First-principle approach to correlated realistic molecular and atomic hydrogen planes: Role of the Heisenberg-type interaction and the superconductivity

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MOTIVATION

The discovery of Dias and Silvera [1] in January 2017 (contested in [2–4]) rekindled the scientific interest in the problem of hydrogen metallization. Similarly, the development in high-pressure physics allowed recently to observe several new phases of solid hydrogen [5–6].

Here we present our approach of tackling this complex and novel problem for hydrogenic system with medium-to-strong interactions. Our aims are:

- to obtain a proper model of interactions in solid hydrogen (without common *double counting problem*);
- to model the electronic part of Hamiltonian from the first principles;
- to determine role of different interaction types;
- to assess whether or not the phases are metallic;
- to provide the phonon, as well as, the electron–phonon parts of the effective Hamiltonian;
- to estimate a first approximation of the critical superconducting temperature of such a system;

As the problem is complex, we analyze triangular H_2 crystal.

EXACT DIAGONALIZATION AB INITIO (EDABI) APPROACH

We use the so-called **E**xact **D**iagonalization **Ab I**nitio (EDABI) approach, where we exactly solve the second-quantized Hamiltonian (here in terms of iterative *Lanczos algorithm*)

$$\mathcal{H} = \sum_{ij}\sum_{\sigma} t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + \sum_{ijkl}\sum_{\sigma,\sigma'}V_{ijkl}\hat{c}^{\dagger}_{i\sigma}\hat{c}^{\dagger}_{j\sigma'}\hat{c}_{l\sigma'}\hat{c}_{k\sigma},$$

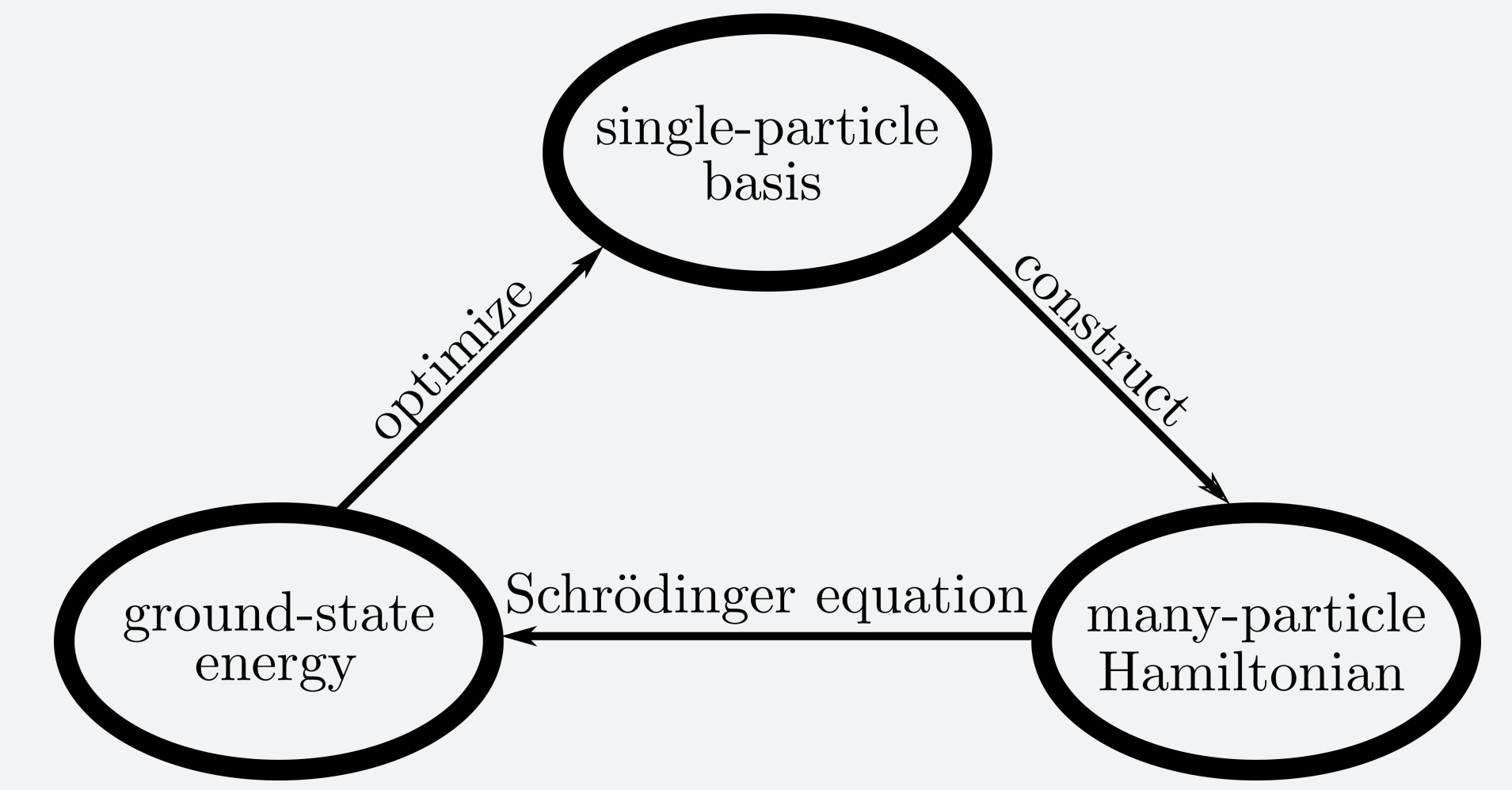where t_{ij} and V_{ijkl} are the microscopic parameters

