$(H_2)_n$ molecule system with an *ab initio* optimization of wave functions in correlated state: Electron-proton couplings and intermolecular microscopic parameters

Andrzej P. Kądzielawa[1*], Agata Bielas[2], Marcello Acquarone[3], Andrzej Biborski[4], Maciej M. Maśka[2], Józef Spałek[1,4]

[1]Instytut Fizyki im. Mariana Smoluchowskiego, Uniwersytet Jagielloński, ul. Reymonta 4, PL-30059 Kraków, Poland
[2]Instytut Fizyki, Uniwersytet Śląski, ul. Uniwersytecka 4, PL-40007 Katowice, Poland
[3]Dipartimento di Fisica e Scienze della Terra dell'Università di Parma, I-43100 Parma, Italy
[4]Akademickie Centrum Materiałów i Nanotechnologii, AGH Akademia Górniczo-Hutnicza, Al. Mickiewicza 30, PL-30-059 Kraków, Poland

[*]kadzielawa@th.if.uj.edu.pl

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY
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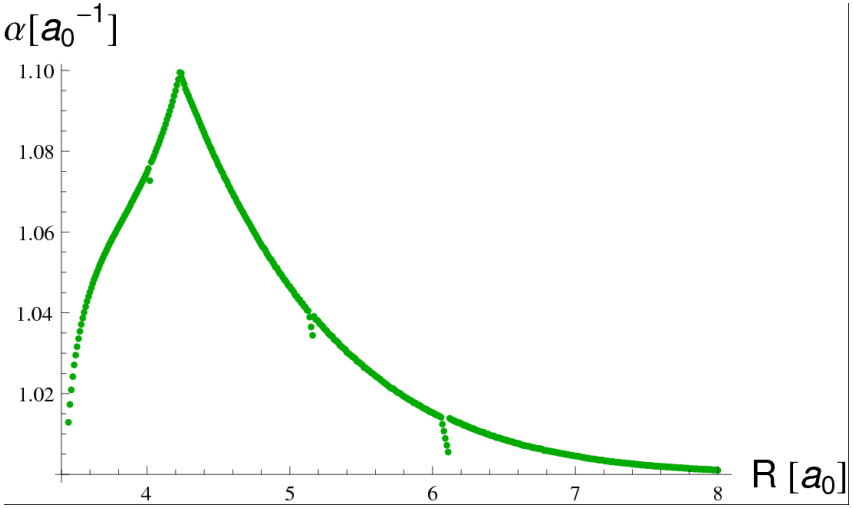
Outline

1. Objective
2. Methods
   - Single-particle basis optimization
   - Hamiltonian
   - Statistically-consistent Gutzwiller Approximation (SGA)
3. Results
   - Metal-insulator transition
   - Quantum critical behavior
   - Metallization pressure

Objective

To apply SGA method for wave function quantum scaling problem near Mott-Hubbard transition.



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Also

- to include the effect of external magnetic field on metal-insulator transition
- to calculate metallization pressure for atomic hydrogen

Base functions

We build our basis by orthogonalizing Slater-type orbitals Ψ_i by introducing mixing coefficients β_j

$$\left\langle w_{\pi_i(j)}(\mathbf{r}) \right| \left. w_i(\mathbf{r}) \right\rangle = \delta_{i\pi_i(j)}, \tag{1}$$

$$w_i\left(\mathbf{r}-\mathbf{R}_i\right) = w_i\left(\mathbf{r}\right) = \sum_{j=0}^{Z} \beta_j \Psi_{\pi_i(j)}\left(\mathbf{r}\right), \tag{2}$$

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

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

Microscopic parameters

Values

We have two classes of microscopic parameters

$$T_{ij} = \langle w_i | \, \mathcal{H}_1 \, | w_j \rangle \,, \tag{4a}$$

$$V_{ijkl} = \left\langle w_i w_j \left| \frac{2}{|\mathbf{r} - \mathbf{r}'|} \right| w_k w_l \right\rangle , \tag{4b}$$

