi di Milano
- 2009–2010 **Membro del Collegio Docenti del Dottorato in Chimica Industriale**
Università degli Studi di Milano
- 2005–2020 **Membro del Consiglio della Biblioteca di Chimica**
Università degli Studi di Milano

Data

05/09/2022

Luogo

Milano