Metallization of atomic solid hydrogen within the extended Hubbard model with renormalized Wannier wave functions

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INNOVATIVE ECONOMY
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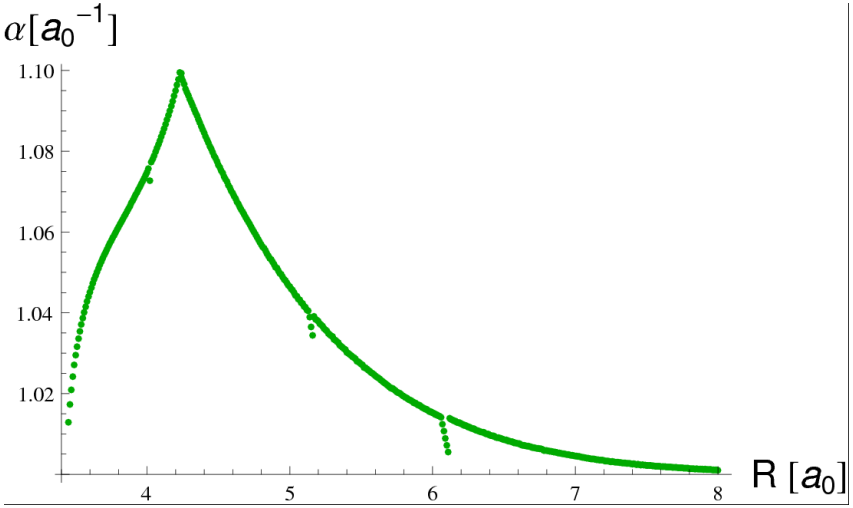
Outline

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.



J. Spałek, J. Kurzyk, R. Podsiadły, W. Wójcik, Eur. Phys. J. B **74**, 63-74 (2010)

Also

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

Base functions

Index i denotes a periodic function: $f_i(\mathbf{r}) \equiv f(\mathbf{r} - \mathbf{R}_i)$

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

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

constant	overlap dependent	minimization $\mathcal{H}_0 \overset{a.u.}{=} -\nabla^2 - 2|\mathbf{r} - \mathbf{R}_i|^{-1}$	minimization of E_G
z, p	β, γ	B_a, Γ_a	α

Accuracy of the STO-*n*G approximation

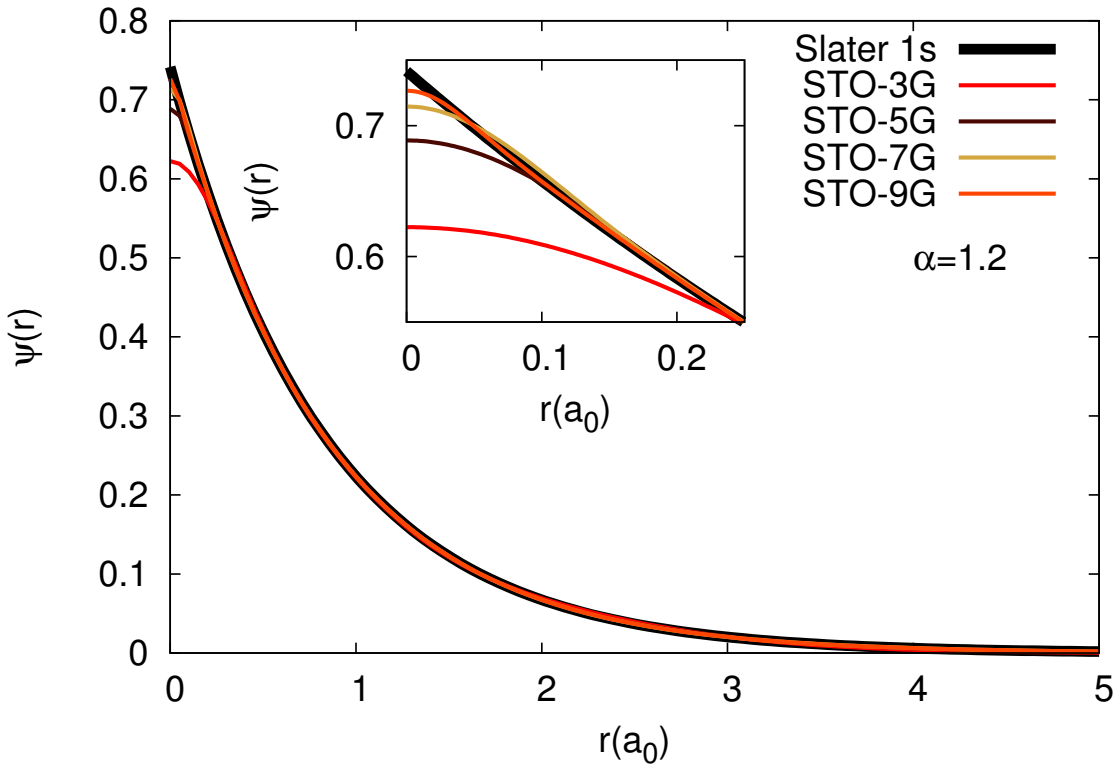


Figure: The accuracy of the STO-*n*G approximation for given basis size $n \in \{3,\ 5,\ 7,\ 9\}$ and inverse wave function size α set to $1.2a_0^{-1}$.

