The Winter School on DFT: Theories and Practical Aspects

Institute of Physics (IOP), Chinese Academy of Sciences (CAS) in Beijing, China, Dec. 19-23, 2016.

Theory of Berry Phase and Wannier Function

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Dec. 19-23@IOP, CAS, Beijing

M. V. Berry

Awards [edit]

Berry has been given the following prizes and awards:[6]

- Maxwell Medal and Prize, Institute of Physics, 1978
- Elected Fellow of the Royal Society of London, 1982
- Elected Fellow of the Royal Society of Arts, 1983
- Elected Fellow o Fellow of the Royal Society of Arts
- Elected Member of the Royal Society of Sciences in Uppsala, Sweden, 1986
- Bakerian Lecturer, Royal Society, 1987
- Elected member of the European Academy, 1989
- Dirac Medal and Prize, Institute of Physics, 1990
- Lilienfeld Prize, American Physical Society, 1990
- Royal Medal, Royal Society, 1990
- Naylor Prize and Lectureship in Applied Mathematics, London Mathematical Society, 1992
- Foreign Member: US National Academy of Science, 1995
- Dirac Medal, International Centre for Theoretical Physics, 1996
- Kapitsa Medal, Russian Academy of Sciences, 1997
- Wolf Prize for Physics, Wolf Foundation, Israel, 1998
- Honorary Fellow of the Institute of Physics, 1999
- Foreign Member: Royal Netherlands Academy of Arts and Sciences, 2000[7]
- Ig Nobel Prize for Physics, 2000 (shared with Andre Geim for "The Physics of Flying Frogs")
- Onsager Medal, Norwegian Technical University, 2001
- Gibbs Lecturer, American Mathematical Society, 2002[8]
- 1st and 3rd prizes, Visions of Science, Novartis/Daily Telegraph, 2002
- Elected to Royal Society of Edinburgh 2005
- Pólya Prize, London Mathematical Society 2005
- Doctor of Science, honoris causa, University of Glasgow 2007
- Doctor of Science, honoris causa, Russian-Armenian (Slavonic) University in Yerevan 2012
- Lorentz Medal (2014)

M. V. Berry and Berry Phase

Proc. R. Soc. Lond. A **392**, 45–57 (1984)
Printed in Great Britain

Quantal phase factors accompanying adiabatic changes

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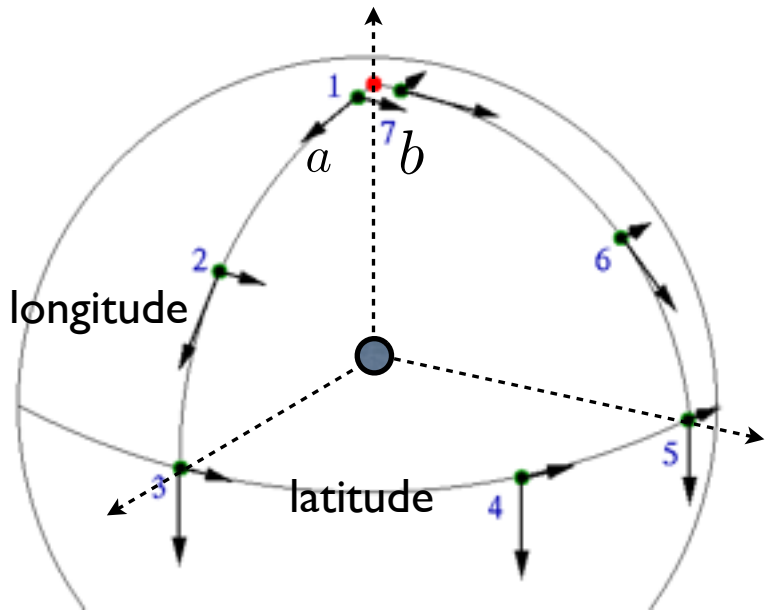
(*Received* 13 *June* 1983)

A quantal system in an eigenstate, slowly transported round a circuit C by varying parameters $\boldsymbol{R}$ in its Hamiltonian $\hat{H}(\boldsymbol{R})$, will acquire a geometrical phase factor $\exp\{i\gamma(C)\}$ in addition to the familiar dynamical phase factor. An explicit general formula for $\gamma(C)$ is derived in terms of the spectrum and eigenstates of $\hat{H}(\boldsymbol{R})$ over a surface spanning C. If C lies near a degeneracy of $\hat{H}$, $\gamma(C)$ takes a simple form which includes as a special case the sign change of eigenfunctions of real symmetric matrices round a degeneracy. As an illustration $\gamma(C)$ is calculated for spinning particles in slowly-changing magnetic fields; although the sign reversal of spinors on rotation is a special case, the effect is predicted to occur for bosons as well as fermions, and a method for observing it is proposed. It is shown that the Aharonov–Bohm effect can be interpreted as a geometrical phase factor.

Geometric phase: A classical Case

Geometric phase: parallel transport of tangent vector on curved surface



1. $a + bi$

$$\downarrow$$

7. $e^{i\frac{\pi}{2}}(a + bi) = -b + ai$

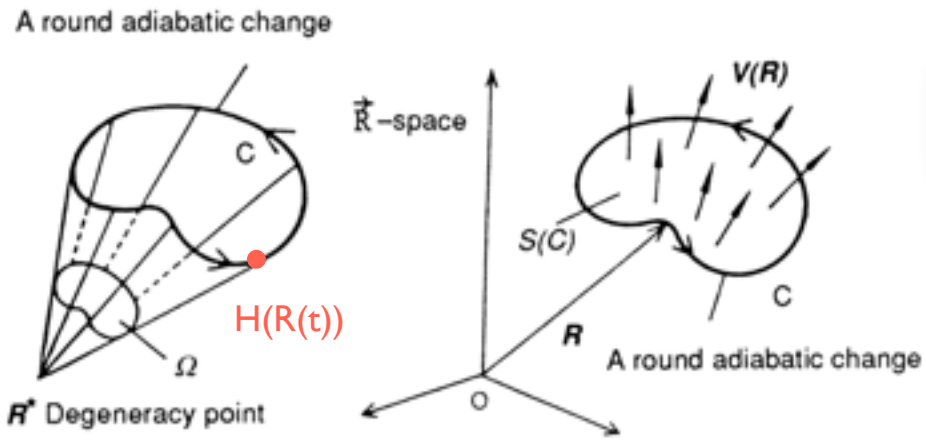
The twisted angle of the tangent vector after a parallel transport loop is equal to the solid angle subtended by the path it transversed.

http://torus.math.uiuc.edu/jms/java/dragsphere/

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

R(t) parameter space



Time dependent cyclic evolution: t -> 0 - T

$$\hat{H}(\boldsymbol{R}(t))\,|\psi(t)\rangle = \mathrm{i}\hbar\,|\dot{\psi}(t)\rangle$$

