



# TREX e-School on Quantum Monte Carlo with TurboRVB

**Selected** applications

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- × Correlation-driven dimerization and topological gap opening in isotropically strained graphene, S.S. et al. arXiv:1804.04479
- × Towards the Solution of the Many-Electron Problem in Real Materials: Equation of State of the Hydrogen Chain with State-of-the-Art Many-Body Methods, Mario Motta,..., Sandro Sorella, ... Shiwei Zhang (Simons Collaboration on the Many-Electron Problem), Phys. Rev. X 7, 031059 (2017)
- Phase Diagram of Hydrogen and a Hydrogen-Helium Mixture at Planetary Conditions by Quantum Monte Carlo Simulations, Guglielmo Mazzola, Ravit Helled, and Sandro Sorella, Phys. Rev. Lett. 120, 025701 (2018)
- × **Spintronics**: stability of spin-edge states in the **oligoacenes**
- × Superconductivity: electron pairing in the iron selenide (FeSe)
- × Proton hopping: zero- and finite-temperature simulations of the protonated water dimer (Zundel ion)



Our system is a chain of equidistant hydrogen atoms where the spacial dimerization is not allowed, it can be considered the realistic version of an Hubbard model in the limit of large **a**. While in three dimensional systems the dimerization of the hydrogen atoms is the responsible for the insulating behavior of the resulting material, in one dimension this is not the case and an the insulating phase survive to the absence of dimerization. This effect is purely 1D and it is due to the commensurability of the coulomb potential to the Fermi surface of the system.

#### The Hydrogen Chain Benchmark

In the Simons Foundation collaboration on the many electron problem, QMC has been used together with some of the other most advanced techniques of simulation for the state of the art benchmark on the hydrogen chain [3].

In Fig. 2 is shown the accuracy of the different methods for the calculation of the equation of state. The QMC provides an excellent accuracy both at long and especially at short hydrogen distances, where all the other methods fail due to basis set problems.



**Figure 2**: Accuracy the methods: the QMC results, indicated by half blue and half white boxes.



- 1. At which pressure does hydrogen become metallic?
  - 2. What is the influence of helium??
  - 3. Is this transition first order or a crossover in Jupiter/Saturn?
- 4. Is helium miscible in metallic hydrogen?

formation of helium rain!





Simulations are **easier** to do compared with experiments, in this regime!





At high temperatures (T > 2000 K) ions are classical, major errors come from treatment of electron correlations.

DFT is not accurate enough for phase transitions and equations of states (EOSs) for dense hydrogen.



QMC methods for electrons are *in principle* more accurate than DFT, relying on controllable approximations



Previous work (G. Mazzola S. Yunoki &S. S. Nat. Comm. '14, PRL '15...) was limited by small basis set





## Hydrogen phase diagram





## Hydrogen phase diagram





### Stretched graphene phase diagram





The Heitler-London bond: \_\_\_\_\_ = 
$$\frac{1}{\sqrt{2}} \left( \uparrow \downarrow \right) - \left| \downarrow \uparrow \right\rangle \left[ \Psi_a(r) \Psi_b(r') + a \leftrightarrow b \right]$$

Kekule' valence bonds.  $\rightarrow 2^3=8$  configurations

Correlation (Jastrow) does not allow overlapping HL-pairs

The spin gap is tuned by the strength of the pairing whereas the charge gap (infinite for exact Gutzwiller projection) controlled by Jastrow: this is quite different by mean-field Peirls or spin-Peirls, when charge gap = spin gap.



## Position relaxation at fixed area for different strains

 $a/a_0 = 1.15$   $a/a_0 = 1.25$ 









Recent work P.A. Lee and coworkers arXiV: 180500478 one band model for twisted bilayer graphene

$$H = H_t + H_U$$

$$H_t = -\sum_{ij} \sum_{\alpha} t_{ij} c_{i\alpha}^{\dagger} c_{j\alpha} + h.c.$$



$$H_U = U \sum_{\bigcirc} (Q_{\bigcirc} - 2)^2$$

Amazingly consistent with our phase diagram for single layer graphene







 $C_{4n+2}H_{2n+4}$  (n: number of benzene rings)



increasing chemical reactivity experimental challenge





*Restricted*: singlet-triplet instability *Unrestricted*: spin-polarized edge



open-shell singlet ground state with spin-edge polarization and diradical character



## Synthesis of nanoribbons with zigzag edge topology



Magnetic edge states in zigzag nanoribbons? Appealing for carbon-based spintronic applications

P Ruffieux et al. Nature 531, 489-492 (2016) doi:10.1038/nature17151



- What is the role of dimensionality and quantum fluctuations for the ground state properties?
- ×Is the magnetic state stable against correlations?
- ×Does the spin-polarization survives beyond the DFT approximation?



