Metallization of molecular and atomic hydrogen in 2D under high pressure

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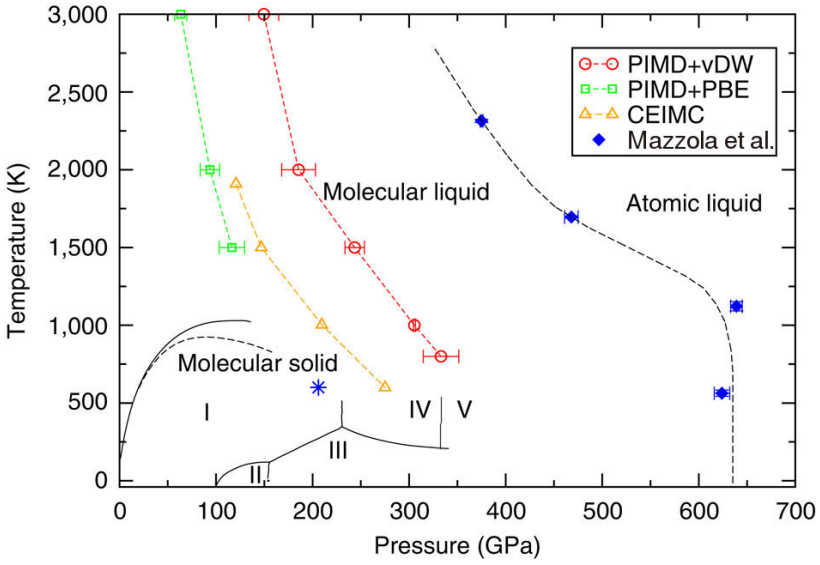
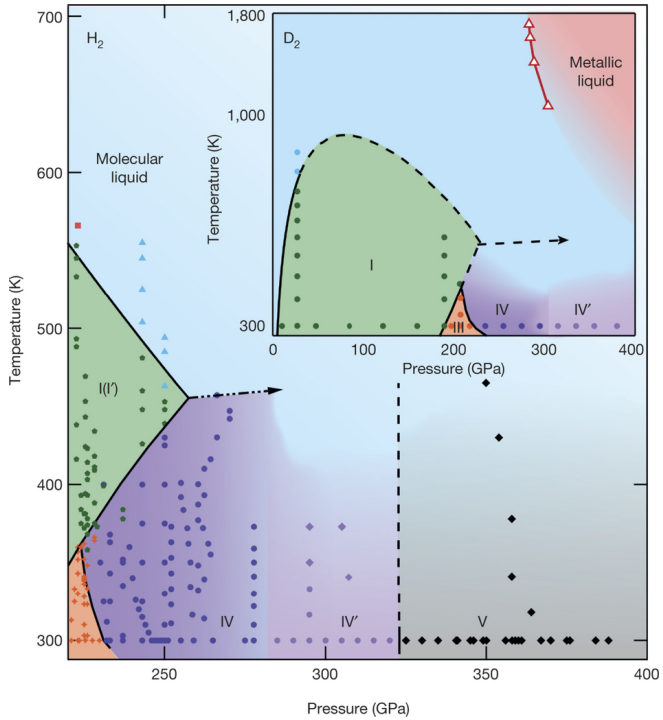
NATIONAL SCIENCE CENTRE

Outline

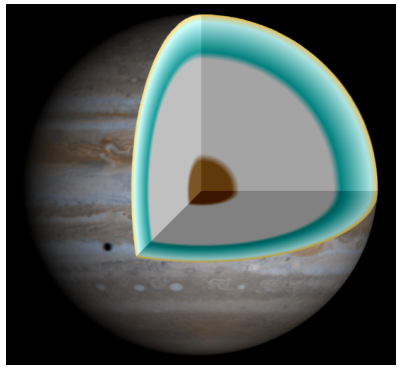
Hydrogen metallization





G. Mazzola, S. Yunoki and S. Sorella, **Nature Communications 5**, 3487, (2014) ↑

P. Dalladay-Simpson, R.T. Howie and E. Gregoryanz, **Nature**, 529, (2016) - phase V ↗



Jupiter interior - potentially metallic hydrogen.
en.wikipedia.org/wiki/Metallic_hydrogen

Hydrogen planes

DFT calculations

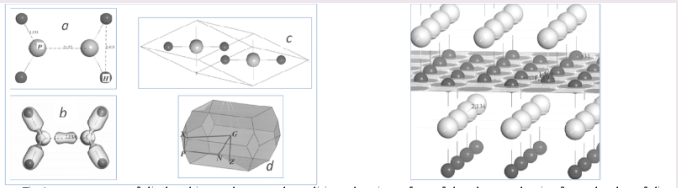


Fig.1. a – structure of di-phosphine under normal conditions; b – isosurface of the electron density for molecules of di-phosphine at the level of 0.6, indicating the covalent bonding in the molecule; c is a primitive cell with two elements of H-P-H at the pressure P=150GPa; d is the Brillouin zone corresponding to the primitive cell at the pressure P =150GPa, e is the structure formed from molecules of di-phosphine at the pressure P=150GPa, The two-dimensional distribution of electron density in the plane with the concentration of hydrogen atoms is shown.