Hamiltonian

We start from the extended Hubbard model:

$$\mathcal{H}_{EH} = \epsilon_a \sum_i n_i + \sum_{i \neq j,\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} K_{ij} n_i n_j + \sum_{i<j} V_{ion-ion}\left(\mathbf{R}_i - \mathbf{R}_j\right) - \sum_{i,\sigma} \sigma h n_{i\sigma}, \tag{3}$$

where ϵ_a is the atomic energy per site, t_{ij} the hopping integral, U the intraatomic interaction, and K_{ij} the interatomic interaction. $V_{ion-ion}\left(\mathbf{R}_i - \mathbf{R}_j\right) = \frac{2}{\left|\mathbf{R}_i - \mathbf{R}_j\right|}$ is classical Coulomb repulsion and $h = \frac{1}{2} g \mu_B H_a$ the reduced magnetic field.

Microscopic parameters

Values

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

$$
\begin{aligned}
t_{ij} &= \langle w_i | \, \mathcal{H}_1 \, | w_j \rangle \,, \\
K_{ij} &= \left\langle w_i w_j \left| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| w_i w_j \right\rangle , \\
U = K_{ii} &= \left\langle w_i w_i \left| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| w_i w_i \right\rangle , \\
\epsilon_a &= \langle w_i | \, \mathcal{H}_1 \, | w_i \rangle \,.
\end{aligned}
\tag{4}
$$

Hamiltonian

We rearrange the Hamiltonian in a way

$$\mathcal{H}_{EH} = \epsilon_a^{eff} \sum_i n_i + \sum_{i \neq j, \sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} K_{ij} \delta n_i \delta n_j - \sum_{i,\sigma} \sigma h n_{i\sigma}, \tag{5}$$

with effective atomic energy per site

$$\epsilon_a^{eff} = \epsilon_a + \frac{1}{2\Lambda} \sum_{i \neq j} \left(K_{ij} + \frac{2}{|R_j - R_i|} \right), \tag{6}$$

and $\delta n = 1 - n$.

SGA:

Ground-state energy

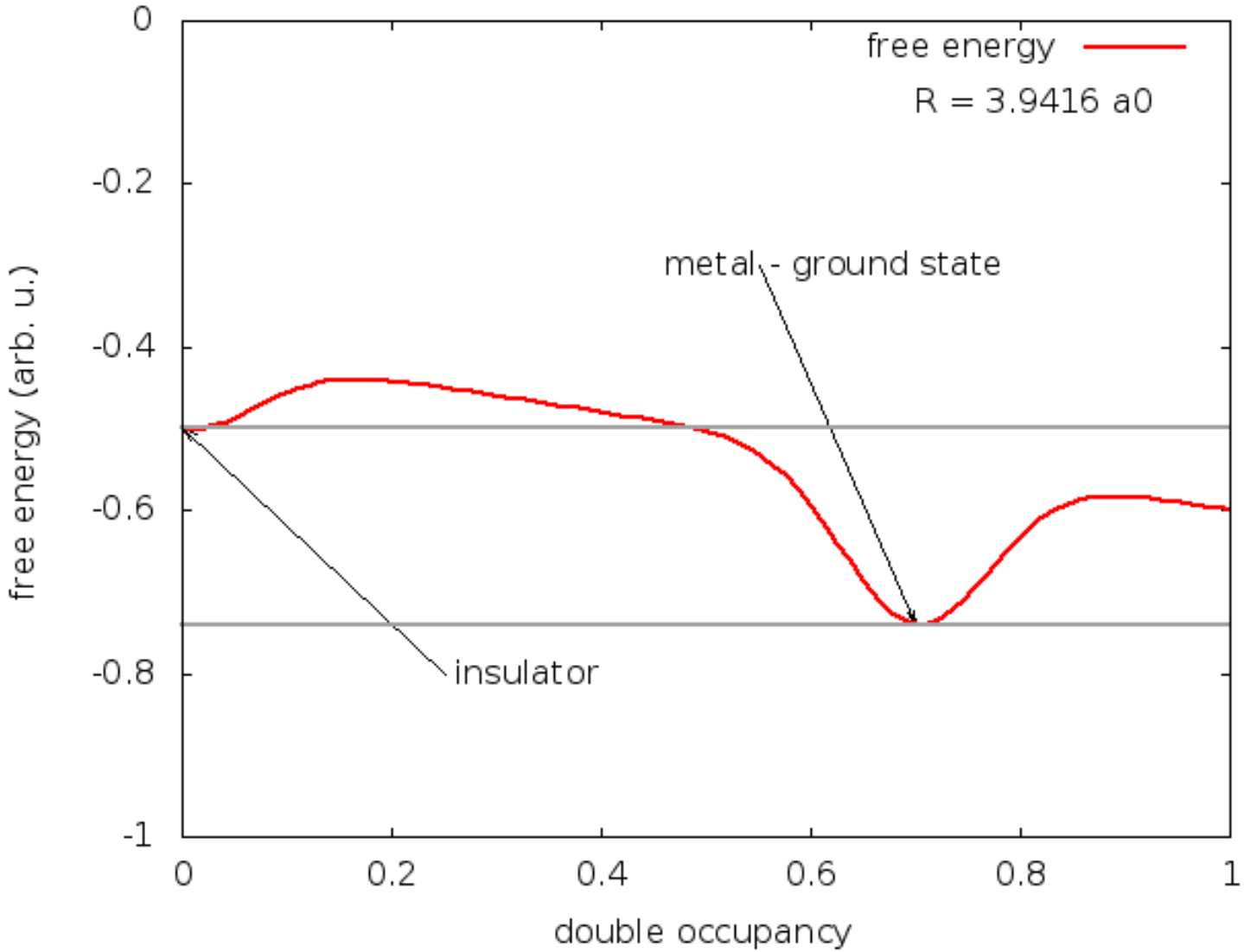
$$\frac{E_G}{\Lambda} = \epsilon_a^{eff} + \frac{1}{\Lambda}\left(\sum_{ij\sigma} t_{ij}\left\langle a_{i\sigma}^{\dagger} a_{j\sigma}\right\rangle + \sum_i U\left\langle a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow}\right\rangle\right) \tag{7}$$

