

Electron-phonon interactions in selected correlated hydrogen systems within the Exact Diagonalization Ab Initio approach

Andrzej Biborski^{1*}, Andrzej P. Kądzielawa², Józef Spałek^{1,2}

¹Akademickie Centrum Materiałów i Nanotechnologii, AGH Akademia Górnictwo-Hutnicza, Al. Mickiewicza 30, PL-30-059 Kraków, Poland

²Instytut Fizyki im. Mariana Smoluchowskiego, Uniwersytet Jagielloński, ul. Reymonta 4, PL-30059 Kraków, Poland

* andrzej.biborski@agh.edu.pl



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Objective

Hydrogen metallization (Wigner and Huntington 1935)

- molecular hydrogen crystal
- molecular 1d and 2d systems - preliminary models in the rigorous treatment

How?

Exact Diagonalization *Ab Initio* approach.

- Electronic correlations consistently taken into account
- Combine first and second quantization pictures

Why?

- Lack of experimental evidence (high pressures)
- Contradictory theoretical results

Questions

- Phonons and electron-phonon couplings in the EDABI?

Hamiltonian

We have Hamiltonian given in the second quantization picture:

$$\mathcal{H} = \sum_{i,\sigma} \epsilon_i \hat{n}_{i\sigma} + \frac{1}{2} \sum_{\sigma, i \neq j} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} V_{ijkl} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma'}^\dagger \hat{c}_{l\sigma} \hat{c}_{k\sigma'} + \mathcal{V}_{c-c}$$
(1)

Microscopic Parameters

And microscopic parameters as integrals over single-particle wave functions

$$T_{ij} = \left\langle w(\mathbf{r})_i \left| -\nabla^2 - \sum_{k=1}^n \frac{2}{|\mathbf{r} - \mathbf{R}_k|} \right| w(\mathbf{r})_j \right\rangle \quad (2)$$

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

Note

We combine first and second quantization pictures

Basis

We build our basis by orthogonalizing Slater-type orbitals Ψ_i^α :

$$\langle w_{\pi_i(j)}(\mathbf{r}) | w_i(\mathbf{r}) \rangle = \delta_{i\pi_i(j)}, \quad (3)$$

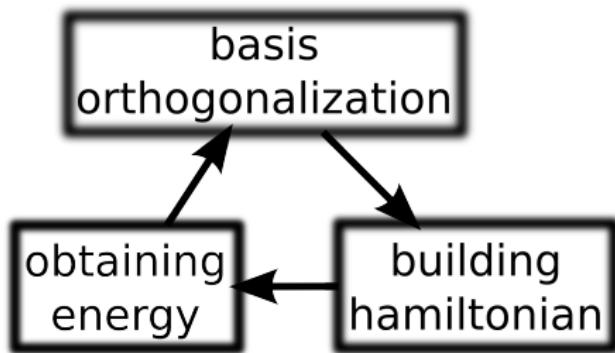
$$w_i(\mathbf{r} - \mathbf{R}_i) = w_i(\mathbf{r}) = \sum_{j=0}^Z \beta_j \Psi_{\pi_i(j)}^\alpha(\mathbf{r}), \quad (4)$$

where π_i is the Z -neighbors mapping function for the node i , where $\pi_i(0) = i$.

Procedure

The core of *EDABI*: since Hamiltonian depends on $\{ \{ T_{ij} \}, \{ V_{ijkl} \} \}$, it does on $\{ w_i^\alpha \}$, and the ground state(-s) might be found in terms of diagonalization in a n -particle Fock space supplied with the optimization procedure via $\{\alpha\}$:

$$E_G \left[\{ w_i^{(\alpha)} \} \right] = \langle n | \mathcal{H}^\alpha | n \rangle \quad (5)$$



Detailed description

J. Spałek et al., J.Phys.: Condens. Matter 19 (2007) 255212 (43pp)

Hamiltonian

Simplified hamiltonian notation

$$\mathcal{H} = \sum_m \sum_{ij} \Xi_{m;ij} \hat{O}_{m;ij}, \quad (6)$$

In general we take Hubbard hamiltonian with *all* two-body interaction, where $\Xi_{m;ij} \in \{\epsilon_i, t_{ij}, U_i, K_{ij}, V_{ij}, J_{ij}\}$ and $\hat{O}_{m;ij}$ is a generic notation of the operator part (i.e. $\hat{O}_{t;ij} = \sum_\sigma \hat{c}_{i\uparrow}^\dagger \hat{c}_{j\sigma}$)