At each R(t)

$$H(\boldsymbol{R}(t))\;|n(\boldsymbol{R}(t))\rangle \;=\; E_n\,(\boldsymbol{R}(t))\;|n(\boldsymbol{R}(t))\rangle$$

but there is arbitrary phase not determined

$$|n(\boldsymbol{R})\rangle \longrightarrow \exp[i\chi(\boldsymbol{R})]\,|n(\boldsymbol{R})\rangle$$

---

adiabatic approximation

At the next neighboring R(t)

$|n(\boldsymbol{R})\rangle$ stays in n-state, but not in m-state (m!=n)

$$\langle m(R(t+\Delta t)|n(R(t))\rangle = 0$$

$$\Longrightarrow\; n(R(t))\rangle \to c_n(t)|n(R(t))\rangle$$

$$c_n(t) = e^{-i/\hbar\int_0^t E_n(t')dt'}\,e^{i\gamma_n(t)}$$

$$|\psi(t)\rangle = \exp\left\{\frac{-\mathrm{i}}{\hbar}\int_0^t \mathrm{d}t' E_n(\boldsymbol{R}(t'))\right\}\exp\left(\mathrm{i}\gamma_n(t)\right)|n(\boldsymbol{R}(t))\rangle$$

additional time-dependent phase

$$\dot{\gamma}_n(t) = \mathrm{i}\langle n(\boldsymbol{R}(t))\,|\,\nabla_{\boldsymbol{R}}\,n(\boldsymbol{R}(t))\rangle\cdot\dot{\boldsymbol{R}}(t)$$

After adiabatic cyclic loop evolution: t -> 0 - T

$$|\psi(T)\rangle = \exp\left(\mathrm{i}\gamma_n(\mathrm{C})\right)\exp\left\{\frac{-\mathrm{i}}{\hbar}\int_0^T \mathrm{d}t\, E_n(\boldsymbol{R}(t))\right\}|\psi(0)\rangle$$

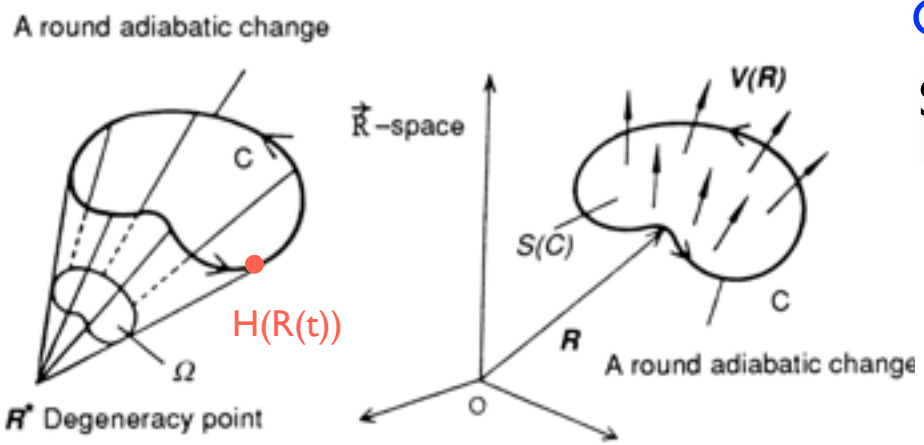
the geometric phase acquired (Berry phase)

$$\gamma_n(\mathrm{C}) = \mathrm{i}\oint_{\mathrm{C}}\langle n(\boldsymbol{R})|\,\nabla_{\boldsymbol{R}}\,n(\boldsymbol{R})\rangle\cdot\mathrm{d}\boldsymbol{R}$$

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

R(t) parameter space



Geometric phase: $\gamma_n(\mathrm{C}) = i\oint_C \langle n(\boldsymbol{R}) \,|\, \nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle d\boldsymbol{R}$

Stoke's theorem

Stoke's theorem is applicable only if $S(C)$ is simply connected.

$$\gamma_n(\mathrm{C}) = -\mathrm{Im}\iint_{\mathrm{C}} \mathrm{d}\boldsymbol{S}\cdot\nabla\times\langle n|\,\nabla n\rangle,$$

$$= -\mathrm{Im}\iint_{\mathrm{C}} \mathrm{d}\boldsymbol{S}\cdot\langle\nabla n|\times|\nabla n\rangle,$$

$$= -\mathrm{Im}\iint_{\mathrm{C}} \mathrm{d}\boldsymbol{S}\cdot\sum_{m\neq n}\langle\nabla n|\,m\rangle\times\langle m\,|\nabla n\rangle$$

$$\hat{H}(\boldsymbol{R})\,|n(\boldsymbol{R})\rangle = E_n(\boldsymbol{R})\,|n(\boldsymbol{R})\rangle$$

$$\langle m|\,\nabla n\rangle = \langle m|\,\nabla\hat{H}\,|n\rangle/(E_n - E_m), \quad m\neq n$$

Thus γ_n can be expressed as

$$\gamma_n(\mathrm{C}) = -\iint_{\mathrm{C}} \mathrm{d}\boldsymbol{S}\cdot\boldsymbol{V}_n(\boldsymbol{R}),$$

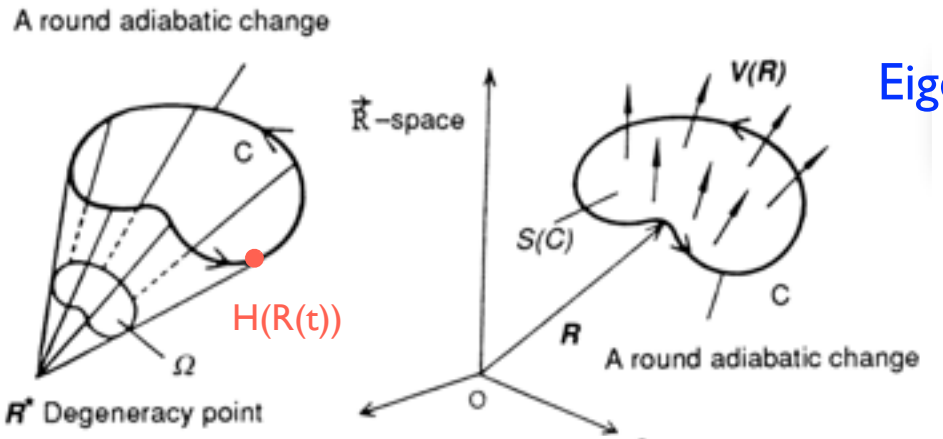
where

$$\boldsymbol{V}_n(\boldsymbol{R}) \equiv \mathrm{Im}\sum_{m\neq n}\frac{\langle n(\boldsymbol{R})|\,\nabla_{\boldsymbol{R}}\hat{H}(\boldsymbol{R})|\,m(\boldsymbol{R})\rangle\times\langle m(\boldsymbol{R})|\,\nabla_{\boldsymbol{R}}\hat{H}(\boldsymbol{R})|\,n(\boldsymbol{R})\rangle}{(E_m(\boldsymbol{R})-E_n(\boldsymbol{R}))^2}$$

