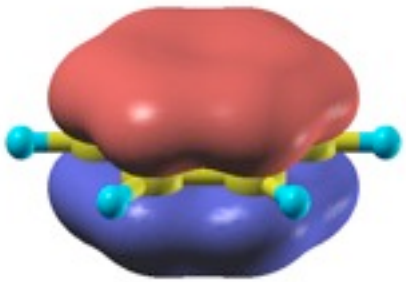

Wannier Functions in OpenMX

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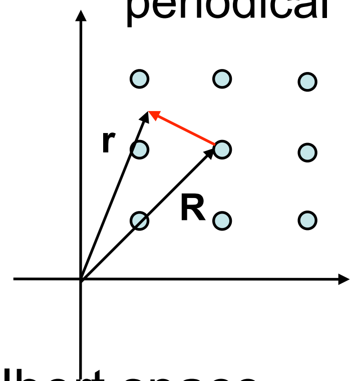
Nov. 23-25@KAIST

Wave-function in Solids

Bloch representation

$$[\mathbf{H},\mathbf{T}_R]=0 \Rightarrow \psi_{n\mathbf{k}}(\mathbf{r})=u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow e^{i\varphi_n(\mathbf{k})}\psi_{n\mathbf{k}}(\mathbf{r})$$

periodical

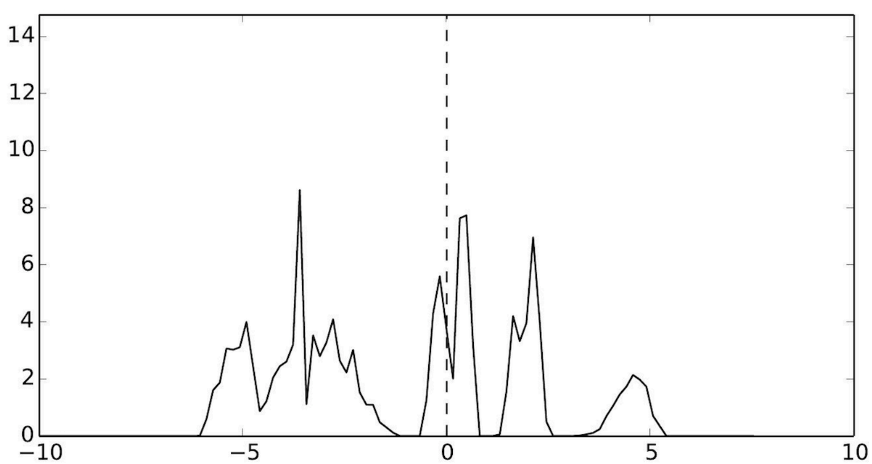


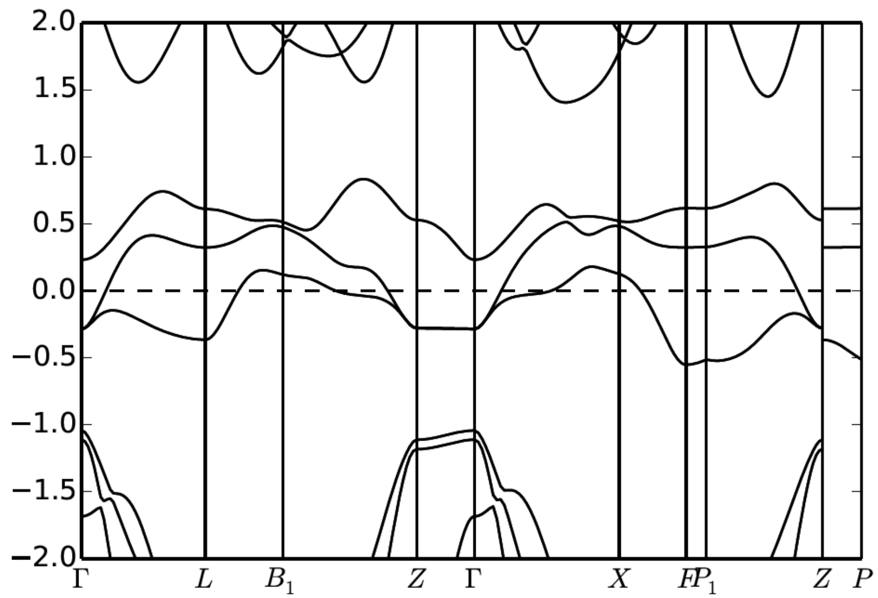
Wannier representation

$$w_n(\mathbf{r}-\mathbf{R})=|\mathbf{R}n\rangle=\frac{V}{(2\pi)^3}\int_{BZ}|\psi_{n\mathbf{k}}(\mathbf{r})\rangle e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{k}$$

Equivalence between two representations: span the same Hilbert space

$$P=\frac{V}{(2\pi)^3}\int_{\mathrm{BZ}}d\mathbf{k}\,|\psi_{n\mathbf{k}}\rangle\langle\psi_{n\mathbf{k}}|=\sum_{\mathbf{R}}|\mathbf{R}n\rangle\langle\mathbf{R}n|$$





Orthonormality & Completeness of Wannier Function

$$\langle \mathbf{R}'m \| \mathbf{R}n \rangle = \left(\frac{V}{(2\pi)^3} \right)^2 \int_{\mathbf{r}} \int_{BZ} \langle \psi_{m\mathbf{k}'}(\mathbf{r}) | e^{-i\varphi_m(\mathbf{k}')+i\mathbf{k}'\cdot\mathbf{R}'} d\mathbf{k}' \int_{BZ} | \psi_{n\mathbf{k}}(\mathbf{r}) \rangle e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k} \cdot d\mathbf{r}$$

$$= \left(\frac{V}{(2\pi)^3} \right)^2 \int_{BZ} \int_{BZ} \langle \psi_{m\mathbf{k}'} | \psi_{n\mathbf{k}} \rangle e^{-i\varphi_m(\mathbf{k}')+i\mathbf{k}'\cdot\mathbf{R}'} d\mathbf{k}' \cdot e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

$$= \left(\frac{V}{(2\pi)^3} \right)^2 \int_{BZ} \int_{BZ} \delta_{m,n} \delta_{\mathbf{k}',\mathbf{k}} e^{-i\varphi_m(\mathbf{k}')+i\mathbf{k}'\cdot\mathbf{R}'} d\mathbf{k}' \cdot e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

$$= \left(\frac{V}{(2\pi)^3} \right)^2 \int_{BZ} \int_{BZ} e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})} d\mathbf{k} d\mathbf{k}$$

$$= \delta_{m,n} \delta_{\mathbf{R}',\mathbf{R}}$$

Arbitrariness of Wannier Function

1. $$\psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow e^{i\varphi_n(\mathbf{k})}\psi_{n\mathbf{k}}(\mathbf{r})$$

The arbitrary phase $\varphi_n(\mathbf{k}) = \varphi_n(\mathbf{k}+\mathbf{G})$ is periodic in reciprocal lattice translation G but not assigned by the Schrodinger equation.

$$w_n(\mathbf{r}-\mathbf{R}) = |\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{BZ} |\psi_{n\mathbf{k}}(\mathbf{r})\rangle e^{i\varphi_n(\mathbf{k}) - i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

2. $$\psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow \sum_m U_{mn}^{\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r})$$

$$w_n(\mathbf{r}-\mathbf{R}) = |\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{BZ} \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}(\mathbf{r})\rangle e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

$$= \frac{V}{(2\pi)^3}\int_{BZ} |\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})\rangle e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

Freedom of Gauge Choice

For composite bands, choice of phase and “band-index labeling” at each k

For entangling bands, the subspace should be optimized.

