Ab initio methods in Mott transition - application to metallization of atomic hydrogen

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June 3, 2013

INNOVATIVE ECONOMY
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FNP
Foundation for Polish Science

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

1. Aims

2. Methods
   - Hamiltonian
   - Single-particle basis optimization
   - Statistically-consistent Gutzwiller Approximation (SGA)

3. Results
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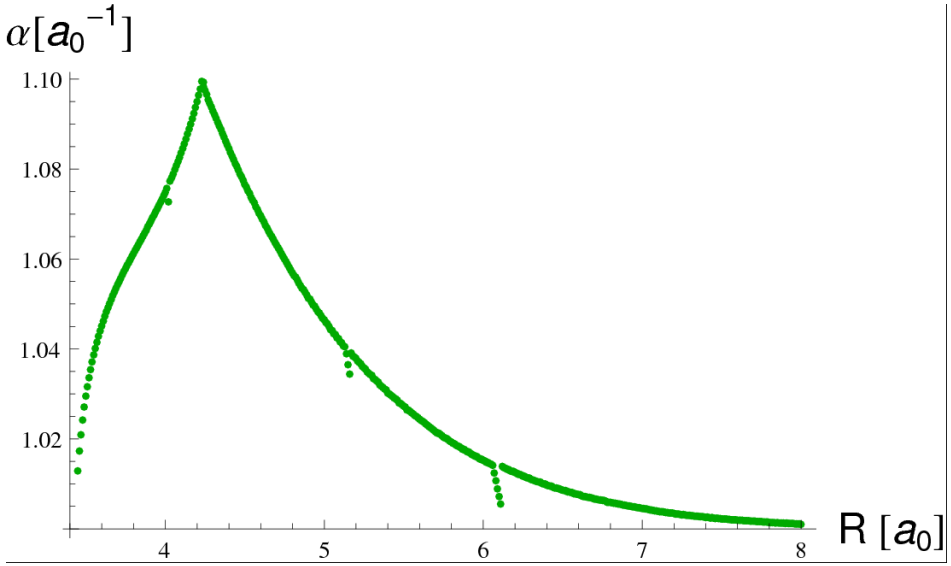
   - Microscopic parameters
   - Results properties: quantum critical behavior
   - Metallization pressure

4. Future

Aim 1

To apply SGA method for wave function quantum scaling problem near Mott-Hubbard transition.
For GA: Eur. Phys. J. B **74**, 63-74 (2010)



Other

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

Hamiltonian

We start from the Extended Hubbard Model:

$$\mathcal{H}_{EH} = \epsilon_a^{eff} \sum_i n_i + \sum_{i \neq j, \sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} K_{ij} \delta n_i \delta n_j, \quad (1)$$

where effective energy

$$\epsilon_a^{eff} = \epsilon_a + \frac{1}{2\Lambda} \sum_{i \neq j} \left(K_{ij} + \frac{2}{|R_j - R_i|} \right), \quad (2)$$

t_{ij} – hopping integral, U – Coulomb interaction on site, a K_{ij} Coulomb interaction between site

Hamiltonian

External field H_a

Zeeman term:

$$\mathcal{H}_Z = -\sum_{i,\sigma} \sigma h n_{i\sigma}, \tag{3}$$

where $h = \frac{1}{2} g \mu_B H_a$ is reduced magnetic field.