$$\Downarrow \text{ minimization}$$

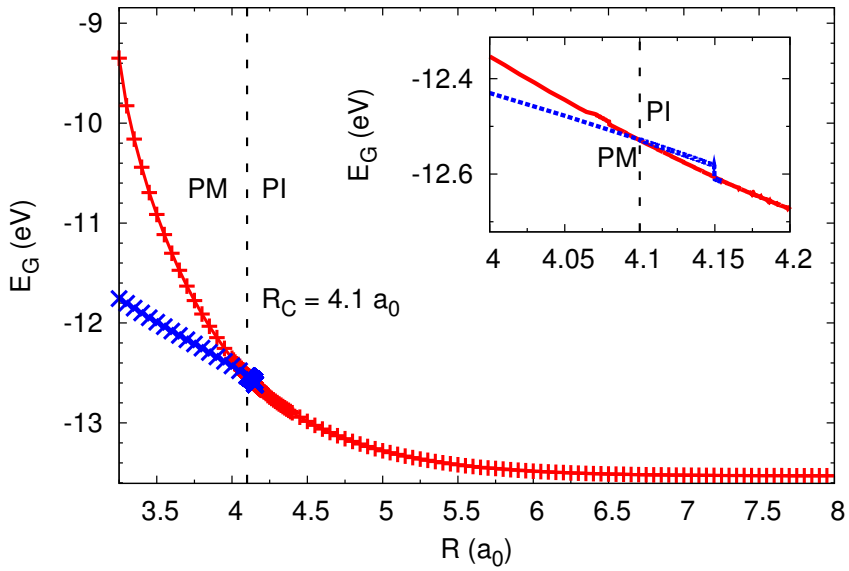
$$\begin{aligned}\mathcal{K} = \epsilon_a^{eff}\sum_{i\sigma} n_{i\sigma} + \sum_{ij\sigma} t_{ij} q_\sigma a_{i\sigma}^{\dagger} a_{j\sigma} + \Lambda U d^2 - \mu\sum_{i\sigma} n_{i\sigma} \\ - \lambda_m\sum_i (m_i - m) - \lambda_n\sum_i (n_i - n)\end{aligned} \tag{8}$$

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

Qualitive behavior of free energy around Mott–Hubbard Transition



Nature of transition



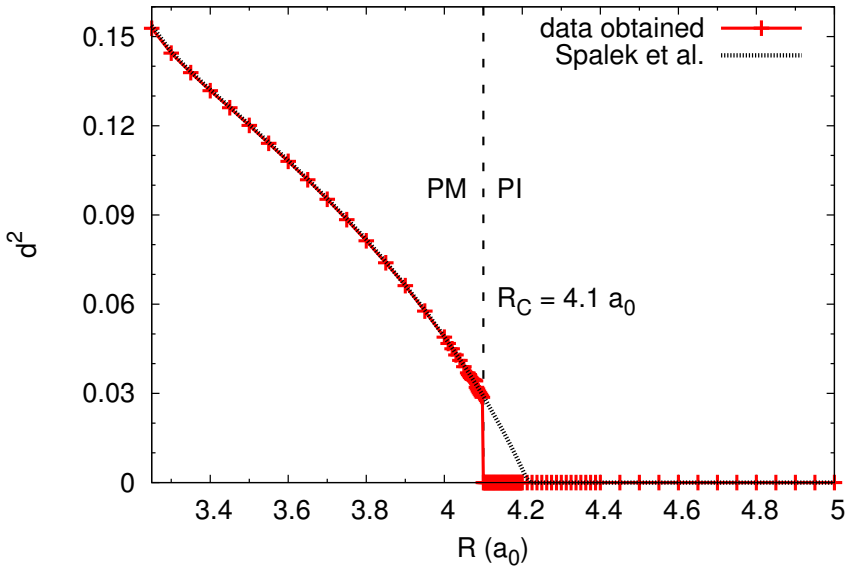


Figure: **G:** Ground-state energy of metallic (blue) and insulating (red) state. **D:** Double occupancies per site for our model vs. last publication.