As we choose w_i to be real all possibilities can be described by

ϵ_i	t_{ij}	U_i	J_{ij}	K_{ij}	V_{ij}
T_{ii}	T_{ij}	V_{iiii}	V_{iijj}	V_{ijij}	V_{iiij}

Hamiltonian

We start from the extended Hubbard model:

$$\mathcal{H} = \sum_i \epsilon_i \hat{n}_i + \sum_{ij\sigma} t_{ij} \hat{c}^\dagger_{i\sigma} \hat{c}_{j\sigma} + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j \qquad (5)$$
$$+ \frac{1}{2} \sum_{ij} \left(K_{ij} - \frac{J_{ij}}{2} \right) \hat{n}_i \hat{n}_j + \sum_{ij} J_{ij} \hat{c}^\dagger_{i\uparrow} \hat{c}^\dagger_{i\downarrow} \hat{c}_{j\downarrow} \hat{c}_{j\uparrow}$$
$$+ \sum_{ij\sigma} V_{ij} \hat{n}_{i\sigma} \left(\hat{c}^\dagger_{i\bar{\sigma}} \hat{c}_{j\bar{\sigma}} + \hat{c}^\dagger_{j\bar{\sigma}} \hat{c}_{i\bar{\sigma}} \right),$$

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

SGA:

Ground-state energy

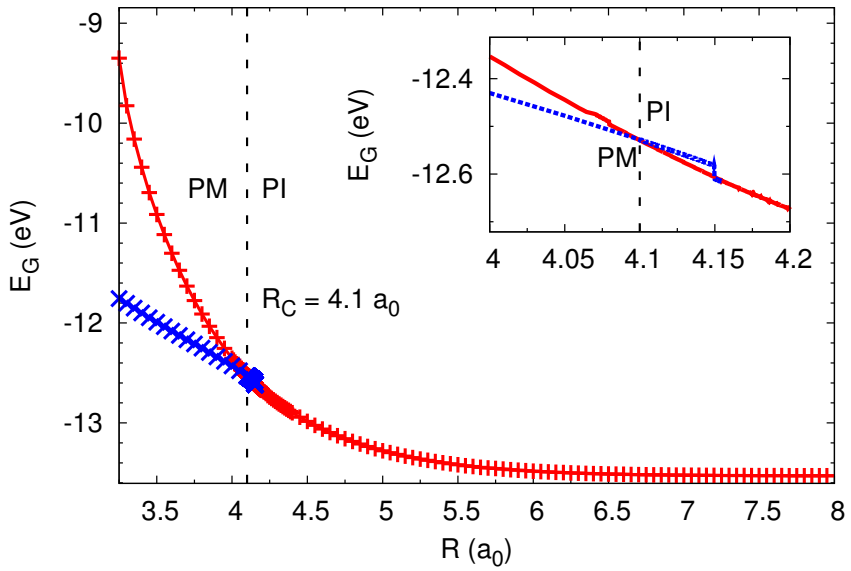
$$\frac{E_G}{\Lambda} = \epsilon_a^{eff} + \frac{1}{\Lambda}\left(\sum_{ij\sigma} t_{ij}\left\langle a_{i\sigma}^{\dagger} a_{j\sigma}\right\rangle + \sum_i U\left\langle a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow}\right\rangle\right) \tag{6}$$

$$\Downarrow \text{ minimization}$$

$$\mathcal{K} = \epsilon_a^{eff}\sum_{i\sigma} n_{i\sigma} + \sum_{ij\sigma} t_{ij} q_\sigma a_{i\sigma}^{\dagger} a_{j\sigma} + \Lambda U d^2 - \mu\sum_{i\sigma} n_{i\sigma} - \lambda_m\sum_i (m_i - m) - \lambda_n\sum_i (n_i - n) \tag{7}$$

n	m	d^2	λ_n	λ_m	μ
band filling	magnetization	no. of double occupancies	molecular field coupled with n	molecular field coupled with m	chemical potential

