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Electron-phonon interactions in selected correlated hydrogen systems within the Exact Diagonalization ab initio approach

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ACMiN AGH

National Science Centre Poland

QMT Quantum Metallization Tools

FNP Foundation for Polish Science

Innovative Economy National Cohesion Strategy

European Union European Regional Development Fund

Motivation

Our goal is to obtain general model of realistic quantum-mechanical system, with

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

We start from simple, but important problem of metallization of hydrogen under pressure, with several $(H_2)_n$ molecular systems.

Obtaining Energy

The approach to obtaining energy of given system may differ depending on its complexity. Although in presented cases we use direct diagonalization in a n-particle Fock space, one is not bounded by this method.

We seek for the solution in a form of α functional

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

For H_2 molecule, the ground-state can be found as

$$|-\rangle = [2\mathcal{D}(\mathcal{D}-U+K)]^{-\frac{1}{2}} \left[b-(\mathcal{D}-U+K)\,|4\rangle + 4|t+V|\,|5\rangle\right],$$

where

$$|4\rangle = \frac{1}{\sqrt{2}}\left(\hat{a}^\dagger_{1\uparrow}\hat{a}^\dagger_{2\downarrow} - \hat{a}^\dagger_{1\downarrow}\hat{a}^\dagger_{2\uparrow}\right)|0\rangle\,,$$
$$|5\rangle = \frac{1}{\sqrt{2}}\left(\hat{a}^\dagger_{1\uparrow}\hat{a}^\dagger_{1\downarrow} + \hat{a}^\dagger_{2\uparrow}\hat{a}^\dagger_{2\downarrow}\right)|0\rangle\,.$$

The eigenvalues

$$E_- = 2\epsilon + \frac{U+K}{2} + J = -\frac{1}{2}\mathcal{D},$$

where $\mathcal{D} = \sqrt{(U-K)^2 + 16\,(t+V)^2}$.

For $(H_2)_n$ systems with boundary conditions we use the *Lanczos algorithm*.

QMT Project

QMT https://bitbucket.org/azja/qmt

Building Hamiltonian

We start from Hubbard hamiltonian with all Coulomb terms

$$\begin{aligned}\mathcal{H} = &\sum_{i,\sigma}\epsilon_i\hat{n}_{i\sigma} + \frac{1}{2}\sum_{\sigma,i\neq j}t_{ij}\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma} + \sum_{i,\sigma}U_i\hat{n}_{i\sigma}\hat{n}_{i\bar{\sigma}}\\ &-\sum_{ij}J_{ij}\mathbf{S}_i\mathbf{S}_j + \frac{1}{2}\sum_{i\neq j}\left(K_{ij}-\frac{J_{ij}}{2}\right)\hat{n}_i\hat{n}_j\\ &+\sum_{i\neq j}J_{ij}\hat{a}^\dagger_{i\uparrow}\hat{a}^\dagger_{i\downarrow}\hat{a}_{j\downarrow}\hat{a}_{j\uparrow}\\ &+\sum_{\sigma,i\neq j}V_{ij}\hat{n}_{i\sigma}\left(\hat{a}^\dagger_{i\bar{\sigma}}\hat{a}_{j\bar{\sigma}} + \hat{a}^\dagger_{j\bar{\sigma}}\hat{a}_{i\bar{\sigma}}\right),\end{aligned}$$

with set of fermionic operators $\{\hat{a}^\dagger_{i\sigma}, \hat{a}_{i\sigma}\}$.

The microscopic parameters are defined via one– and two-body integrals

$$\mathcal{T}_{ij} = \left\langle w(\mathbf{r})_i\right| -\nabla^2 - \sum_{k=1}^{n}\frac{2}{|\mathbf{r}-\mathbf{R_k}|}\left|w(\mathbf{r})_j,\right\rangle$$
$$\mathcal{V}_{ijkl} = \left\langle w(\mathbf{r})_i w(\mathbf{r}')_j\right| \frac{2}{|\mathbf{r}-\mathbf{r}'|}\left|w(\mathbf{r}')_k w(\mathbf{r})_l,\right\rangle$$

where $w(\mathbf{r})_i$ is an orthogonal basis (see Frame *Basis orthogonalization*).

ϵ_i	t_{ij}	U_i	J_{ij}	K_{ij}	V_{ij}
$\mathcal{T}_{ii}$	$\mathcal{T}_{ij}$	$\mathcal{V}_{iiii}$	$\mathcal{V}_{iijj}$	$\mathcal{V}_{ijij}$	$\mathcal{V}_{iiij}$

For simplicity we use notation

$$\mathcal{H} = \sum_i \Xi_i \hat{O}_i,$$

where Ξ_i is a microscopic parameter, and $\hat{O}_i$ is symbol for *all* fermionic operators next to said parameter.

Basis Orthogonalization

We start from $1s$ Slater-type atomic orbitals (calculations with $2s$ and $2p$ orbitals are currently tested).

Orthogonalization is conducted by mixing the atomic orbitals with coefficients β_i (expanded in terms of the nearest neighbors (*nn*) 1s atomic orbitals (*tight binding*)), so that new so-called Wannier functions $w_i(\mathbf{r})$ will satisfy the orthonormality condition $\langle w_i|\ w_j\rangle = \delta_{ij}$.