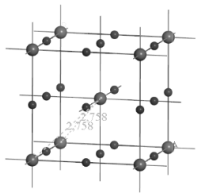


Fig.1. The SH3 structure investigated in the present paper is shown. Sulfur atoms are represented by a larger size balls. The Fig.1 is taken from [26].

PH_4 - N. Degtyarenko, E. A. Mazur, J. Exp. Theor. Phys. **123**, 2 (2016),
H, H_2S, H_3S - N. Degtyarenko, E. A. Mazur, unpublished work

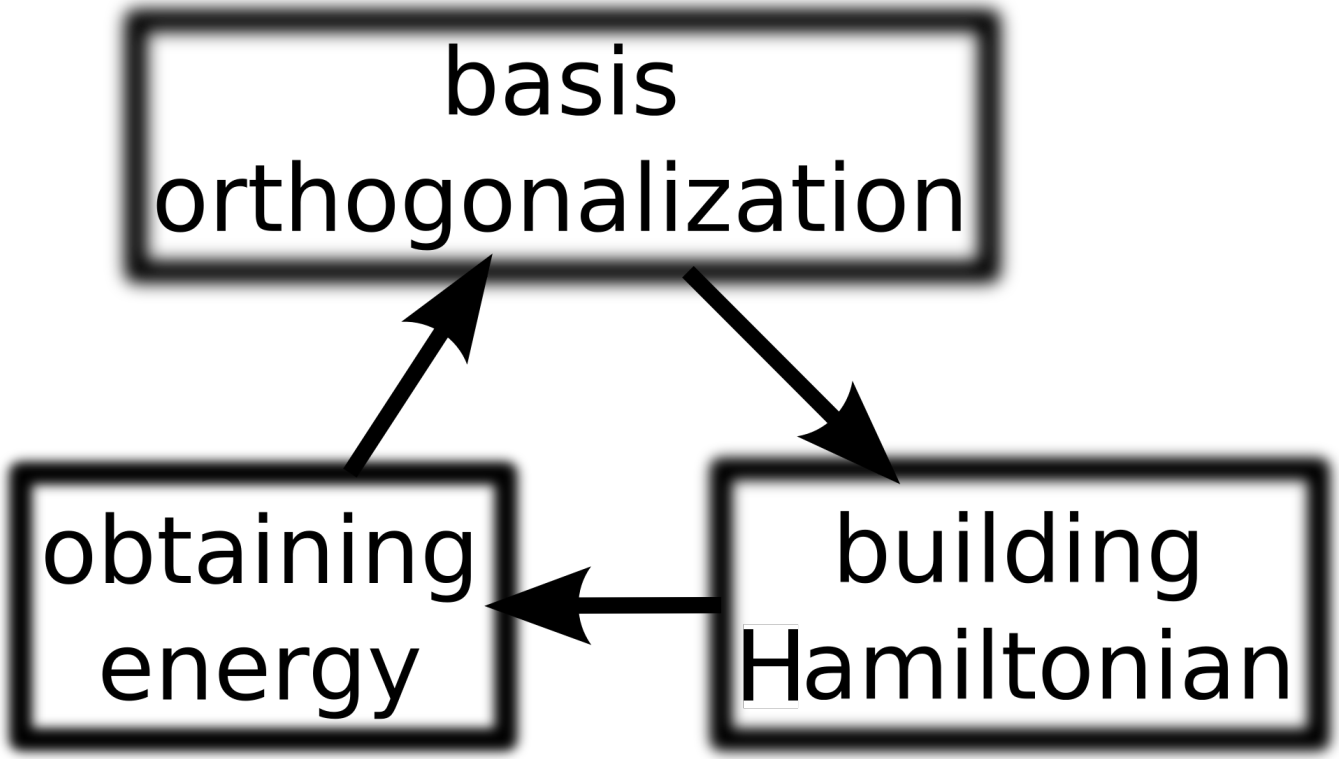
Comment

Two-dimensional planes contribute to the metallization and superconductivity with strong hydrogen-hydrogen correlations and electron-phonon coupling.

Method: Exact Diagonalization Ab Initio (EDABI)

Exact Diagonalization ab Initio approach

Quantum mechanical method to describe light-element structures with proper correlations picture, combining the first and second quantization.



