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Generating Wannier Function within OpenMX

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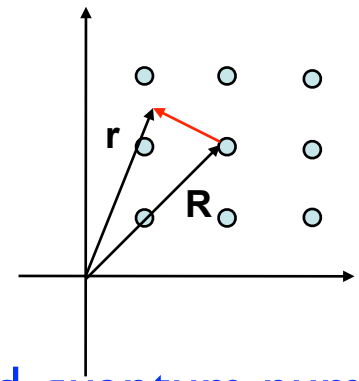
Wave-function in Solids

1, Bloch representation

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

$$\psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow e^{i\varphi_n(\mathbf{k})}\psi_{n\mathbf{k}}(\mathbf{r})$$ phase factor of periodic

periodical boundary condition



2, Wannier representation

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

good quantum number:

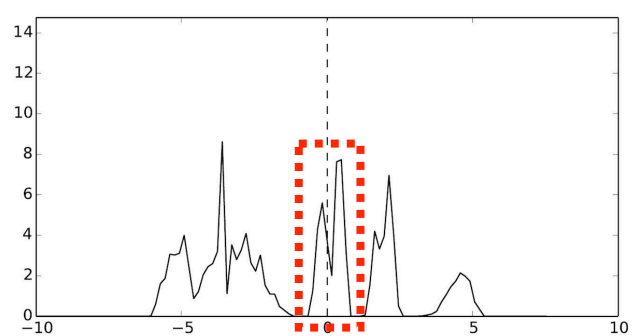
n — band index

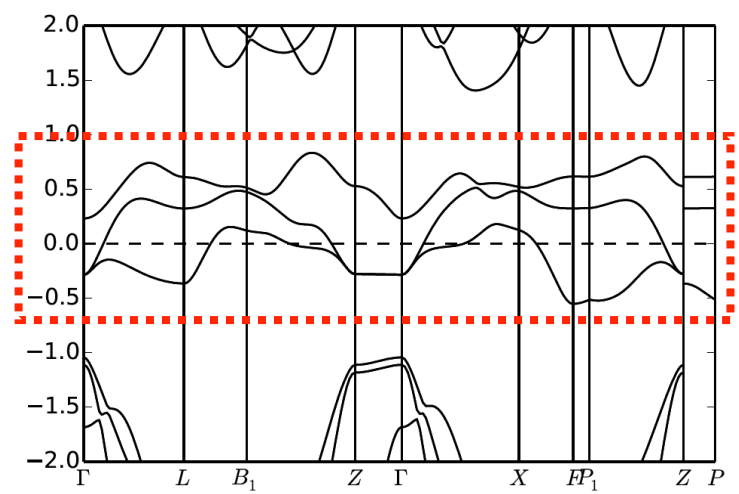
k — crystal momentum

R — Lattice

Equivalence of these 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

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

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

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

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

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

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.

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

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

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

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

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 $U_{mn}^{(\mathbf{k})}$ 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 $U_{mn}^{(\mathbf{k})}$. $U_{mn}^{(\mathbf{k})}$ 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

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

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

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

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

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

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:

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

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

$$\mathbf{v} = -\frac{i}{\hbar}[\mathbf{r}, H]$$

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

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

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

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

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

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

Gradient of Spread Functional

$$\left| u_{n\mathbf{k}} \right\rangle \Leftarrow \left| u_{n\mathbf{k}} \right\rangle + \sum_m dW_{mn}^{(\mathbf{k})} \left| u_{m\mathbf{k}} \right\rangle \xrightarrow{M_{nn}^{(\mathbf{k},\mathbf{b})} = \left\langle u_{n\mathbf{k}} \middle| u_{n\mathbf{k}+\mathbf{b}} \right\rangle}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Benefit from initial guess:

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

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

Initial guess for MLWF in OpenMX

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

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:

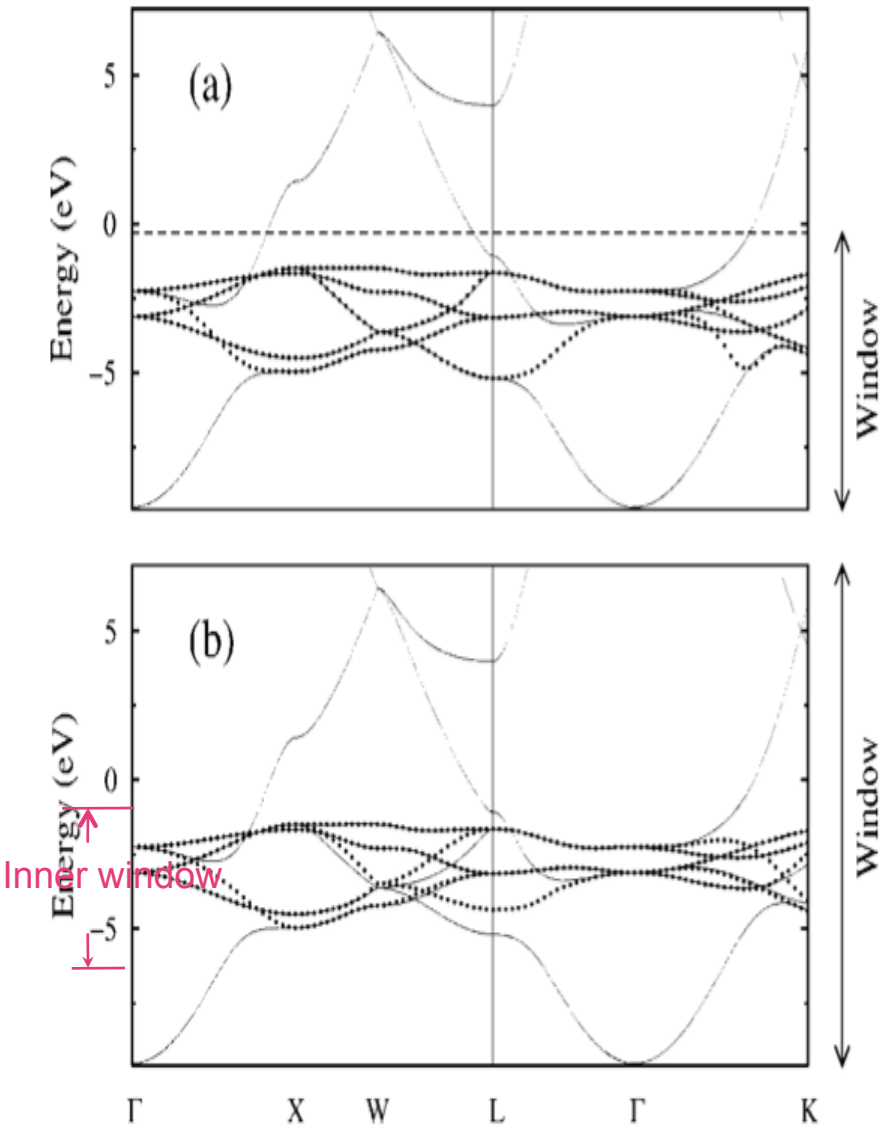
$$A_{mn}^{(k)} = \langle \psi_{m\in win}^{(k)}(r) | g_n(r) \rangle = \frac{1}{\sqrt{N}} \sum_{p}^{N} e^{-iR_p k} \sum_{i,\alpha} C_{n\in win,i\alpha}^{(k)\,*} \langle \phi_{i\alpha}(r - \tau_i - R_p) | \phi_{j,\beta}(r) \rangle$$

Advantages over other ab-initio program based on plane-wave basis:

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.

Entangled Bands Case

to optimize Ω_I



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

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

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

P_k is the operator which project onto a set of bands while Q_{k+b} is projecting onto the left set of bands. Therefore, Ω_I measures the mismatch between two sets of bands at neighboring k and k+b points, respectively.

Iterative minimization of Ω_I

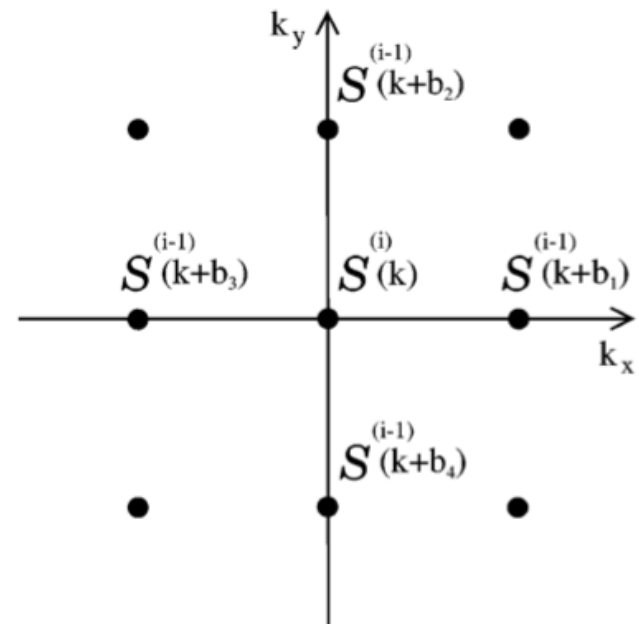
Using Lagrange multipliers to enforce orthonormality and the stationary condition at *i*-th iteration is:

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

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

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

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



If inner window is set, the space needed to be optimized is smaller.