Single-particle basis optimization

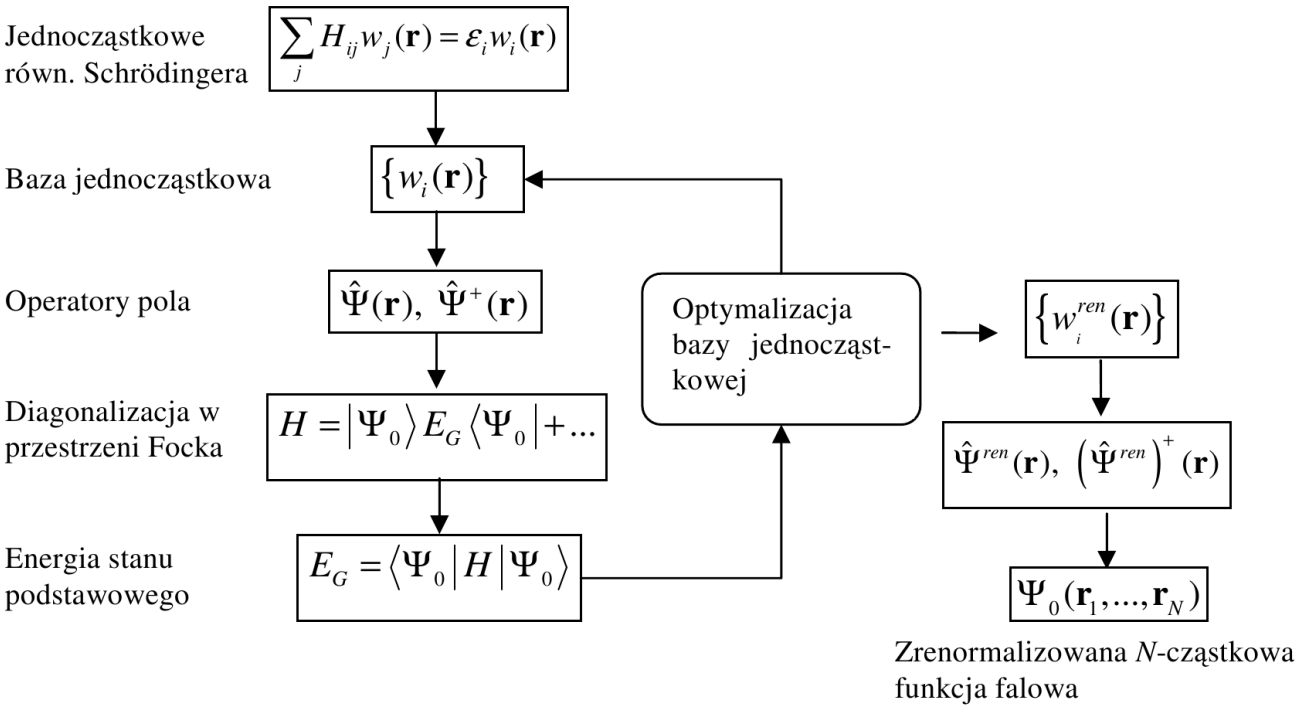


Figure: Flow chart from Dr. J. Kurzyk PhD thesis (UJ 2010)

Base functions

On site $i = R_i$:

$$w_i(\vec{r}) = \beta\Psi_i(\vec{r}) - \gamma\sum_{j=1}^{z}\Psi_j(\vec{r}),$$

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

constant	overlap	minimization $\mathcal{H}_1 \overset{a.u.}{=} -\nabla^2 - 2\left\|\vec{r}-\vec{R}_i\right\|^{-1}$	minimization
dependent	dependent		with respect to E_G
z, p	β, γ	B_a, Γ_a	α

Microscopic parameters

Values

Microscopic parameters ϵ_a, t_{ij}, U, and K_{ij} are expressed by integrals

$$
\begin{aligned}
t_{ij} &= \langle w_i | \, \mathcal{H}_1 \, | w_j \rangle \, , \\
U &= \left\langle w_i \, w_i \left| \, \frac{\mathrm{e}^2}{|\vec{r}_1 - \vec{r}_2|} \, \right| w_i \, w_i \right\rangle , \\
K_{ij} &= \left\langle w_i \, w_j \left| \, \frac{\mathrm{e}^2}{|\vec{r}_1 - \vec{r}_2|} \, \right| w_i \, w_j \right\rangle , \\
\epsilon_a &= \langle w_i | \, \mathcal{H}_1 \, | w_i \rangle \, .
\end{aligned}
\tag{5}
$$