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

R(t) parameter space



Eigenstate: $|\psi(t)\rangle = \exp\left\{\frac{-i}{\hbar}\int_0^t dt' E_n(\boldsymbol{R}(t'))\right\} \exp(i\gamma_n(t)) |n(\boldsymbol{R}(t))\rangle$

Geometric phase: $\gamma_n(C) = i\oint_C \langle n(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle d\boldsymbol{R} = -\iint_{S(C)} \boldsymbol{V}_n(\boldsymbol{R}) \cdot d\boldsymbol{S},$

Berry connection & $\boldsymbol{A}(\boldsymbol{R}) = i\langle n(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle$

Berry curvature: $\boldsymbol{V}_n(\boldsymbol{R}) = \nabla_{\boldsymbol{R}} \times i\langle n(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle$

$\boldsymbol{B}(\boldsymbol{r}) = \nabla \times \boldsymbol{A}(\boldsymbol{r})$

Stoke's theorem is applicable only if $S(C)$ is simply connected.

Gauge dependence: $|n(\boldsymbol{R})\rangle \rightarrow \exp[i\chi(\boldsymbol{R})]|n(\boldsymbol{R})\rangle$

$\langle n(\boldsymbol{R})\nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle \rightarrow \langle n(\boldsymbol{R})\nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle + i\nabla_{\boldsymbol{R}}\chi(\boldsymbol{R})$

$\nabla_{\boldsymbol{R}} \times \nabla_{\boldsymbol{R}}\chi(\boldsymbol{R}) = 0$

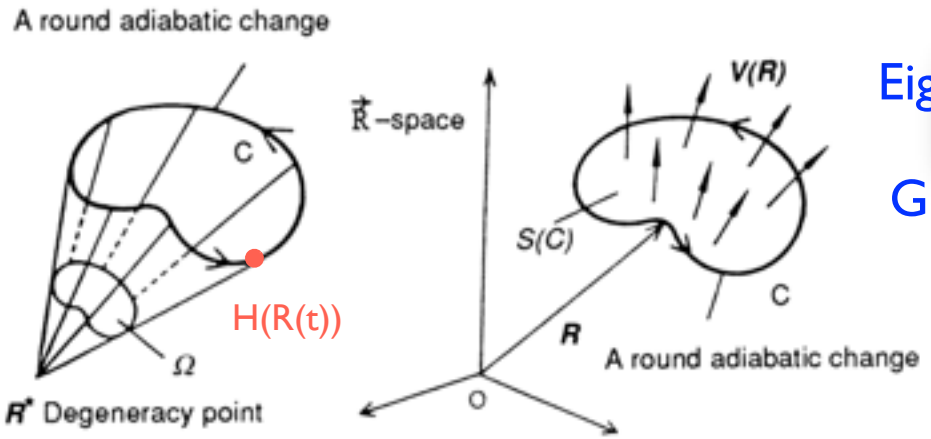
$\boldsymbol{A}(\boldsymbol{R})$ is gauge-dependent, while $\boldsymbol{V}_n(\boldsymbol{R})$ is gauge-invariant.

a 'magnetic field' (in parameter space) whose 'vector potential' is Im $\langle n|\nabla n\rangle$

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

R(t) parameter space



Eigenstate: $|\psi(t)\rangle = \exp\left\{\frac{-\mathrm{i}}{\hbar}\int_0^t \mathrm{d}t' E_n(\boldsymbol{R}(t'))\right\} \exp(\mathrm{i}\gamma_n(t)) |n(\boldsymbol{R}(t))\rangle$

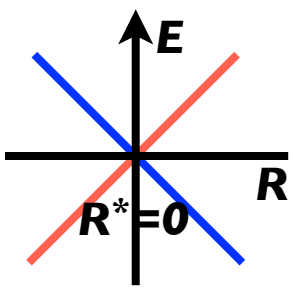
Geometric phase:

$$\gamma_n(\mathrm{C}) = i\oint_{\mathrm{C}} \langle n(\boldsymbol{R}) \,|\, \nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle d\boldsymbol{R} = -\iint_{S(\mathrm{C})} \boldsymbol{V}_n(\boldsymbol{R})\cdot d\boldsymbol{S},$$

$$\boldsymbol{V}_n(\boldsymbol{R}) = \mathrm{Im}\sum_{m\neq n} \frac{\langle n(\boldsymbol{R}) \,|\, \nabla_{\boldsymbol{R}} H(\boldsymbol{R}) \,|\, m(\boldsymbol{R})\rangle \times \langle m(\boldsymbol{R}) \,|\, \nabla_{\boldsymbol{R}} H(\boldsymbol{R}) \,|\, n(\boldsymbol{R})\rangle}{(E_m(\boldsymbol{R}) - E_n(\boldsymbol{R}))^2}.$$

$\boldsymbol{R}^*$ is the point where $E_m(\boldsymbol{R}^*)=E_n(\boldsymbol{R}^*)$ with energy degeneracy or band crossing.

around $\boldsymbol{R}^*$:



$$H(\boldsymbol{R}) = \tfrac{1}{2}\begin{pmatrix} Z & X-iY \\ X+iY & -Z \end{pmatrix} = \tfrac{1}{2}\,\boldsymbol{R}\cdot\boldsymbol{\sigma}$$

$$E_{\pm}(\boldsymbol{R}) = \pm\tfrac{1}{2}R$$

$$V_{+}(\boldsymbol{R}) = R/2R^3.$$

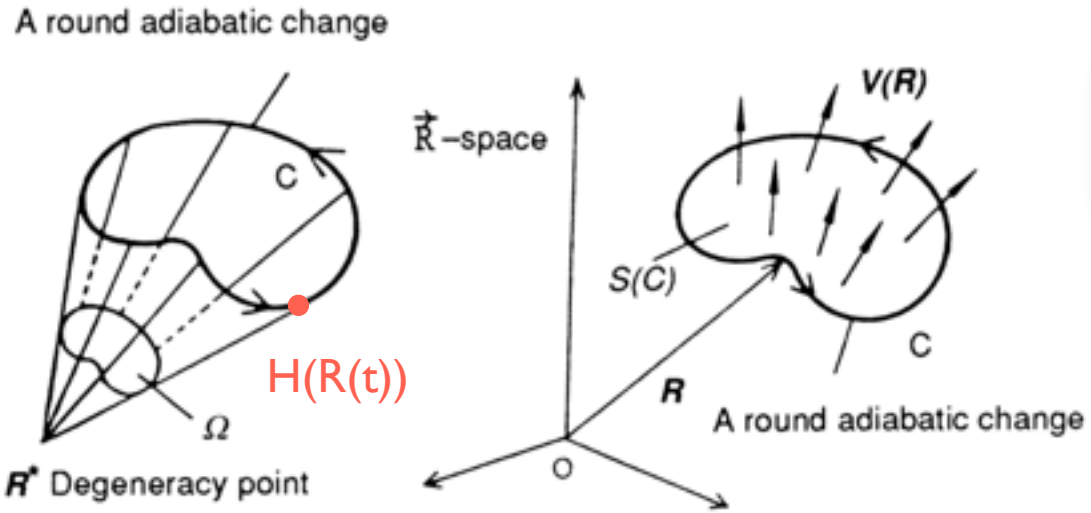
Magnetic monopole in R-space

$$\exp\{\mathrm{i}\gamma_{\pm}(\mathrm{C})\} = \exp\{\mp\tfrac{1}{2}\mathrm{i}\Omega(\mathrm{C})\}$$

Berry phase:
1, accumulated phase along loop-path *C* inside of vector potential;
2, magnetic flux through *S*;
3, the solid angle subtended by *S*(*C*) related to R*.