$S_{(\mathbf{k})}^{(i)}$ 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

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

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

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

Hamiltonian in Wannier gauge can be diagonalized and the bands inside the inner window will have the same eigenvalues as in original Hamiltonian gauge.
Other operators can be transferred into 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:

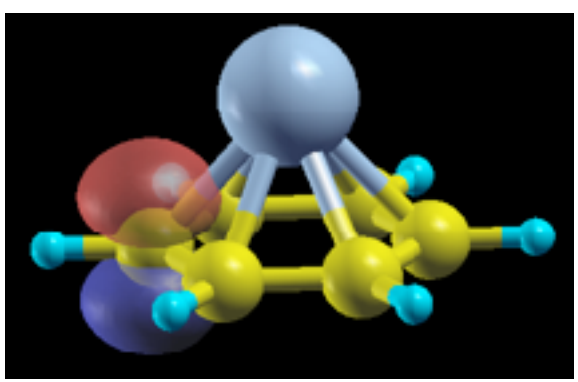
$$H_{nm}^{(W)}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H_{nm}^{(W)}(\mathbf{R})$$

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

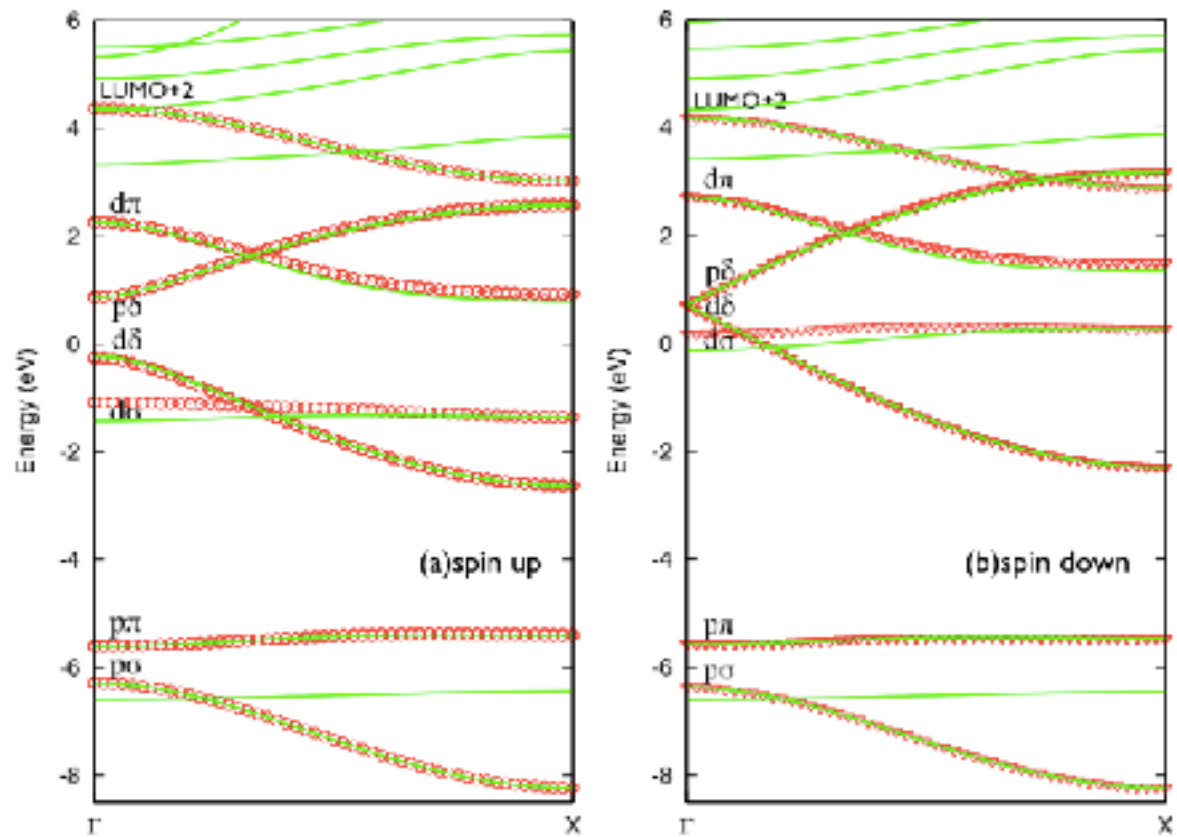
This is directly related to Slater-Koster interpolation, with MLWFs playing the role of the TB basis orbitals.

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
```



a chain of V-Benzene



Wannier in OpenMX

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Species.Number        5
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 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>
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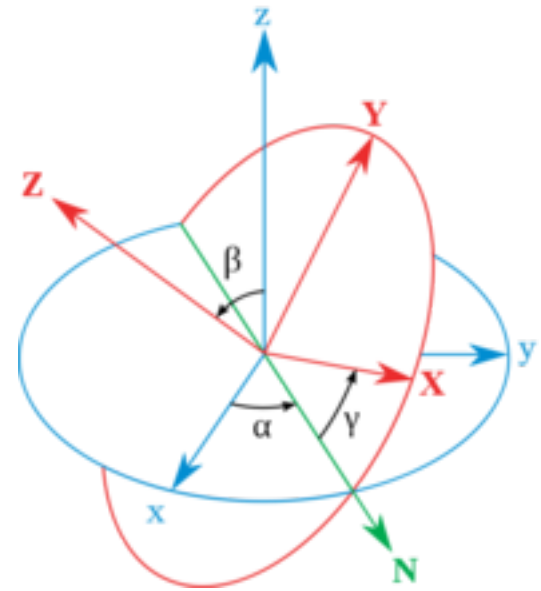


redefined local coordinate axis of z' and x'.
y' is automatically checked to be satisfied in right-handed system.