H_2 molecule

H_2 basis

$$w_i(\mathbf{r}) = \beta_0 \Psi_i(\mathbf{r}) + \beta_1 \Psi_{\bar{i}}(\mathbf{r}) \quad (7)$$

Microscopic parameters

$$\Xi_m = \Xi_m(R, \alpha). \quad (8)$$

R interatomic distance (set)

α inverse function size (variational parameter)

Exact results

See: J. Spałek, R. Podsiadły, W. Wójcik, A. Rycerz, PRB **61**, 15676 (2000);
Andrzej P. Kądzielawa, A. Bielas, M. Acquarone, A. Biborski, M. M. Maśka, J. Spałek, New Journal of Physics 2014

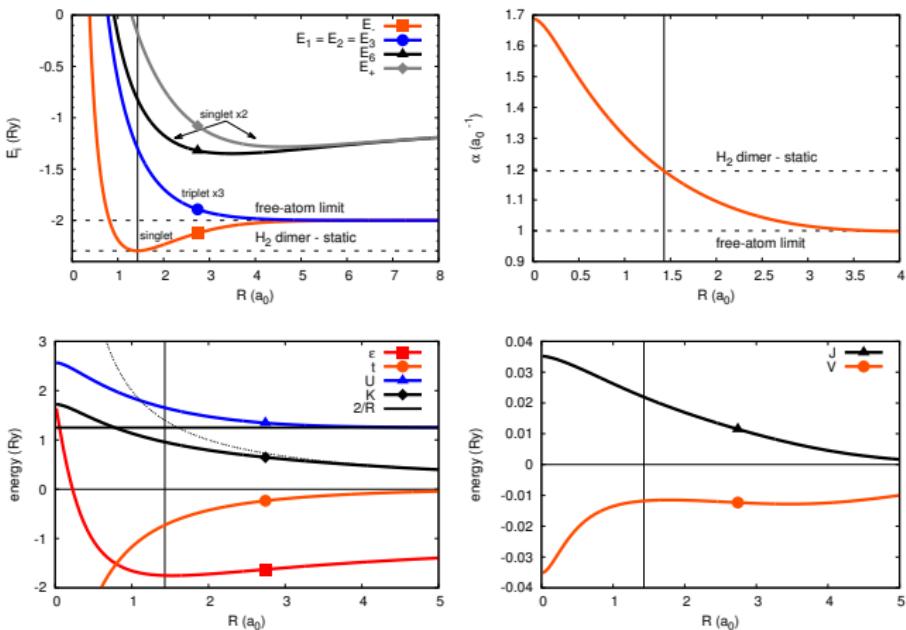


Figure : **TL:** energies of the spin-triplets ($E_1 = E_2 = E_3$) and the spin-singlets (E_{\pm}, E_6) versus the interionic distance R , **TR:** the optimal inverse wave-function size α versus the interionic distance R , **B:** microscopic parameters versus the interionic distance R

Electron–ion coupling

Simplified hamiltonian notation

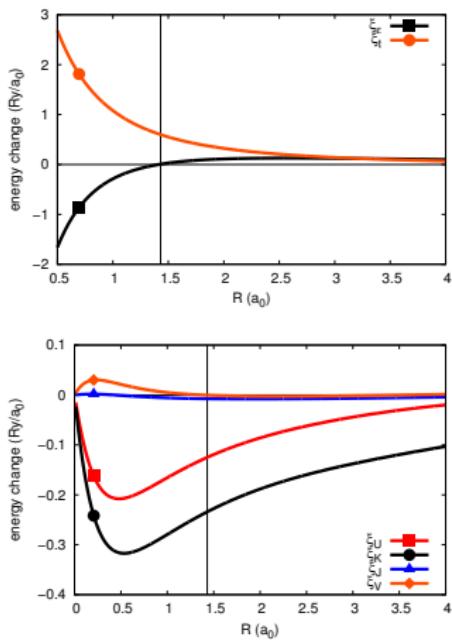
$$\mathcal{H} = \sum_i \Xi_i \hat{O}_i, \quad (9)$$