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)



$$\boldsymbol{R} = (x, y, z)$$

$$H(\boldsymbol{R}) = \frac{1}{2}\begin{pmatrix} Z & X-iY \\ X+iY & -Z \end{pmatrix} = \frac{1}{2}\,\boldsymbol{R}\cdot\boldsymbol{\sigma}$$

mapping from ***R*** space to ***H***-space

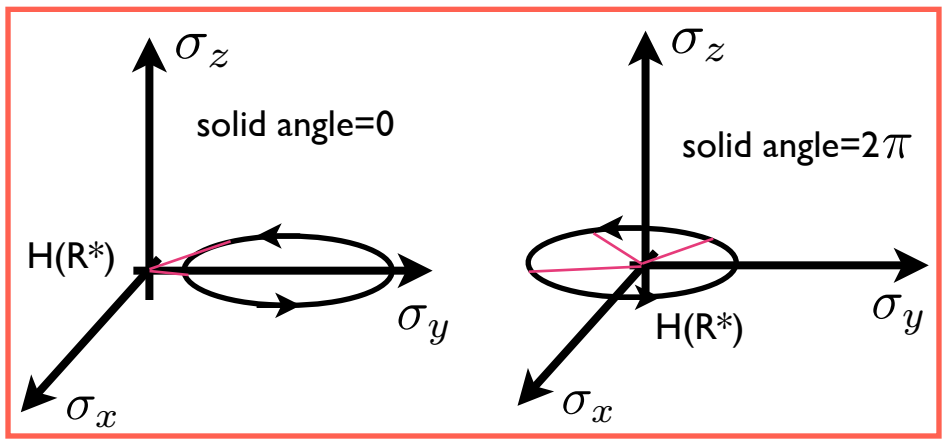
$H_{\sigma x}(R)=X$

$H_{\sigma y}(R)=Y$

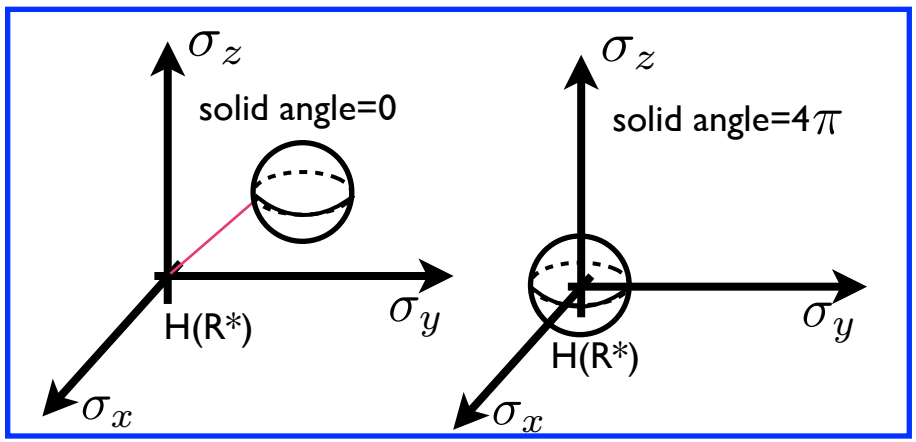
$H_{\sigma z}(R)=Z$

Berry phase depends on the topology of H(R) related to H(R*) !

two-Dimensional case: no kz



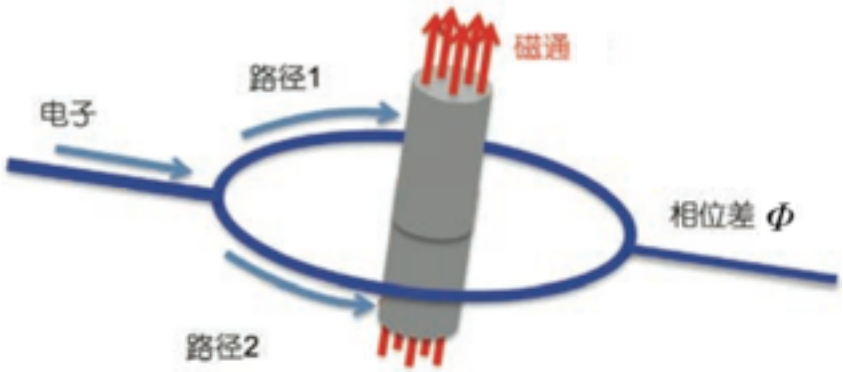
three-Dimensional case: with kz



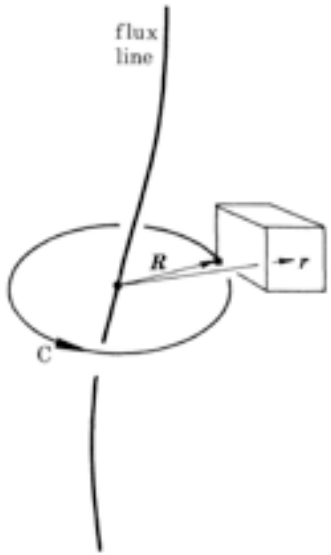
Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

Aharonov-Bohm Effect (1959)



$$\oint_C \boldsymbol{A}(\boldsymbol{R})\cdot \mathrm{d}\boldsymbol{R} = \Phi$$



$$H(\hat{\boldsymbol{p}} - q\boldsymbol{A}(\hat{\boldsymbol{r}}), \hat{\boldsymbol{r}} - \boldsymbol{R})\,|\,n(\boldsymbol{R})\rangle = E_n\,|n(\boldsymbol{R})\rangle$$

$$\langle \boldsymbol{r}\,|\,n(\boldsymbol{R})\rangle = \exp\left\{\frac{\mathrm{i}q}{\hbar}\int_{\boldsymbol{R}}^{\boldsymbol{r}} \mathrm{d}\boldsymbol{r}'\cdot\boldsymbol{A}(\boldsymbol{r}')\right\}\psi_n(\boldsymbol{r}-\boldsymbol{R}).$$

$$\begin{aligned}\langle n(\boldsymbol{R})|\,\nabla_{\boldsymbol{R}} n(\boldsymbol{R})\rangle &= \iiint \mathrm{d}^3\boldsymbol{r}\,\psi_n^*(\boldsymbol{r}-\boldsymbol{R})\left\{\frac{-\mathrm{i}q}{\hbar}\boldsymbol{A}(\boldsymbol{R})\,\psi_n(\boldsymbol{r}-\boldsymbol{R}) + \nabla_{\boldsymbol{R}}\psi_n(\boldsymbol{r}-\boldsymbol{R})\right\} \\ &= -\mathrm{i}q\boldsymbol{A}(\boldsymbol{R})/\hbar.\end{aligned}$$

$$\gamma_n(\mathrm{C}) = \frac{q}{\hbar}\oint_C \boldsymbol{A}(\boldsymbol{R})\cdot\mathrm{d}\boldsymbol{R} = q\Phi/\hbar$$