Hamiltonian

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

$$\{\hat{c}^{\dagger}_{i\sigma}, \hat{c}^{\dagger}_{j\bar{\sigma}}\} \equiv \{\hat{c}_{i\sigma}, \hat{c}_{j\bar{\sigma}}\} \equiv 0 \quad \text{and} \quad \{\hat{c}^{\dagger}_{i\sigma}, \hat{c}_{j\bar{\sigma}}\} \equiv \delta_{ij}\delta_{\sigma\bar{\sigma}}$$

Microscopic parameters

$$t_{ij} \overset{a.u.}{=} \left\langle w(\mathbf{r})_i \right| -\nabla^2 - \sum_{k=1}^{n} \frac{2}{|\mathbf{r}-\mathbf{R_k}|} \left| w(\mathbf{r})_j \right\rangle$$

$$V_{ijkl} \overset{a.u.}{=} \left\langle w(\mathbf{r})_i w(\mathbf{r}')_j \right| \frac{2}{|\mathbf{r}-\mathbf{r}'|} \left| w(\mathbf{r})_k w(\mathbf{r}')_l \right\rangle$$

Benchmark: H_2 molecule

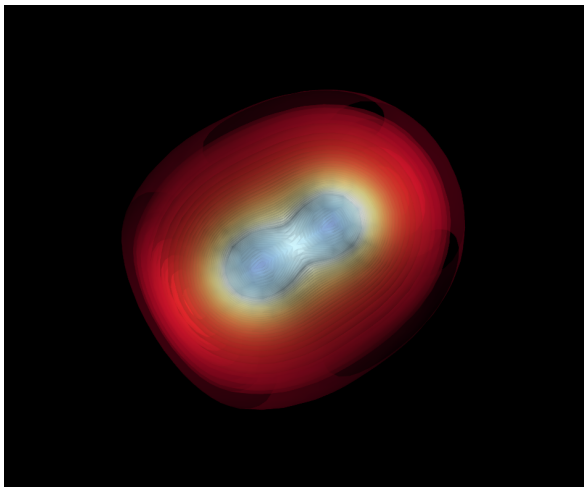
Extended basis

Orbitals: $1s, 2s, 2p_x, 2p_y, 2p_z$

Results

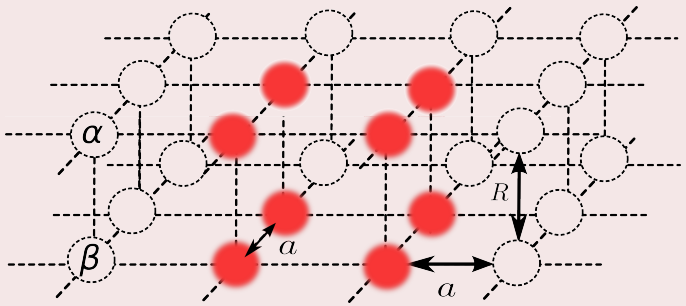
$R_B = 1.395(1.4010)\ a_0$,
$E_B = -2.33766(-2.3291)\ Ry$.
Comparable to the best with only 4 variational parameters!
(Kołos, Wolniewicz, Piszczatowski)

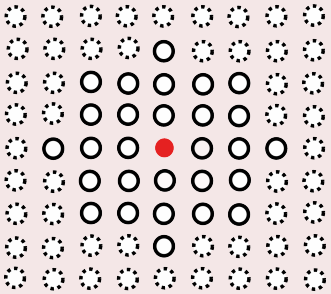
http://cccbdb.nist.gov/energy2.asp



Two-dimensional molecular crystal - model

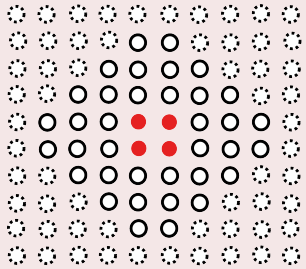
Two-dimensional molecular lattice





$t^{\alpha\beta}_{\bullet\circ} \neq 0,\ t^{\alpha\alpha}_{\bullet\circ} \neq 0,\ t^{\beta\beta}_{\bullet\circ} \neq 0$

$t^{\alpha\beta}_{\bullet\circ} = t^{\alpha\alpha}_{\bullet\circ} = t^{\beta\beta}_{\bullet\circ} = 0$



$K^{\alpha\beta}_{\bullet\bullet} \neq 0,\ K^{\alpha\beta}_{\bullet\circ} \neq 0$