$\Xi_i \in \{\epsilon, t, U, K, V, J\}$, \hat{O}_i is a generic notation of the operator part of the hamiltonian (i.e. $\hat{O}_t = \hat{c}_{2\uparrow}^\dagger \hat{c}_{1\uparrow} + \hat{c}_{1\uparrow}^\dagger \hat{c}_{2\uparrow} + \hat{c}_{2\downarrow}^\dagger \hat{c}_{1\downarrow} + \hat{c}_{1\downarrow}^\dagger \hat{c}_{2\downarrow}$)

Electron–ion coupling

$$\delta\mathcal{H} = \sum_i \delta\Xi_i \hat{O}_i = \sum_i \xi_i \delta R \hat{O}_i, \quad (10)$$

where $\xi_i = \delta\Xi_i / \delta R$.



Results

$R_B = 1.43042(1.4010) \text{ } a_0,$
 $E_B = -2.29587(-2.33221) \text{ } Ry,$
 $E_{ZPM} = 0.024072(0.02) \text{ } Ry.$

Full derivation

APK *et al.*, New Journal of Physics 2014

Figure : Coupling constants ξ_i versus intersite distance R .

Gaussian contraction

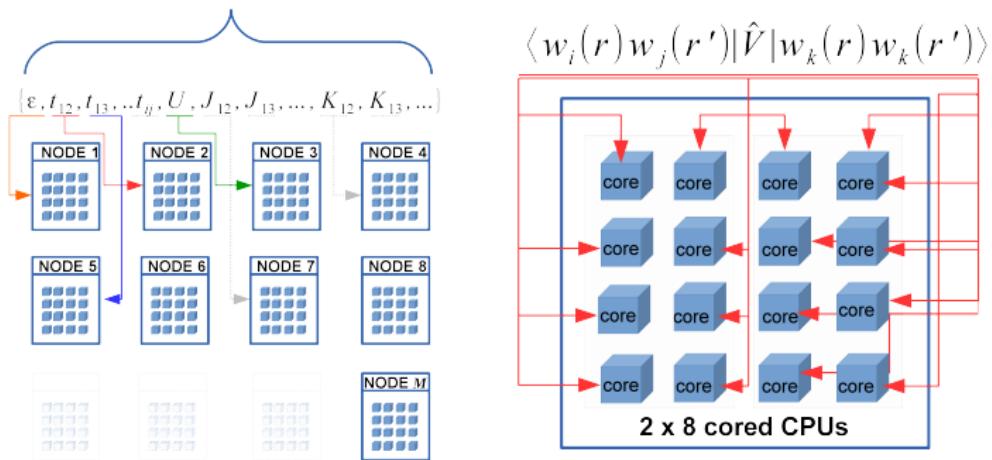
In general the V_{ijkl} integrals are hardly to obtain analytically (lack of/low symmetries). It is not the case if Gaussian contraction is applied:

$$\Psi_i^{1s}(\vec{r}) \approx \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\vec{r}-\vec{a}_i|} \approx \alpha^{3/2} \sum_{a=0}^n \left(\frac{2\alpha^2 \Gamma_a^2}{\pi} \right)^{3/4} e^{-\alpha^2 \Gamma_a^2 |\vec{r}-\vec{a}|^2} \quad (11)$$

Computational complexity

Computational effort for diagonalization is negligible for small systems, V_{ijkl} is **bottleneck** if satisfactory accuracy and/or significant number of integrals ($\propto 10^2 \div 10^3$) are desired since its calculation complexity is $\mathcal{O}(N_G^4 \times Z^4)$. Where N_G is a number of Gaussians used.