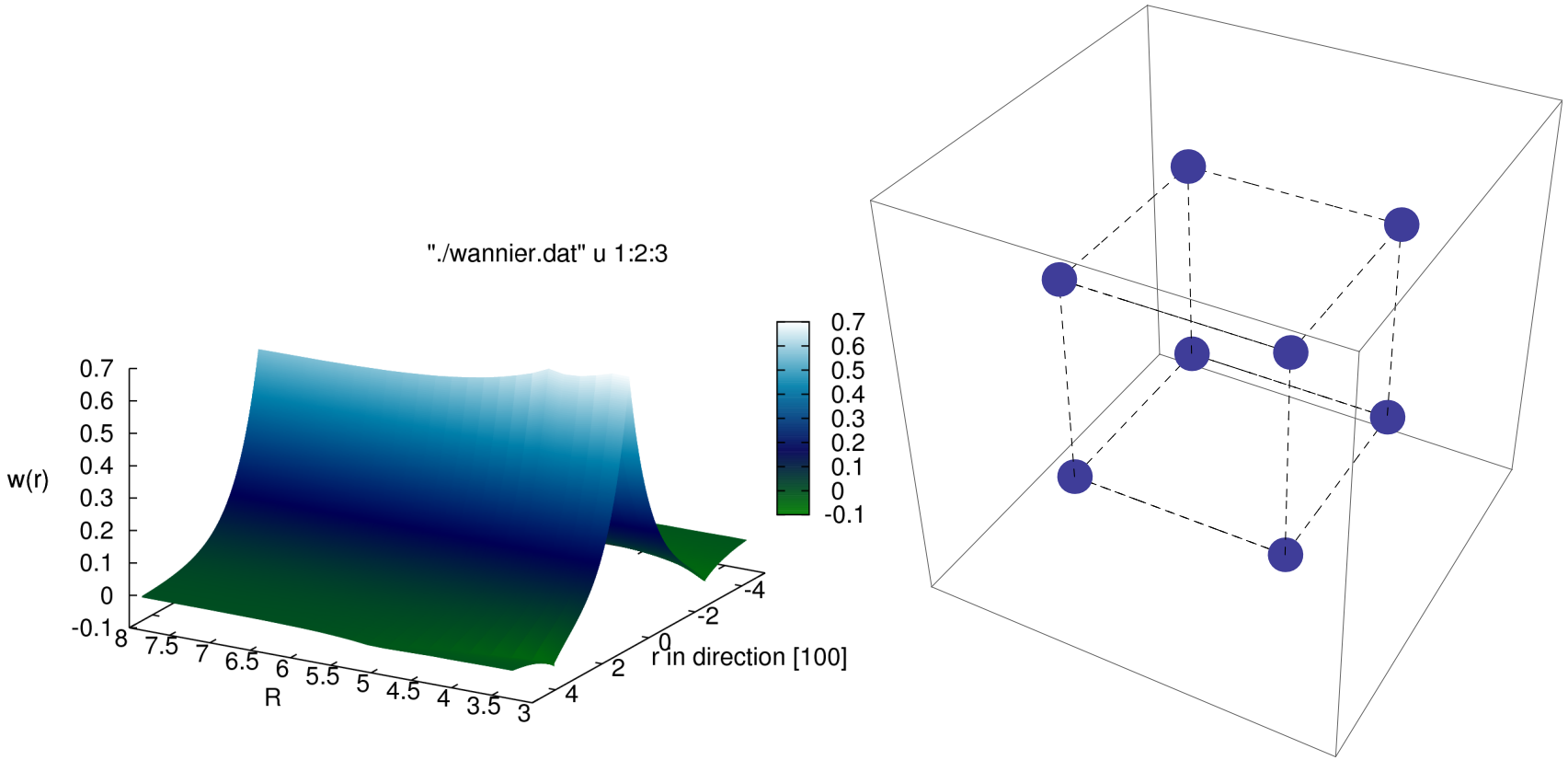


Figure: **L:** Wannier function in the direction of one of the lattice axis vs. lattice parameter R, **P:** SC structure

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

$$\mathcal{F}^{(SGA)} = -\frac{1}{\beta}\sum_{\vec{k}\sigma}\log\left(1+e^{-\beta E^{(SGA)}_{\vec{k}\sigma}}\right) + \Lambda\left(\lambda_n n + \lambda_m m + Ud^2 + \mu n\right), \tag{6}$$

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

$$E^{(SGA)}_{\vec{k}\sigma} \equiv q_\sigma \varepsilon_{\vec{k}} - \sigma\left(h+\lambda_m\right) - \left(\mu+\lambda_n\right),$$
$$q_\sigma = \frac{\left(\sqrt{\left(n_\sigma - d^2\right)\left(1-n_\sigma-n_{\overline{\sigma}}+d^2\right)} + d\sqrt{n_{\overline{\sigma}}-d^2}\right)^2}{n_\sigma\left(1-n_\sigma\right)} \tag{7}$$

β	n	m	d	λ_n	λ_m	μ
$\frac{1}{k_B T}$	occup. density	magne– tization	num. doub. occupancy	mol. field con. w. n	mol. field con. w. m	chem. pot.