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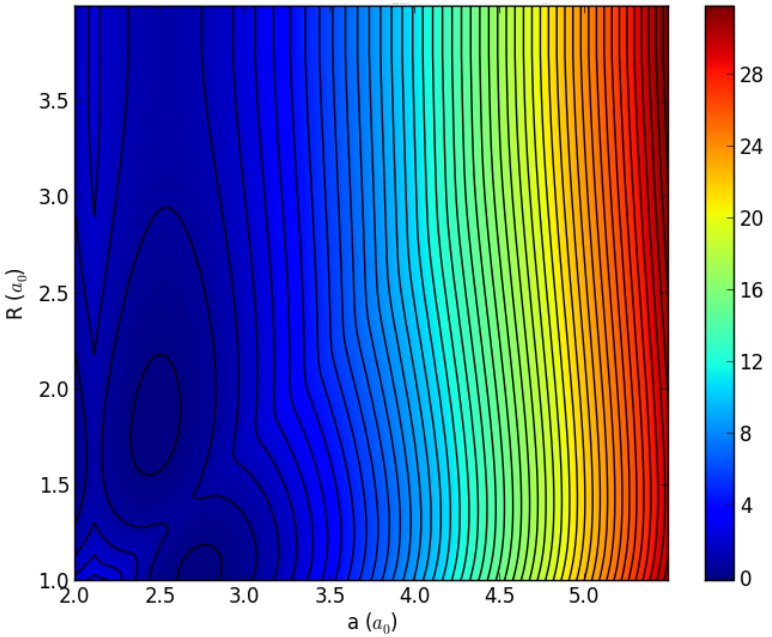
$K^{\alpha\beta}_{\bullet\circ} = K^{\alpha\alpha}_{\bullet\circ} = K^{\beta\beta}_{\bullet\circ} = 0$

- periodic boundary conditions in xy plane
- 8 atoms in supercell
- hoppings up to 13th neighbor
- Coulomb repulsion K_{ij} up to 13th neighbor

Function of state



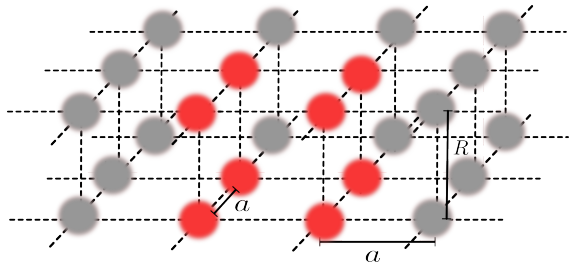
Generalized enthalpy near the metal–insulator transition