Optimal Subspace

Maximally Localized Wannier Functions

N. Marzari and D. Vanderbilt PRB56, 12847 (1997)

- Localization criterion

Minimizing the **spread functional** defined as

$$\Omega = \sum_n \left[\langle 0n|\mathbf{r}^2|0n\rangle - \langle 0n|\mathbf{r}|0n\rangle^2 \right] = \sum_n \left[\langle \mathbf{r}^2\rangle_n - \bar{\mathbf{r}}_n^2 \right]$$

by finding the proper choice of $U_{mn}^{(k)}$ for a given set of Bloch functions.

- Optimization with the knowledge of Gradient

$$G = \frac{d\Omega}{dW} \longrightarrow dW = \varepsilon \cdot (-G)$$

$$\longrightarrow U_{mn}^{(\mathbf{k})} \Leftarrow U_{mn}^{(\mathbf{k})} + dW_{mn}^{(\mathbf{k})} \longrightarrow |u_{n\mathbf{k}}\rangle \Leftarrow |u_{n\mathbf{k}}\rangle + \sum_n dW_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle$$

$$\longrightarrow w_n(\mathbf{r}-\mathbf{R}) = |\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}(\mathbf{r})\rangle e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

The equation of motion for $U_{mn}^{(k)}$. $U_{mn}^{(k)}$ is moving in the direction opposite to the gradient to decrease the value of Ω, until a minimum is reached. **A proper Gauge choice.**

Spread functional in real-space

$$\Omega = \sum_n \left[\langle 0n | \mathbf{r}^2 | 0n \rangle - \langle 0n | \mathbf{r} | 0n \rangle^2 \right]$$

$$= \sum_n \left[\langle 0n | \mathbf{r}^2 | 0n \rangle - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m | \mathbf{r} | 0n \rangle \right|^2 + \sum_{\mathbf{R}m \neq 0n} \left| \langle \mathbf{R}m | \mathbf{r} | 0n \rangle \right|^2 \right]$$

$$= \sum_n \left[\langle 0n | \mathbf{r}^2 | 0n \rangle - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m | \mathbf{r} | 0n \rangle \right|^2 \right] + \sum_n \sum_{\mathbf{R}m \neq 0n} \left| \langle \mathbf{R}m | \mathbf{r} | 0n \rangle \right|^2 = \Omega_I + \tilde{\Omega}$$

$$= \Omega_I + \sum_n \sum_{\mathbf{R} \neq 0} \left| \langle \mathbf{R}n | \mathbf{r} | 0n \rangle \right|^2 + \sum_{m \neq n} \sum_{\mathbf{R}} \left| \langle \mathbf{R}m | \mathbf{r} | 0n \rangle \right|^2$$

$$= \Omega_I + \Omega_D + \Omega_{OD}$$

Ω_I, Ω_D and Ω_{OD} are all *positive-definite*. Especially Ω_I is *gauge-invariant*, means it will not change under any arbitrary unitary transformation of Bloch orbitals. Thus, only Ω_D+Ω_{OD} should be minimized.

Spread functional in Reciprocal-space

$$\Omega = \Omega_I + \sum_n \sum_{\mathbf{R}\neq 0} \left|\langle \mathbf{R}n|\mathbf{r}|0n\rangle\right|^2 + \sum_{m\neq n}\sum_{\mathbf{R}} \left|\langle \mathbf{R}m|\mathbf{r}|0n\rangle\right|^2$$

$$= \Omega_I + \Omega_D + \Omega_{OD}$$

Using the following transformations, matrix elements of the position operator in WF basis can be expressed in Bloch function basis:

$$\langle \mathbf{R}n|\mathbf{r}|0m\rangle = i\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{m\mathbf{k}}\rangle$$

$$\langle \mathbf{R}n|\mathbf{r}^2|0m\rangle = -\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla^2_{\mathbf{k}}|u_{m\mathbf{k}}\rangle$$

$$\bar{\mathbf{r}}_n = -\frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b\,\mathbf{b}\,\mathrm{Im}\ln M_{nn}^{(\mathbf{k},\mathbf{b})}$$

$$\Omega_I = \sum_n\left[\langle 0n|\mathbf{r}^2|0n\rangle - \sum_{\mathbf{R}m}\left|\langle \mathbf{R}m|\mathbf{r}|0n\rangle\right|^2\right] = \frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b\left(J - \sum_{m,n}\left|M_{mn}^{(\mathbf{k},\mathbf{b})}\right|^2\right)$$

$$\Omega_{OD} = \frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m\neq n}\left|M_{mn}^{(\mathbf{k},\mathbf{b})}\right|^2$$

$$\Omega_D = \frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \sum_n\left(-\mathrm{Im}\ln M_{nn}^{(\mathbf{k},\mathbf{b})} - \mathbf{b}\cdot\bar{\mathbf{r}}_n\right)^2$$

$$\sum_{\mathbf{b}} w_b b_\alpha b_\beta = \delta_{\alpha\beta}$$

$$M_{nn}^{(\mathbf{k},\mathbf{b})} = \langle u_{n\mathbf{k}}|u_{n\mathbf{k}+\mathbf{b}}\rangle$$

Gradient of Spread Functional

$$M_{nn}^{(\mathbf{k},\mathbf{b})} = \langle u_{n\mathbf{k}} | u_{n\mathbf{k}+\mathbf{b}} \rangle$$

$$|u_{n\mathbf{k}}\rangle \Leftarrow |u_{n\mathbf{k}}\rangle + \sum_m dW_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle \quad \Longrightarrow$$

$$dM_{nn}^{(\mathbf{k},\mathbf{b})} = -\sum_m dW_{nm}^{(\mathbf{k})} M_{mn}^{(\mathbf{k},\mathbf{b})} + \sum_l M_{nl}^{(\mathbf{k},\mathbf{b})} dW_{ln}^{(\mathbf{k}+\mathbf{b})}$$

$$= -\left[dW^{(\mathbf{k})} M^{(\mathbf{k},\mathbf{b})}\right]_{nn} + \left[M^{(\mathbf{k},\mathbf{b})} dW^{(\mathbf{k}+\mathbf{b})}\right]_{nn} \quad \Longrightarrow$$

$$d\Omega_{I,OD} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \, 4\,\mathrm{Re}\left(\sum_{m,n} dW_{nm}^{(\mathbf{k})} M_{mn}^{(\mathbf{k},\mathbf{b})} M_{nn}^{(\mathbf{k},\mathbf{b})^*} \right) = \frac{4}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \,\mathrm{Re}\,\mathrm{tr}\left[dW^{(\mathbf{k})} R^{(\mathbf{k},\mathbf{b})}\right]$$

$$d\Omega_D = -\frac{4}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \,\mathrm{Re}\,\mathrm{tr}\left[dW^{(\mathbf{k})} T^{(\mathbf{k},\mathbf{b})}\right] \quad \Longrightarrow$$

$$G^{(\mathbf{k})} = \frac{d\Omega}{dW^{(\mathbf{k})}} = 4 \sum_{\mathbf{b}} w_b \left(\mathcal{A}\left[R^{(\mathbf{k},\mathbf{b})}\right] - \mathbb{S}\left[T^{(\mathbf{k},\mathbf{b})}\right] \right)$$

Overlap Matrix $M_{mn}^{(\mathbf{k},\mathbf{b})}$

$$\psi_{m\in win}^{(k)}(r) = e^{ikr} u_{m\in win}^{(k)}(r) = \frac{1}{\sqrt{N}} \sum_{p}^{N} e^{iR_p k} \sum_{i,\alpha} C_{m\in win,i\alpha}^{(k)} \phi_{i\alpha}(r - \tau_i - R_p)$$