Ground energy

$$\frac{E_G}{\Lambda} = \epsilon_a^{eff} + \frac{1}{\Lambda}\left(\sum_{ij\sigma} t_{ij}\left\langle a_{i\sigma}^{\dagger} a_{j\sigma}\right\rangle + \sum_i U\left\langle a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow}\right\rangle\right) \tag{8}$$

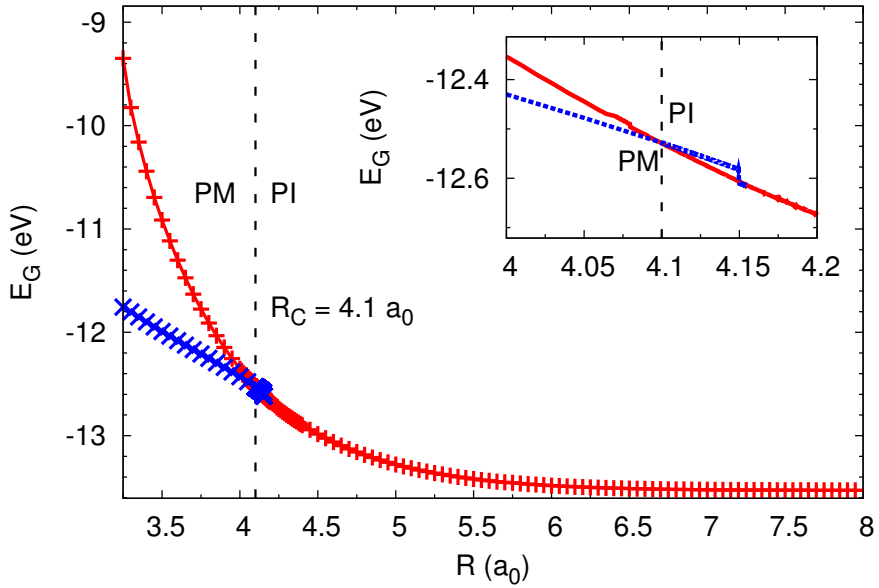
$$\Downarrow \text{ minimization}$$

$$\begin{aligned}\mathcal{K} = \epsilon_a^{eff}\sum_{i\sigma} n_{i\sigma} + \sum_{ij\sigma} t_{ij} q_\sigma a_{i\sigma}^{\dagger} a_{j\sigma} + \Lambda U d^2 - \mu\sum_{i\sigma} n_{i\sigma} \\ - \lambda_m\sum_i (m_i - m) - \lambda_n\sum_i (n_i - n)\end{aligned} \tag{9}$$

Remark

No Zero Point Motion of protons.

Type of transition



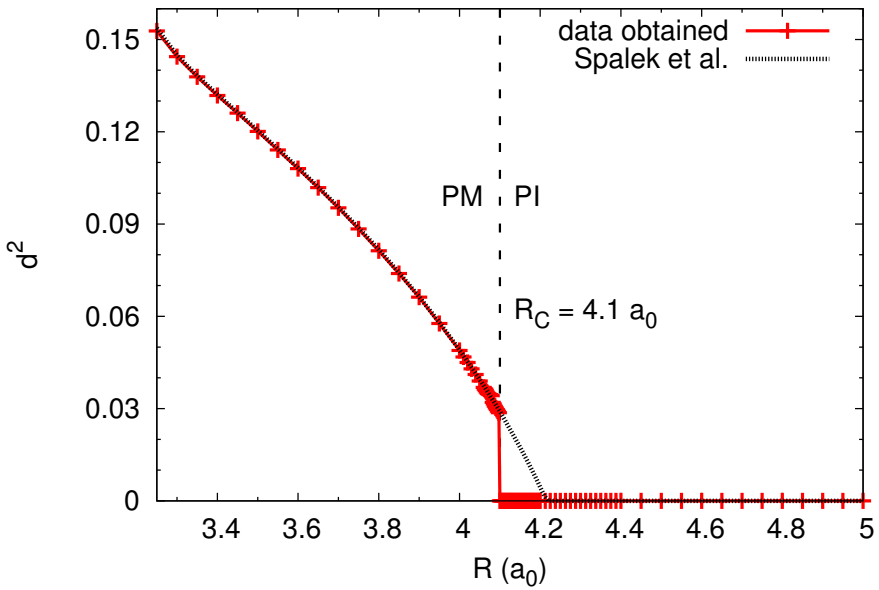


Figure: **G:** Ground energy of metallic (blue) and insulating (red) state. **D:** Double occupancies per site for our model vs. last publication.