Nature of transition



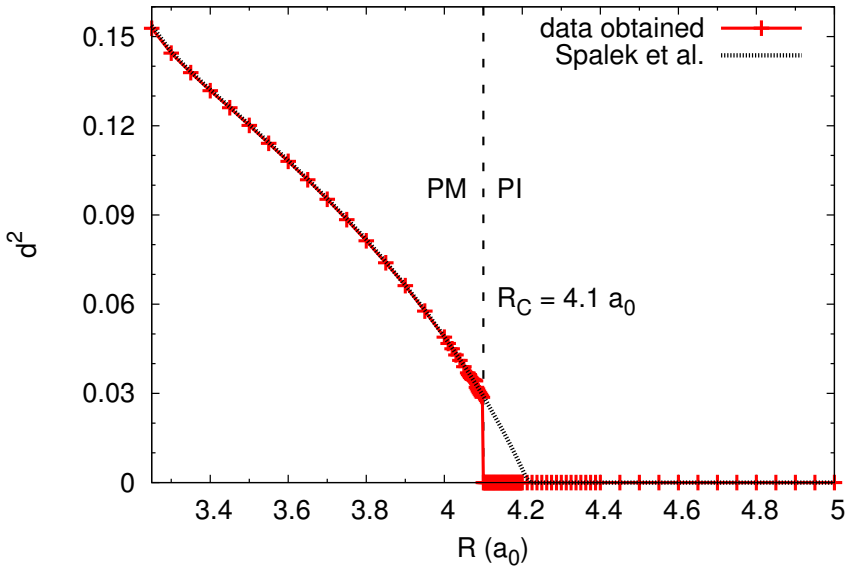


Figure: **G:** Ground-state energy of metallic (blue) and insulating (red) state. **D:** Double occupancies per site for our model vs. last publication.

1st order

Discontinuity of first derivative of energy (upper plot) $\rightarrow$ metal-insulator transition of weakly first order.

Zero-point motion for ion lattice

The uncertainties of momentum δP and distance between ions δR:

$$\Delta E = \frac{(\delta P)^2}{2M} + \sum_{i=1}^{3} \frac{1}{2} \left(\frac{1}{R + \delta R^i} + \frac{1}{R - \delta R^i} \right) \tag{8}$$

using Heisenberg Principle $(\delta \mathbf{P})(\delta \mathbf{R}) \geqslant \frac{3}{4}$ and minimizing with respect to $\delta \mathbf{R}$, we obtain results (at MIT):

	axis–aligned	plane–aligned	**diagonal**
$\lvert\delta \mathbf{R}\rvert$ (a_0)	0.3432	0.3438	**0.3440**
$\Delta E - \frac{3}{R}$ (Ry)	0.003455	0.003449	**0.003447**

Remark 1

All the calculations are done in atomic units.

Remark 2

This is only estimation of the magnitude of ZPM.