```
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
```

disentangling

Wannier in OpenMX

Files:

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

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

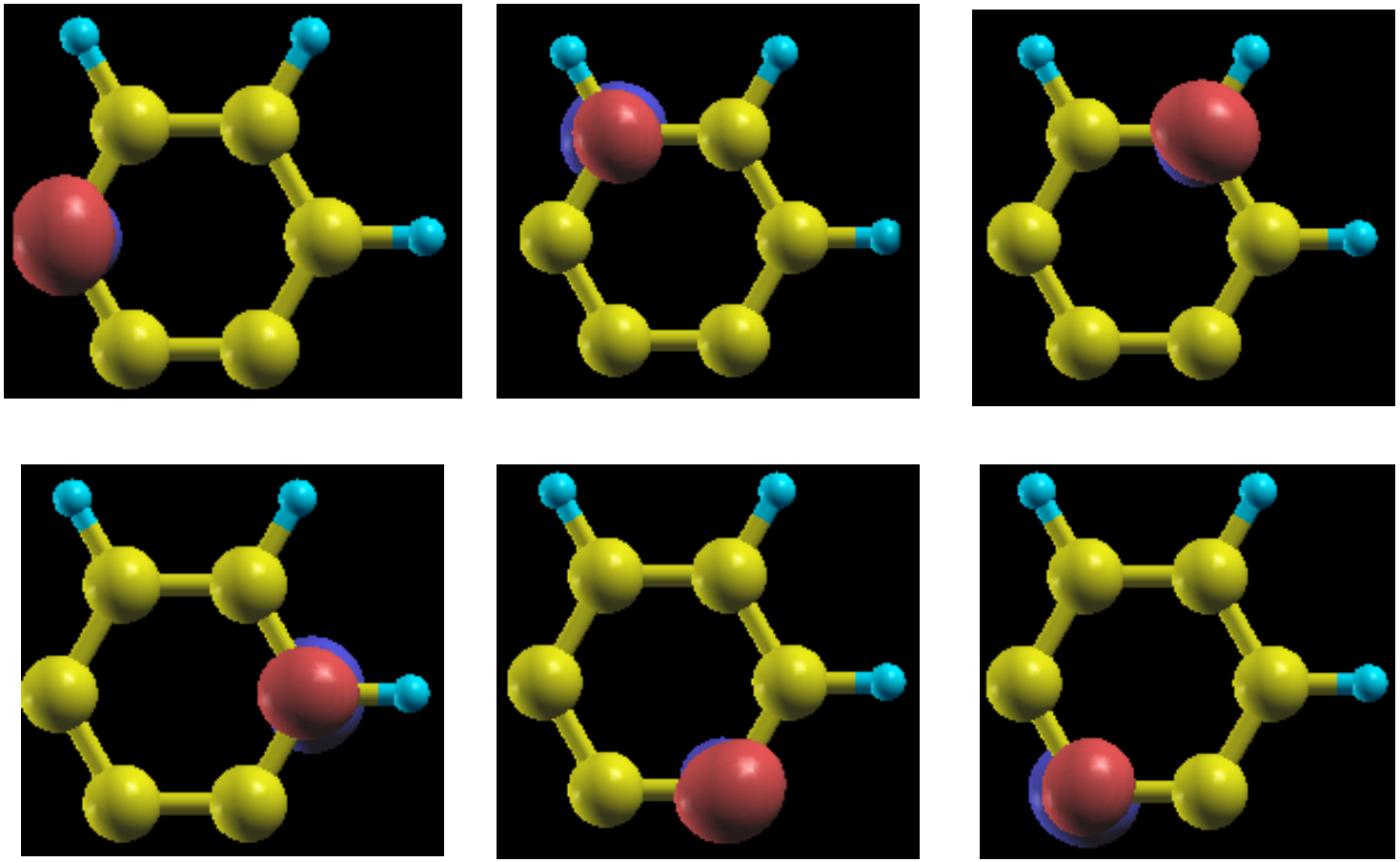
physical and chemical intuition is required here and important!

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

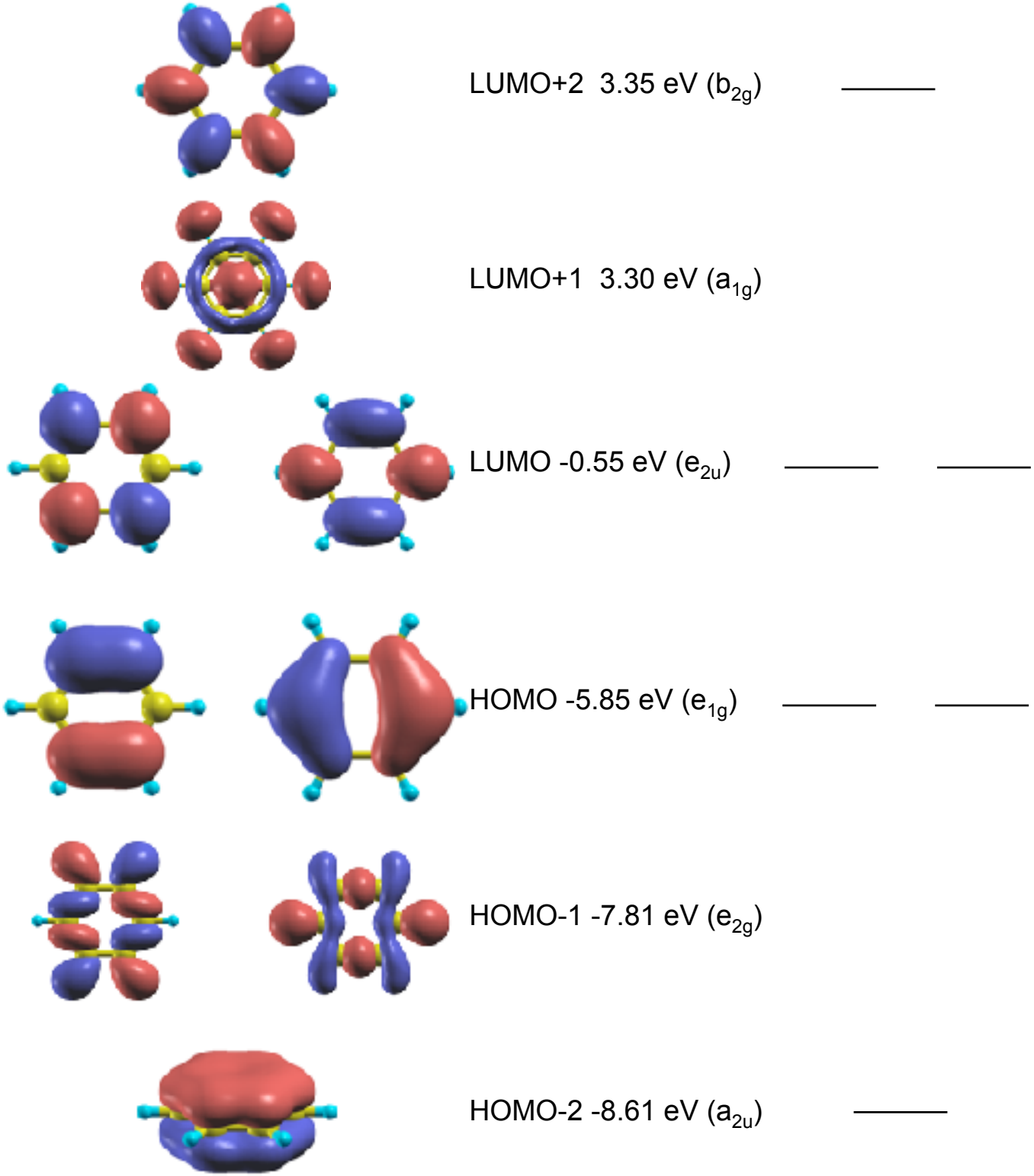