Generalized enthalpy

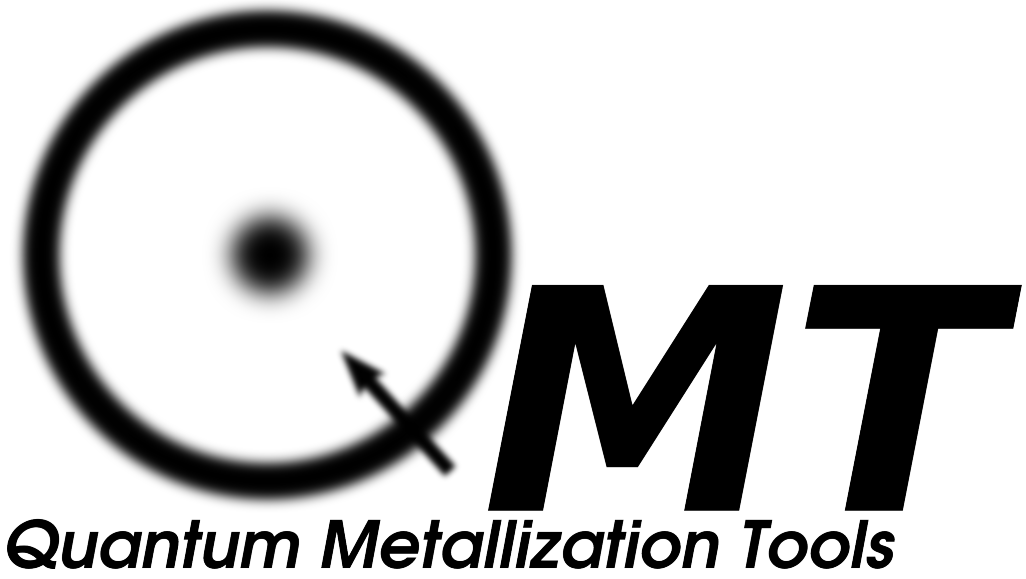
Generalized pressure

$$p \Leftrightarrow p_{2D}\ (Rya_0^{-2})$$

$$H/\text{atom} \equiv E_G/\text{atom} + p_{2D}a^2/2$$



Software: QMT



QMT

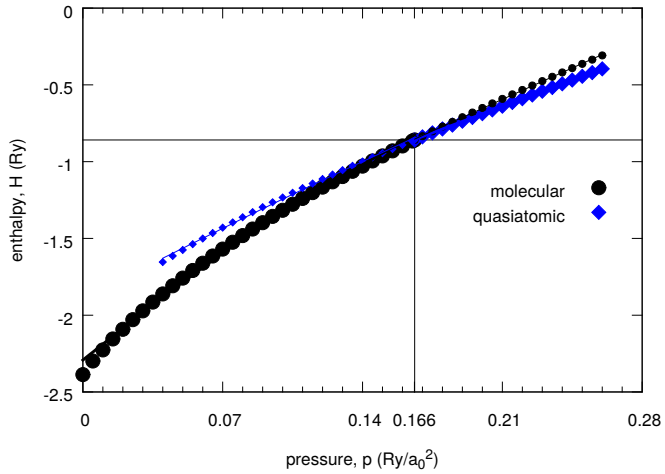
(**Q**uantum **M**etallization **T**ools)

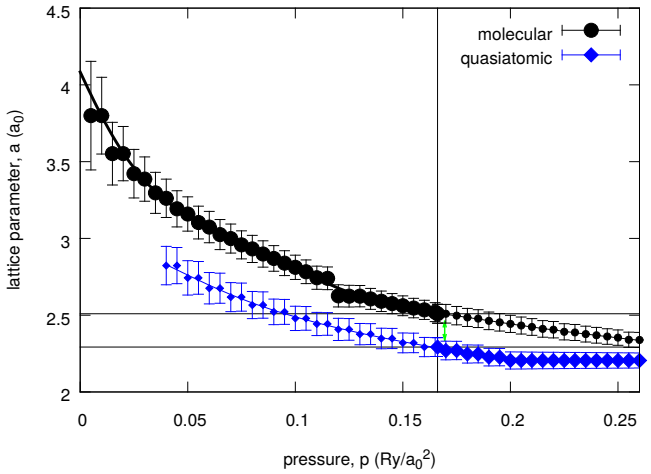
`bitbucket.org/azja/qmt`

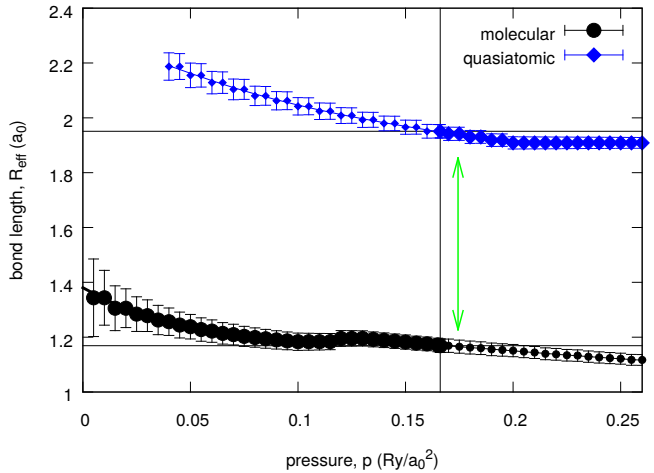
Process–pool solution for integral calculation

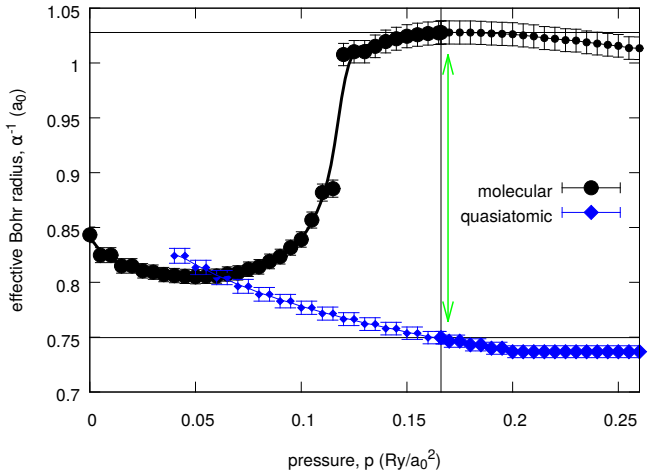
AB, APK, JS, Comput. Phys. Commun. **197**, 7 (2015)

