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Correlation-induced transition in one-dimensional molecular hydrogen crystal

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Motivation

Even though metallization of hydrogen was predicted in 1935 by Wigner and Huntington [1] it is still unclear if and under what pressure the transition occurs. As the critical temperature for superconductivity is proportional to $M^{-1/2}$ it is possible for hydrogen to be a room temperature superconductor [2].

Our goal is to model the hydrogen system in $T = 0$ using realistic quantum-mechanical method, with

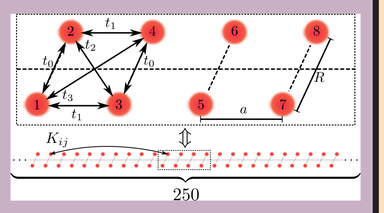
- proper correlations picture (avoid double counting),
- modeling of phase transitions (in particular metal–insulator transition (MIT)),
- possible inclusion of phonons in the system (both frequencies and electron–phonon interactions),
- *ab-initio* combination of first– and second-quantizatioan language.

Hamiltonian

We start with the extended Hubbard model with additional term $V_{\text{ion–ion}}$ expressing ion–ion repulsion namely,

$$\hat{\mathcal{H}} = \sum_i \epsilon_i \hat{n}_i + \sum_{\sigma, i \neq j} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \qquad (1)$$
$$+ \frac{1}{2} \sum_{i \neq j} K_{ij} \hat{n}_i \hat{n}_j + V_{\text{ion–ion}},$$

where ϵ_i is the single-particle energy, t_{ij} are the so-called hopping integrals (t_0 (intramolecular) and t_1, t_2, and t_3 (intermolecular)), U is the on-site Coulomb repulsion, and K_{ij} is the amplitude of intersite Coulomb repulsion, here taken into account for the interaction radius up to $250a$ in the starting atomic representation, where a is the intermolecular distance.



Parameters evaluation

We choose the Slater $1s$ basis

$$\Psi_i(\mathbf{r}) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\mathbf{r}-\mathbf{R_i}|},$$

where α is the inverse size of the orbital. Orthogonalization is conducted by mixing the atomic orbitals with coefficients β_i, so that new so-called Wannier functions $w_i(\mathbf{r})$ will satisfy the orthonormality condition $\langle w_i | w_j \rangle = \delta_{ij}$.

$$w_i(\mathbf{r}) = \sum_{j=0}^{Z_{nn}} \beta_j \phi_j(\mathbf{r}).$$

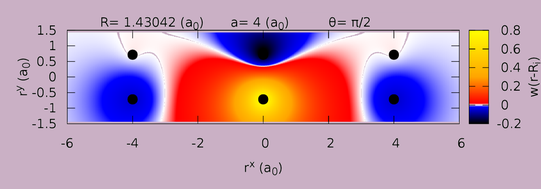


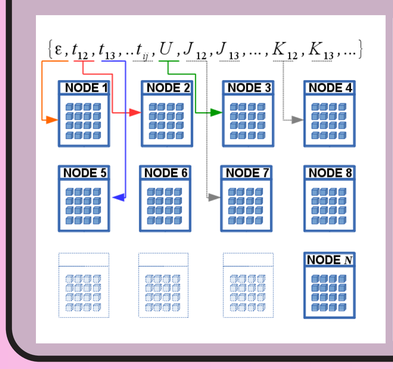
Fig: Wannier function $w_i(\mathbf{r})$ for the $(H_2)_n$ chain.

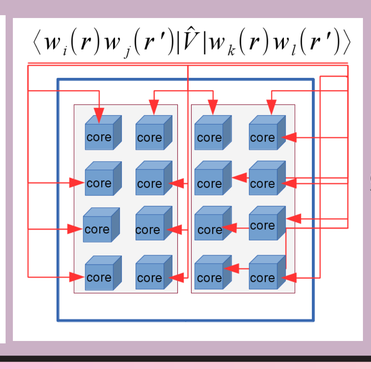
Microscopic Parameters

As the complexity of our problem increases exponentially, we need a way to use the parallel computing.

Computations of each of "N" microscopic parameters t_{ij}, V_{ijkl} distributed over "M" cluster nodes. Inter-process communication via *Message Passing Interface* (MPI).

On each reserved node V_{ijkl} calculation loops are paralleled via OpenMP and computed utilizing all available CPU cores.