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \left\langle u_m^{\mathbf{k}}(\mathbf{r}) \middle| u_n^{\mathbf{k}+\mathbf{b}}(\mathbf{r}) \right\rangle = \left\langle \psi_m^{\mathbf{k}}(\mathbf{r}) \middle| e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i(\mathbf{k}+\mathbf{b})\cdot\mathbf{r}} \middle| \psi_n^{\mathbf{k}+\mathbf{b}}(\mathbf{r}) \right\rangle$$

$$= \frac{1}{N} \sum_{p,q}^{N} e^{-i\mathbf{R}_p\mathbf{k}} e^{i\mathbf{R}_q(\mathbf{k}+\mathbf{b})} \sum_{\substack{i,\alpha \\ j,\beta}} C_{m,i\alpha}^{(\mathbf{k})*} C_{n,j\beta}^{(\mathbf{k}+\mathbf{b})} \left\langle \phi_{i\alpha}(r - \tau_i - \mathbf{R}_p) \middle| e^{-i\mathbf{b}\cdot\mathbf{r}} \middle| \phi_{j\beta}(r - \tau_j - \mathbf{R}_q) \right\rangle$$

$$= \frac{1}{N} \sum_{p,q}^{N} e^{-i(\mathbf{R}_p - \mathbf{R}_q)\mathbf{k}} \sum_{\substack{i,\alpha \\ j,\beta}} C_{m,i\alpha}^{(\mathbf{k})*} C_{n,j\beta}^{(\mathbf{k}+\mathbf{b})} \left\langle \phi_{i\alpha}(r - \tau_i - \mathbf{R}_p) \middle| e^{-i(\mathbf{r}-\mathbf{R}_q)\cdot\mathbf{b}} \middle| \phi_{j\beta}(r - \tau_j - \mathbf{R}_q) \right\rangle$$

$$r' \equiv r - \tau_i - \mathbf{R}_p$$

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \frac{1}{N} \sum_{p,q}^{N} e^{-i(\mathbf{R}_p - \mathbf{R}_q)\mathbf{k}} \sum_{\substack{i,\alpha \\ j,\beta}} C_{m,i\alpha}^{(\mathbf{k})*} C_{n,j\beta}^{(\mathbf{k}+\mathbf{b})} \left\langle \phi_{i\alpha}(r') \middle| e^{-i(\mathbf{r}' + \tau_i + \mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{b}} \middle| \phi_{j\beta}(r' + \tau_i - \tau_j + \mathbf{R}_p - \mathbf{R}_q) \right\rangle$$

$$= \sum_{q}^{N} e^{i\mathbf{R}_q\cdot\mathbf{k}} \sum_{\substack{i,\alpha \\ j,\beta}} C_{m,i\alpha}^{(\mathbf{k})*} C_{n,j\beta}^{(\mathbf{k}+\mathbf{b})} \left\langle \phi_{i\alpha}(r') \middle| e^{-i(\mathbf{r}' + \tau_i - \mathbf{R}_q)\cdot\mathbf{b}} \middle| \phi_{j\beta}(r' + \tau_i - \tau_j - \mathbf{R}_q) \right\rangle$$

$$= \sum_{q}^{N} e^{i\mathbf{R}_q\cdot(\mathbf{k}+\mathbf{b})} \sum_{\substack{i,\alpha \\ j,\beta}} e^{-i\mathbf{b}\cdot\tau_i} C_{m,i\alpha}^{(\mathbf{k})*} C_{n,j\beta}^{(\mathbf{k}+\mathbf{b})} \left\langle \phi_{i\alpha}(r') \middle| e^{-i\mathbf{b}\cdot\mathbf{r}'} \middle| \phi_{j\beta}(r' + \tau_i - \tau_j - \mathbf{R}_q) \right\rangle$$

Initial guess for MLWF

$$A_{mn}^{(\mathbf{k})} = \langle u_{m\mathbf{k}} | g_n \rangle \qquad |\phi_{n\mathbf{k}}\rangle = \sum_{m}^{N_{win}^{(\mathbf{k})}} A_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle$$

The resulting N functions can be orthonormalized by Löwdin transformation

$$|u_{n\mathbf{k}}^{opt}\rangle = \sum_{m=1}^{N} (S^{-1/2})_{mn} |\phi_{m\mathbf{k}}\rangle \qquad S_{mn} \equiv S_{mn}^{(\mathbf{k})} = \langle \phi_{m\mathbf{k}} | \phi_{n\mathbf{k}} \rangle = (A^{+}A)_{mn}$$

$$= \sum_{m=1}^{N} (S^{-1/2})_{mn} \sum_{p=1}^{N_{win}^{(\mathbf{k})}} A_{pm}^{(\mathbf{k})} |u_{p\mathbf{k}}\rangle$$

$$= \sum_{p=1}^{N_{win}^{(\mathbf{k})}} (AS^{-1/2})_{pn} |u_{p\mathbf{k}}\rangle$$

1. to avoid the local minima and accelerate the convergence;
2. to eliminate the random phase factor of Bloch function

Therefore, $AS^{-1/2}$ is used as the initial guess of $U^{(\mathbf{k})}$

Initial guess for MLWF

$$A_{mn}^{(\mathbf{k})} = \langle u_{m\mathbf{k}} | g_n \rangle \qquad \psi_{m\in win}^{(k)}(r) = \frac{1}{\sqrt{N}} \sum_{p}^{N} e^{iR_p k} \sum_{i,\alpha} C_{m\in win,i\alpha}^{(k)} \phi_{i\alpha}(r - \tau_i - R_p)$$

In OpenMX, we use the pesudo-atomic orbital as initial trial functions.

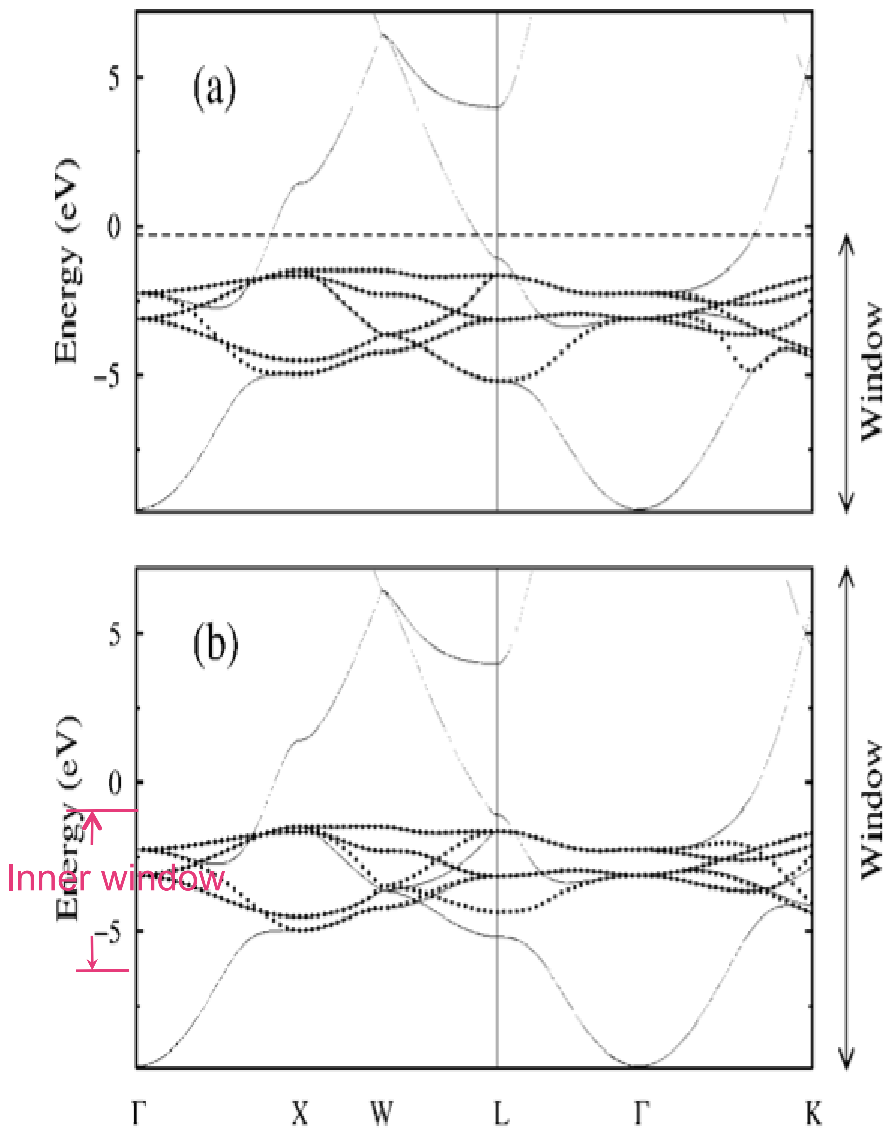
$$g_n(r) = g_{j,\beta}(r) = \phi_{j,\beta}(r)$$