Enthalpy and structural parameters





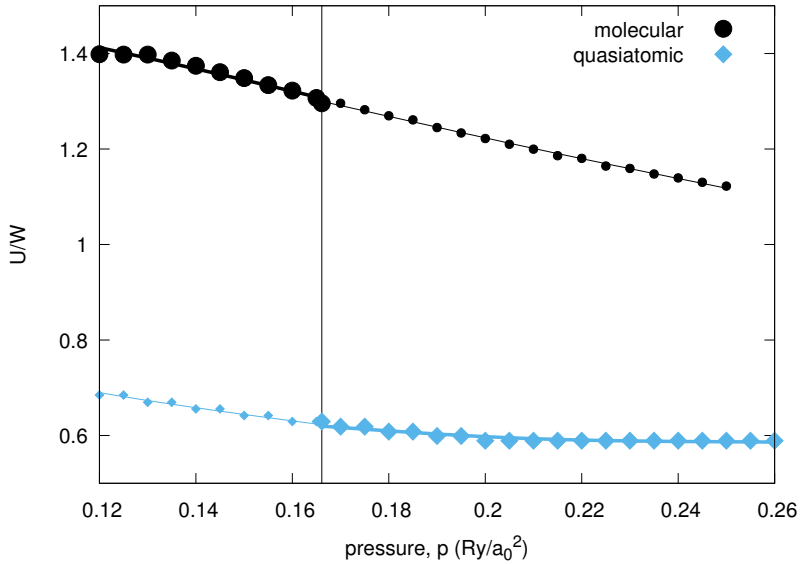


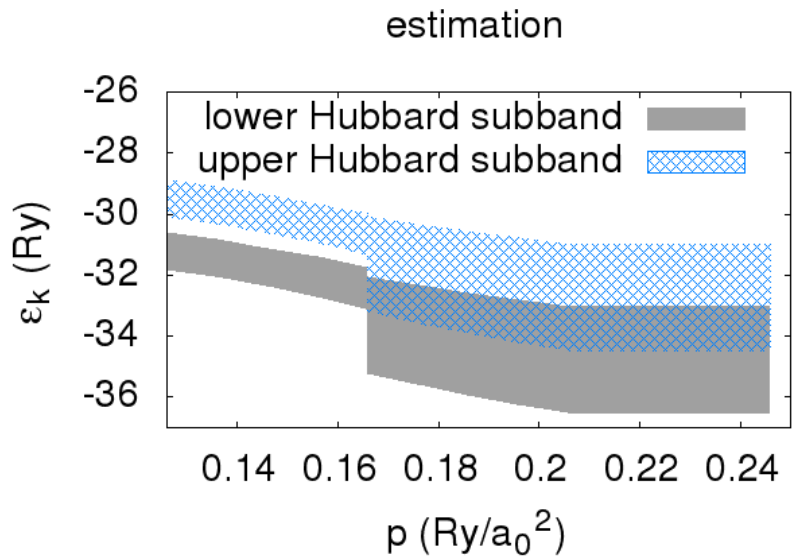


Transition

Metal-insulator

Nature of transition



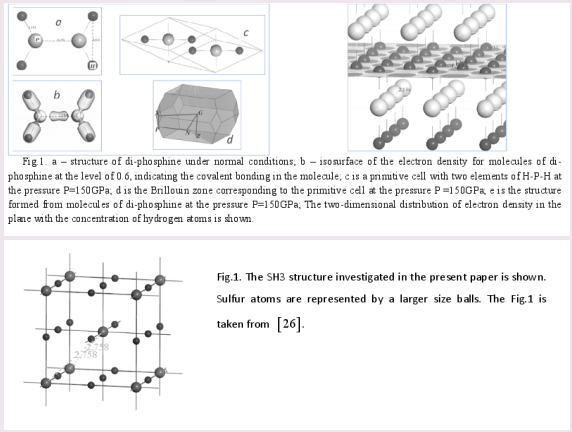


Metallization of solid hydrogen

We observe concomitant atomization and metallization of molecular plane, as shown on on-site Coulomb repulsion U to bandwidth W ratio, as well as the overlap of Hubbard subbands after transition.

Atomic triangular plane

DFT calculations



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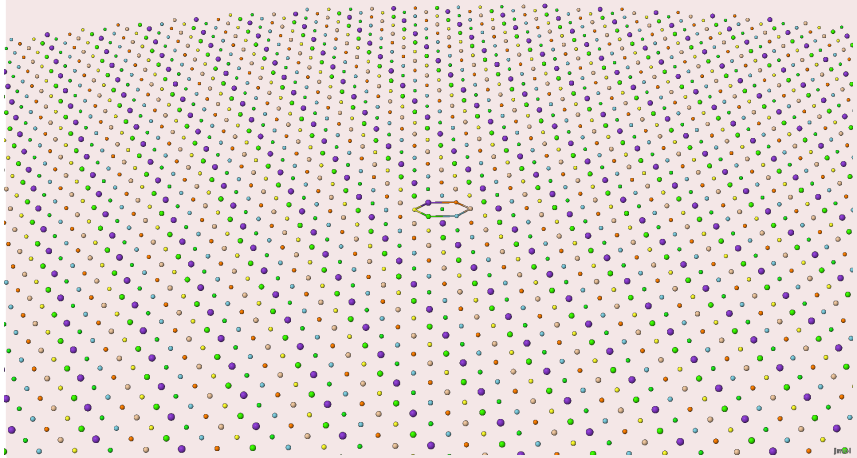
H, H_2S, H_3S - N. Degtyarenko, E. A. Mazur, unpublished work