Two level parallelization and Qmt



QMT framework

QMT framework: bitbucket.org/azja/qmt



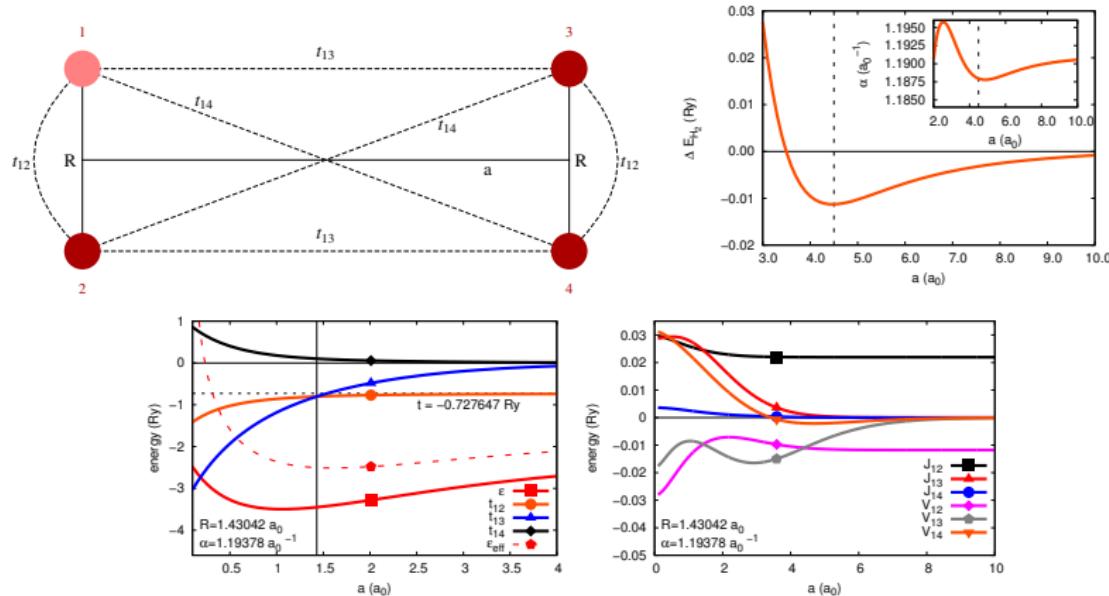
$(H_2)_2$ molecule

Figure : **TL:** model of two H_2 molecules, **TR:** the difference of energies of the $(H_2)_2$ system an that of the free molecules (per molecule) vs. intermolecular distance a , **B:** microscopic parameters vs. intermolecular distance a

$(H_2)_n$ chain

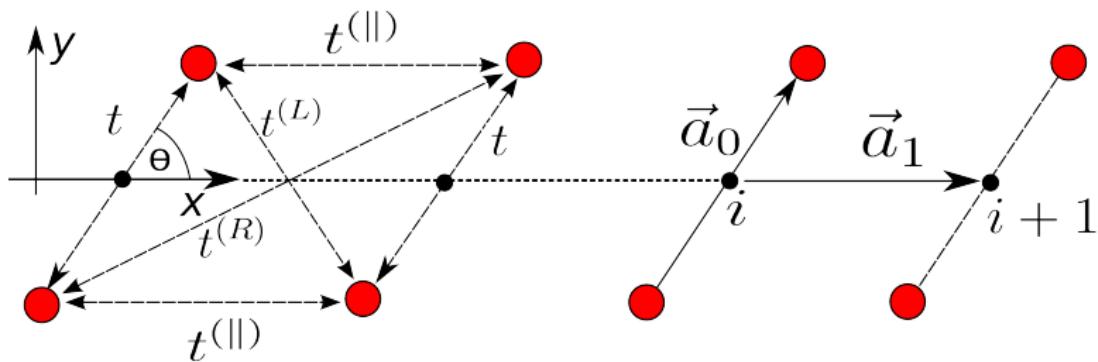


Figure : Molecular chain scheme.

Purpose

- Hydrogen "molecular crystal" model
- Real space treatment - possibility to study phonon spectra in terms of direct method
- All with the correlations directly taken into account

