

1 Conventions

First of all, let us agree to use atomic units, i.e. to measure lengths in Bohr and energies in Hartree.

We arrange N hydrogen atoms on a ring of radius R , such that the distance between neighbouring atoms is a desired value ΔR :

$$R = \frac{\Delta R}{2 \sin(\alpha/2)} \quad , \alpha = \frac{2\pi}{N} \quad (1)$$

For each atom $i = 0 \dots N-1$ we define the atomic orbital (we use the minimal STO-6G basis)

$$\langle r|i \rangle_A = \phi_i(r) = \sum_{k=1}^n c_k g(\alpha_k, r - r_i) \quad , \quad (2)$$

with $r_i = \cos(i\alpha)e_x + \sin(i\alpha)e_y$, $n = 6$ and

$$g(\alpha, r) = \left(\frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha r^2} \quad . \quad (3)$$

The coefficients α_k , c_k read (from <https://bse.pnl.gov/bse/portal>):

k	α_k	c_k
1	35.52322122	0.00916359628
2	6.513143725	0.04936149294
3	1.822142904	0.16853830490
4	0.625955266	0.37056279970
5	0.243076747	0.41649152980
6	0.100112428	0.13033408410

and matrix elements between ϕ_i , ϕ_j are computed with formulas taken from the book "Modern Quantum Chemistry" by A. Szabo and N. Ostlund.

2 Orthogonalisation of the basis

Atomic orbitals are localised around atomic sites in the ring, but not mutually orthogonal. For instance, the overlap between ϕ_1 , ϕ_2 is:

$$\langle 1|2 \rangle_A = \sum_{ij} c_i c_j \left(\frac{2\alpha_i}{\pi} \right)^{\frac{3}{4}} \left(\frac{2\alpha_j}{\pi} \right)^{\frac{3}{4}} \int d^3r e^{-\alpha_i|r|^2} e^{-\alpha_j|r-r_1|^2} \quad (4)$$

and since:

$$\int d^3r e^{-\alpha_i|r|^2} e^{-\alpha_j|r-r_1|^2} = \left(\frac{\pi}{\alpha_i + \alpha_j} \right)^{\frac{3}{2}} e^{-\frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} |r_1|^2} \quad (5)$$

it finally reads

$$\langle 1|2\rangle = \sum_{ij} c_i c_j \left(\frac{2\alpha_i}{\pi} \right)^{\frac{3}{4}} \left(\frac{2\alpha_j}{\pi} \right)^{\frac{3}{4}} \left(\frac{\pi}{\alpha_i + \alpha_j} \right)^{\frac{3}{2}} e^{-\frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} |r_1|^2} . \quad (6)$$

Therefore $\langle 1|2\rangle_A \neq 0$.

We now construct an orthonormal basis of localised orbitals addapting the procedure for constructing the tight binding Hamiltonian to the case of electrons on this H ring.

Thanks to the ring geometry the overlap matrix is a cyclic Toeplitz matrix:

$$S_{ij} = s(i - j) \quad , \quad s(l + N) = s(l) \quad . \quad (7)$$

So, writing

$$s(l) = \sum_{p=0}^{N-1} \tilde{s}_p \frac{e^{i\frac{2\pi}{N}pl}}{N} \rightarrow S_{ij} = \sum_{p=0}^{N-1} \tilde{s}_p (u_p)_i (u_p)_j^* \quad , \quad (8)$$

where $(u_p)_l = \frac{e^{i\frac{2\pi}{N}pl}}{\sqrt{N}}$ and

$$\tilde{s}_p = \sum_{l=0}^{N-1} s(l) e^{-i\frac{2\pi}{N}pl} \quad , \quad (9)$$

we find that

- $\sum_{j=0}^{N-1} (u_q)_j (u_p)_j^* = \sum_{j=0}^{N-1} \frac{e^{i\frac{2\pi}{N}(q-p)j}}{N} = \delta_{qp}$
- $(Su_p)_i = \tilde{s}_p (u_p)_i$
- the states