$$T_{ij} = \langle w_i | \mathcal{T} | w_j \rangle,$$
$$V_{ijkl} = \langle w_i w_j | \mathcal{V}_{12} | w_k w_l \rangle,$$

build in terms of single-particle wavefunctions w_i, where in atomic units $\mathcal{T} = -\nabla^2 - \sum 2/|\mathbf{r} - \mathbf{R}|$, and $\mathcal{V} = 2/|\mathbf{r} - \mathbf{r}'|$.

We optimize our system with respect to *inverse wavefunction size* ζ, using the direct dependence of the ground-state energy
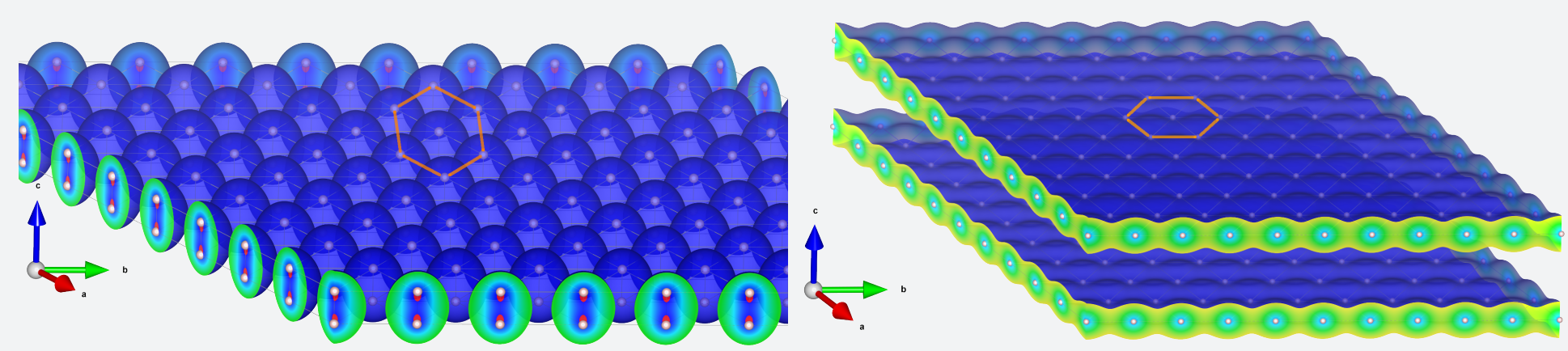
$$E_G\left[\{w_i^{(\zeta)}\}\right] = \langle n | \mathcal{H}^{\zeta} | n \rangle.$$


The general scheme of EDABI method.

MODEL

More about the model on Thursday, poster **Th-1-17** *Metallization of the solid molecular hydrogen as the Mott-Hubbard transition* by Biborski et al. [7–8].