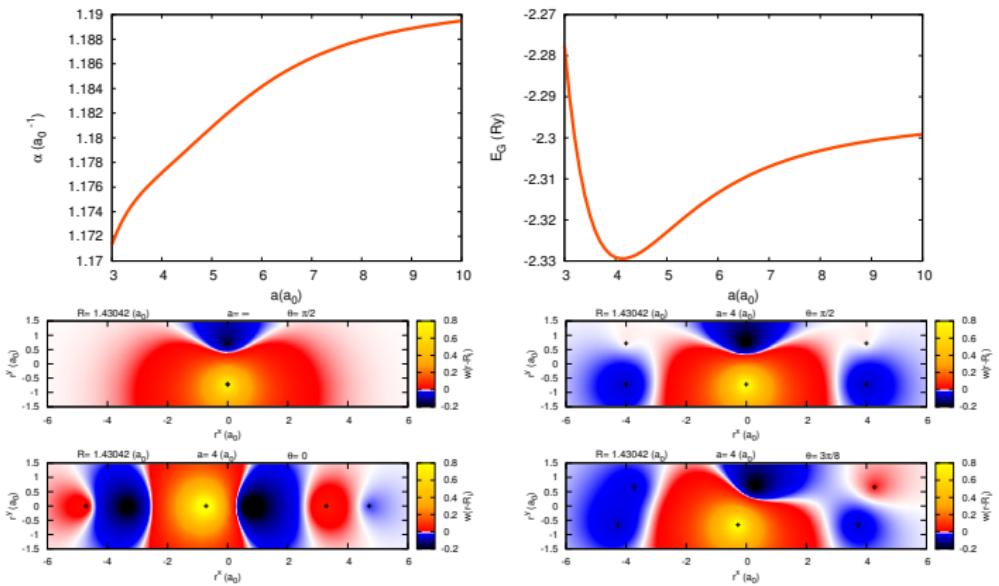
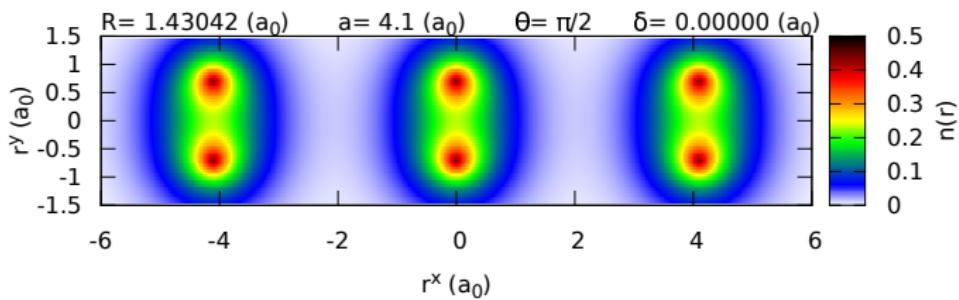


Figure : **TL:** the optimal inverse wave-function size α vs. intermolecular distance a , **TR:** the energy of the $(H_2)_n$ (per molecule) vs. intermolecular distance a **C,B:** single-particle wave function (orthogonalized for $(H_2)_3$) in xy -plane

Electron density



Possibility of conductivity

Correlation functions ($n = 1$)

$$\langle 2e^- \text{ per } H_2 \rangle = \left\langle \sum_{i\nu} \hat{n}_{i\uparrow}^{\nu} \hat{n}_{i\downarrow}^{\nu} (1 - \hat{n}_{i\uparrow}^{\bar{\nu}}) (1 - \hat{n}_{i\downarrow}^{\bar{\nu}}) \right\rangle \quad (12)$$

$$\langle 3e^- \text{ per } H_2 \rangle = \left\langle \sum_{i\nu\sigma} \hat{n}_{i\uparrow}^{\nu} \hat{n}_{i\downarrow}^{\nu} \hat{n}_{i\sigma}^{\bar{\nu}} (1 - \hat{n}_{i\sigma}^{\bar{\nu}}) \right\rangle \quad (13)$$

$$\langle 4e^- \text{ per } H_2 \rangle = \left\langle \sum_{i\nu} \hat{n}_{i\uparrow}^{\nu} \hat{n}_{i\downarrow}^{\nu} \hat{n}_{i\uparrow}^{\bar{\nu}} \hat{n}_{i\downarrow}^{\bar{\nu}} \right\rangle \quad (14)$$

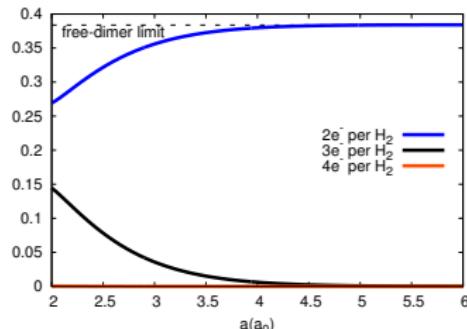


Figure: Averages of operator sums above vs. intermolecular distance a

Direct method

Idea: Direct method in EDABI

- Real space calculations - we can move ions (protons) and compute ΔE for each displacement
- Apply adiabatic approximation
- Impose harmonic approximation and calculate force constants
$$\Phi_{\mu\nu}^{ij} = \frac{\delta E_{\mu\nu}^{ij}}{\delta i_\mu \delta j_\nu}$$
 numerically

Lost in the forest...