For selected Bloch function, the projection matrix element can be expressed as:

$$A_{mn}^{(k)} = \langle \psi_{m\in win}^{(k)}(r) | g_n(r) \rangle = \frac{1}{\sqrt{N}} \sum_{p}^{N} e^{-iR_p k} \sum_{i,\alpha} C_{n\in win,i\alpha}^{(k)}{}^{*} \langle \phi_{i\alpha}(r - \tau_i - R_p) | \phi_{j,\beta}(r) \rangle$$

1. Easier to calculate;
2. Can be tuned by generating new PAO;
3. Can be put anywhere in the unit cell;
4. Quantization axis and hybridizations can also be controlled.

Disentangle bands in metal



Select $N_{win}^{(k)}$ bands locates in an energy window. These bands constitute a large space $F(\mathbf{k})$. The number of bands at each k inside the window should be larger or equal to the number of WF.

Target is to find an optimized subspace $S(\mathbf{k})$, which gives the smallest Ω_I

$$\Omega_I = \frac{1}{N_{kp}} \sum_{k=1}^{N_{kp}} \sum_b w_b T_{k,b}$$

$$T_{k,b} = N - \sum_{m,n} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2 = Tr\left[\mathbf{P_k Q_{k+b}}\right]$$

P is the operator which project onto a set of bands while Q is projecting onto the left set of bands. Therefore, Ω_I measures the mismatch between two sets of bands at k and k+b, respectively.

Iterative minimization of Ω_I

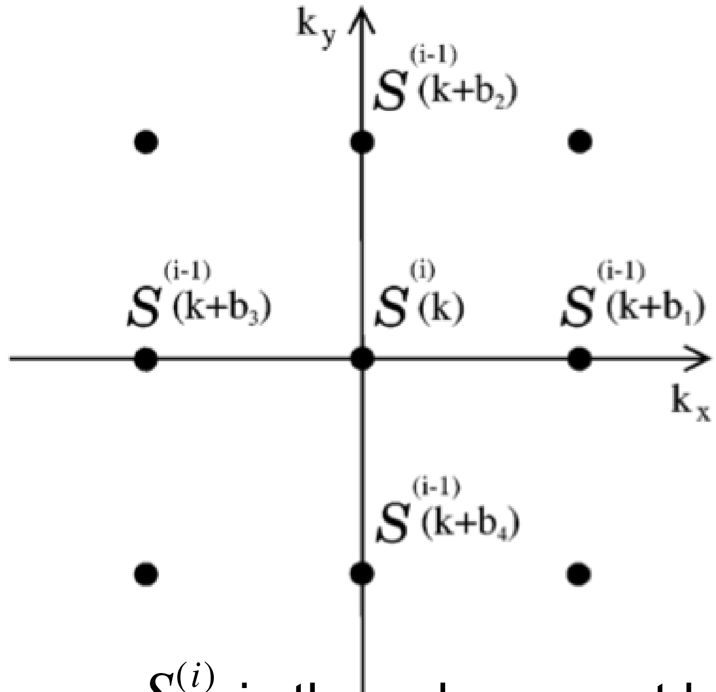
Using Lagrange multipliers to enforce orthonormality and the stationary condition at *i*-th iteration is:

$$\frac{\delta \Omega_I^{(i)}}{\delta u_{mk}^{(i)*}} + \sum_{n=1}^{N} \Lambda_{nm,k}^{(i)} \frac{\delta}{\delta u_{mk}^{(i)*}} \left[\left\langle u_{mk}^{(i)} \middle| u_{nk}^{(i)} \right\rangle - \delta_{m,n} \right] = 0$$

$$\Omega_I^{(i)} = \frac{1}{N_{kp}} \sum_{k=1}^{N_{kp}} \omega_I^{(i)}(k)$$

$$\omega_I^{(i)}(k) = \sum_b w_b T_{k,b}^{(i)} = \sum_b w_b T_{k,b}^{(i)}$$

$$= \sum_b w_b \sum_{m=1}^{N} \left[1 - \sum_{n=1}^{N} \left| \left\langle u_{mk}^{(i)} \middle| u_{n,k+b}^{(i-1)} \right\rangle \right|^2 \right]$$



If inner window is set, the full space shrink.

$S_{(\mathbf{k})}^{(i)}$ is the subspace at k point in the *i*-th iteration

Interpolation of band structure

q is the grid of BZ used for constructing MLWF

$$\left|u_{n\mathbf{q}}^{(W)}\right\rangle = \sum_{m=1}^{N_{\mathbf{q}}} U_{mn}(\mathbf{q})\left|\phi_{m\mathbf{q}}\right\rangle \qquad \left|n\mathbf{R}\right\rangle = \frac{1}{N_{\mathbf{q}}}\sum_{\mathbf{q}=1}^{N_{\mathbf{q}}} e^{-i\mathbf{q}\cdot\mathbf{R}}\left|u_{n\mathbf{q}}^{(W)}\right\rangle$$

$$H_{nm}^{(W)}(\mathbf{q}) = \left\langle u_{n\mathbf{q}}^{(W)}\right|\mathbf{H}(\mathbf{q})\left|u_{m\mathbf{q}}^{(W)}\right\rangle = \sum_{i} U_{in}^{*}(\mathbf{q})\left\langle u_{i\mathbf{q}}\right|\mathbf{H}(\mathbf{q})\sum_{j} U_{jm}(q)\left|u_{j\mathbf{q}}\right\rangle$$

$$= \sum_{i,j} U_{in}^{*}(\mathbf{q})\left\langle u_{i\mathbf{q}}\right|\mathbf{H}(\mathbf{q})\left|u_{j\mathbf{q}}\right\rangle U_{jm}(q) = \left[U^{+}\mathbf{H}(\mathbf{q})U\right]_{nm}$$

Hamiltonian in Wannier gauge can be diagonalized and the bands inside the inner window will have the same eigen-value as in original Hamiltonian gauge.
Other operators can be transferred to Wannier gauge in the similar way.

Interpolation of band structure

Fourier transfer into the R space:

$$H_{nm}^{(W)}(\mathbf{R}) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}=1}^{N_{\mathbf{q}}} e^{-i\mathbf{q}\cdot\mathbf{R}} H_{nm}^{(W)}(\mathbf{q})$$

Here R denotes the Wigner-Seitz supercell centered home unit cell.