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 wave-functions w_i, where in atomic units $\mathcal{T} = -\nabla^2 - 2/|\mathbf{r} - \mathbf{R}|$, and $\mathcal{V} = 2/|\mathbf{r} - \mathbf{r}'|$.

We optimize our system with respect to *inverse wave-function size* α, using the direct dependence of the ground-state energy

$$E_G\left[\{w_i^{(\alpha)}\}\right] = \langle n | \mathcal{H}^{\alpha} | n \rangle.$$

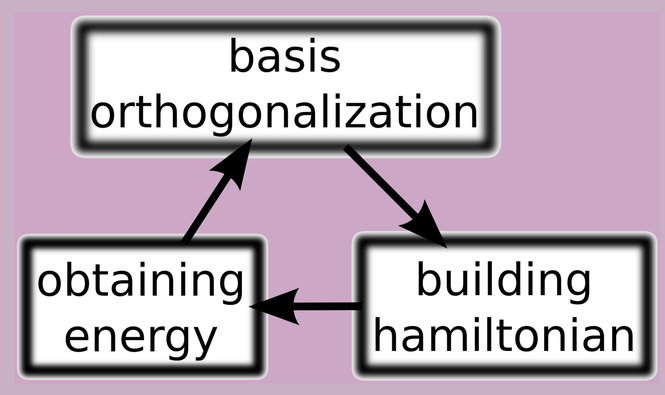
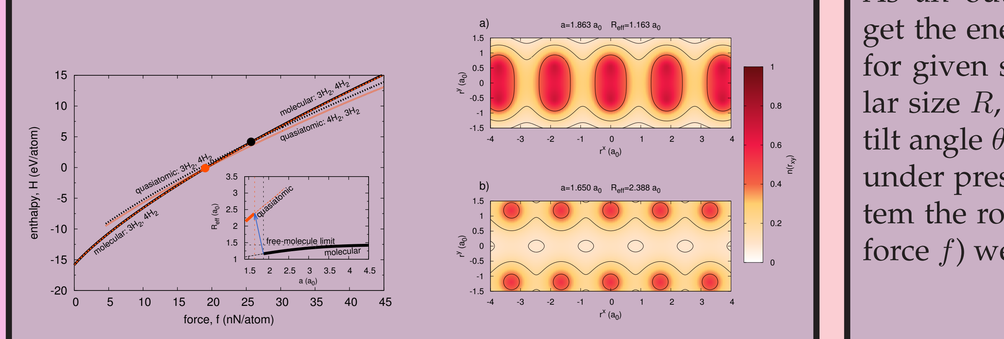


Fig: The general scheme of EDABI method.

Mol. →quasiat. transition



Figs: **L:** Enthalpy versus applied force. **Inset:** Effective molecular size R_{eff} vs. intermolecular distance a. **R:** Electron density $n(\mathbf{r})$ projected onto xy-plane for molecular (top) and quasiatomic (bottom) configuration near the transition.

Electron density defined as

$$n(\mathbf{r}) = \left\langle \hat{\Psi}^{\dagger}(\mathbf{r}) \hat{\Psi}(\mathbf{r}) \right\rangle = \sum_{i,j,\sigma} w_i^*(\mathbf{r}) w_j(\mathbf{r}) \left\langle \Phi_G \middle| \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} \middle| \Phi_G \right\rangle,$$