Zero-point motion

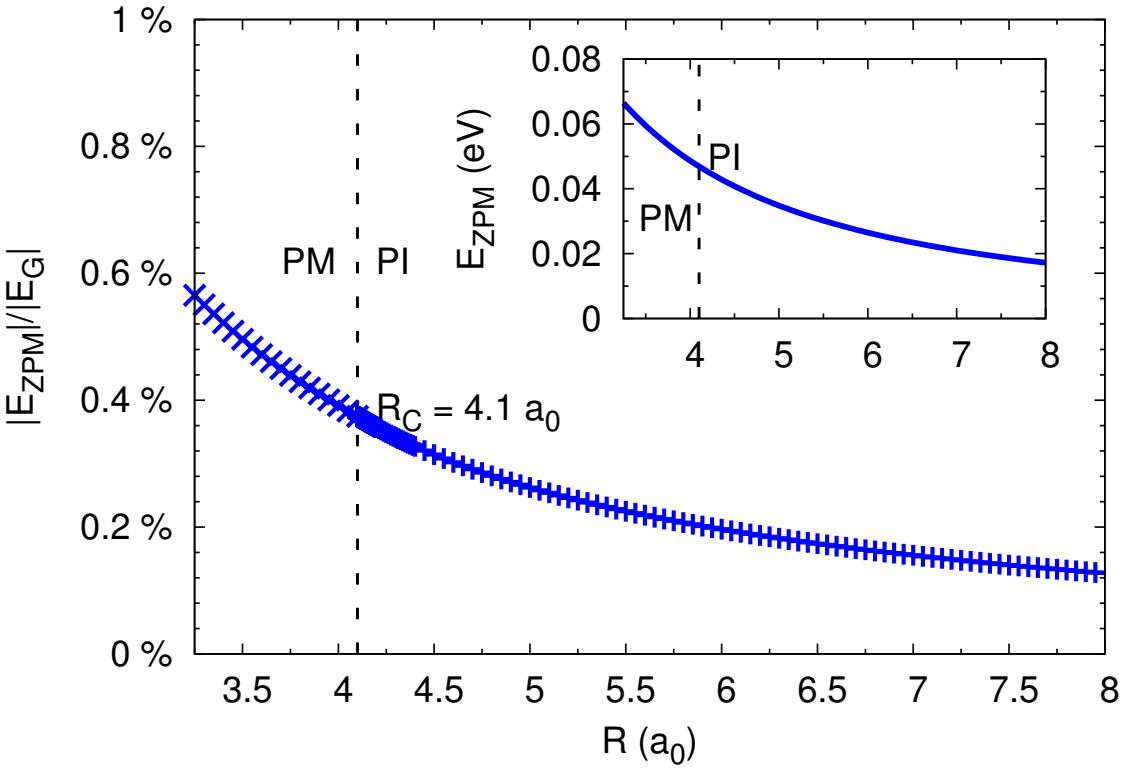


Figure: The relative magnitude of the zero-point motion energy with respect to ground state vs. lattice parameter R.
Inset: The explicit value of the energy of zero-point motion vs. lattice parameter R.