To do the interpolation of band structure at arbitrary k point, inverse Fourier transform is performed:

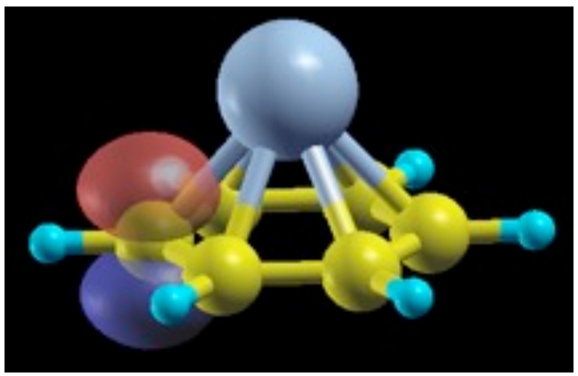
$$H_{nm}^{(W)}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H_{nm}^{(W)}(\mathbf{R})$$

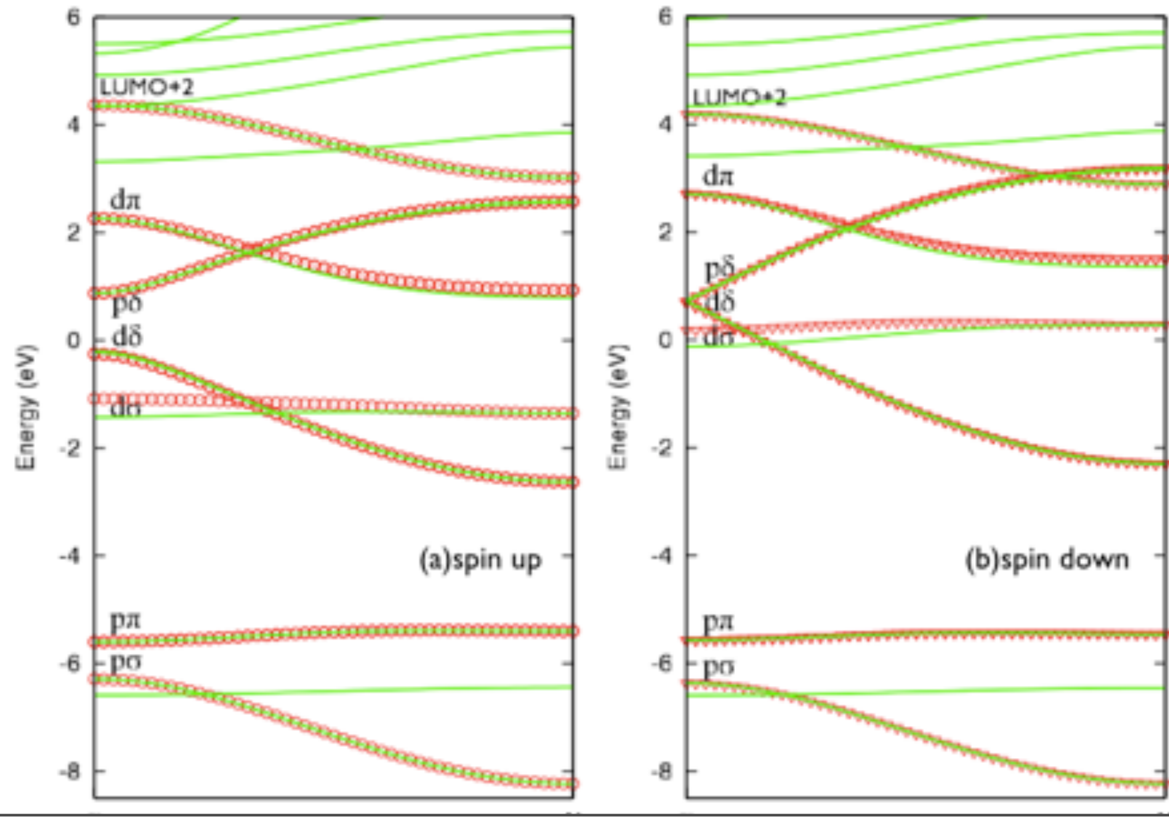
Diagonalize this Hamiltonian, the eigenvalues and states will be gotten.

This is directly related to Slater-Koster interpolation, with MLWFs playing the role of the TB basis orbitals.

Wannier in OpenMX

```
Wannier.Func.Calc           on
Wannier.Func.Num            11
Wannier.Outer.Window.Bottom -8.7
Wannier.Outer.Window.Top     6.0
Wannier.Inner.Window.Bottom  -4.0
Wannier.Inner.Window.Top      0.0
Wannier.Initial.Guess         on
Wannier.Initial.Projectors.Unit ANG     # AU, ANG or FRAC
```





Wannier in OpenMX

```
Species.Number       5
<Definition.of.Atomic.Species
 H    H5.0-s2p2         H_PBE13
 C    C5.0-s2p2d1       C_PBE13
 V    V6.0-s2p2d2f1     V_PBE13
 Cpro C5.0-s1p1d1       C_PBE13
 Vpro V6.0-s1p1d1       V_PBE13
Definition.of.Atomic.Species>
```

```
Wannier.Initial.Guess              on
Wannier.Initial.Projectors.Unit ANG     # AU, ANG or FRAC
<Wannier.Initial.Projectors
 Cpro-pz   7.02378   8.50000   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Cpro-pz   7.76209   9.77664   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Cpro-pz   9.23791   9.77664   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Cpro-pz   9.97623   8.50000   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Cpro-pz   9.23791   7.22336   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Cpro-pz   7.76209   7.22336   0.00000     0.0 0.0 1.0 1.0 0.0 0.0
 Vpro-d    8.5       8.5       1.65        0.0 0.0 1.0 1.0 0.0 0.0
Wannier.Initial.Projectors>
```

Wannier in OpenMX

```
Wannier.Kgrid                              2 2 20
Wannier.MaxShells                          12

Wannier.Interpolated.Bands                 on   # on|off, default=off

Wannier.Function.Plot                      on   # on|off, default=off
Wannier.Function.Plot.SuperCells           0 0 1   # default=0 0 0

Wannier.Dis.Mixing.Para                    0.5
Wannier.Dis.Conv.Criterion                  1e-10
Wannier.Dis.SCF.Max.Steps                  5000

Wannier.Minimizing.Max.Steps               800
Wannier.Minimizing.Scheme                  2  # 0 Steepest-descent;  1 conjugate gradient; 2 Hybrid
Wannier.Minimizing.StepLength              2.0
Wannier.Minimizing.Secant.Steps            2
Wannier.Minimizing.Secant.StepLength       2.0
Wannier.Minimizing.Conv.Criterion           1e-10

Wannier.Readin.Overlap.Matrix              off
```

Wannier in OpenMX

Files:

case.mmn overlap matrix $M_{mn}^{(\mathbf{k},\mathbf{b})}$
case.amn initial guess $A_{mn}^{(\mathbf{k})}$
case.eigen eigenvalue and Bloch wavefunction

case.HWR $H_{nm}^{(W)}(\mathbf{R})$
case.Wannier_Band interpolated bands

Wannier in OpenMX

```
Disentangling the attached bands ......
Disentangling spin component 0.
****************************************************
  Iteration(s) to minimize OMEGA_I ......
****************************************************
|  Iter   | Omega_I (Angs^2) | Delta_I (Angs^2) |   ---> DISE
|      1  |  152.171064809446|  152.171064809446|   ---> DISE
|      2  |  134.186576107804| -17.984488701642|   ---> DISE
|      3  |  127.128501721323|  -7.058074386481|   ---> DISE
|      4  |  121.733285733873|  -5.395215987451|   ---> DISE
|      5  |  117.693911475738|  -4.039374258134|   ---> DISE
|      6  |  114.660891433347|  -3.033020042391|   ---> DISE
```

```
Starting minimization of OMEGA_D and OMEGA_OD ......
For spin component 0:
Using guide for WF center.
Initialized Wannier Function before optimization:
         Center of Wannier Function (Angs)    |    Spread (Angs^2)
WF   1 ( 4.87597228, 2.80809912, 1.90020848) |  12.79052017  --->CENT
WF   2 ( 4.30237955, 2.57899410, 1.90020855) |  13.49934260  --->CENT
WF   3 ( 4.16434220, 2.20733676, 1.90020851) |  11.54921471  --->CENT
WF   4 ( 3.99284591, 2.60432905, 1.90020856) |   8.78137563  --->CENT
WF   5 ( 4.29825726, 2.19887731, 1.90020852) |   6.88813886  --->CENT

*************************************************************  ---> CONV
                 CONVERGENCE ACHIEVED !                         ---> CONV
*************************************************************  ---> CONV
```