I order

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

Zero Point Motion for ion chain

The uncertainties of momentum δP and distance between ions δR:

$$\Delta E = \frac{(\delta P)^2}{2M} + \frac{1}{2}\left(\frac{e^2}{R+\delta R} + \frac{e^2}{R-\delta R}\right) \overset{\delta R \ll R}{=} \frac{(\delta P)^2}{2M} + \frac{e^2}{R} + 2\frac{e^2}{R}\left(\frac{\delta R}{R}\right)^2 \tag{10}$$

using Heisenberg Principle $(\delta P)(\delta R) \geqslant \frac{3}{4}\hbar^2$ and minimizing with respect to δR

$$\begin{aligned} \delta R &= \left(\frac{3\hbar^2 R^3}{8Me^2}\right)^{\frac{1}{4}} \\ \Delta E &= \frac{e^2}{R} + \hbar\left(\frac{6e^2}{MR^3}\right)^{\frac{1}{2}} \end{aligned} \tag{11}$$

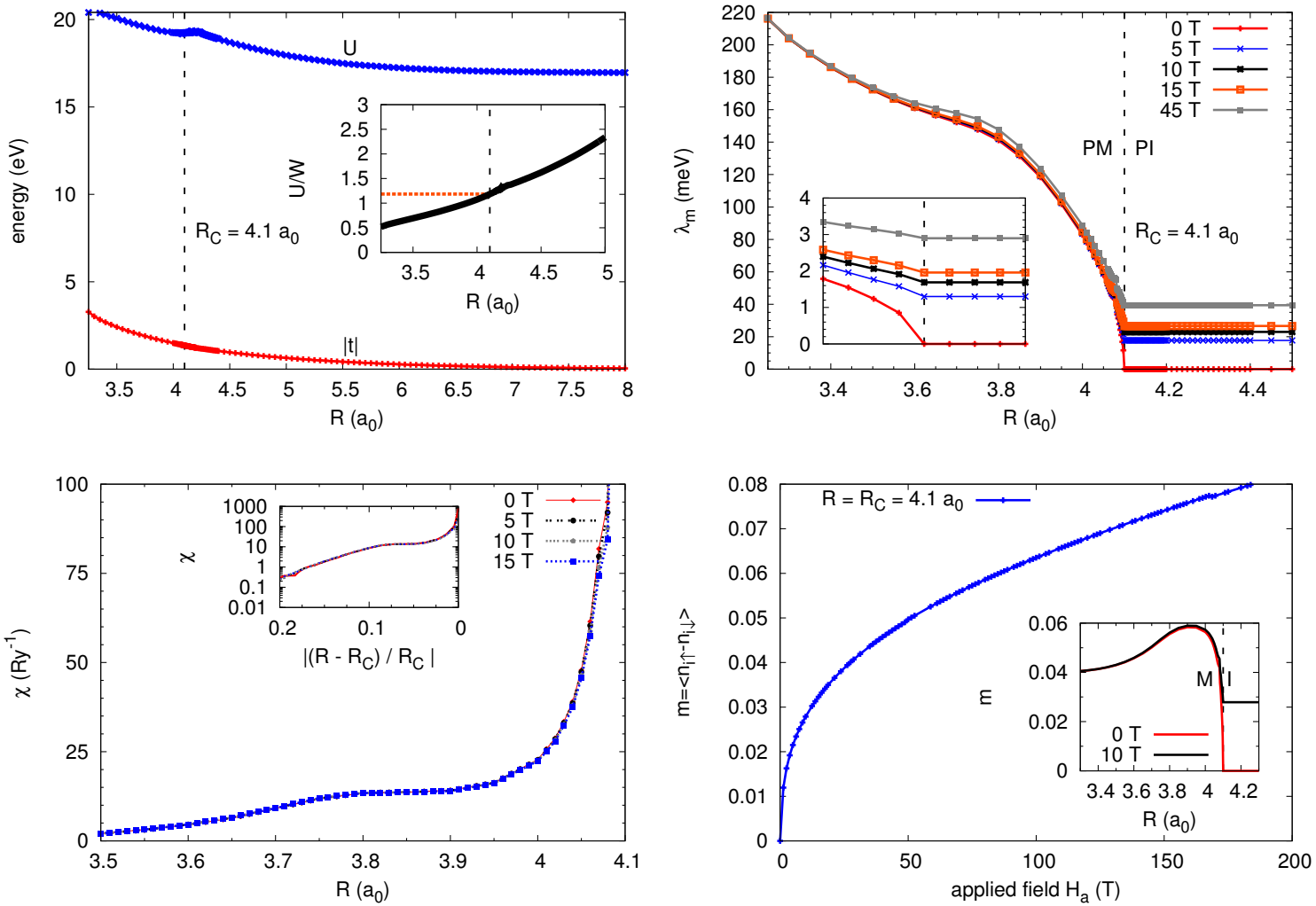


Figure: **GL:** microscopic parameters vs. lattice parameter R, **GP:** effective magnetic field λ_m vs. lattice parameter R, **DL:** magnetic susceptibility vs. lattice parameter R, **DP:** magnetization m vs. external magnetic field H_a

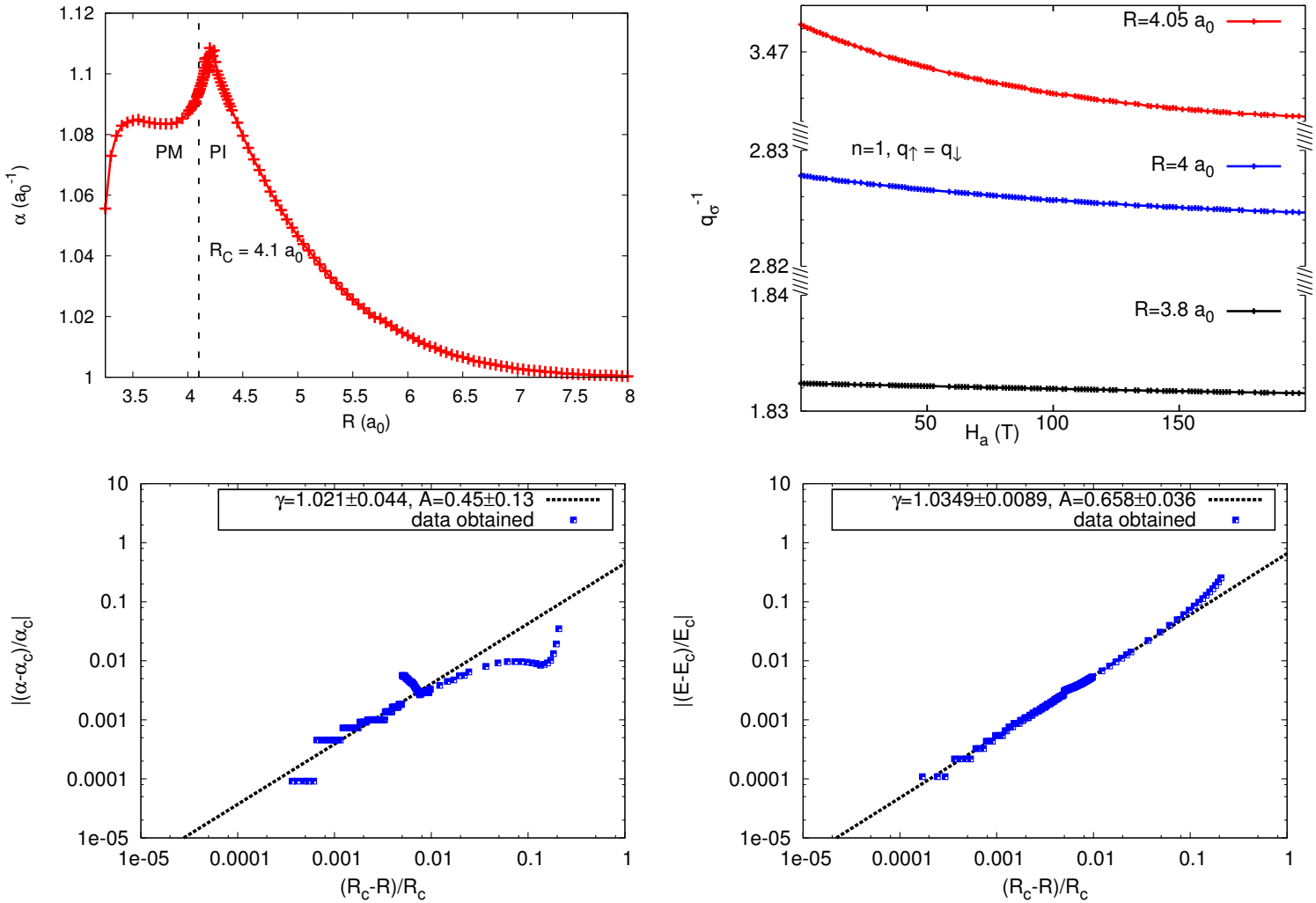
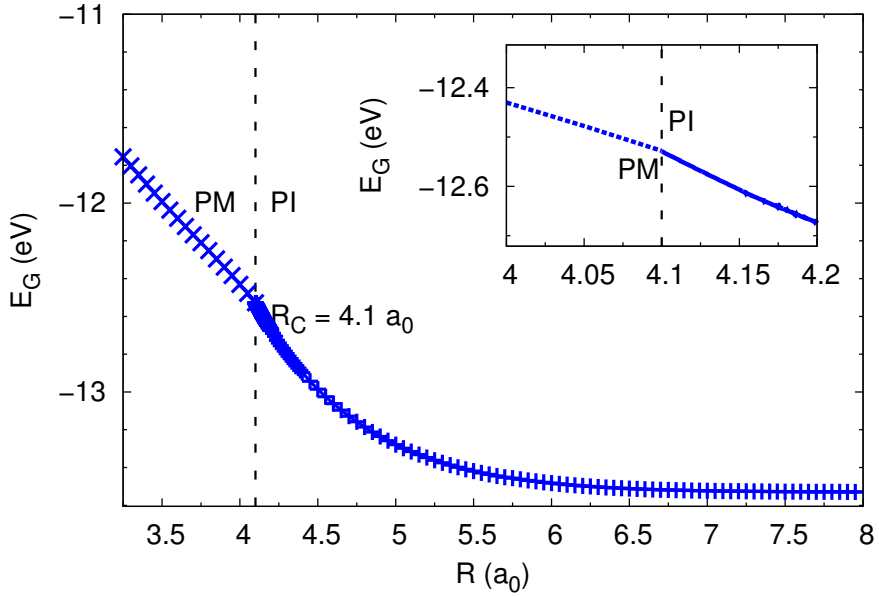