System of molecules on the triangular lattice in molecular (left) and quasiatomic (right) states.
We study the thermodynamical state function

$$h = e + p \cdot A,$$

where h is enthalpy per molecule, e is energy per molecule, p is effective pressure, and $A = \frac{\sqrt{3}}{2}a^2$ is the area per molecule (a is the intermolecular distance).
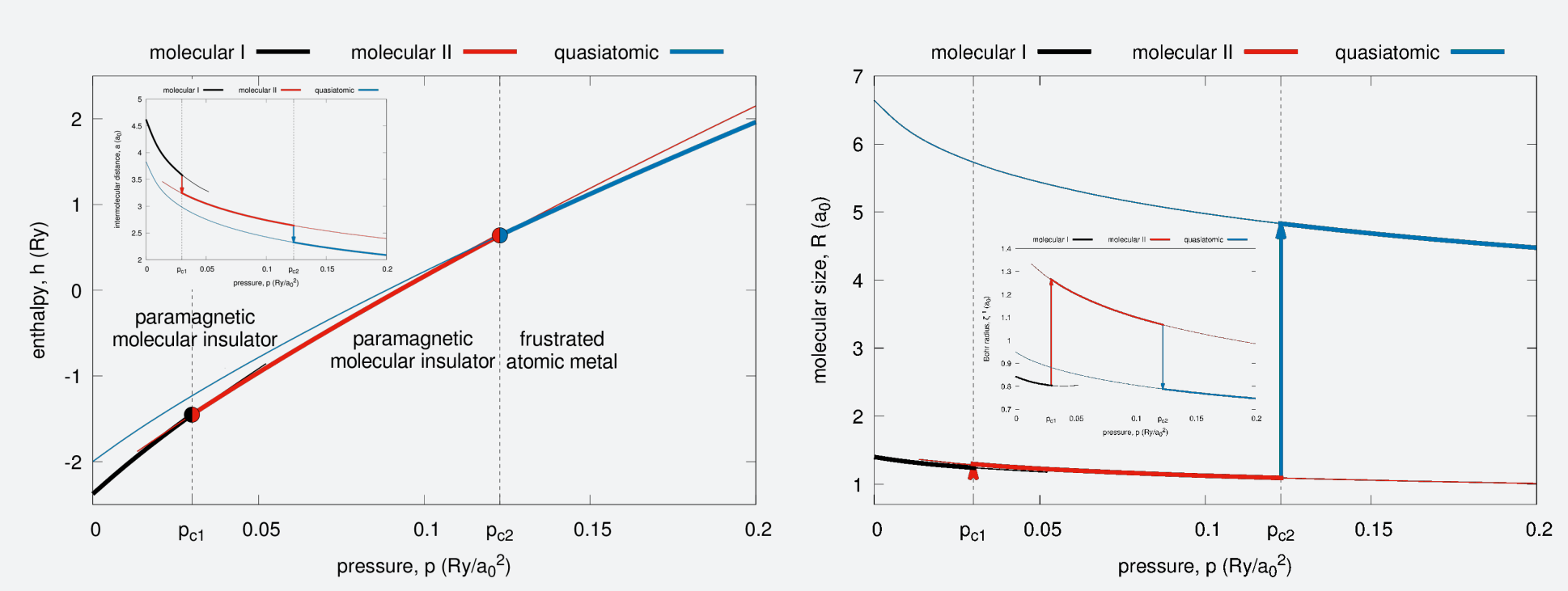

(LEFT) Effective enthalpy e versus effective pressure p, with the transition points marked explicitly;
(LEFT INSET) Intermolecular distance a vs p (left inset, note the abrupt effective volume changes at the transitions: $11.13a_0^2 \overset{p=p_1}{\rightarrow} 9.11a_0^2$ and $6.03a_0^2 \overset{p=p_2}{\rightarrow} 4.68a_0^2$);
(RIGHT) Molecular size R vs p (note that $R \approx 3a$ for quasiatomic phase suggesting the van-der-Waals-like attraction of the separated triangular planes. The crystal is susceptible to quantum melting along z-axis.
(RIGHT INSET) Effective Bohr radius for electrons in all three phases, ζ^{-1} vs p.