$$|p\rangle_B = \frac{1}{\sqrt{\tilde{s}_p}} \sum_{j=0}^{N-1} (u_p)_j |j\rangle_A \quad (10)$$

are an orthonormal set:

$$\langle p|q\rangle_B = \frac{1}{\sqrt{\tilde{s}_p \tilde{s}_q}} \sum_{j,l=0}^{N-1} (u_p)_l^* (u_q)_j \langle l|j\rangle_A = \frac{1}{\sqrt{\tilde{s}_p \tilde{s}_q}} \sum_{j,l=0}^{N-1} (u_p)_l^* S_{lj} (u_q)_j = \delta_{qp} \quad (11)$$

We call those states $|p\rangle_B$ because they are the analogue of the Bloch waves in this ring geometry. Indeed, they are delocalised over the ring as we understand considering

$$|0\rangle_B = \frac{1}{\sqrt{\tilde{s}_0} N} \sum_{j=0}^{N-1} |j\rangle_A \quad (12)$$

We can produce a basis of "Wannier" orbitals, localised and orthonormal, by performing the Fourier transform

$$|l\rangle_W = \sum_{p=0}^{N-1} (u_p)_l^* |p\rangle_B \quad (13)$$

We have that

- $\sum_{p=0}^{N-1} (u_p)_m (u_p)_l^* = \sum_{p=0}^{N-1} \frac{e^{i \frac{2\pi}{N} (m-l)p}}{N} = \delta_{ml}$
- $\langle l|m\rangle_W = \delta_{lm}$
-

$$|l\rangle_W = \sum_{j=0}^{N-1} \sum_{p=0}^{N-1} \frac{(u_p)_{j-l}}{\sqrt{\tilde{s}_p} N} |j\rangle_A \equiv \sum_{j=0}^{N-1} W_{lj} |j\rangle_A \quad (14)$$

- $\lim_{N \rightarrow \infty} W_{lj} = \delta_{lj}$ (no pathologies)
- for a one-body operator A

$$(A_W)_{lm} = \langle l|A|m\rangle_W = \sum_{ij=0}^{N-1} W_{li}^* (O_A)_{ij} W_{mj} \quad (15)$$

- for a two-body operator A

$$(A_W)_{ll'mm'} = \langle ll'|A|mm'\rangle_W = \sum_{ijj'=0}^{N-1} W_{li}^* W_{l'i'}^* (O_A)_{ii'jj'} W_{mj} W_{m'j'} \quad (16)$$

In the basis of "Wannier" orbitals, we might either retain all the matrix elements of the core and interaction Hamiltonian, and working with the operator:

$$H = \sum_{lm\sigma} (T_W)_{lm} a_{l\sigma}^+ a_{m\sigma} + \frac{1}{2} \sum_{lm'l'm'\sigma\rho} (U_W)_{ll'mm'} a_{l\sigma}^+ a_{l'\rho}^+ a_{m'\rho} a_{m\sigma} \quad (17)$$

or retain just part of those matrix elements, ending up with a simplified operator like the Hubbard hamiltonian:

$$H = \sum_{lm}^* \sum_{\sigma} (T_W)_{lm} a_{l\sigma}^+ a_{m\sigma} + \sum_l (U_W)_{lll} a_{l\uparrow}^+ a_{l\downarrow}^+ a_{l\downarrow} a_{l\uparrow} \quad (18)$$

where $*$ indicates summation over nearest neighbors only (in PBC). With this approach we could compute the elements $U = (U_W)_{lll}$ and $t = (T_W)_{l,l+1}$ and take advantage of the exact solution by Lieb and Wu.