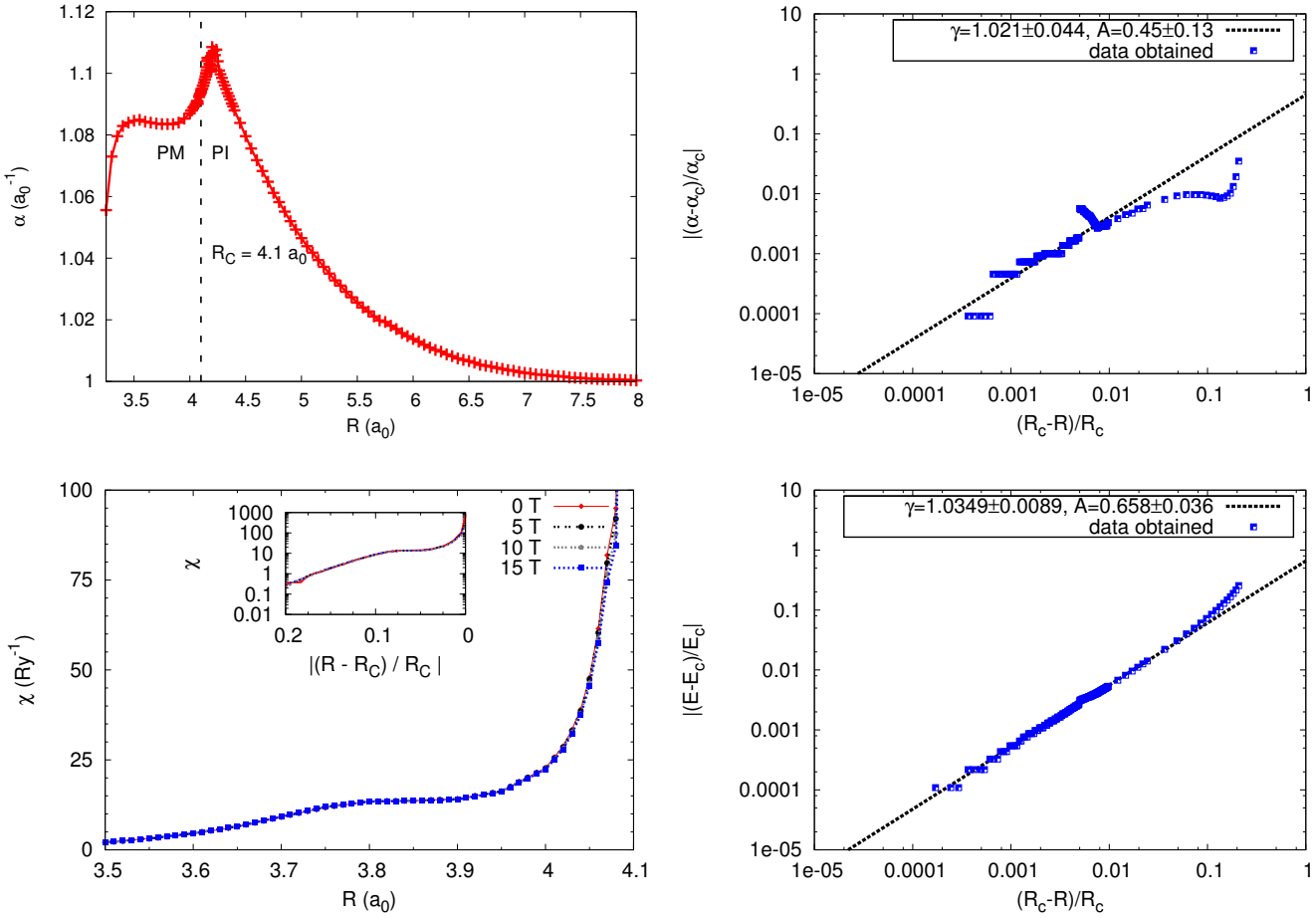


Figure:

left: reverse wave function size α (**top**), and magnetic susceptibility (**bottom**) vs. lattice parameter R,

right: scaling of reverse wave function size α (**top**) and energy E (**bottom**) near critical point ($\sim A\left((R_C - R)/R_C\right)^{\gamma}$).