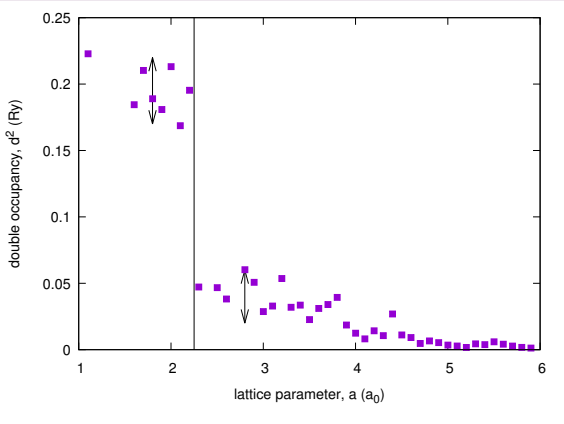
Model

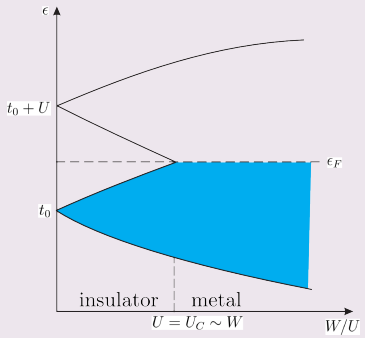


Constant interaction radius $R_{cutoff} = 50a_0$,
No. of interaction parameters:
$M_{a=6.0a_0} = 36$
$M_{a=1.0a_0} = 645$
Hoppings up to 17th neighbor.

Atomic triangular plane

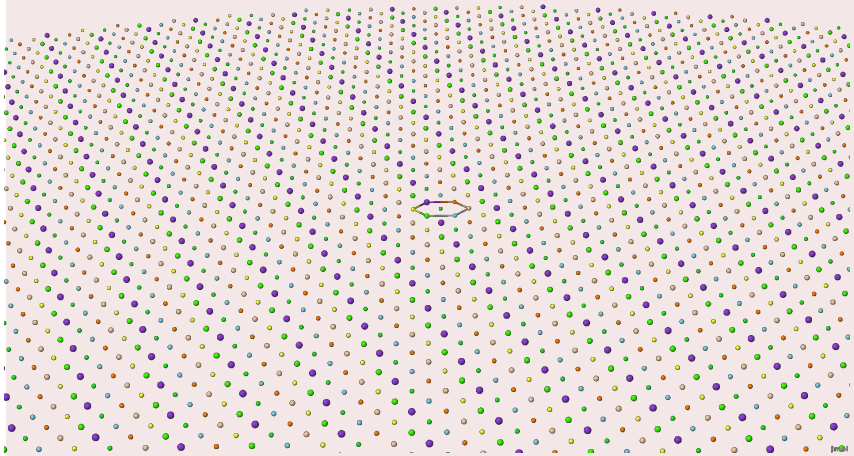
Results - Metallization under pressure





Wstęp do fizyki materii skondensowanej, Józef Spałek, PWN, Warszawa 2015

Model



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Summary

- successful *ab-initio* description of infinite systems with proper correlation picture
- atomization and metallization pressure estimated for molecular plane $p_C = 0.166 Ry/a_0^2$
- metallization of atomic planes in di-phosphine under pressure confirmed

To do

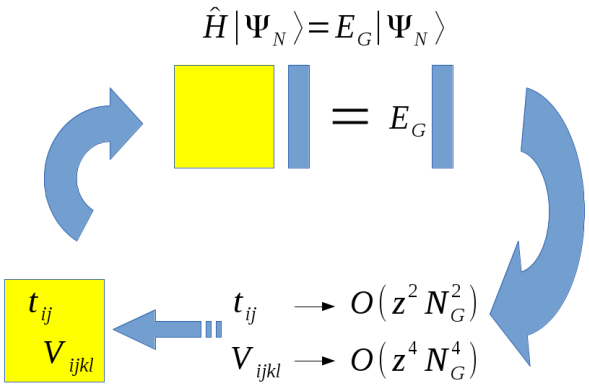
- charge and spin gap (more computational resources)
- larger suprecell size (VMC - already in the testing phase)
- phonon spectra

Thank you!