Orbital name	Number of included projector	Description
s	1	s orbital from PAOs
p	3	p_x, p_y, p_z from PAOs
px	1	p_x from PAOs
py	1	p_y from PAOs
pz	1	p_z from PAOs
d	5	$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ from PAOs
dz2	1	d_{z^2} from PAOs
dx2-y2	1	$d_{x^2-y^2}$ from PAOs
dxy	1	d_{xy} from PAOs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

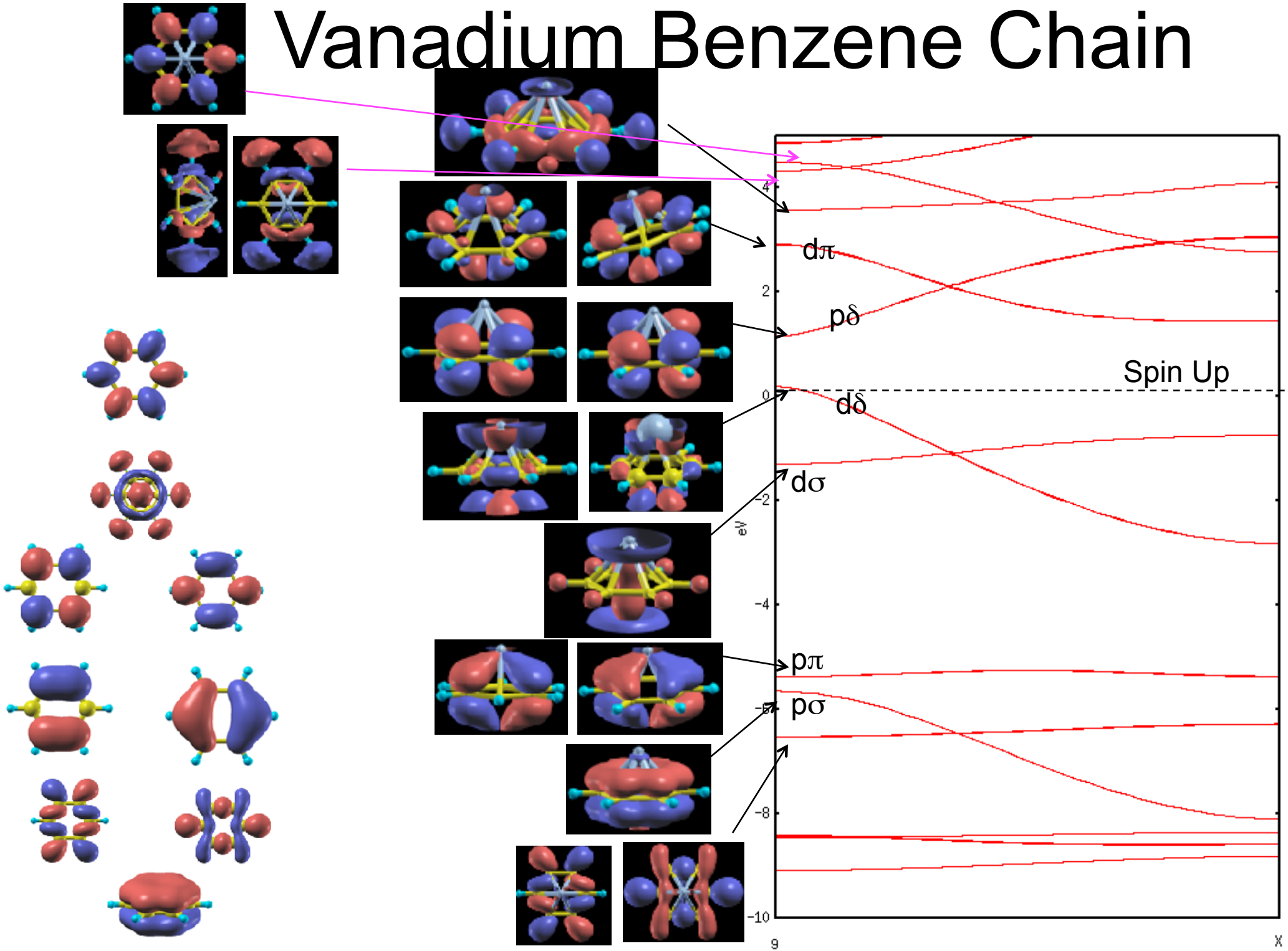