1st order

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

The effect of the basis resolution

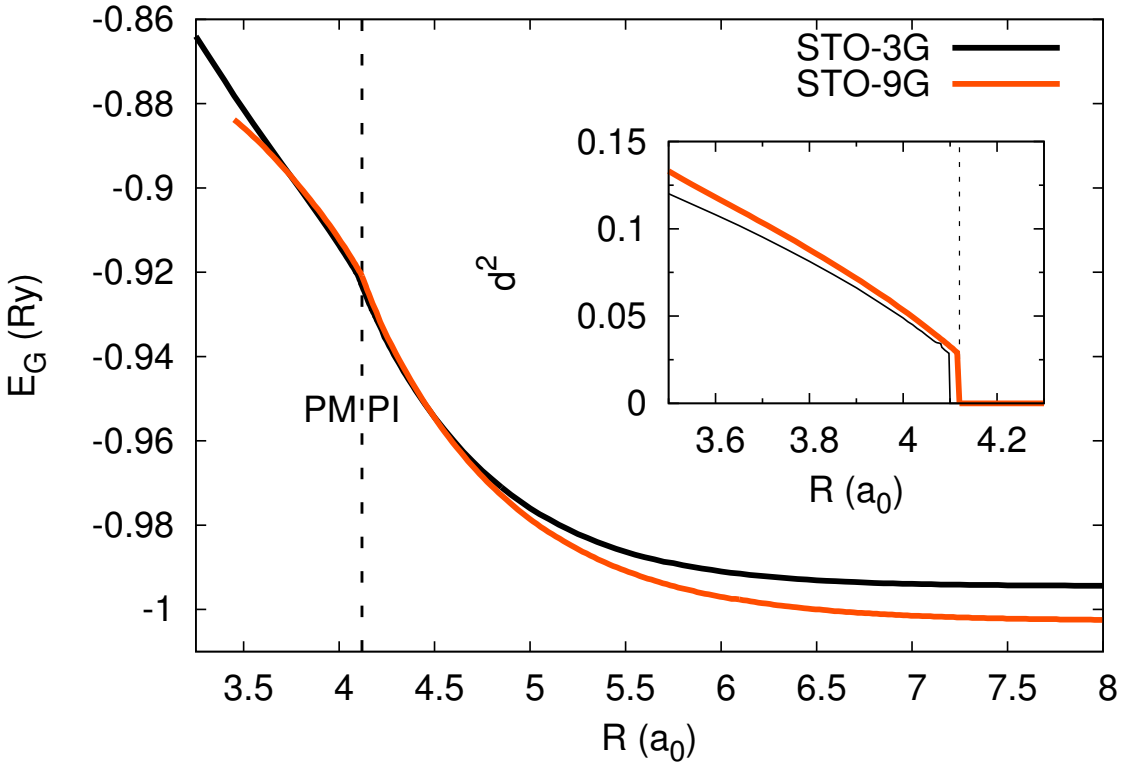


Figure: The effect of the basis resolution on the results. The ground-state energy E_G versus the lattice parameter R. Inset: the double occupancy mean-field d^2 related to the conductivity of the model system versus the lattice parameter R.

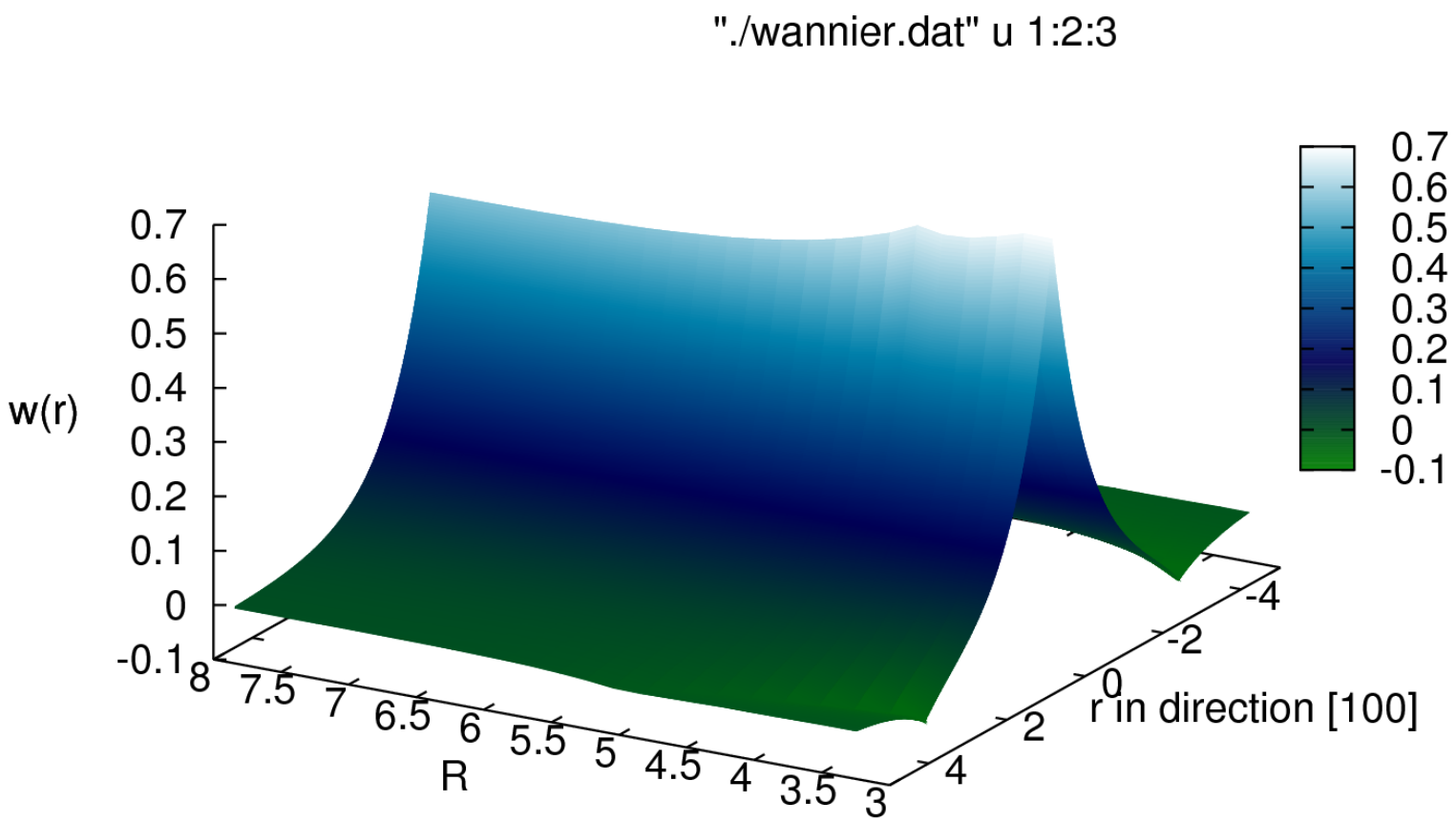


Figure: Overall space profiles of the renormalized Wannier function for sc lattice as a function of lattice parameter R and along [100] direction r.