EDABI:

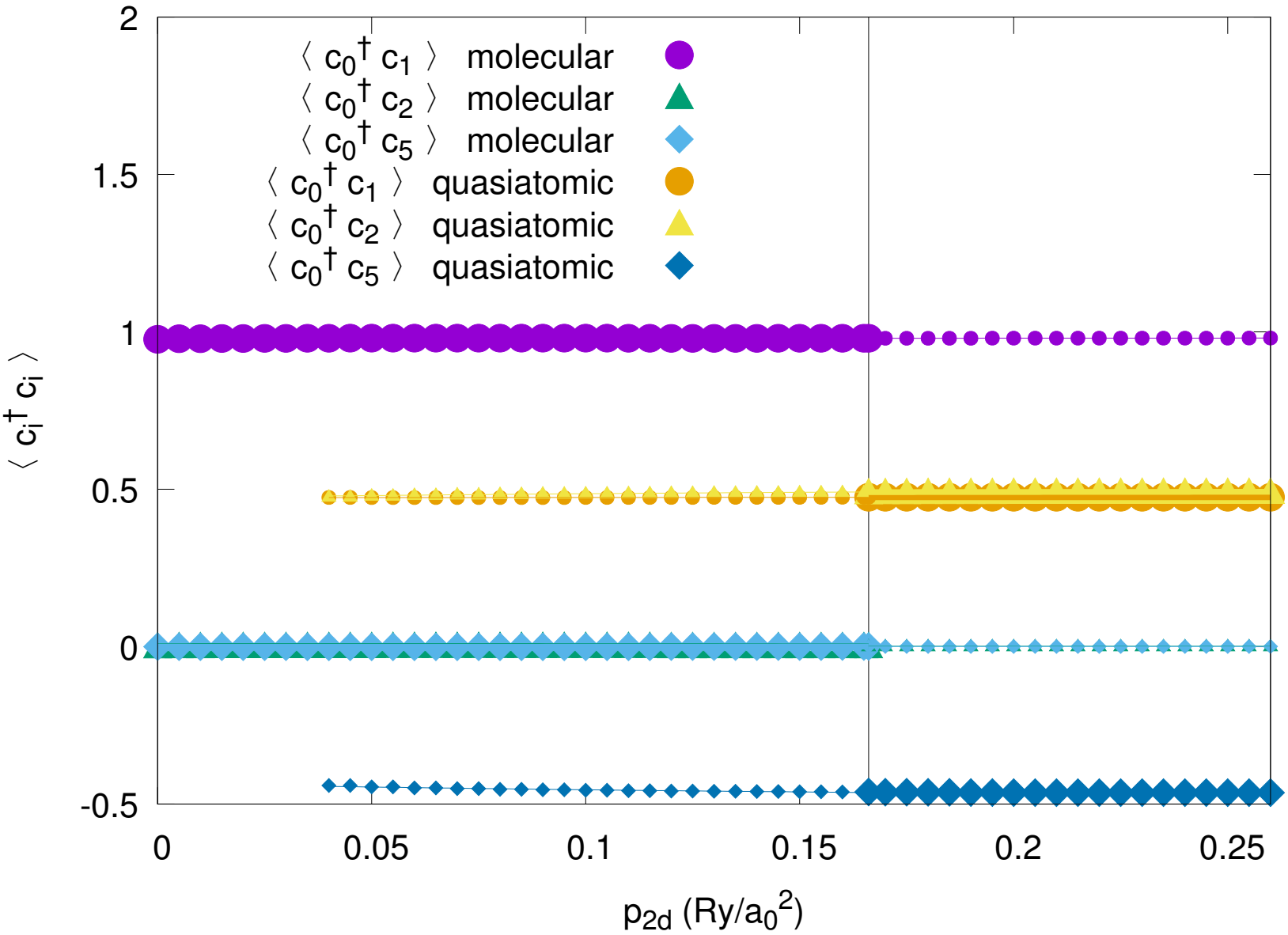
Computational procedure:

- starting with the single-particle basis $\{w_i^{\{\alpha(i)\}}(r)\}$ (eg. LCAO)
- calculating the microscopic parameters $t_{ij}\left(w_i, w_j\right)$, $V_{ijkl}\left(w_i, w_j, w_k, w_l\right)$
- diagonalizing the Hamiltonian $\hat{H}_N\left(\{t_{ij}\}, \{V_{ijkl}\}\right)$ in the second quantization picture



$$\begin{cases} \langle w_i | \, w_j \rangle = \delta_{ij} \\ \hat{H}\,|\Psi_N\rangle = E_G\left(\left\{w_i^{\{\alpha(i)\}}\right\}\right)|\Psi_N\rangle \\ \delta_{w_i} E_G\left(\left\{w_i^{\{\alpha(i)\}}\right\}\right) = 0 \end{cases}$$

Correlation functions



Dispersion relation