CORRELATION FUNCTIONS - METALLICITY
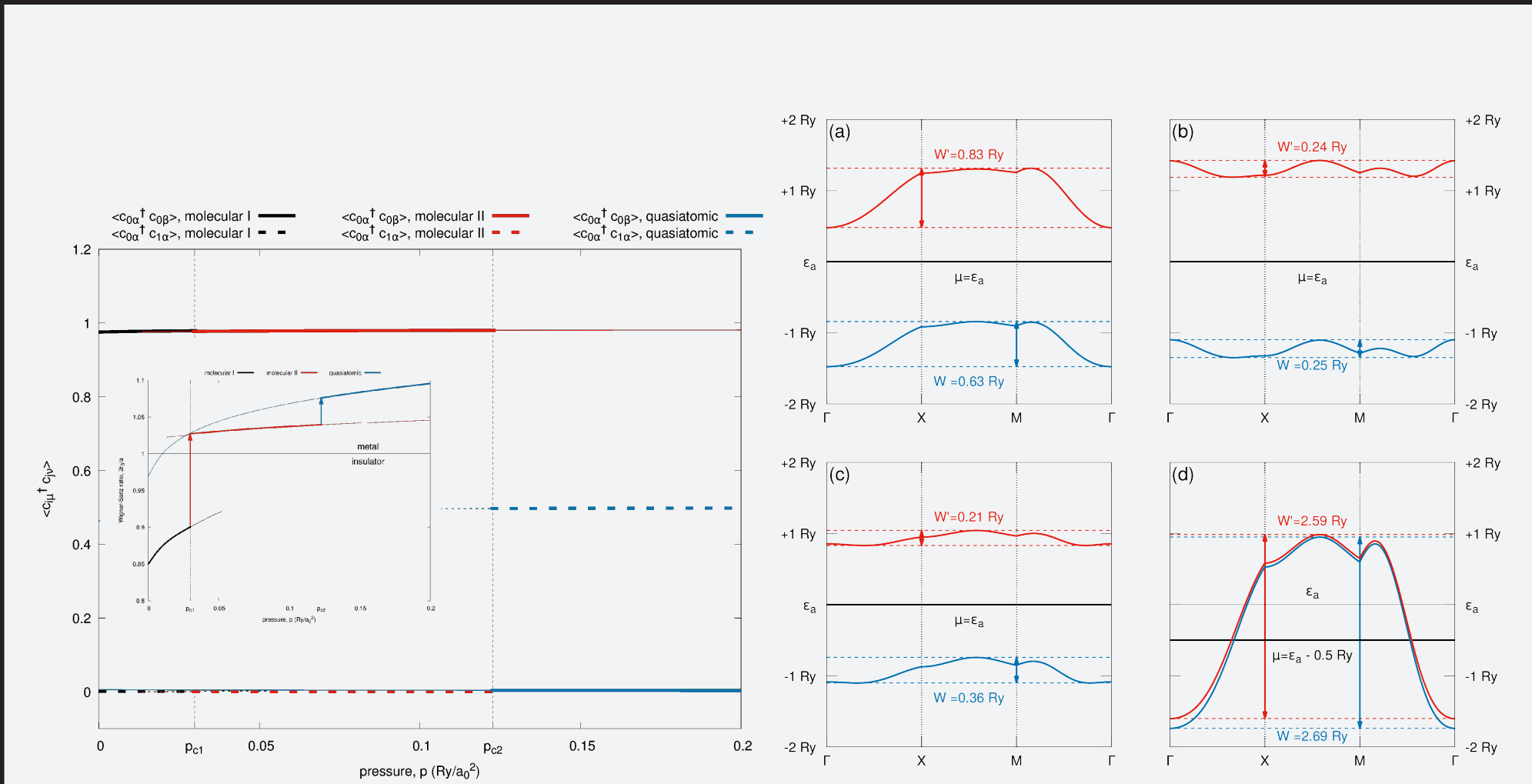
(LEFT) Correlation functions connected with electrons inside a molecule (solid lines) and between molecules (dashed lines). Note that for the molecular phases the electron is swapped only within the molecule, whereas for the quasiatomic phase it is swapped along the crystal directions suggesting an insulator-to-metal transition.
(INSET) The Wigner-Seitz criterion for the metallization of hydrogen $\frac{2r_S}{a} > 1$, where r_S is the Wigner-Seitz radius (cf. box *Electron-phonon coupling and superconductivity* for detail on how the Wigner-Seitz radius was obtained) and a is the interatomic distance in the crystal direction. **Note that according to the (weaker) Wigner-Seitz criterion, the