Zero-point motion for ion lattice

The uncertainties of momentum δP and distance between ions δR:

$$\Delta E = \frac{(\delta P)^2}{2M} + \sum_{i=1}^{3} \frac{1}{2} \left(\frac{2}{R + \delta R^i} + \frac{2}{R - \delta R^i} \right) \tag{9}$$

using Heisenberg Principle $(\delta \mathbf{P})^2 (\delta \mathbf{R})^2 \geqslant \frac{3}{4}$ 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**
$\Delta E - \frac{6}{R}$ (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

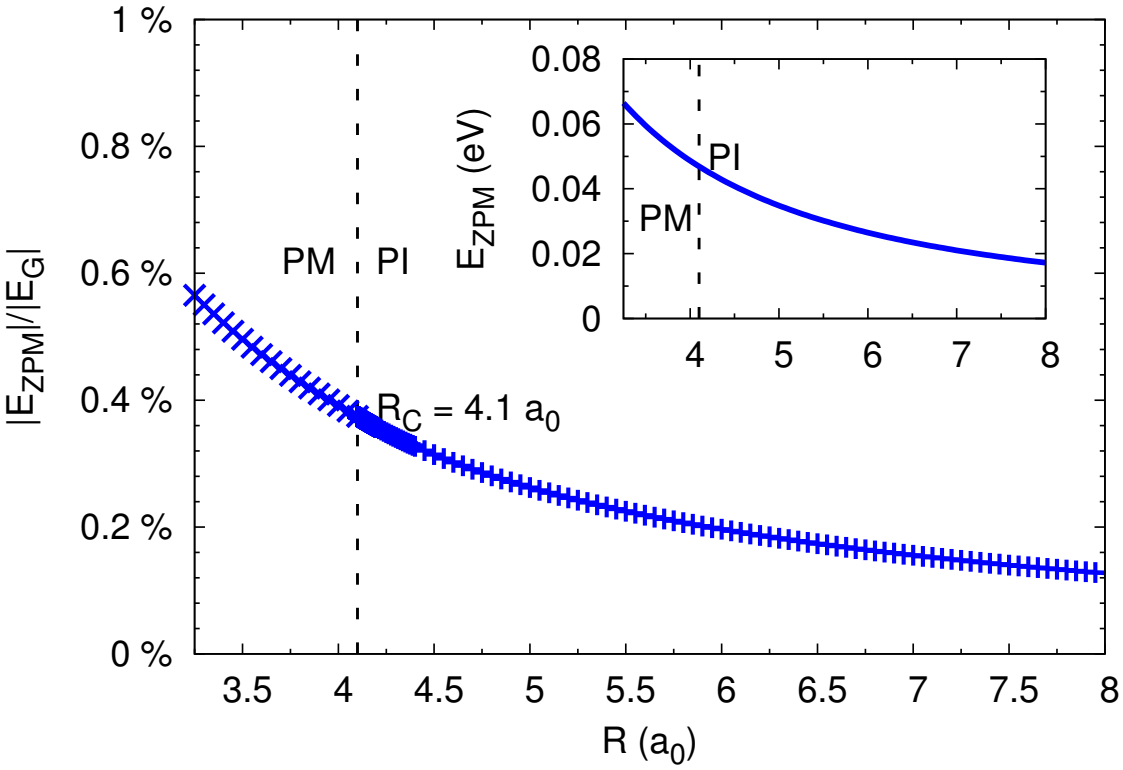


Figure: The relative magnitude of the zero-point motion energy with respect to ground state vs. lattice parameter R.
Inset: The explicit value of the energy of zero-point motion vs. lattice parameter R.