## RVB natural orbitals occupations





## RVB natural orbitals occupations



## No signature of open-shell singlet instability in RVB



## RVB range and aromaticity in nonacene



Long-ranged RVB correlations in nonacene
 → enhanced aromaticity
 → suppression of edge localization



× Correlations are detrimental for the formation of the open-shell singlet and magnetic edge states

× Enhanced aromaticity in wave function acts against edge localization

#### **References for this work**

N. Dupuy, S. Bouaouli, F. Mauri, S. Sorella, and M. Casula, JCP 142, 214109 (2015)

Nicolas Dupuy PhD thesis: "Electronic correlations in the acenes toward the longlength limit : a Monte Carlo study", https://tel.archives-ouvertes.fr/tel-01398365

N. Dupuy, M. Casula, JCP 148, 134112 (2018)



- Discovery of high-T<sub>c</sub> in iron pnictides in 2008: new excitement
- Electron-phonon coupling cannot account for T<sub>c</sub>
- New family of unconventional high-T<sub>c</sub> superconductors: cuprates are not the only ones!
- Proximity of spin ordered phases
- Multi-band physics

BaFe<sub>2</sub>As<sub>2</sub>





## Superconductivity in FeSe



## LETTERS nature PUBLISHED ONLINE: 14 JUNE 2009 | DOI: 10.1038/NIMAT2491 materials

# Electronic and magnetic phase diagram of $\beta$ -Fe<sub>1.01</sub>Se with superconductivity at 36.7 K under pressure

S. Medvedev<sup>1,2</sup>, T. M. McQueen<sup>3</sup>, I. A. Troyan<sup>2,4</sup>, T. Palasyuk<sup>2,5</sup>, M. I. Eremets<sup>2</sup>, R. J. Cava<sup>3</sup>, S. Naghavi<sup>1</sup>, F. Casper<sup>1</sup>, V. Ksenofontov<sup>1</sup>, G. Wortmann<sup>6</sup> and C. Felser<sup>1 \*</sup>



Open questions

- ×What is the origin of the superconducting gap?
- ×Underlying electron pairing symmetry?
- ×Pairing mechanism?
- ×Can we predict these properties from first principles?







N<sub>nuclei</sub> N

4x4x1 lattice with periodic boundary conditions in QMC Fe atom: 16 electron pseudo  $H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i,j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N_{\text{nuclei}}} \sum_{j=1}^{N} v_i (\mathbf{R}_i - \mathbf{r}_j)$ Se atom: 6 electron pseudo 352 electrons i < j10000 variational parameters



## parity under reflection through the iron (xy) plane



d<sub>xz</sub>, d<sub>yz</sub> orbitals: odd parity

 $d_{xy}$ ,  $d_{x2-y2}$ ,  $d_{z2}$  orbitals: even parity

$$\begin{split} F_{ee}(\mathbf{r}, \mathbf{r}') &= \sum_{\{\nu, \mu\} \in \text{even}} f(\mathbf{k})_{\nu, \mu} d_{\mathbf{k}, \nu, \uparrow}(\mathbf{r}) d_{-\mathbf{k}, \mu, \downarrow}(\mathbf{r}'), \\ F_{eo}(\mathbf{r}, \mathbf{r}') &= \sum_{\substack{\{\nu\} \in \text{even} \\ \{\mu\} \in \text{odd}}} f(\mathbf{k})_{\nu, \mu} d_{\mathbf{k}, \nu, \uparrow}(\mathbf{r}) d_{-\mathbf{k}, \mu, \downarrow}(\mathbf{r}'), \\ F_{oe}(\mathbf{r}, \mathbf{r}') &= \sum_{\substack{\{\nu\} \in \text{odd} \\ \{\mu\} \in \text{even}}} f(\mathbf{k})_{\nu, \mu} d_{\mathbf{k}, \nu, \uparrow}(\mathbf{r}) d_{-\mathbf{k}, \mu, \downarrow}(\mathbf{r}'), \\ F_{oo}(\mathbf{r}, \mathbf{r}') &= \sum_{\substack{\{\nu, \mu\} \in \text{odd}}} f(\mathbf{k})_{\nu, \mu} d_{\mathbf{k}, \nu, \uparrow}(\mathbf{r}) d_{-\mathbf{k}, \mu, \downarrow}(\mathbf{r}'). \end{split}$$

## odd-odd & even-even QMC pairing





## even-odd & odd-even QMC pairing











C.-L. Song et al., Science 332, 1410 (2011)



At z=0.25 c (almost at the Se height) C<sub>2</sub> broken symmetry from s+d<sub>xy</sub> superposition!