Quantum Geometric phase: Berry Phase

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 15 (1984)

M.V. Berry, *Proc.R. Soc. Lond.* A **392**, 45 (1984)

Proc. R. Soc. Lond. A **392**, 15–43 (1984)
Printed in Great Britain

Diabolical points in the spectra of triangles

BY M. V. BERRY, F.R.S., AND M. WILKINSON
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(*Received 27 April* 1983)

'Accidental' degeneracies between energy levels E_j and E_{j+1} of a real Hamiltonian can occur generically in a family of Hamiltonians labelled by at least two parameters $X, Y, \ldots$ Energy-level surfaces in E, X, Y space have (locally) a double-cone (diabolo) connection and we refer to the degeneracies themselves as 'diabolical points'. We studied the family of

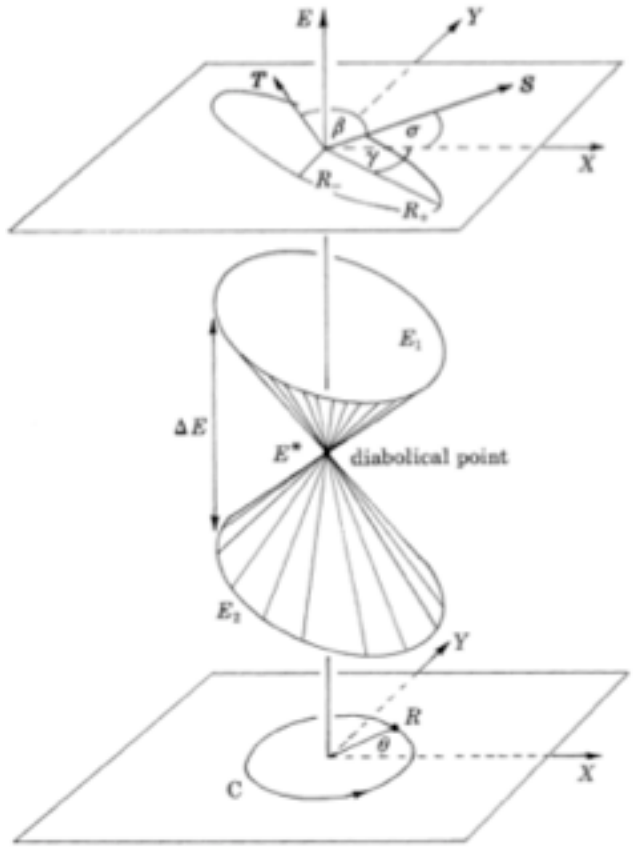


FIGURE 8. Geometry and notation near a diabolical point.

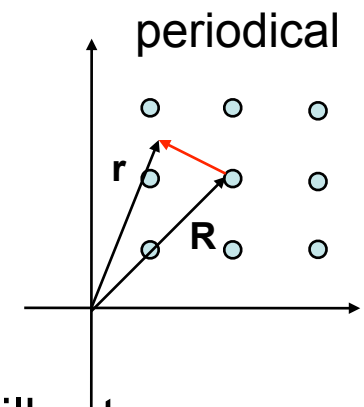
Wave-function in Solids

Bloch representation

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

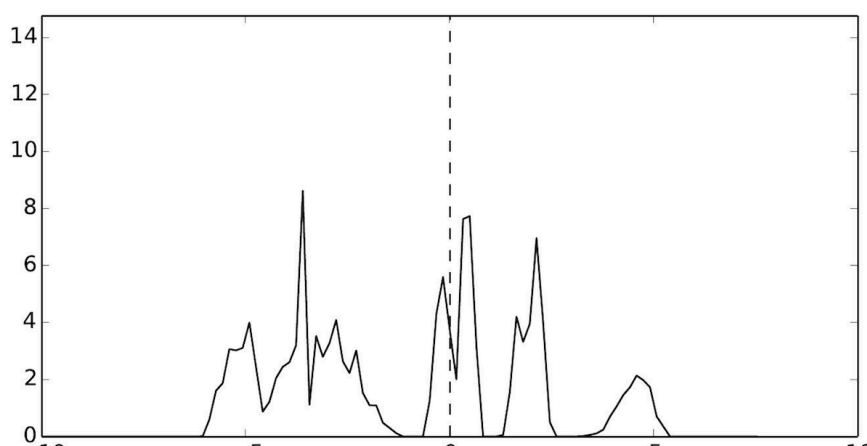
Wannier representation

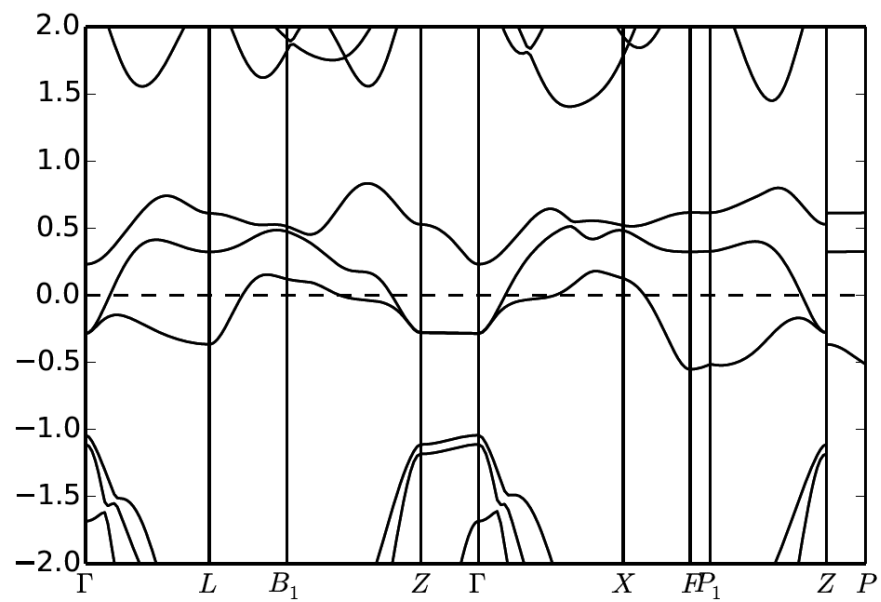
$$w_n(\mathbf{r}-\mathbf{R})=\left|\mathbf{R}n\right\rangle=\frac{V}{(2\pi)^3}\int_{BZ}\left|\psi_{n\mathbf{k}}(\mathbf{r})\right\rangle e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{k}$$



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.