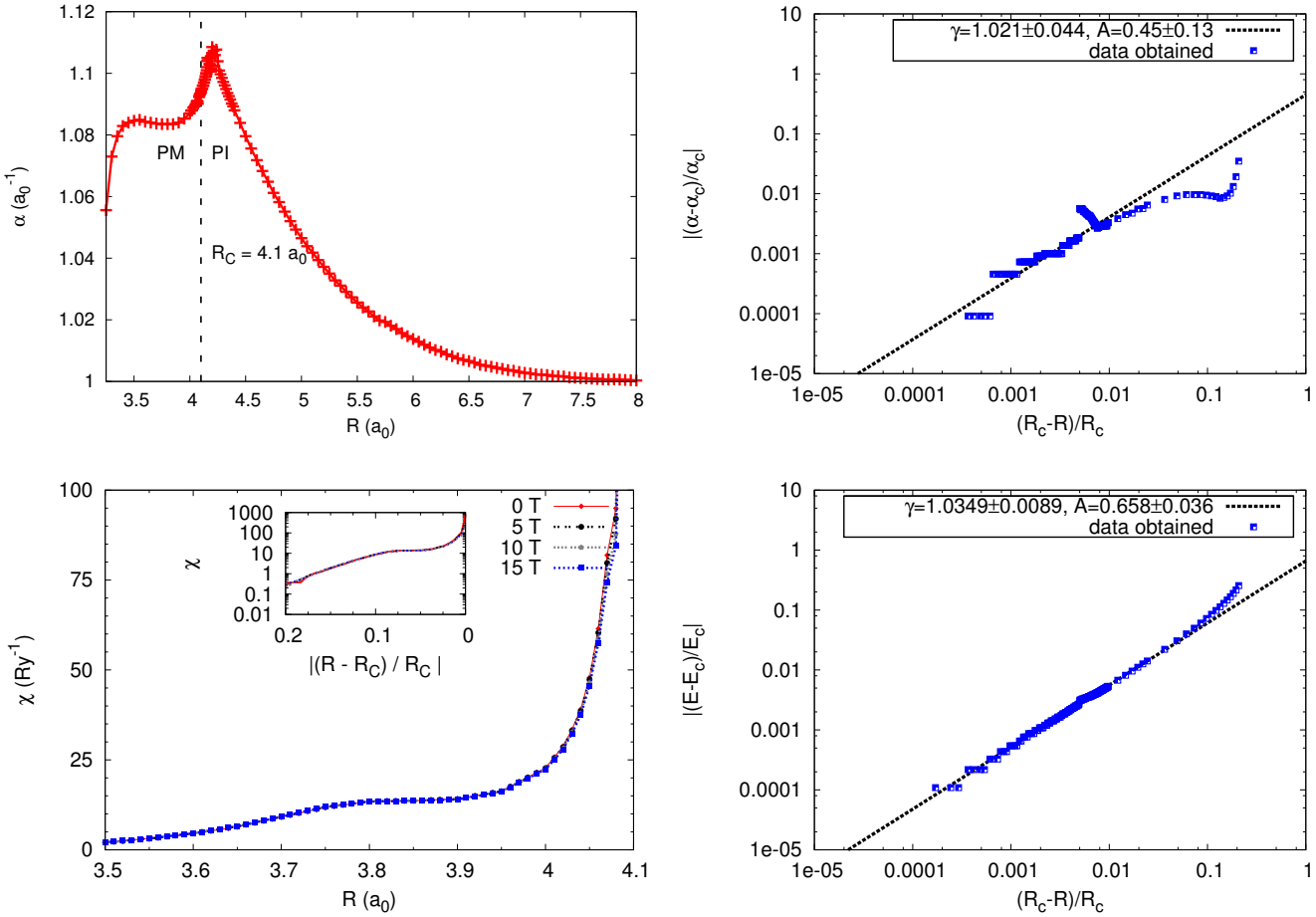


Figure:

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 ($\sim A((R_C - R)/R_C)^{\gamma}$).