molecular phase II is already metallic, the conclusion *not* supported by either the correlation function, or the Mott-Hubbard criterion analysis.** (RIGHT) Bare bands at the transitions: phase I (a) to phase II (c), and phase II (b) to phase III (c).
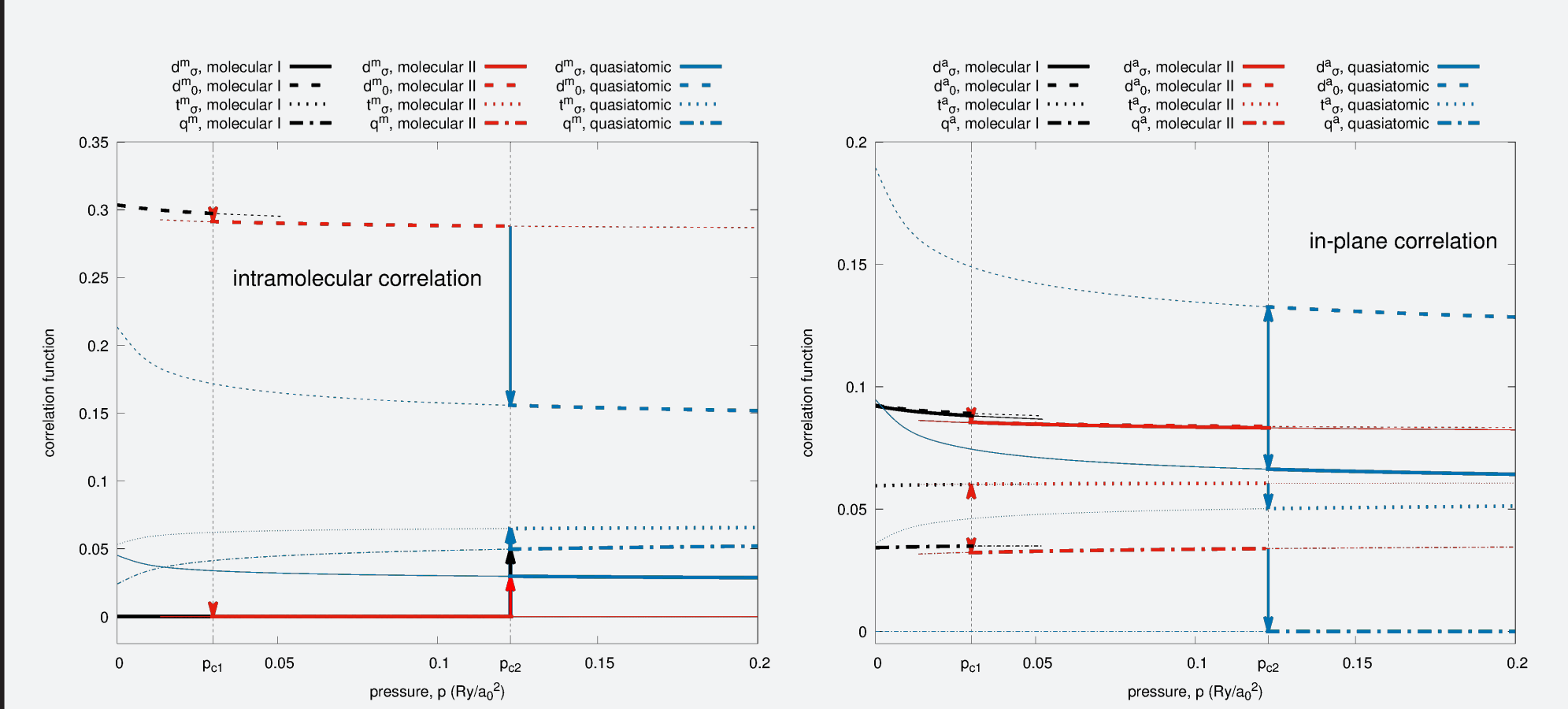
Average exact double d_σ, d_0, triple t_σ, and quadruple q occupancies on **the molecule (LEFT), and the pair of neighboring sites in the crystal direction (RIGHT)**, versus pressure p in all three phases. Note that in both molecular phases there is only possibility of having 2 electrons per molecule, supporting the conclusion that they are, in fact, insulating, whereas in the quasiatomic case all on-molecular configurations are possible (suggesting metallicity).