Figure: **GL:** reverse wave function size α vs. lattice parameter R, **GP:** effective mass enhancement vs. external magnetic field H_a, **D:** scaling of reverse wave function size α(**L**) and energy E(**P**) near critical point.



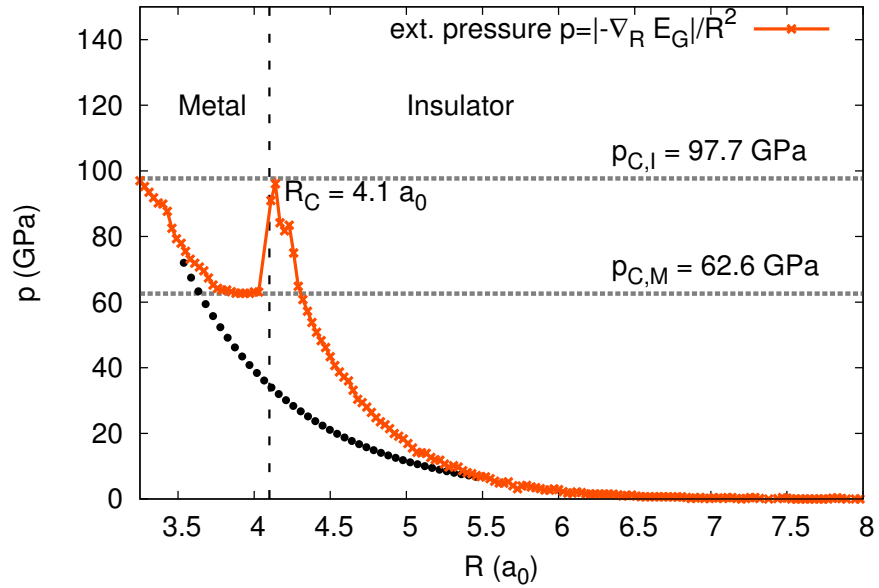


Figure: **G:** Ground energy vs. lattice parameter R, **D:** crystal stabilizing pressure vs. lattice parameter R - numerical (orange), naive approach with no phase transition (czarny).