- With pz on each C atom as initial guess



Benzene Molecular Orbitals

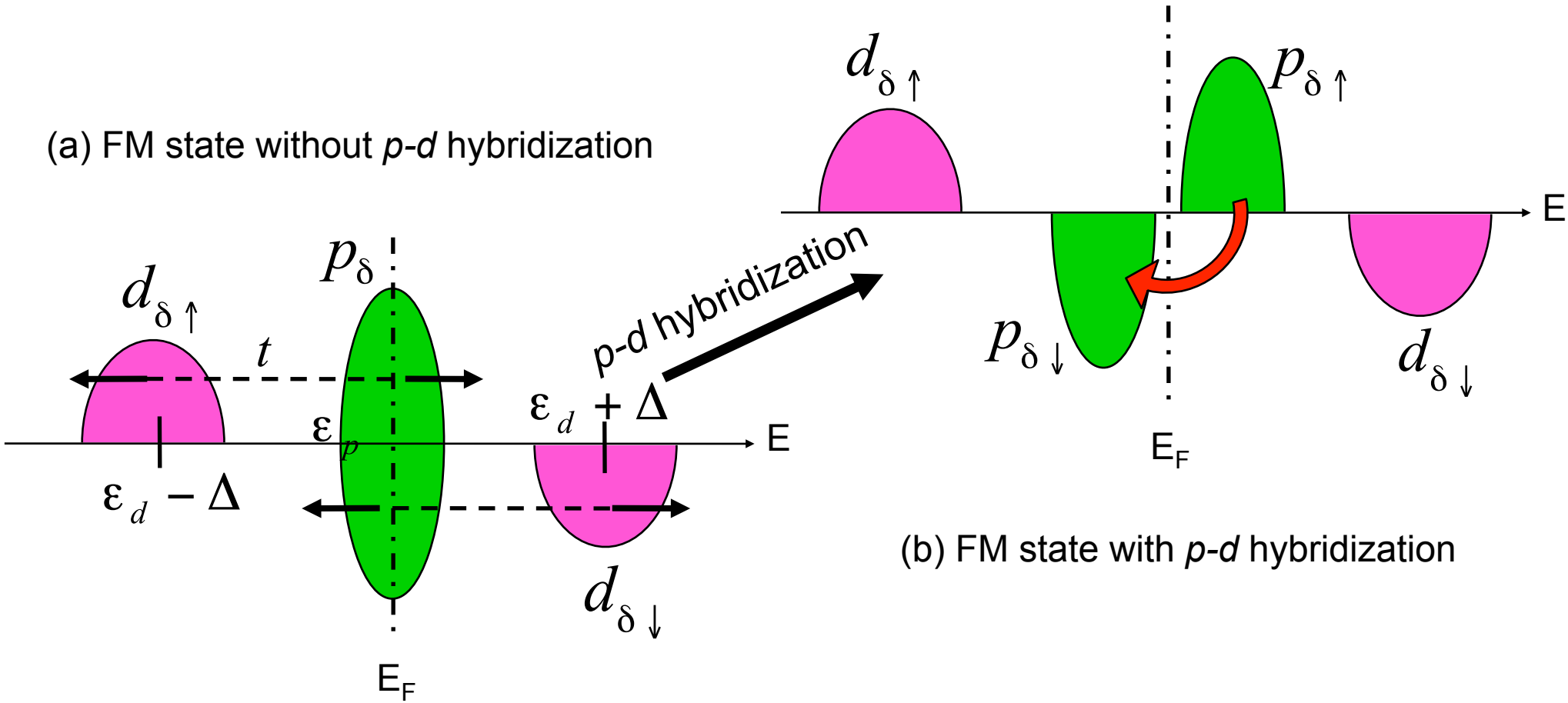


Vanadium Benzene Chain



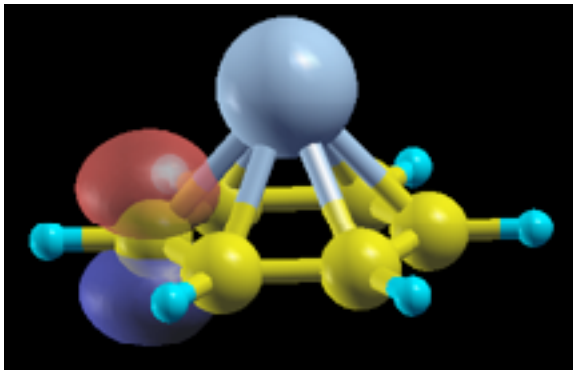
Model of V-Bz electronic structure

Now we can propose model to clarify the essence of the electronic structures.

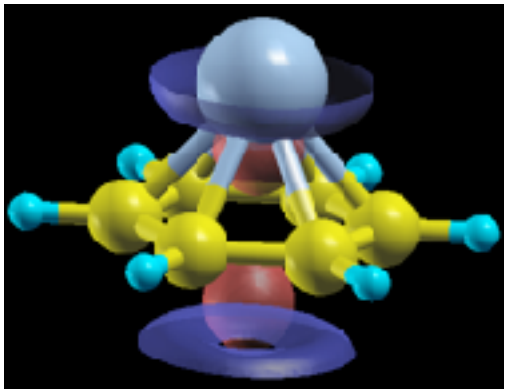


VBz Chain FM GGA MLWF