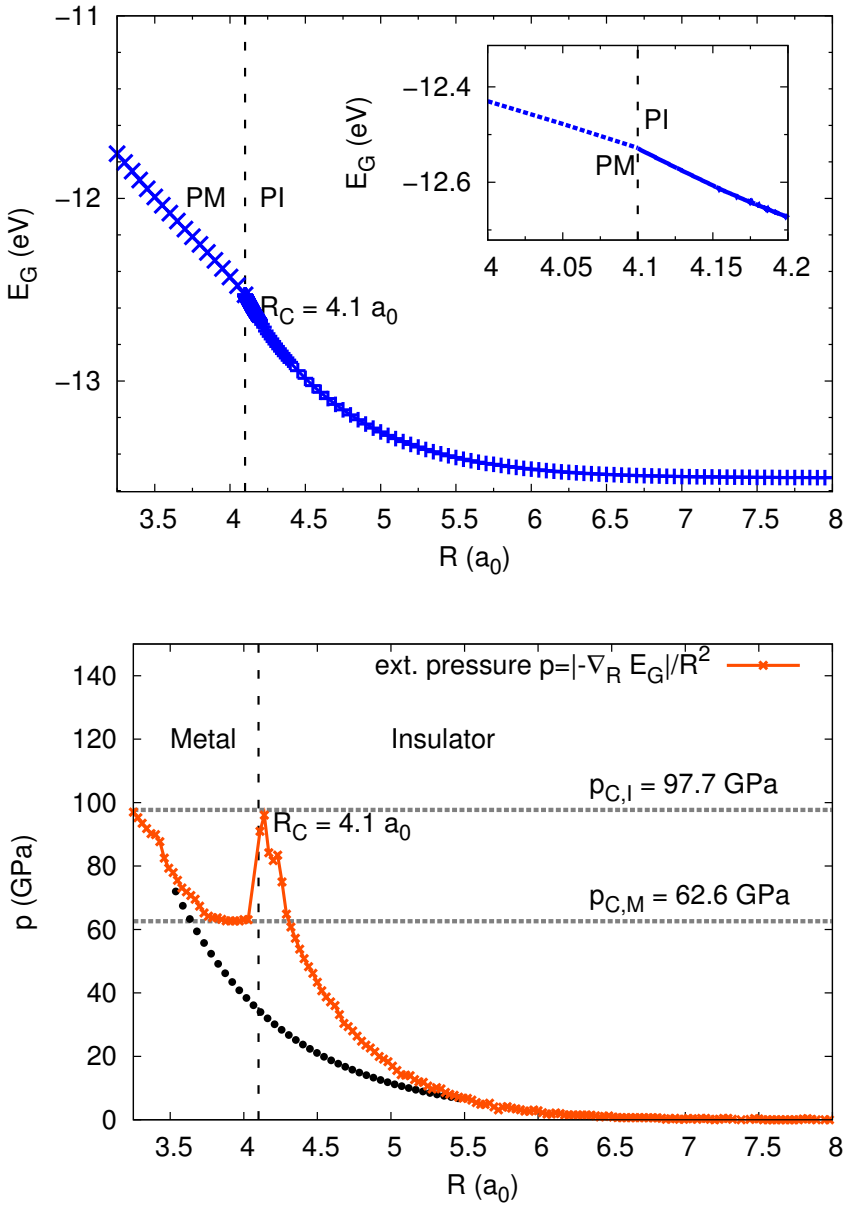


Figure: **top:** Ground energy vs. lattice parameter R, **bottom:** crystal stabilizing pressure vs. lattice parameter R - numerical (orange) and naive fit (black).

Pressure stabilizing hydrogen crystal

$p_C = 97.7\,GPa$

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Thank you!