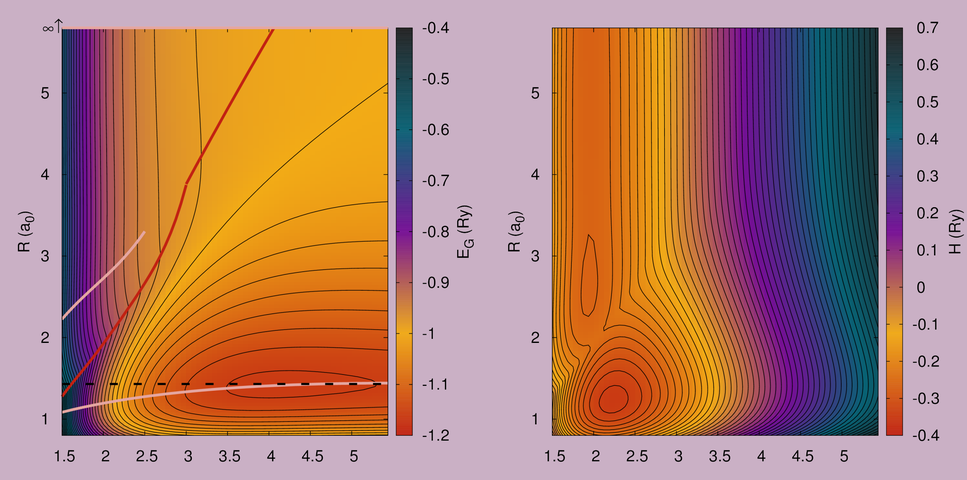
Thermodynamic potential

As an output from EDABI method we get the energy and system characteristics for given structural parameters: molecular size R, intermolecular distance a, and tilt angle θ. To study the system behavior under pressure (for one-dimensional system the role of "pressure" is assumed by force f) we are required to use enthalpy

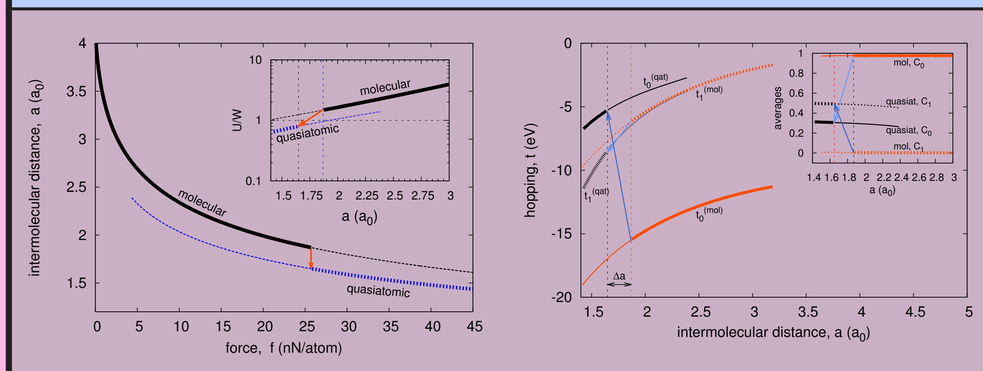
$$H = E_G + fa,$$

where a, the intermolecular distance, is the system volume in one dimension.

Figs: System energy (**L**) and system *enthalpy* for arbitrary force $f = 12.358nN$ (**R**) as a function of structural parameters a, R and $\theta = \pi/2$.



Transition details



Figs: **L:** Intermolecular distance (unit volume) vs. pressure. **Inset:** Hubbard U to bandwidth W ratio. **R:** Intramolecular and intermolecular hoppings and related averages $\left\langle \hat{c}^{\dagger}_i \hat{c}_j \right\rangle$, t_0, C_0 and t_1, C_1 respectively, for both molecular and quasi-atomic phases.

At this moment we are not sure if quasiatomic phase is metallic. However, there indications that the nature of the transition might be of Mott-Hubbard type. Namely, the unit volume (here a) changes in a discontinuous manner (see left figure). Similarly, the Hubbard U/W ratio (inset of the left figure) drops from ~ 1.5 to ~ 0.8 at the transition. Interestingly, the hopping probabilities C_0 and C_1 change their values dramatically form $C_0 \approx 1$ and $C_1 \approx 0$ in molecular to $C_0 \sim C_1$ in quasiatomic state.

Quantum Metallization Tools

https://bitbucket.org/azja/qmt

Acknowledgments

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References

[1] E. Wigner and H. B. Huntington, J. Chem. Phys. **3**, 764 (1935).

[2] N. W. Ashcroft , Phys. Rev. Let. **21**, 1748 (1968).

[3] G. Mazolla, S. Yunoki and S. Sorella, Nature Comm. **5**, 3487 (2014).

[4] A. Kądzielawa, A. Bielas, M. Acquarone, A. Biborski, M. M. Maśka, and J. Spałek, New J. Phys. **16**, 123022 (2014).

[5] A. Biborski, A. P. Kądzielawa, and J. Spałek, arXiv:1504.00500 (2015).

[6] A. P. Kądzielawa, A. Biborski, and J. Spałek, arXiv:1506.03356 (2015).