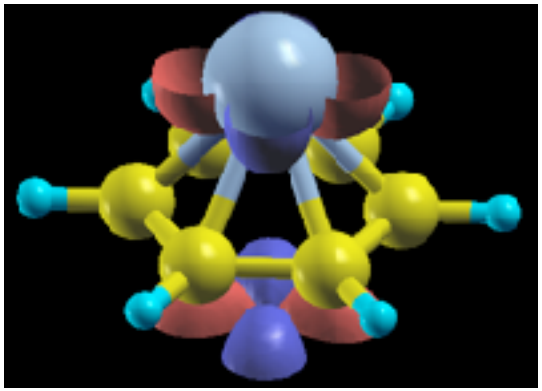
Initial guess: pz orbital on each C atom and 5d on V atom

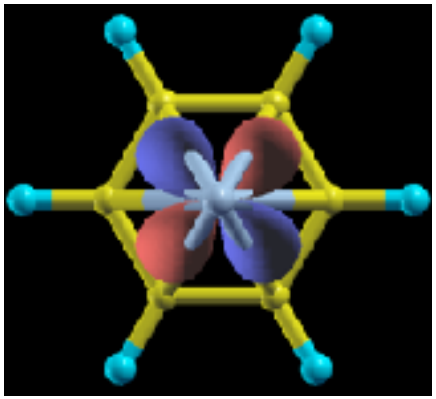


Spread 1.200



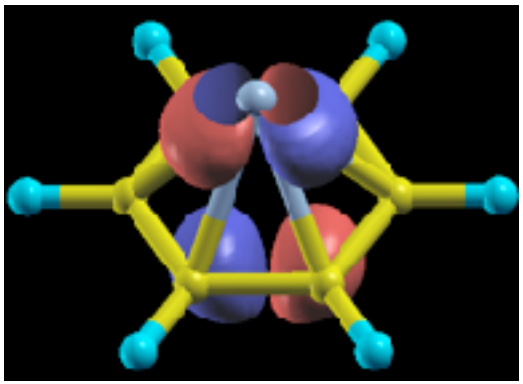
Spread 1.235

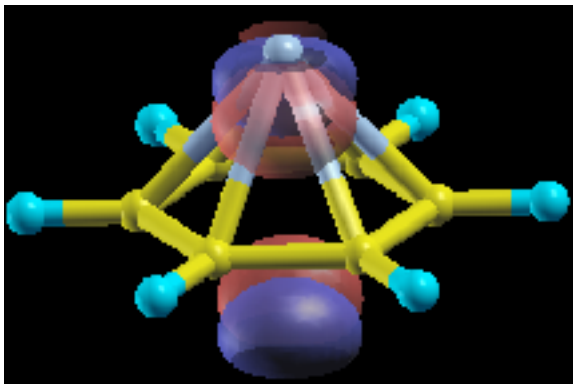




Spread 0.857

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

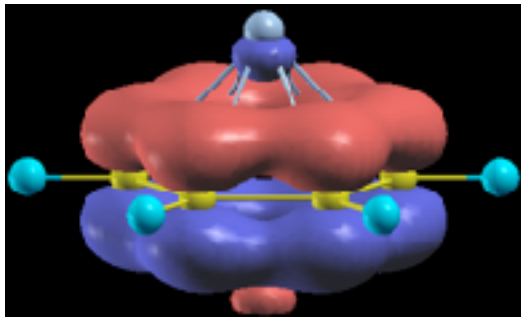




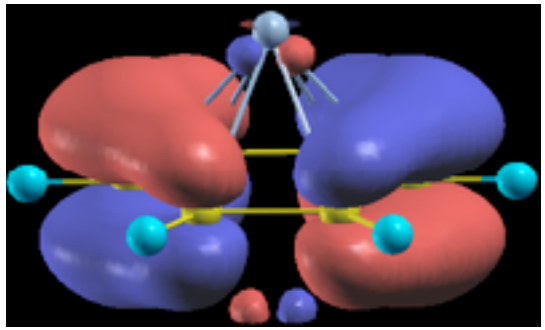