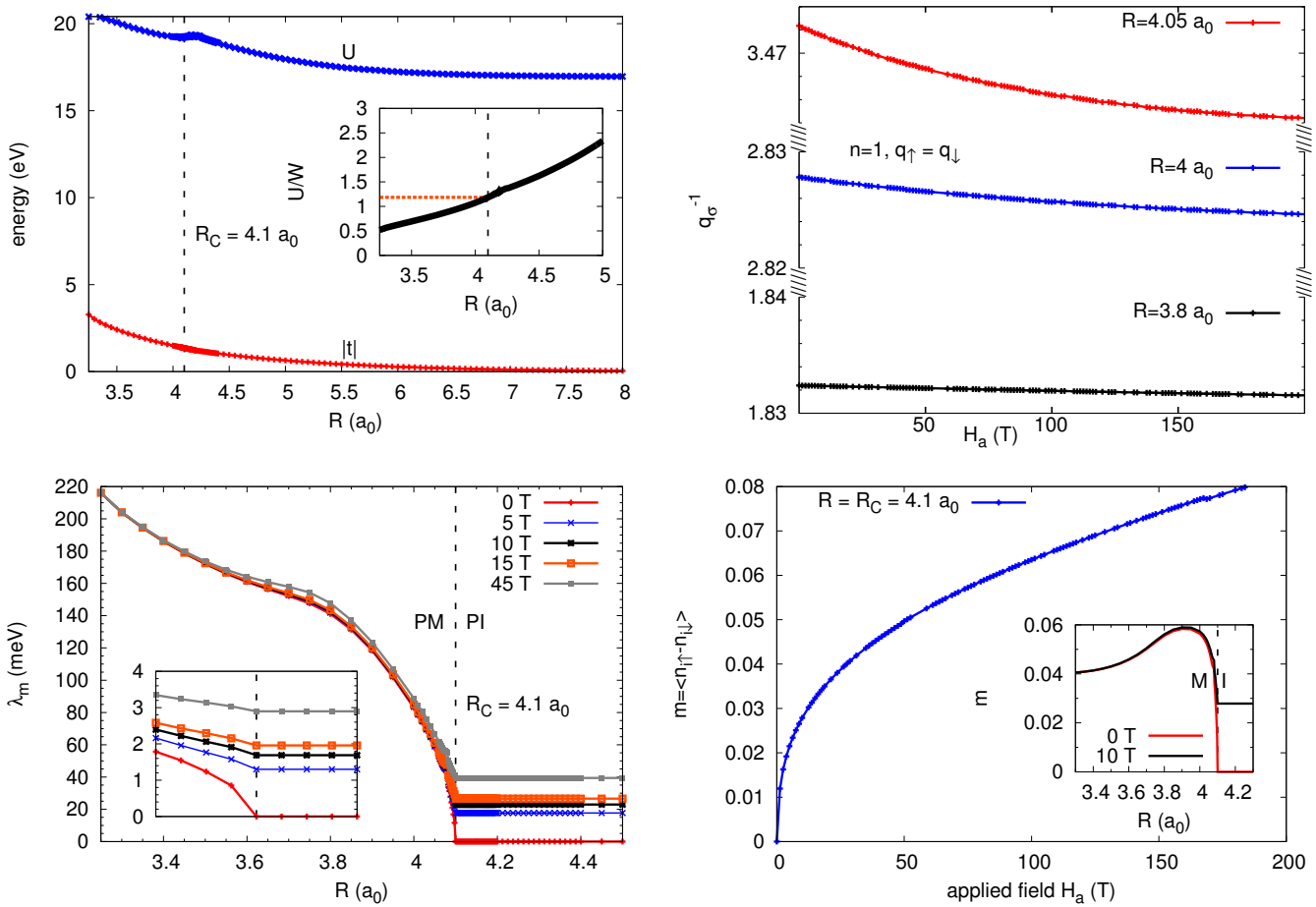

Figure: **TL:** microscopic parameters vs. lattice parameter R, **TR:** effective mass enhancement vs. external magnetic field H_a, **BL:** effective magnetic field λ_m vs. lattice parameter R, **BR:** magnetization m vs. external magnetic field H_a

Table: Values calculated using SGA method as a function of lattice parameter for SC. Units, if not written explicitly, are set to be *rydbergs* (Ry). $\chi(0)$ for $R \geqslant R_c$ is infinite.

$R(a_0)$	E_G^{SGA}	E_G^{GA}	t	U	$\alpha^{-1}(a_0)$	d^2	λ_m	$\chi(Ry^{-1})$	q^{-1}
3.25	-0.8640	-0.8644	-0.2409	1.4996	0.9474	0.152774	0.015884	0.1809	1.17728
3.50	-0.8814	-0.8816	-0.1773	1.4749	0.9220	0.120128	0.012641	2.0598	1.36818
4.00	-0.9136	-0.9136	-0.1098	1.4152	0.9200	0.048886	0.006084	22.6577	2.82781
4.05	-0.9171	-0.9171	-0.1046	1.4139	0.9175	0.038973	0.004256	47.3562	3.47235
4.09	-0.9200		-0.1005	1.4140	0.9147	0.030193	0.027281	253.7567	4.40375
4.10	-0.9209	-0.9207	-0.0995	1.4143	0.9138	0.000000	0.000000	∞	∞
4.20	-0.9315	-0.9288	-0.0896	1.4217	0.9021	0.000000	0.000000		
4.50	-0.9544	-0.9517	-0.0705	1.3742	0.9263	0.000000	0.000000		
5.00	-0.9760	-0.9732	-0.0471	1.3200	0.9556	0.000000	0.000000		
7.00	-0.9939		-0.0082	1.2504	0.9972	0.000000	0.000000		
∞	-1.0000	-1.0000	0.0000	1.2500	1.0000	0.000000	0.000000		

Minimization of free energy functional $\mathcal{F}$:

$$\mathcal{F}^{(SGA)} = -\frac{1}{\beta}\sum_{\mathbf{k}\sigma}\log\left(1+e^{-\beta E^{(SGA)}_{\mathbf{k}\sigma}}\right) + \Lambda\left(\lambda_n n + \lambda_m m + Ud^2 + \mu n\right), \tag{9}$$

where the test eigenvalues $E^{(SGA)}_{\mathbf{k}\sigma}$

$$E^{(SGA)}_{\mathbf{k}\sigma} \equiv q_\sigma \varepsilon_{\mathbf{k}} - \sigma\left(h+\lambda_m\right) - \left(\mu+\lambda_n\right),$$
$$q_\sigma = \frac{\left(\sqrt{\left(n_\sigma - d^2\right)\left(1-n_\sigma-n_{\overline{\sigma}}+d^2\right)} + d\sqrt{n_{\overline{\sigma}}-d^2}\right)^2}{n_\sigma\left(1-n_\sigma\right)} \tag{10}$$