We need to calculate Hellmann – Feynman forces to build dynamic matrix. How to do that? Some attempts were done but without desired results though further perspectives promising.

Summary

First- and second-quantization language

- successful combination of both pictures
- full symmetry **not** required for calculation

H_2 chain

- zero-point motion estimated for H_2 molecule
- description of one-dimensional molecular crystal

To do

- phonon spectra for molecular and atomic crystals
- electron–phonon couplings
- inclusion of 2s and 2p orbitals

To do

- more configurations of H_2 crystals
- other methods of obtaining energy

A lot of to do, see:

- "Unexpectedly high pressure for molecular dissociation in liquid hydrogen by electronic simulation", G. Mazzola et al., Nature Communications (2014)
- "Fate of density functional theory in the study of high-pressure solid hydrogen", S. Azadi et al., Phys. Rev. B 88, 014115 (2013)

Thank you!

Hamiltonian

$$\begin{aligned}\mathcal{H} = & \sum_i \epsilon_i \hat{n}_i + \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j \quad (15) \\ & + \frac{1}{2} \sum_{ij} \left(K_{ij} - \frac{J_{ij}}{2} \right) \hat{n}_i \hat{n}_j + \sum_{ij} J_{ij} \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow}^\dagger \hat{c}_{j\downarrow} \hat{c}_{j\uparrow} \\ & + \sum_{ij\sigma} V_{ij} \hat{n}_{i\sigma} \left(\hat{c}_{i\bar{\sigma}}^\dagger \hat{c}_{j\bar{\sigma}} + \hat{c}_{j\bar{\sigma}}^\dagger \hat{c}_{i\bar{\sigma}} \right),\end{aligned}$$

where $\hat{c}_{i\sigma}$ and $\hat{c}_{i\sigma}^\dagger$ are the fermionic operators of annihilation and creation of the electron with spin σ on $1s$ orbital of hydrogen atom $i \bmod 2$ in H_2 molecule $\lfloor \frac{i}{2} \rfloor$.

Two level parallelization

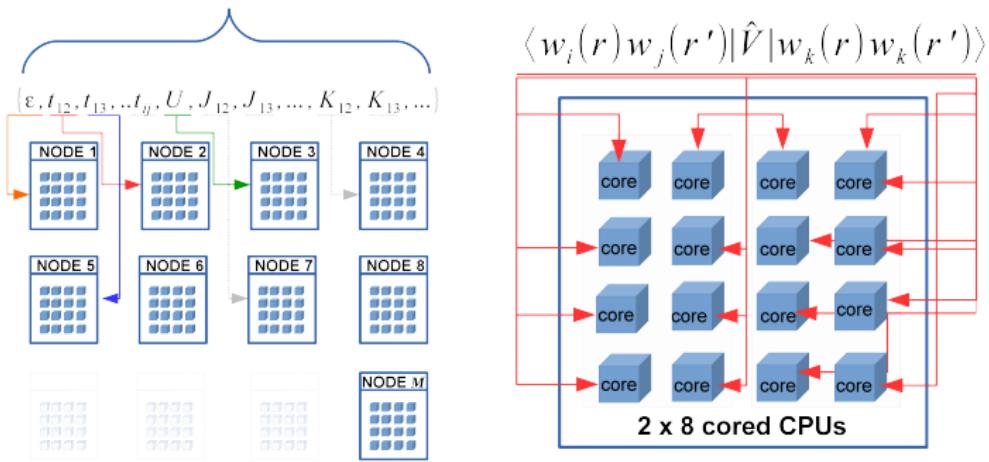


Figure: General approach to parallelization of microscopic parameters calculation.