ATOMICITY OF THE PHASE III

There is a relevant question concerning the condition of atomicity. We do not expect the monolayers to be completely independent of each other In fact, the van-der-Waals-like attraction is to be expected. Thus condition of $R \to \infty$ seems to be not sufficient to decide whether phase is or not atomic.

There is an intuitive way of looking at such a problem. We define

$$\delta d \equiv (d^2 - q)^2,$$

as the difference between double occupancy d on both atoms in "molecule" (hence d^2) and the quadruple *molecular* occupation (q). Now $\delta d > 0$ for molecular, and $\delta d = 0$ for atomic phases.
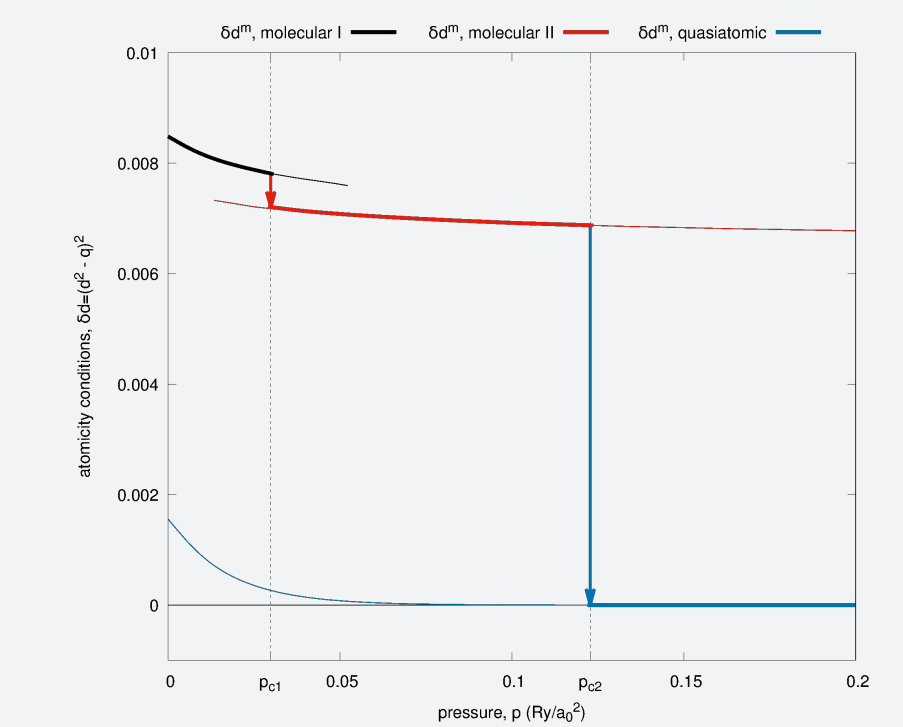

The atomicity condition versus pressure p.

SPIN CORRELATION FUNCTIONS

One can argue that being an s electron system, hydrogen solids are not influenced in a qualitative manner by the Heisenberg-type exchange J. As we calculated the results both with and without additional term

$$\hat{\mathcal{H}}_J = -\sum_{ij} J_{ij}\mathbf{S}_i\mathbf{S}_j - \frac{1}{4}\sum_{i\neq j}J_{ij}\hat{n}_i\hat{n}_j + \sum_{i\neq j}J_{ij}\hat{c}^{\dagger}_{i\uparrow}\hat{c}^{\dagger}_{i\downarrow}\hat{c}_{j\downarrow}\hat{c}_{j\uparrow}$$