Initial guess in OpenMX

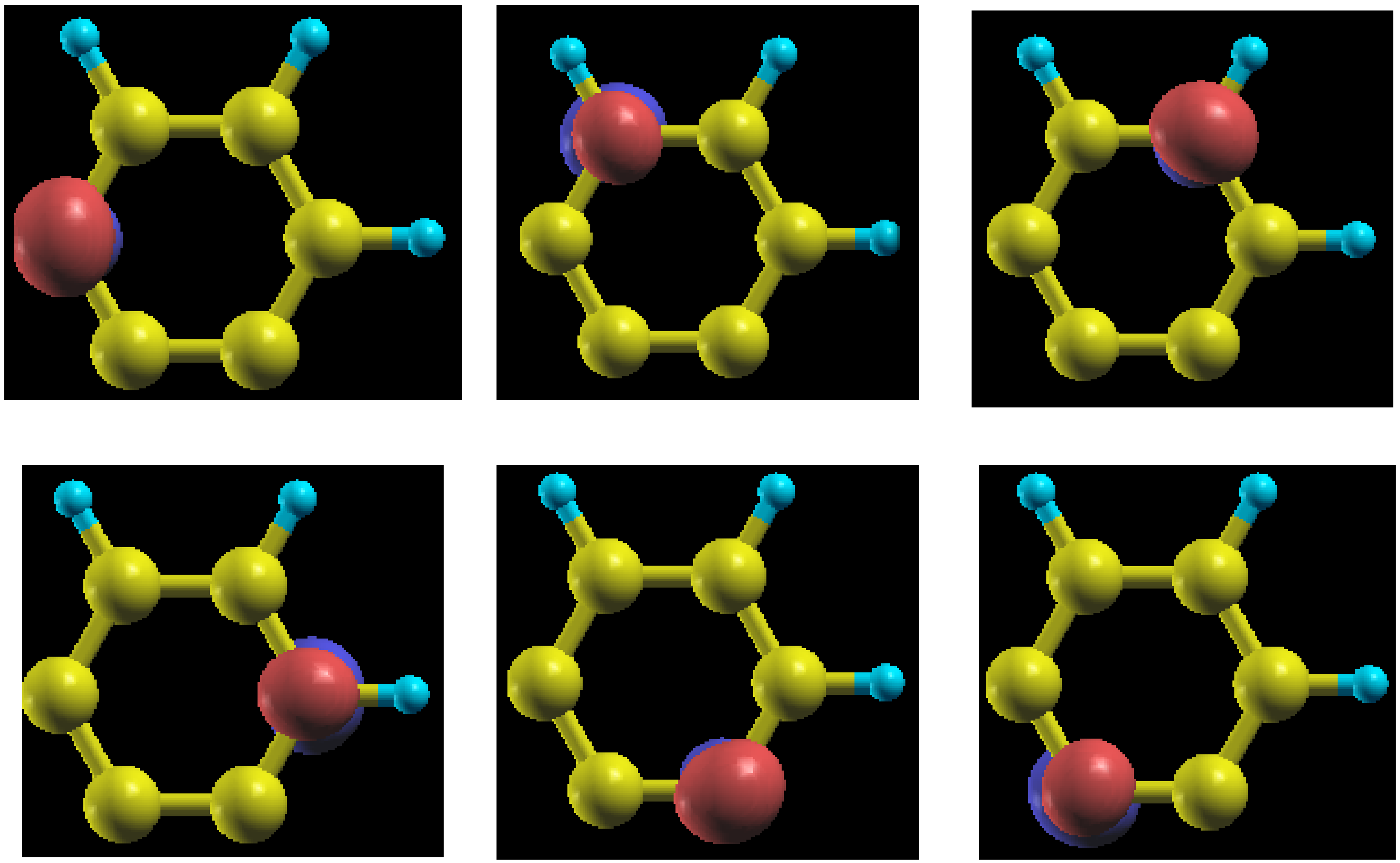
physical intuition is here and important!

Table 7: Orbitals and hybrids used as projector. The hybridization is done within the new coordinate system defined by z-axis and x-axis.

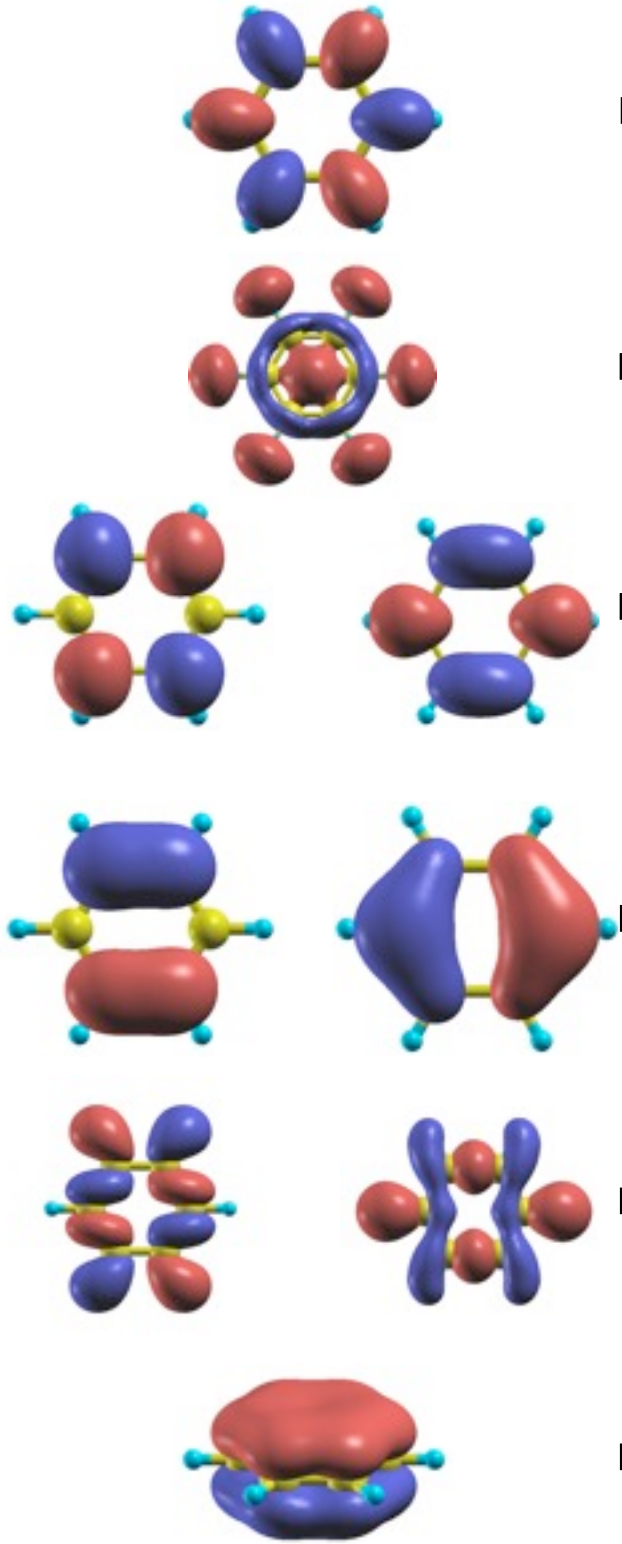
Orbital name	Number of included projector	Description
s	1	s orbital from PAOs
p	3	p_x, p_y, p_z from PAOs
px	1	p_x from PAOs
py	1	p_y from PAOs
pz	1	p_z from PAOs
d	5	$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ from PAOs
dz2	1	d_{z^2} from PAOs
dx2-y2	1	$d_{x^2-y^2}$ from PAOs
dxy	1	d_{xy} from PAOs
dxz	1	d_{xy} from PAOs
dyz	1	d_{xy} from PAOs
f	7	$f_{z^3}, f_{xz^2}, f_{yz^2}, f_{zx^2}, f_{xyz}, f_{x^3-3xy^2}, f_{3yx^2-y^3}$ from PAOs
sp	2	Hybridization between s and px orbitals including $\frac{1}{\sqrt{2}}(s+p_x)$ and $\frac{1}{\sqrt{2}}(s-p_x)$
sp2	3	Hybridization among s, px, and py orbit including $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x-\frac{1}{\sqrt{2}}p_y$ and $\frac{1}{\sqrt{3}}s+\frac{2}{\sqrt{6}}p$
sp3	4	Hybridization among s, px, py and pz o $\frac{1}{\sqrt{2}}(s+p_x+p_y+p_z)$, $\frac{1}{\sqrt{2}}(s+p_x-p$ $\frac{1}{\sqrt{2}}(s-p_x+p_y-p_z)$, $\frac{1}{\sqrt{2}}(s-p_x -$
sp3dz2	5	Hybridization among s, p_x, p_y, p_z and orbitals: $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{1}{\sqrt{6}}p_x+\frac{1}{\sqrt{2}}p_y$, $\frac{1}{\sqrt{3}}s-\frac{2}{\sqrt{6}}p_x$ $\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{2}}d_{z^2}$, $-\frac{1}{\sqrt{2}}p_z+\frac{1}{\sqrt{2}}d_{z^2}$
sp3deg	6	Hybridization among s, p_x, p_y, p_z and