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

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

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

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

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 $\Omega_D+\Omega_{OD}$ 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:

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

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

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

for local potential, but can be generalized to non-local case.

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

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

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

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

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

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

Gradient of Spread Functional

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

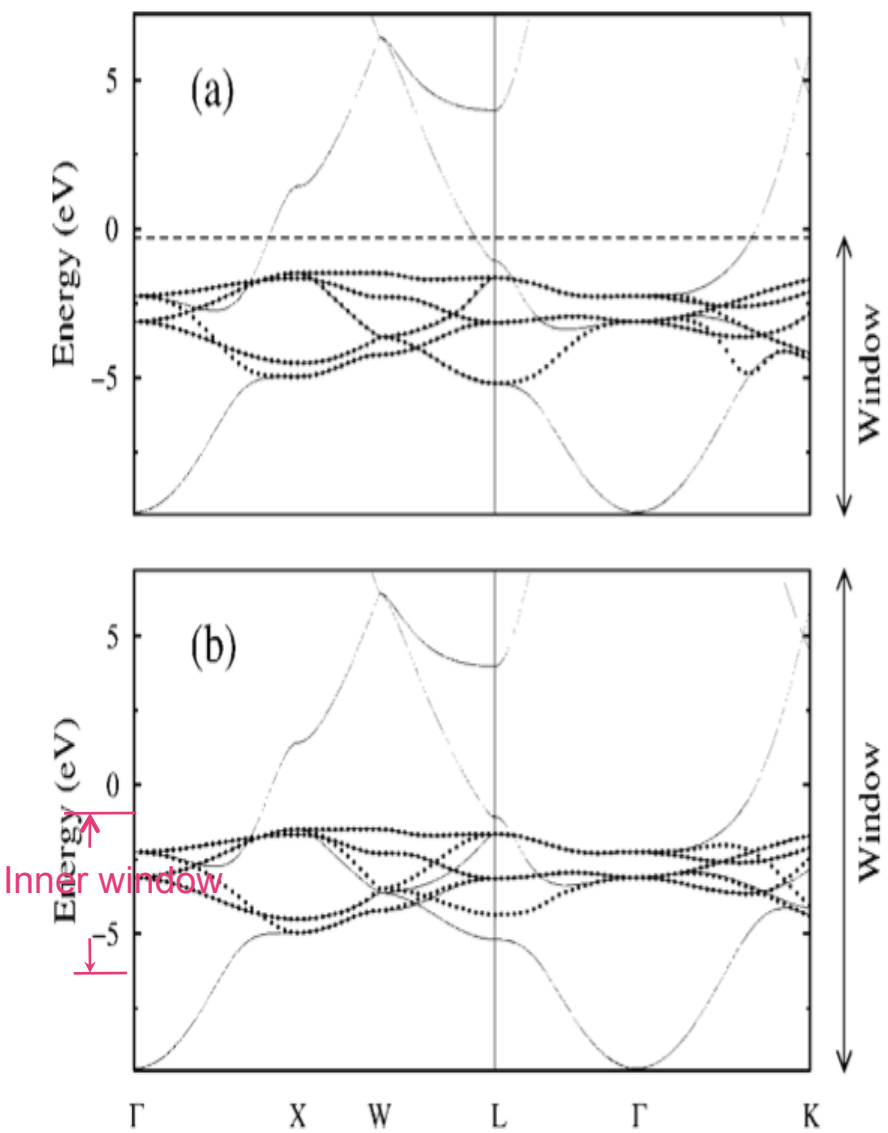
$$g_n(r) = g_{j,\beta}(r) = \phi_{j,\beta}(r)$$

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

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

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

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

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

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

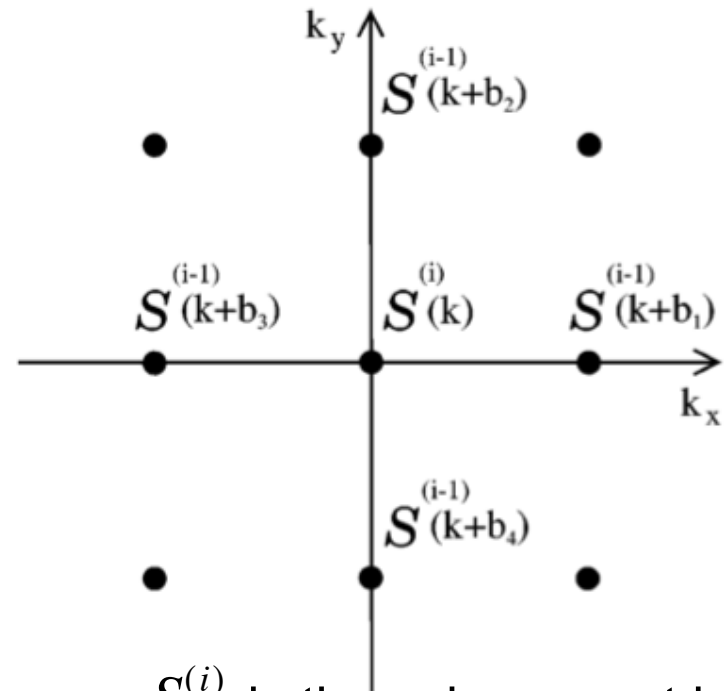
Using Lagrange multipliers to enforce orthonormality and the stationary condition at *i*-th iteration is:

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

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

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

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



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

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

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

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

Hamiltonian in Wannier gauge can be diagonalized and the bands inside the inner window will have the same 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:

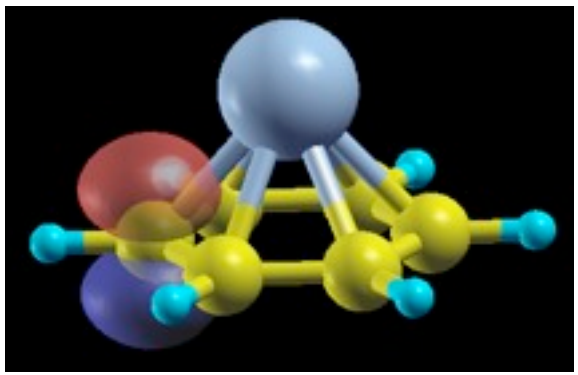
$$H_{nm}^{(W)}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H_{nm}^{(W)}(\mathbf{R})$$