in Hamiltonian, the stability of quasiatomic phase at pressure $p = 0$ depends on a proper treatment of Heisenberg-type interaction.
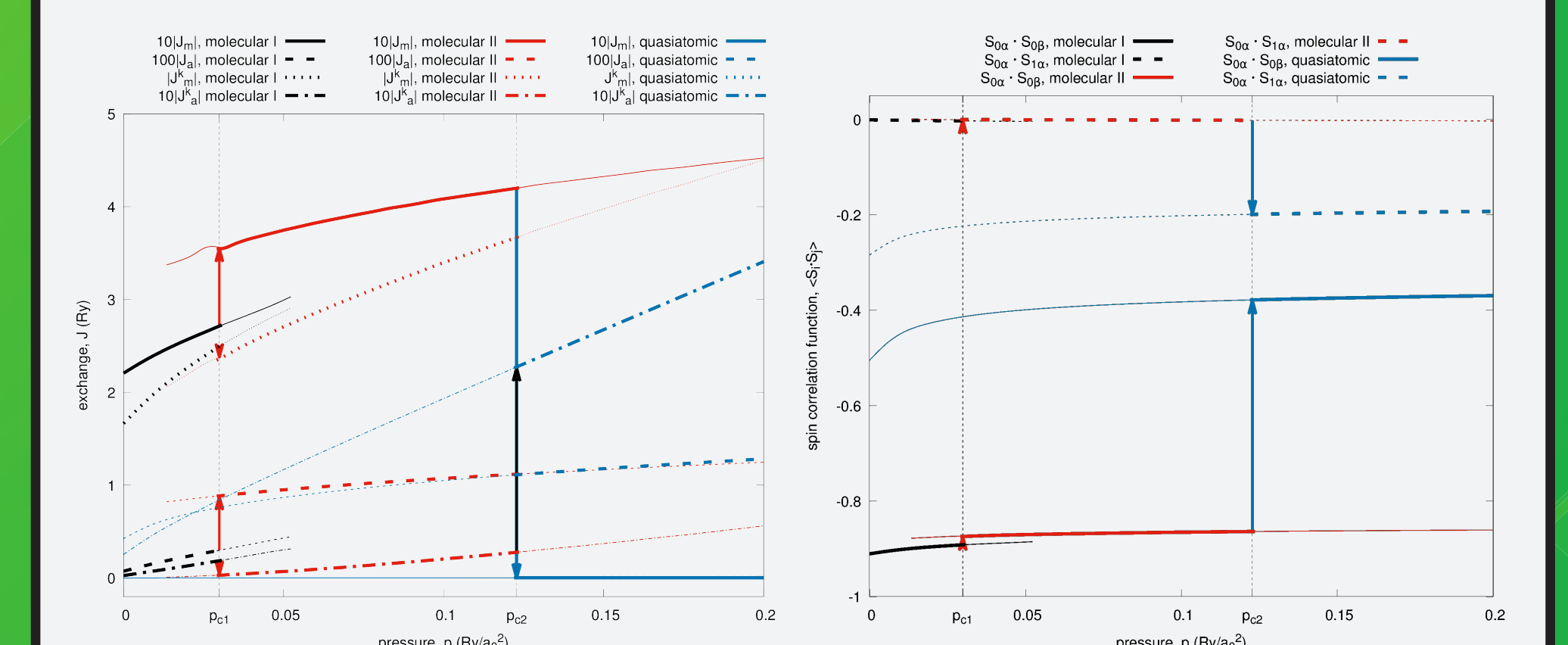
(LEFT) Values of both Heisenberg-type exchange J and the kinetic exchange $J^k \equiv \frac{4t^2}{U}$ versus pressure p. (RIGHT) Values of spin-spin correlation functions $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. Note that for molecular phases, spin-spin exhibits paramagnetic behavior, whereas for the quasiatomic phase we deal with a frustrated system. In all cases the kinetic exchange dominates the Heisenberg-type one.

ELECTRON-PHONON COUPLING AND SUPERCONDUCTIVITY

We follow Ashcroft [9] using the MacMillan formula:

$$T_C = 0.85\Theta_D e^{-\lambda^2\left(\frac{1}{\alpha^2}\left[1+\frac{\lambda^2}{0.25^{2/3}}\ln\left(\frac{\lambda^2+1}{\lambda^2 0.25^{2/3}}\right) - \frac{2}{0.25^{2/3}(\lambda^2+1)}\right] - \ln\left(\frac{\lambda^2+1}{\lambda^2}\right)\right)},$$