Spread 1.122

VBz Chain FM GGA MLWF

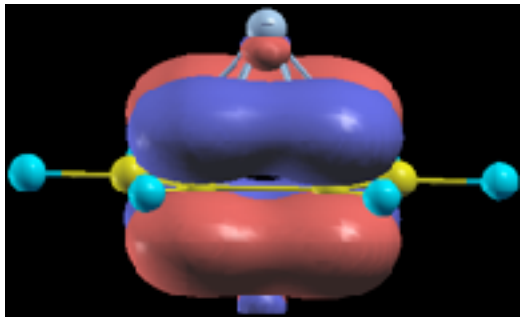
Initial guess: Benzene molecular orbitals and 5d on V atom



2.831 σ



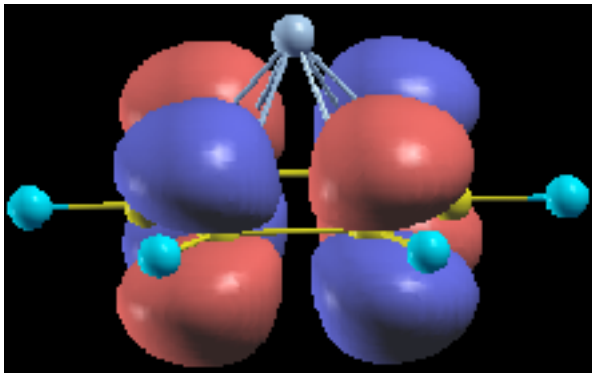
3.391 π



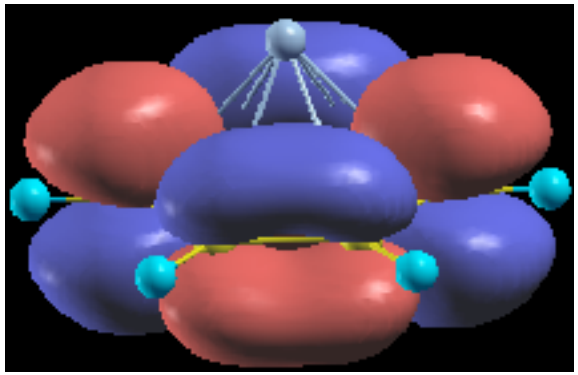
3.390 π

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

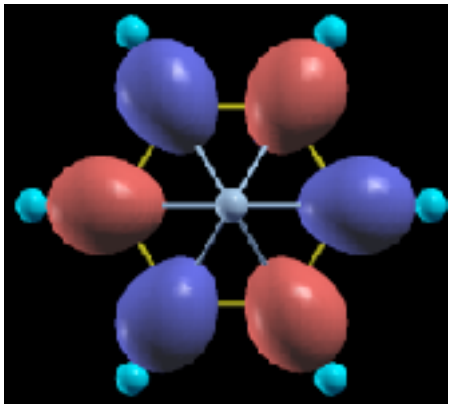
3.622 δ



3.616 δ



3.920



Thank you for your attention!