Time consumption

Maximal speed-up (first- and second-level) defined as:

$$f_{FL+SL}^{\max}(M) = \frac{t_{FL+SL}(M)}{t_{FL}(M=1)} \quad (16)$$

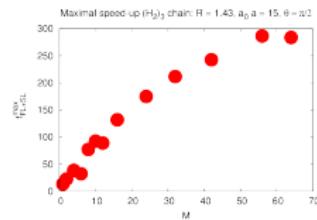


Figure : Maximal speed-up factor for $p = 15$ Gaussians vs. number of nodes M .

Wave functions

Slater 1s wave functions (approximated by series of p Gaussians.

$$\Psi_i^\alpha(\mathbf{r}) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha|\mathbf{r}-\mathbf{R}_i|} \approx \alpha^{\frac{3}{2}} \sum_{a=1}^p B_a \left(\frac{2\alpha^2 \Gamma_a^2}{\pi} \right)^{\frac{3}{4}} e^{-\alpha^2 \Gamma_a^2 |\mathbf{r}-\mathbf{R}_i|^2}. \quad (17)$$

Table : The numerical values of coefficients in Taylor series of ground-state energy. Up to the term $E_B^{(6)}$ all of the derivatives are calculated analytically. Orders seventh–ninth (marked by an asterisk) were calculated numerically due to complicated analytical expression for ground-state energy.

$E_B^{(1)} \left(\frac{Ry}{a_0} \right)$	0.0
$\frac{1}{2!} E_B^{(2)} \left(\frac{Ry}{a_0^2} \right)$	0.430045
$\frac{1}{3!} E_B^{(3)} \left(\frac{Ry}{a_0^3} \right)$	-0.464021
$\frac{1}{4!} E_B^{(4)} \left(\frac{Ry}{a_0^4} \right)$	0.354584
$\frac{1}{5!} E_B^{(5)} \left(\frac{Ry}{a_0^5} \right)$	-0.253393
$\frac{1}{6!} E_B^{(6)} \left(\frac{Ry}{a_0^6} \right)$	0.174863
$\frac{1}{7!} E_B^{(7)} \left(\frac{Ry}{a_0^7} \right)^*$	-0.119178
$\frac{1}{8!} E_B^{(8)} \left(\frac{Ry}{a_0^8} \right)^*$	0.0817586
$\frac{1}{9!} E_B^{(9)} \left(\frac{Ry}{a_0^9} \right)^*$	-0.0563837

Table : The values (in atomic units) of the microscopic parameters of H_2 Hamiltonian and the electron–ion coupling constants at the hydrogen-molecule equilibrium ($R = R_B$ and $\alpha = \alpha_B$).

microscopic paramters (Ry)		coupling constants (Ry/ a_0)	
ϵ	-1.75079	ξ_ϵ	0.00616165
t	-0.727647	ξ_t	0.598662
U	1.65321	ξ_U	-0.124934
K	0.956691	ξ_K	-0.234075
J	0.0219085	ξ_J	-0.00746303
V	-0.0117991	ξ_V	-0.000426452

Table : The values (in atomic units) of the second-order electron–ion coupling constants $\xi_i^2 = \delta^2 \Xi / \delta R^2$ at the hydrogen-molecule equilibrium ($R = R_B$ and $\alpha = \alpha_B$).

coupling constants (Ry/a_0^2)	
ξ_{ϵ}^2	0.327335
ξ_t^2	-0.560426
ξ_U^2	0.0504027
ξ_K^2	0.013028
ξ_J^2	-0.00671566
ξ_V^2	-0.0105204