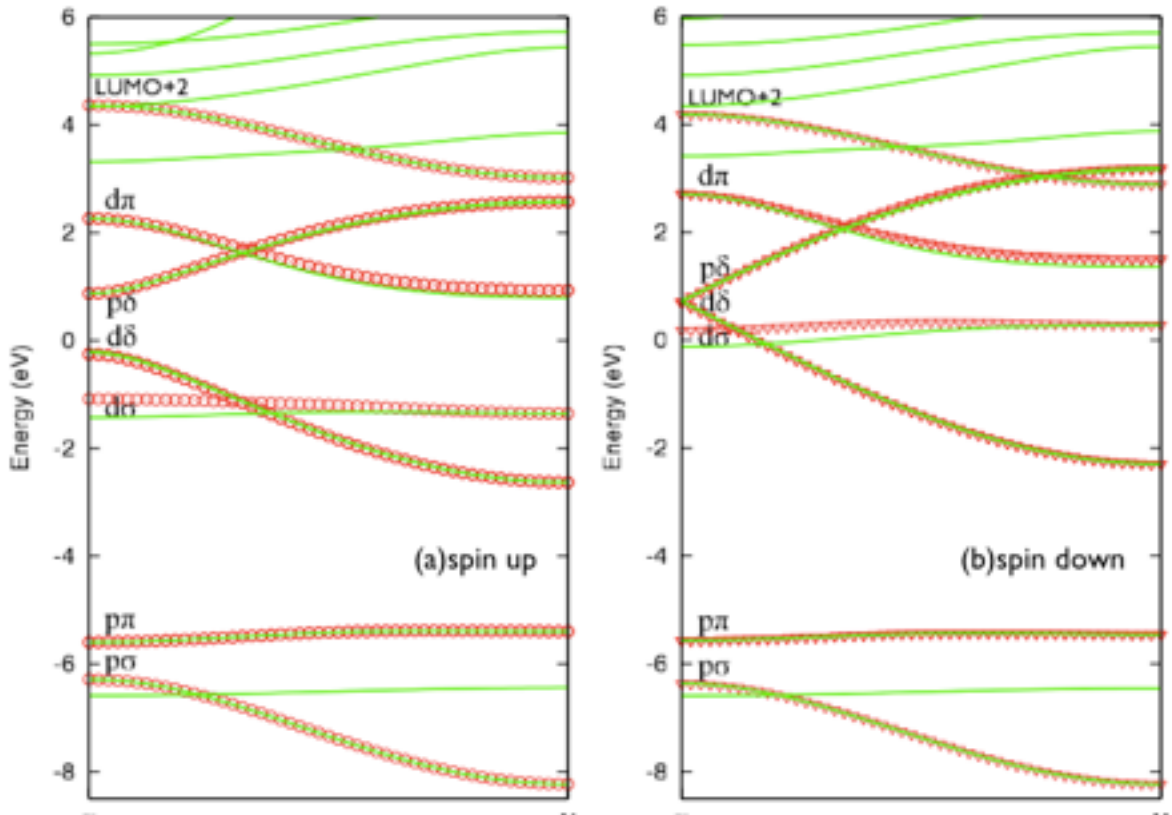
Diagonalize this Hamiltonian, the eigenvalues and states will be gotten.

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

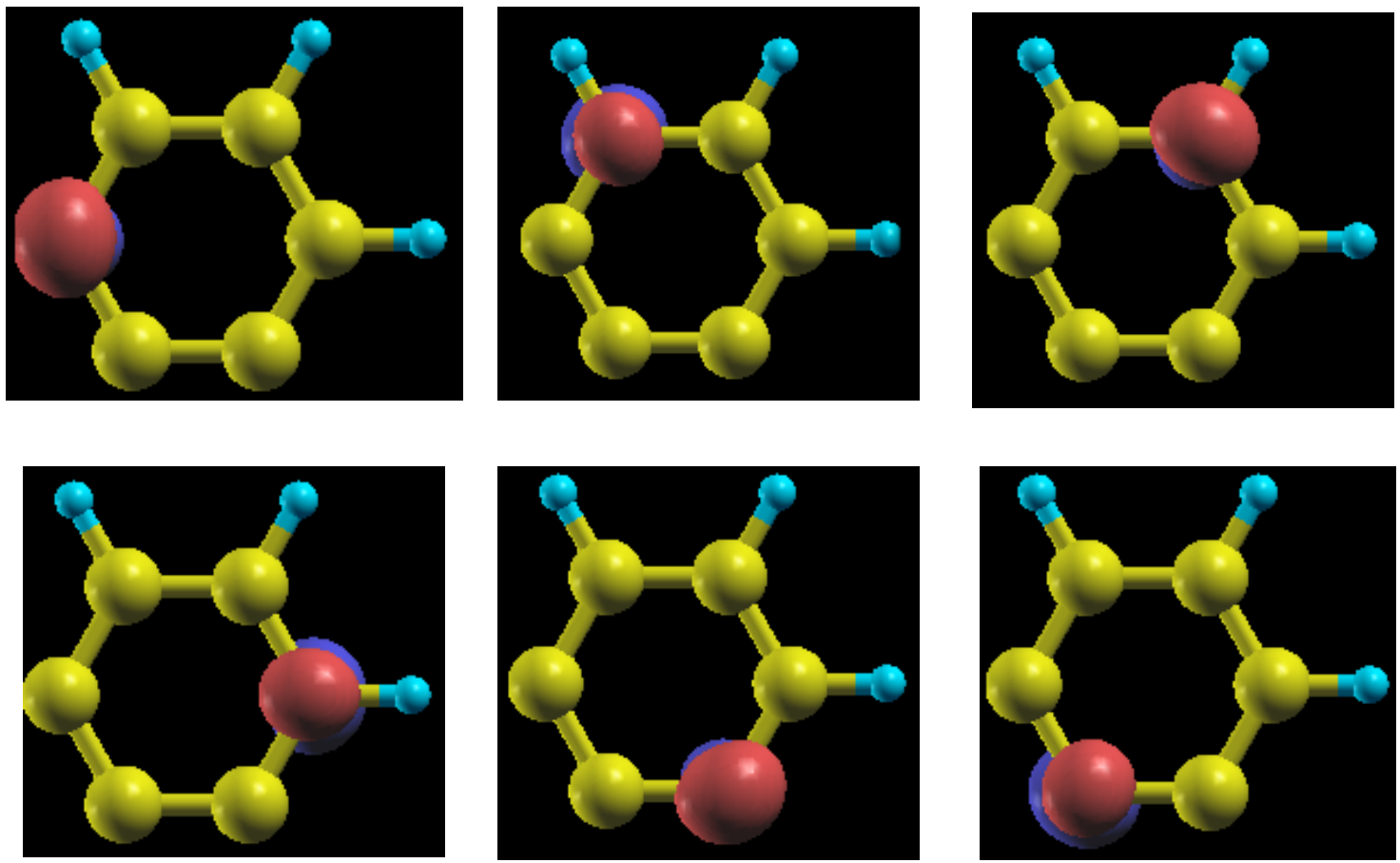
physical intuition is here and important!