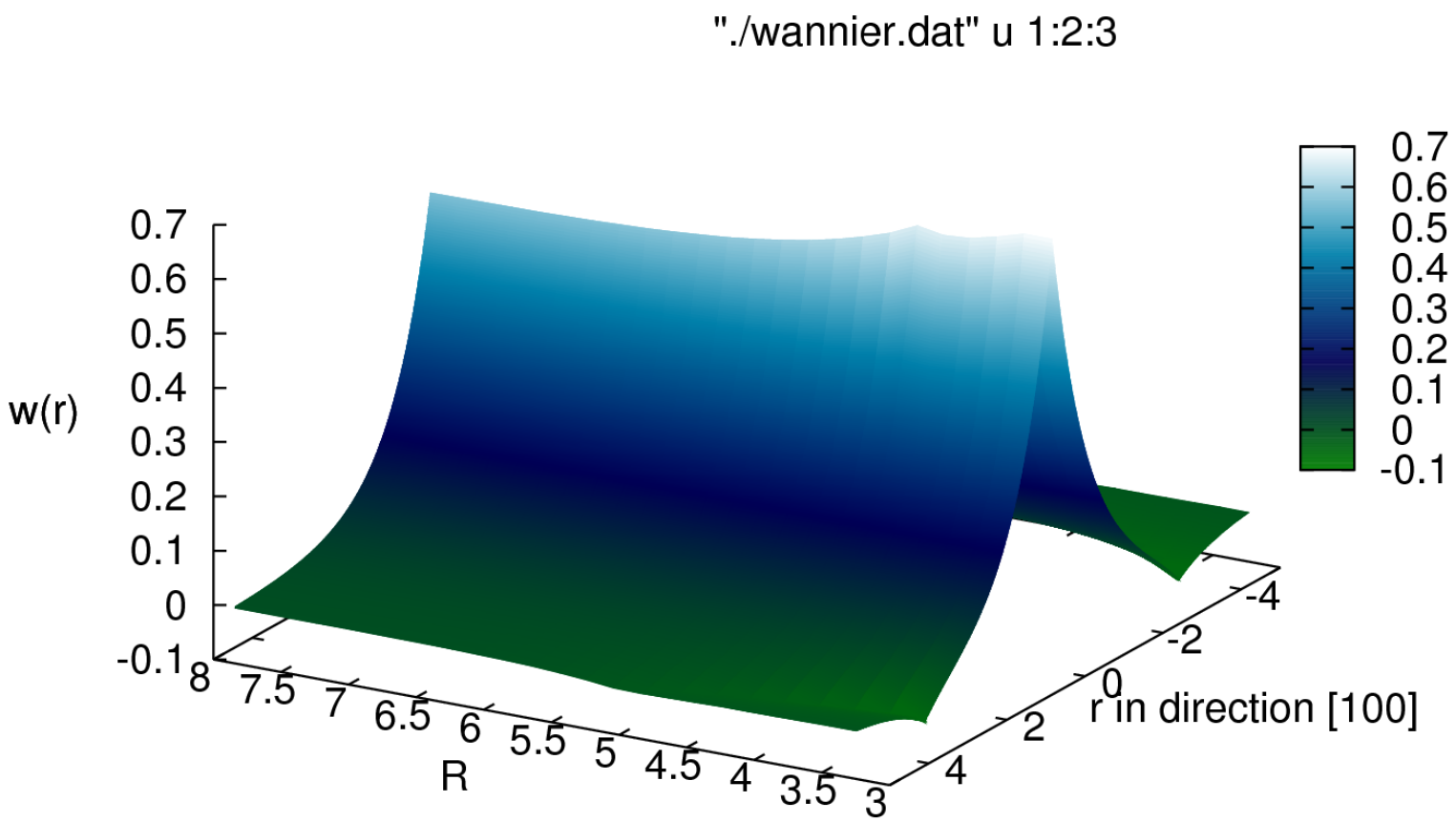

Figure: Overall space profiles of the renormalized Wannier function for sc lattice as a function of lattice parameter R and along [100] direction r.