Benzene Molecule MLWF

- With pz on each C atom as initial guess



Benzene Molecular Orbitals



LUMO+2 3.35 eV (b_{2g})

LUMO+1 3.30 eV (a_{1g})

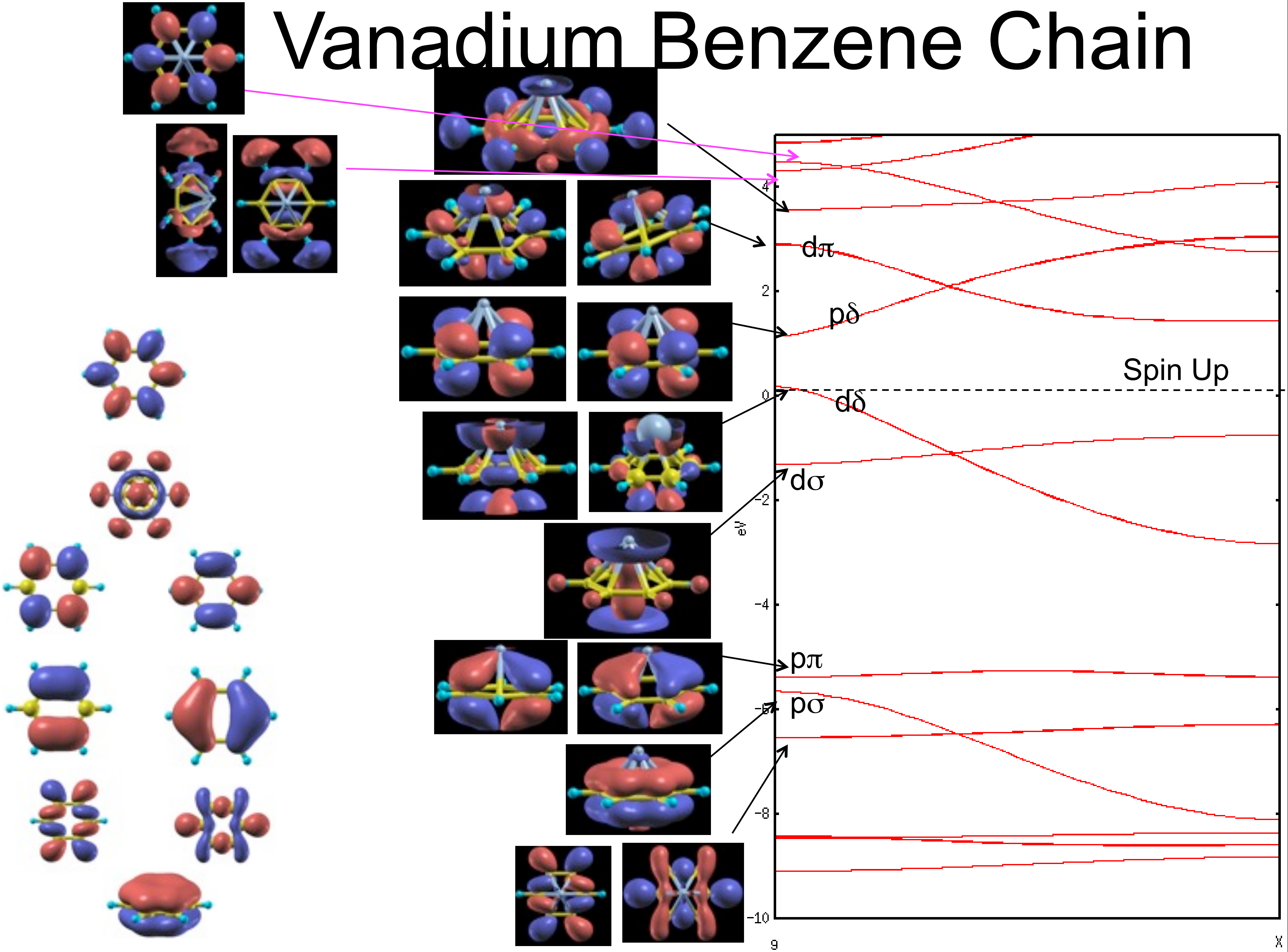
LUMO -0.55 eV (e_{2u})

HOMO -5.85 eV (e_{1g})

HOMO-1 -7.81 eV (e_{2g})

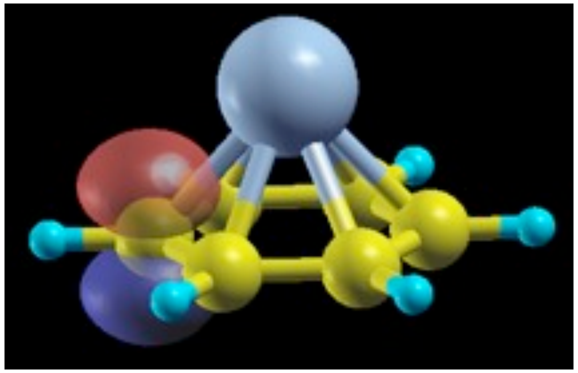
HOMO-2 -8.61 eV (a_{2u})