Pressure stabilizing hydrogen crystal

$p_C = 97.7 GPa$

Remark

To do: bulk modulus

$\kappa = -\frac{1}{V}\frac{dV}{dp}$.

Next steps

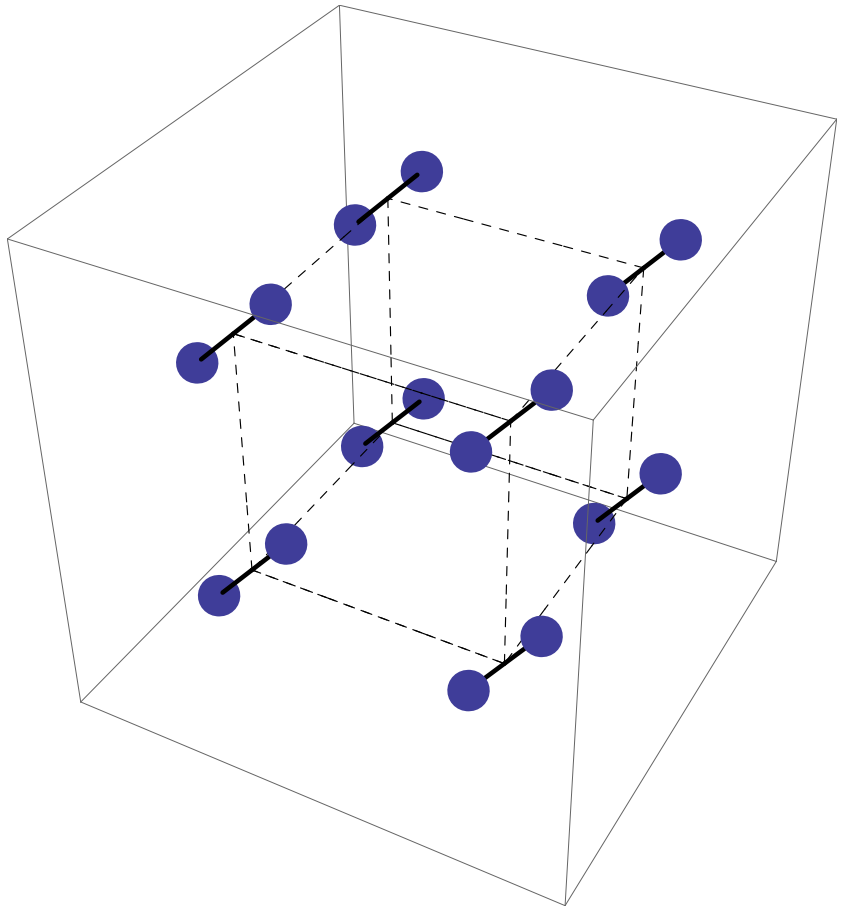
Modification 1

More realistic crystal structures:

- fcc
- hcp (antiferromagnetism ?)

Modification 2

Metal-insulator transition for molecular hydrogen



Electron-phonon interaction

Phononic part

$$\mathcal{H}_{ph} = \hbar\Omega_d \left(d^\dagger d + \frac{1}{2} \right) + \hbar\Omega_e \left(e^\dagger e + \frac{1}{2} \right) \tag{12}$$

Holstein term

$$\mathcal{H}_H = \hbar\Omega_d \xi \sum_\sigma \left(c_{1\sigma}^\dagger c_{1\sigma} - c_{2\sigma}^\dagger c_{2\sigma} \right) \left(d^\dagger + d \right) \tag{13}$$

Su-Schrieffer-Heeger term

$$\mathcal{H}_{SSH} = \hbar\Omega_e \zeta \sum_\sigma \left(c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma} \right) \left(e^\dagger + e \right) \tag{14}$$

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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		