# Condensation energy: E<sub>RVB</sub>-E<sub>JHF</sub> energy per d electron (assuming nominal value of 6) meV





× First *ab initio* calculation of the pairing function of an iron-based superconductor

- Improper s-wave symmetry with planar s + d<sub>xy</sub> channels from pointgroup considerations
- Consistency with the gap anisotropy probed by specific heat and the C<sub>2</sub> broken symmetry seen by STM
- ×"Meaningful" estimate of T<sub>c</sub> from first principles

References for this work M. Casula and S. Sorella PRB 88, 155125 (2013)

Other relevant papers on the S<sub>4</sub> improper s-wave symmetry: J. Hu and N. Hao, PRX **2**, 021009 (2012) J. Hu, PRX **3**, 031004 (2013) Chia-Hui Lin, Chung-Pin Chou, Wei-Guo Yin, Wei Ku, arXiv:1403.3687



Exploring properties of hydrogen bond in water and water clusters

Water self-ionization:  $2 H_2 O \rightleftharpoons OH^- + H_3 O^+$ very high ionic mobility of hydroxide and hydronium hard to explain quantitatively

Hydrogen-bond network defect (by excess proton) to study proton hopping



#### Infrared pump-probed spectra of the proton transfer mode in water Dahms *et al.*, Science **357**, 491 (2017)

Zundel ion as a key structure





- Develop a reliable and accurate framework to study the impact of *quantum nuclear effects* in the **proton transfer** at finite temperature
- Theoretical challenge in describing quantum nuclei from first principles: three necessary ingredients must be taken into account
  - 1. very accurate treatment of the electronic part  $\rightarrow$  QMC wave functions
  - 2. include thermal effects
    - $\rightarrow$  Langevin Dynamics at finite temperature
  - 3. propagate equations of motion for quantum nuclei
    - $\rightarrow$  Path Integral + Langevin Dynamics (PILD)

### Zundel cation





- 2 regimes: symmetric for  $dO_1O_2 \le d_c$ , otherwise asymmetric.
- PBE overestimates symmetric region → high-level treatment of electronic correlations is essential
- QMC results are in good agreement with the CCSD(T) level of theory (X.Huang et al., J. Chem. Phys. 2005, **122**, 044308)



In *ab initio* MD, the nuclei move in a potential energy landscape provided by the electrons, via nuclear forces  $f = -\nabla_q V(q)$ 

$$V(\mathbf{q}) = \frac{\langle \Psi_{\mathbf{q}} | H(\mathbf{q}) | \Psi_{\mathbf{q}} \rangle}{\langle \Psi_{\mathbf{q}} | \Psi_{\mathbf{q}} \rangle} \quad \begin{array}{l} \text{QMC-DRIVEN MOLECULAR DYNAMICS} \\ \text{Way to include temperature effects} \end{array}$$

How to incorporate accurate but noisy QMC forces into classical and quantum MD simulations?  $\rightarrow$  Langevin Dynamics! (Attaccalite, Sorella PRL 2007)

$$\left\{ egin{array}{lll} \dot{\mathbf{p}} &=& -oldsymbol{\gamma}\mathbf{p}+\mathbf{f}(\mathbf{q})+oldsymbol{\eta}(t)\ \dot{\mathbf{q}} &=& \mathbf{p}\ oldsymbol{\eta} &=& oldsymbol{\eta}^{ ext{ext}}+oldsymbol{\eta}^{ ext{QMC}} \end{array} 
ight.$$

Generalized fluctuation-dissipation theorem (FDT)  $2k_B T \gamma_{ij} = \langle \eta_i^{\text{ext}} \eta_j^{\text{ext}} \rangle + \langle \delta f_i \delta f_j \rangle$ 



Quantum-to-classical isomorphism

$$H_M = \sum_{k=1}^M \left[ \sum_{i=1}^{3N} \left( \frac{\left[ p_i^{(k)} \right]^2}{2m_i} + \frac{1}{2} m_i \omega_M^2 \left[ q_i^{(k)} - q_i^{(k-1)} \right]^2 \right) + \frac{1}{M} V \left( q_1^{(k)}, \dots, q_{3N}^{(k)} \right) \right]$$

Quantum kinetic term replaced by a set of M beads, subject to ring boundary conditions (Boltzmannon), and interacting via a harmonic potential, whose coupling  $\omega_M = \frac{M}{\beta\hbar}$ 



Two different energies scales: Born-Oppenheimer forces and quantum kinetic term

### QMC-PIOUD in the Zundel ion









### Quantum versus thermal effects



# In the zundel ion, zero-point energy and NQE prevail over thermal fluctuations

 $\rightarrow$  weak thermal dependence of the radial distribution functions up to 300 K



- New PIOUD algorithm with better performances than standard PILE, thanks to the mapping onto an Ornstein-Uhlenbeck process
- Extension of a QMC-driven MD to the quantum case
- Strong quantum effects even at room temperature in the Zundel ion
- Alternative method to the nuclear quantum version of the CEIMC algorithm (see Pierleoni, Holzmann, Ceperley)

#### **Reference of this work**

Félix Mouhat, Sandro Sorella, Rodolphe Vuilleumier, Antonino Marco Saitta, and Michele Casula, J. Chem. Theory Comput. **13** (6), 2400 (2017)