$(H_2)_2$ molecule

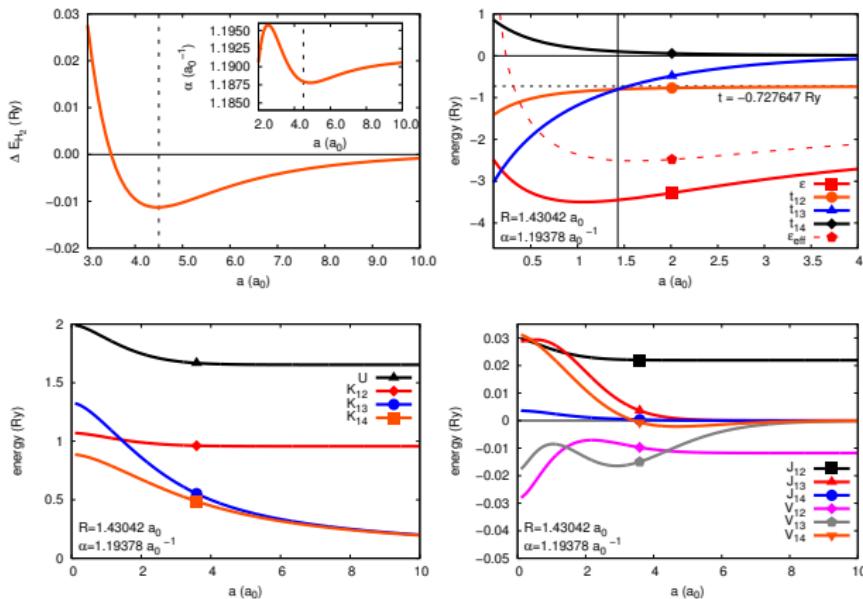


Figure : TL: the difference of energies of the $(H_2)_2$ system an that of the free molecules (per molecule) vs. intermolecular distance a , **TR:** the one-particle microscopic parameters for two H_2 molecules system vs. intermolecular distance a , **B:** microscopic parameters vs. intermolecular distance a

Table : The numerical values of single-particle energy and the hopping integrals for the two-molecule system.

R (a_0)	a (a_0)	ϵ (Ry)	t_1 (Ry)	t_2 (Ry)	t_3 (Ry)
0.715	1.43	-3.42645	-1.55344	-0.931964	0.279925
0.715	2.86	-2.90683	-1.39477	-0.234881	0.099267
0.715	4.29	-2.52287	-1.36709	-0.0498632	0.0338935
1.43	1.43	-3.44995	-0.802954	-0.802954	0.102336
1.43	2.86	-3.00071	-0.750421	-0.22323	0.0279053
1.43	4.29	-2.64834	-0.737967	-0.0535184	0.00961135
2.145	1.43	-3.23442	-0.42775	-0.765119	0.0500421
2.145	2.86	-2.88048	-0.421111	-0.229361	0.00128325
2.145	4.29	-2.56678	-0.418513	-0.0609803	-0.0019108
2.86	1.43	-3.00071	-0.22323	-0.750421	0.0279053
2.86	2.86	-2.71928	-0.235403	-0.235403	-0.00747347
2.86	4.29	-2.44103	-0.238535	-0.0670113	-0.006626

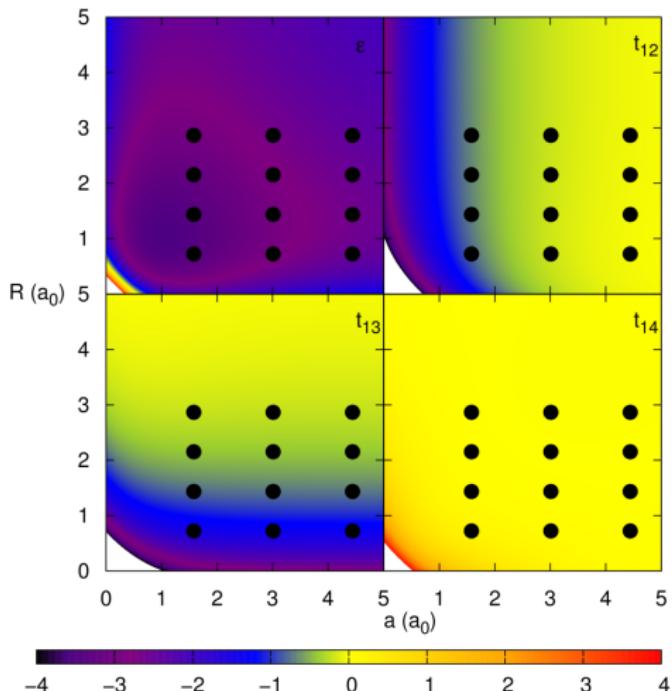


Figure : The one-particle microscopic parameters (in Ry) for two H_2 molecules system vs. intermolecular distance a and interionic distance R . Note the symmetry of ϵ and t_{14} . As expected for relatively small distances values of t_{12} and t_{13} are negative, whereas t_{14} is positive. When approaching point $(0, 0)$ all parameters diverge to minus (t_{12} and t_{13}) or plus (ϵ and t_{14}) infinity.