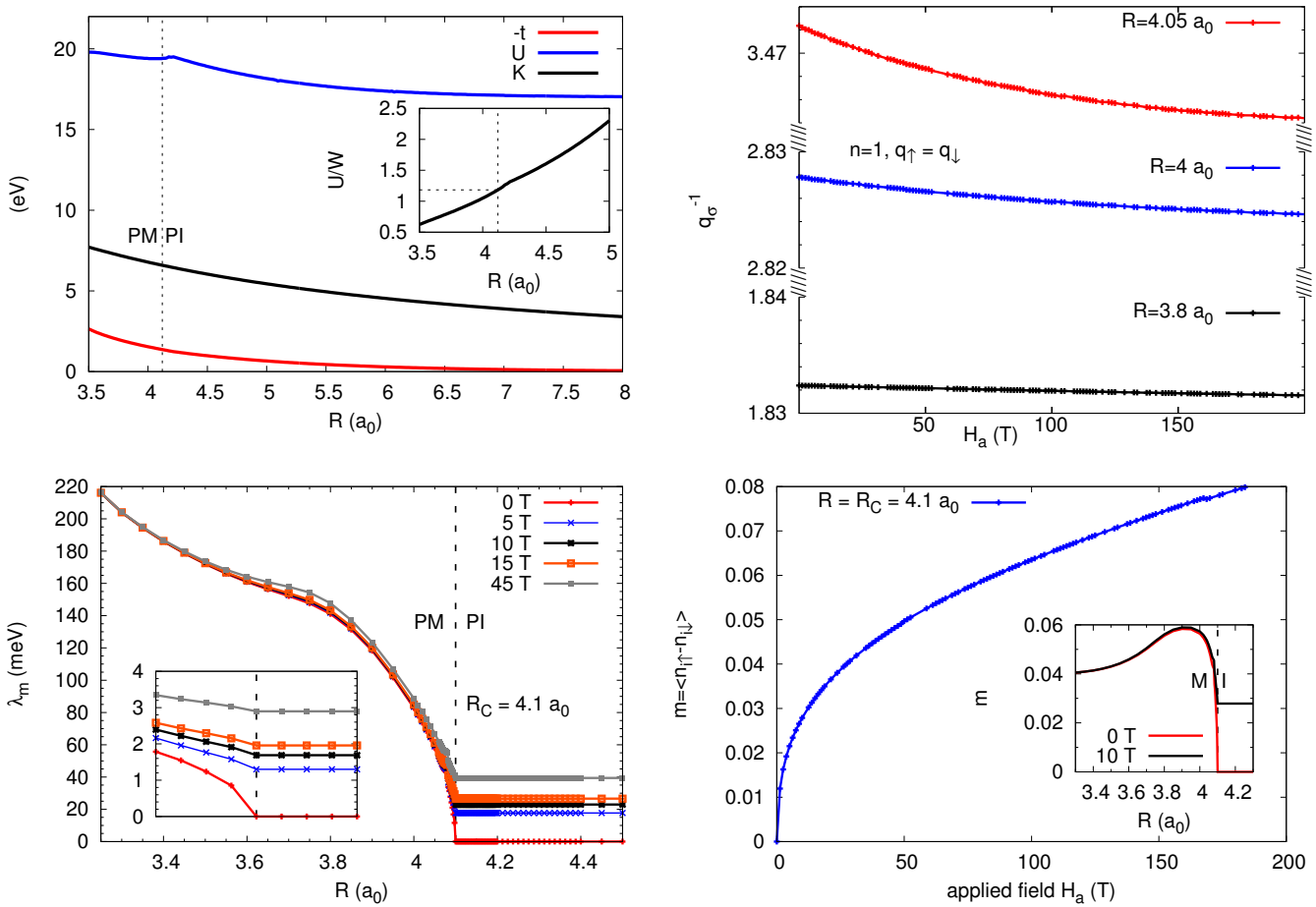


Figure: **TL:** microscopic parameters vs. lattice parameter R, **TR:** effective mass enhancement vs. external magnetic field H_a, **BL:** effective magnetic field λ_m vs. lattice parameter R, **BR:** magnetization m vs. external magnetic field H_a

Mott and Hubbard Criteria

Mott Criterion

$$n_C^{1/3} a_B \sim 0.2, \qquad (10)$$

where n_C is the particle density and a_B is the effective Bohr radius.

The result

$$n_C = R_C^{-3} \quad a_B = \alpha_C^{-1}$$

$$R_C^{-1} \alpha_C^{-1} \approx 0.22, \qquad (11)$$

Hubbard Criterion

$$\frac{U}{W} = 1, \qquad (12)$$

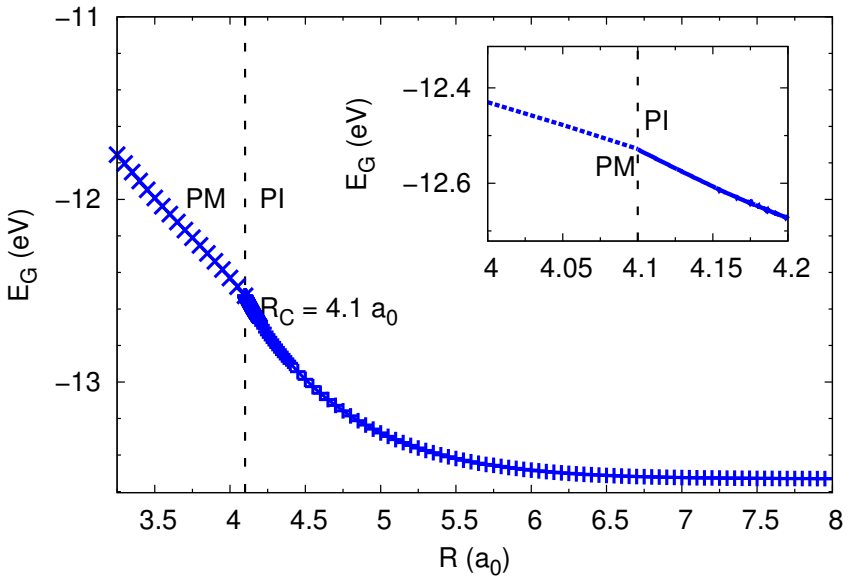
where U is the on-site electron repulsion and W is the bandwidth.

The result

$$W = 2z|t|,$$

where z is the number of nearest neighbors ($z = 6$ for sc).

$$\frac{U_C}{W_C} \approx 1.18, \qquad (13)$$



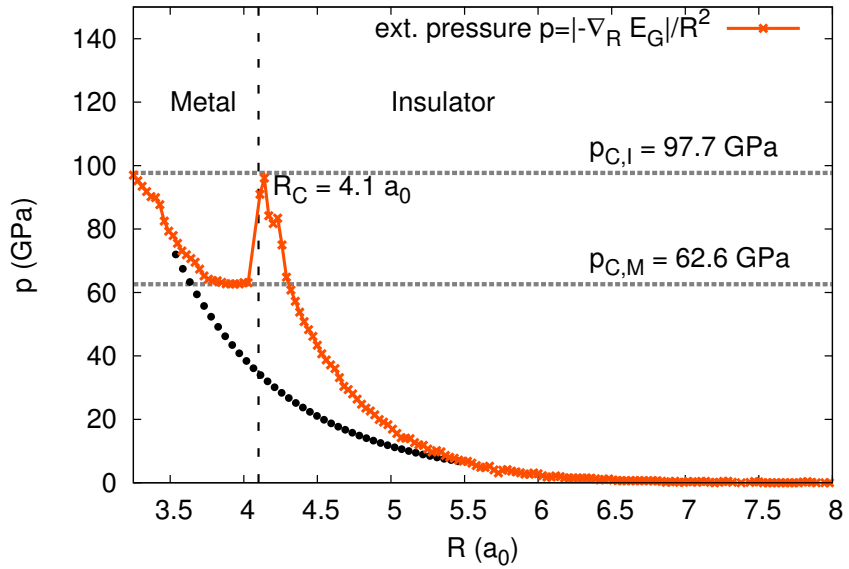
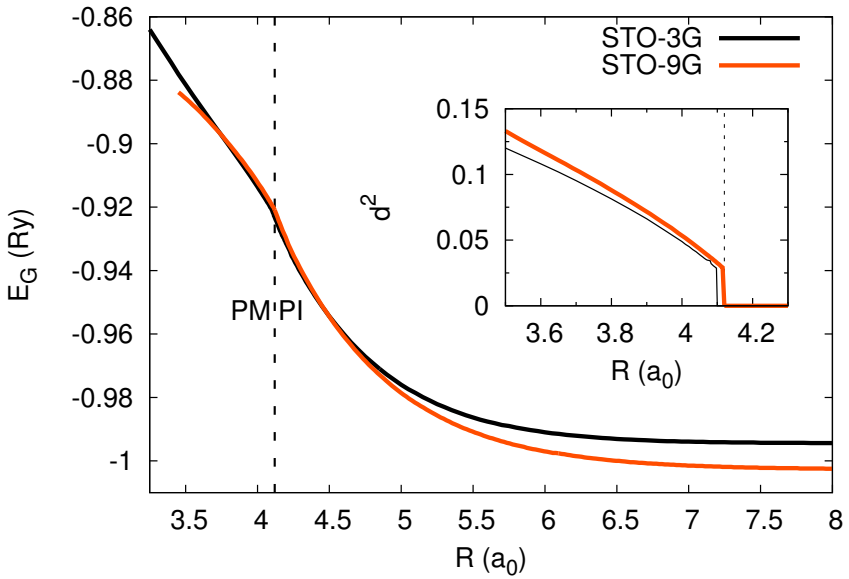