Vanadium Benzene Chain

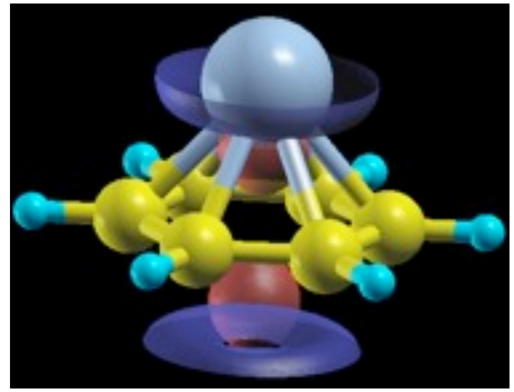


VBz Chain FM GGA MLWF

Initial guess: pz orbital on each C atom and 5d on V atom



Spread 1.200



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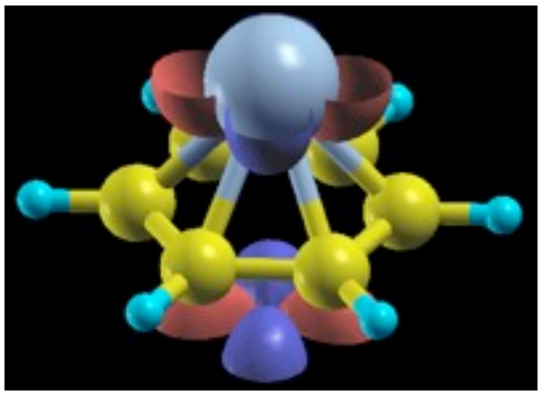
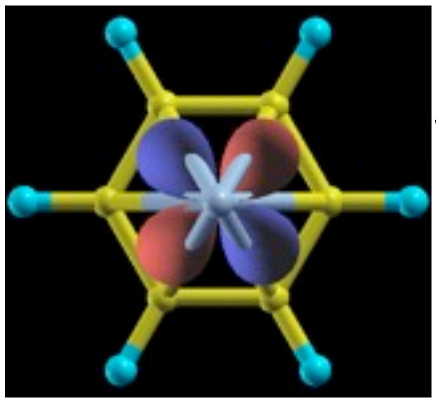
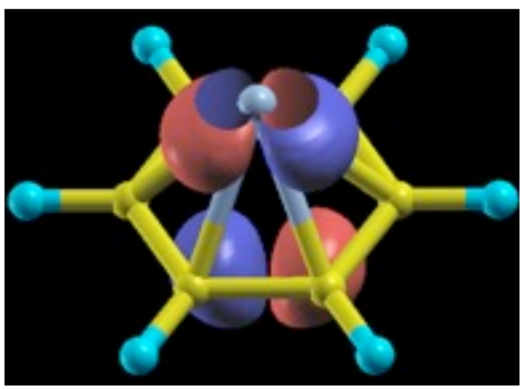
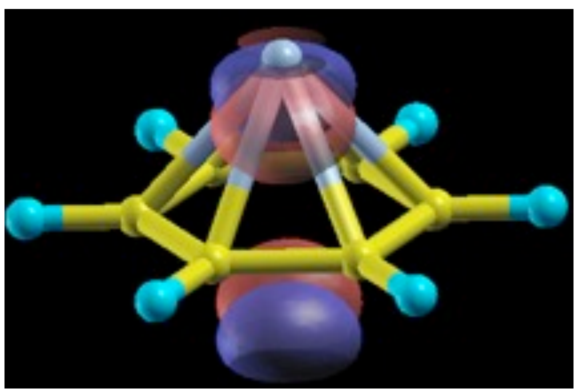




Spread 0.857

Omega_I=12.19080
Omega_D= 0.0021
Omega_OD= 0.2059
Total_Omega=12.3988

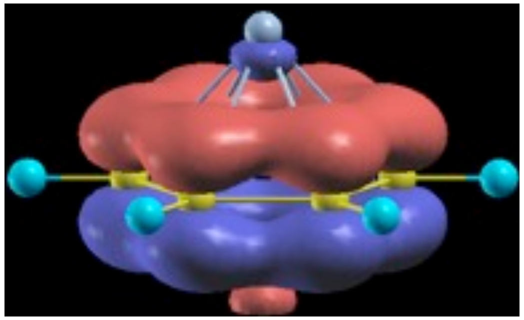




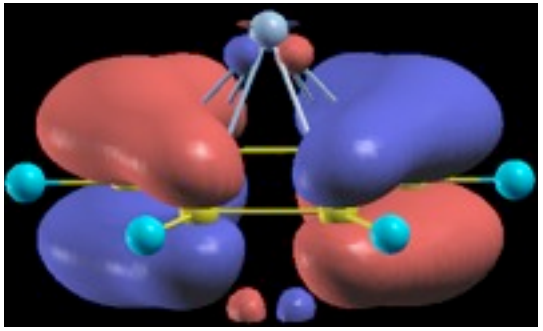
Spread 1.122

VBz Chain FM GGA MLWF

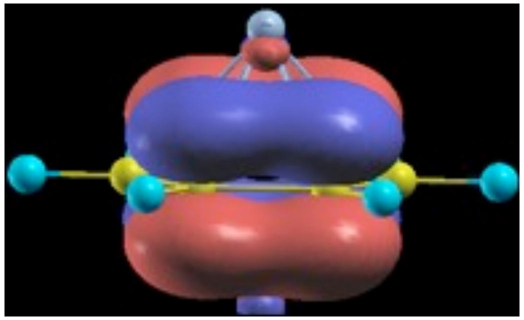
Initial guess: Benzene molecular orbitals and 5d on V atom



2.831 σ



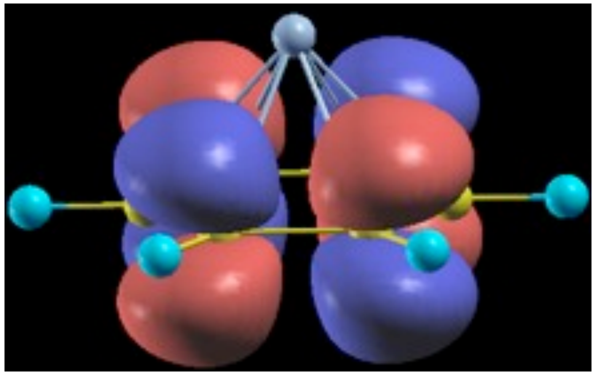
3.391 π



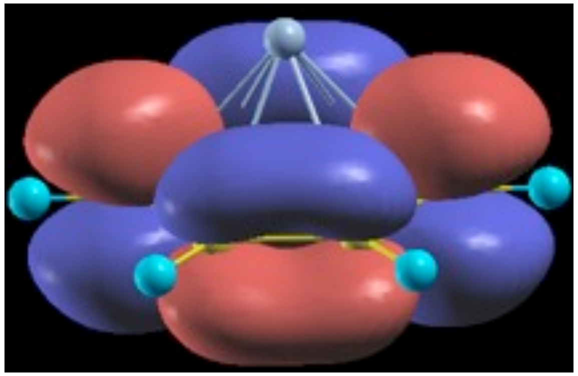
3.390 π

Omega_I=12.1908
Omega_D= 0.00
Omega_OD=13.7714 Total_Omega=25.9622

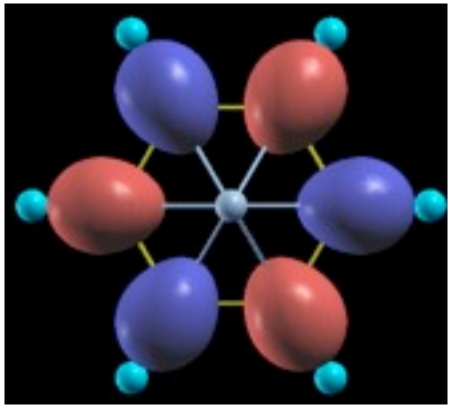
3.622 δ



3.616 δ



3.920



Thank you for your attention!

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