where Θ_D is the Debye temperature calculated from the phonon mode with the highest frequency (assessed as in [10]), $\lambda^2 \equiv 0.166 r_S$ depends on the Wigner-Seitz radius r_S, and $\alpha \approx 1.0$ is an electron–lattice parameter estimated.
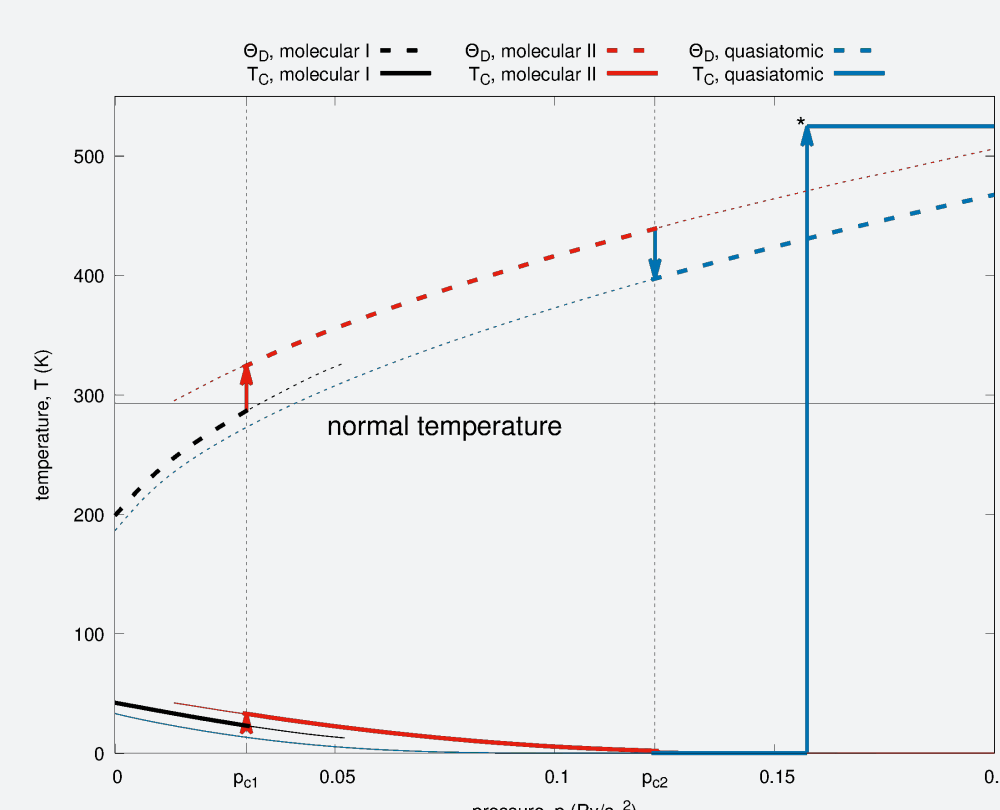
Wigner-Seitz radius

For molecular phases the Wigner-Seitz radius is defined as

$$r_s \equiv \sqrt[3]{\frac{3\frac{\sqrt{3}}{2}a^2(R + \frac{2}{\zeta})}{4\pi \cdot 2_{el}}},$$

where a is the intermolecular distance, R - molecular size, $\frac{1}{\zeta}$ - effective Bohr radius, and 2_{el} - electrons per molecule. For the quasiatomic phase it takes different form:

$$r_s \equiv \sqrt[3]{\frac{3\frac{\sqrt{3}}{2}a^2\frac{2}{\zeta}}{4\pi}}.$$

The Debye temperature Θ_D and the critical superconducting temperature T_C, both vs pressure p. Note that even though Θ_D for quasiatomic phase is smaller than that for molecular phase II, around $p_c = 0.1574 \frac{Ry}{a_0^2}$, the system is undergoing another phase transition to the superconducting state with very high T_C (* MacMillan formula diverges for $T_C > \Theta_D$, thus not allowing to assess the T_C reliably).

article	method	r_s (a_0)
J. McMinis et al. (arXiv:1309.7051)	DMC	2.27
G. Mazzola et al. (Nat. Commun. **5**, 3487 (2014))	DMC	**1.28**
J.-L. Li et al. (Phys. Rev. B **66**, 035102 (2002))	LSDA	2.78
J.-L. Li et al. (Phys. Rev. B **66**, 035102 (2002))	GGA	2.50
B. I. Min et al. (Phys. Rev. B **33**, 324 (1986))	LMTO-LSDA	2.85
A. Svane et al. (Solid State Commun. **76**, 851 (1990))	SIC-LSDA	2.45
B. G. Pfrommer et al. (Phys. Rev. B **58**, 12680 (1998))	GGA-PW91	2.5
APK, AB, JS (Phys. Rev. B **96**, 085101 (2017))	EDABI	**1.265**
R. P. Dias et al. (Science: 10.1126/science.aal1579 (2017))	experiment	**1.255 − 1.34**

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