Figure: **top:** Ground energy vs. lattice parameter R, **bottom:** crystal stabilizing pressure vs. lattice parameter R - numerical (orange) and naive fit (black).

Pressure stabilizing hydrogen crystal

$p_C = 97.7 GPa$

APK, J. Spałek, K. Kurzyk, W. Wójcik, Eur. Phys. J. B **86**, 252 (2013)



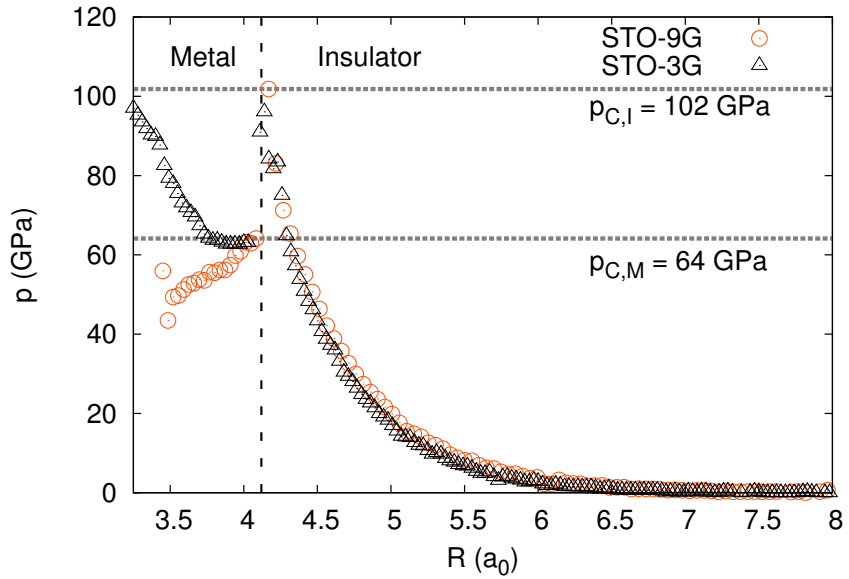


Figure: **top:** Ground energy vs. lattice parameter R for two different STO-nG basis, **bottom:** crystal stabilizing pressure vs. lattice parameter R for two different STO-nG basis.

Pressure stabilizing hydrogen crystal

$p_C = 102 GPa$

Thank you!

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		

Table: B_a and Γ_a coefficients of the STO-nG basis.

STO-3G		STO-5G		STO-7G		STO-9G		
B_a	Γ_a^2	B_a	Γ_a^2	B_a	Γ_a^2	B_a	Γ_a^2	a
0.7079069	0.4037496	0.4862397	0.3428813	0.3347926	0.3073439	0.2333815	0.2832535	1
0.3460096	0.8919739	0.4687430	0.6489746	0.4947580	0.5341995	0.4735227	0.4656983	2
0.0691531	1.9705714	0.1446282	1.2283203	0.2218991	0.9285009	0.2825582	0.7656564	3
		0.0307340	2.3248533	0.0674427	1.6138428	0.1065788	1.2588187	4
		0.0093803	4.4002717	0.0188009	2.8050467	0.0341750	2.0696289	5
				0.0038829	4.8754978	0.0099417	3.4026852	6
				0.0018480	8.4741829	0.0032307	5.5943683	7
						0.0006094	9.1977233	8
						0.0004466	15.1220138	9

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

$$\begin{aligned}\mathcal{F}^{(SGA)} = &-\frac{1}{\beta}\sum_{\mathbf{k}\sigma}\log\left(1+e^{-\beta E^{(SGA)}_{\mathbf{k}\sigma}}\right)\\ &+\Lambda\left(\lambda_n n+\lambda_m m+Ud^2+\mu n\right),\end{aligned} \tag{14}$$

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

$$\begin{aligned}E^{(SGA)}_{\mathbf{k}\sigma} &\equiv q_\sigma\varepsilon_{\mathbf{k}}-\sigma\left(h+\lambda_m\right)-\left(\mu+\lambda_n\right),\\ q_\sigma &= \frac{\left(\sqrt{\left(n_\sigma-d^2\right)\left(1-n_\sigma-n_{\overline{\sigma}}+d^2\right)}+d\sqrt{n_{\overline{\sigma}}-d^2}\right)^2}{n_\sigma\left(1-n_\sigma\right)}\end{aligned} \tag{15}$$