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

Method

We base our approach on Exact Diagonalization **Ab-I**nitio approach

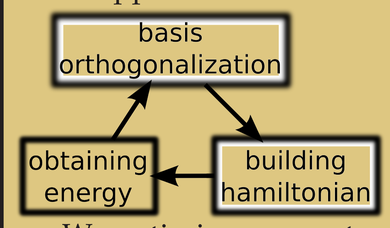


Fig: The general scheme of EDABI method. For details on each step please refer to the proper Frame on this poster.

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

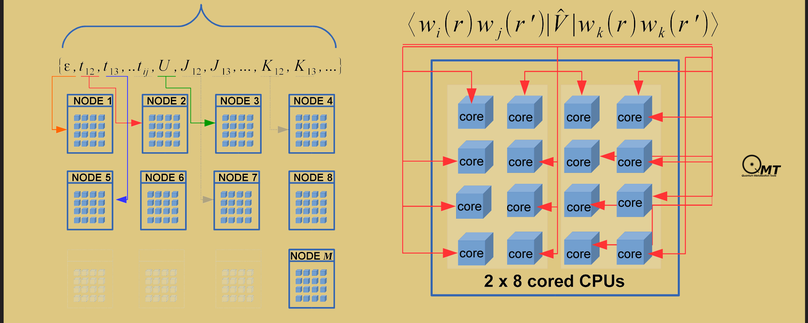
$$E_G\left[\left\{w_i^{(\alpha)}\right\}\right] = \langle n|\mathcal{H}^\alpha|n\rangle.$$

Parallel computation

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

Computations of each of "N" microscopic parameters distributed over "M" cluster nodes. Inter-process communication via *Message Passing Interface* (MPI).

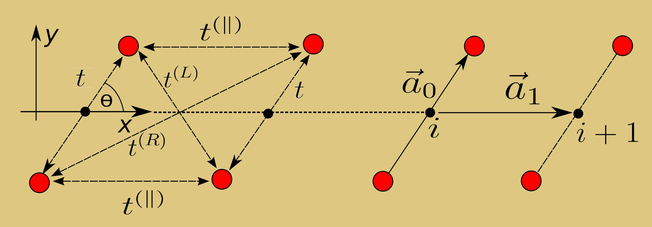
On each reserved node V_{ijkl} calculation loops are paralleled via OpenMP and computed utilizing all available CPU cores.



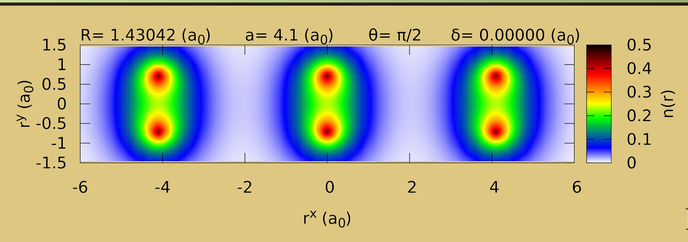
Systems

We analyze hydrogen molecular systems:

- (H_2) without periodic boundary conditions (*PBC*)
- linear molecular chain as $(H_2)_3$ with *PBC*



Results



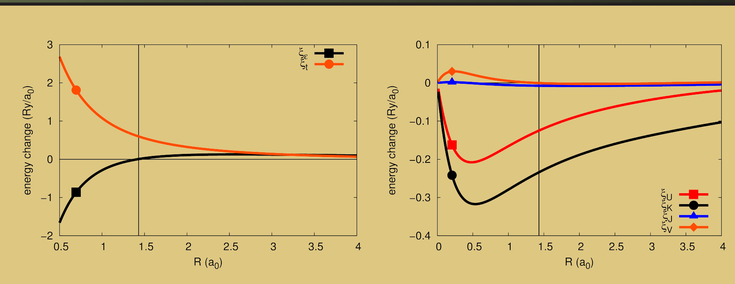
Electron density defined as

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

where $n(\mathbf{r})$ is said density, $w_i(\mathbf{r})$ is the previously obtained Wannier function, and the average $\langle\Psi_G\rangle\cdot\Psi_G$ is calculated in Fock space, with $|\Psi_G\rangle$ being the ground state of our hamiltonian.

ELECTRON–ION INTERACTIONS $\xi_i \equiv \delta\Xi_i/\delta R$

We use adiabatic approximation to determine wavefunction for the given state.



Electron–ion couplings (effectively in units of characteristic frequencies).

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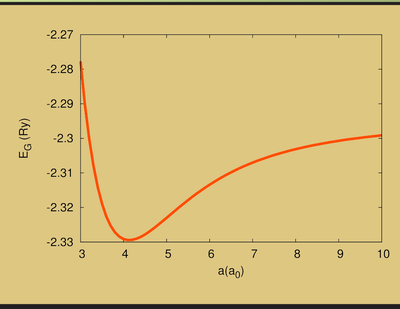
Conclusions



The energy of $(H_2)_N$ chain. Note the van-der-Waals-like attractive behavior.

1. functional way to approach correlated systems
2. realistic results for hydrogen systems
3. in perspective - *ab-initio* phonons without double counting

Acknowledgments

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