Or we could retain more matrix elements and obtain a richer model:

$$H = \sum_{lm}^{**} \sum_{\sigma} (T_W)_{lm} a_{l\sigma}^{\dagger} a_{m\sigma} + \sum_{ll'} (U_W)_{ll'} a_{l\uparrow}^{\dagger} a_{l'\downarrow}^{\dagger} a_{l'\downarrow} a_{l\uparrow} \quad (19)$$

where ** indicates summation over nearest and second-nearest neighbors, and the interaction tensor can be written as $\sum_l \rho_{l\uparrow} \rho_{l\downarrow} + \sum_{l \neq l'} V(l, l') \rho_{l\uparrow} \rho_{l'\downarrow}$ where $\rho_{l\uparrow}$ indicates the density of spin-up electrons at site l .

3 Some Results

In this table we list:

- the **binding energy** of H chains in the TDL, from AFQMC (minimal basis)
- the $U/|t|$ ratio and the t hopping amplitude in the Wannier basis
- the binding energy of the 1D Hubbard model with $U/|t|$, t as in the previous case, obtained from numeric integration of the Lieb-Wu equation of state

$$\frac{E}{|t|} = -4 \int_0^{\infty} \frac{J_0(\omega) J_1(\omega)}{\omega(1 + e^{\frac{\omega}{2} \frac{U}{|t|}})} d\omega \quad (20)$$

- the difference between the two binding energies

R	BE_{afqmc}	$U/ t $	t	t'	BE_{wann}	$BE_{wann} - BE_{afqmc}$
3.6	-0.0112	13.5499	-0.0582	0.00541	-0.0117	-0.0005
3.2	-0.0205	9.6722	-0.0827	0.00998	-0.0228	-0.0023
2.8	-0.0346	6.8867	-0.1179	0.01804	-0.0441	-0.0095
2.4	-0.0522	4.9537	-0.1707	0.03225	-0.0837	-0.0315

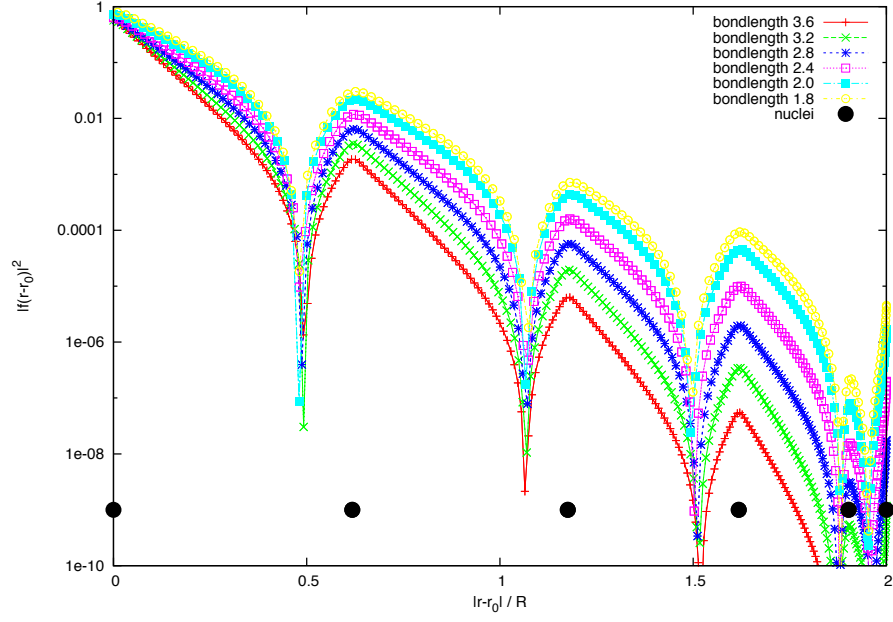


Figure 1: Square norm of the Wannier orbital $\psi_0(r) = \langle r|0\rangle_W$ along the circle $|r| = R$, for rings of $N = 10$ atoms with $\Delta R = 1.8, 2.0, 2.4, 2.8, 3.2, 3.6$. Positions of nuclei are marked with black points.