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

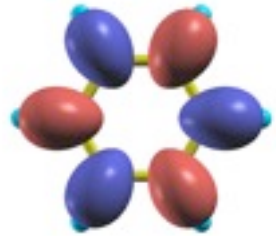
Orbital name	Number of included projector	Description
s	1	s orbital from PAOs
p	3	p_x, p_y, p_z from PAOs
px	1	p_x from PAOs
py	1	p_y from PAOs
pz	1	p_z from PAOs
d	5	$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$ from PAOs
dz2	1	d_{z^2} from PAOs
dx2-y2	1	$d_{x^2-y^2}$ from PAOs
dxy	1	d_{xy} from PAOs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

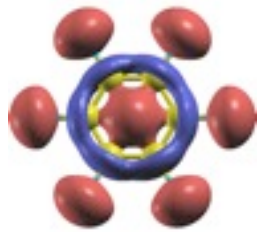
- With pz on each C atom as initial guess



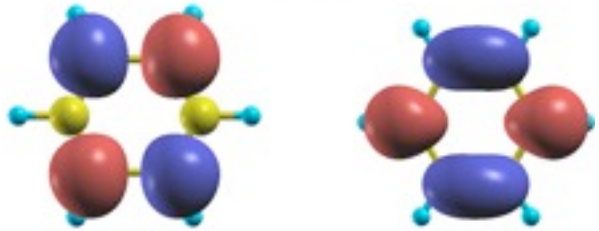
Benzene Molecular Orbitals



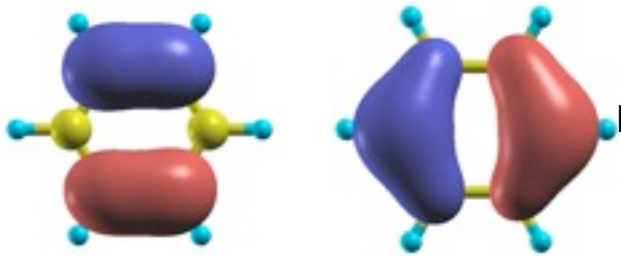
LUMO+2 3.35 eV (b_{2g}) ———



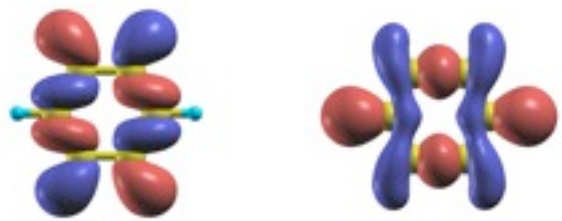
LUMO+1 3.30 eV (a_{1g})



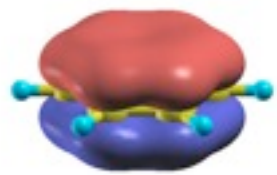
LUMO -0.55 eV (e_{2u}) ——— ———



HOMO -5.85 eV (e_{1g}) ——— ———

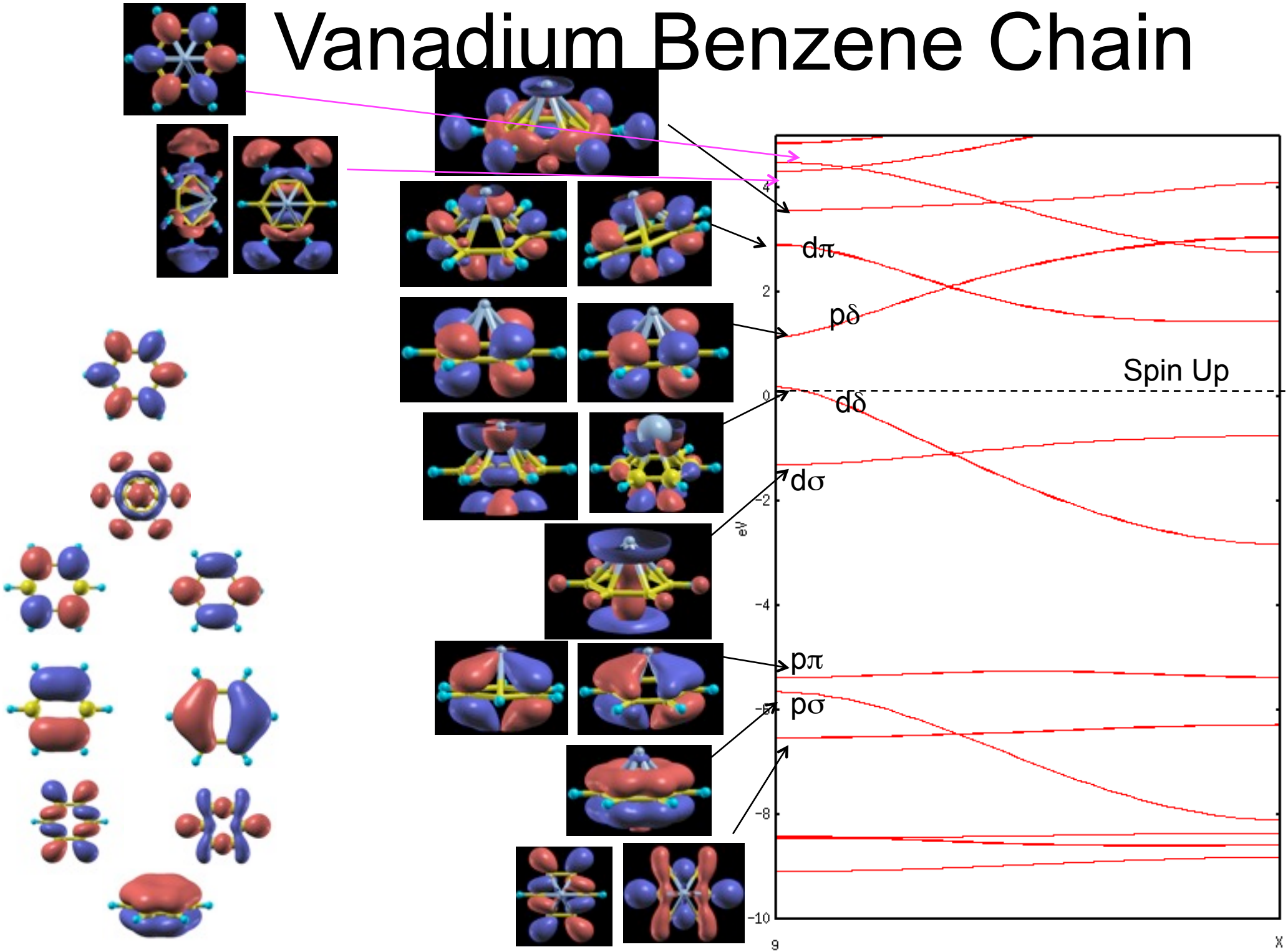


HOMO-1 -7.81 eV (e_{2g})



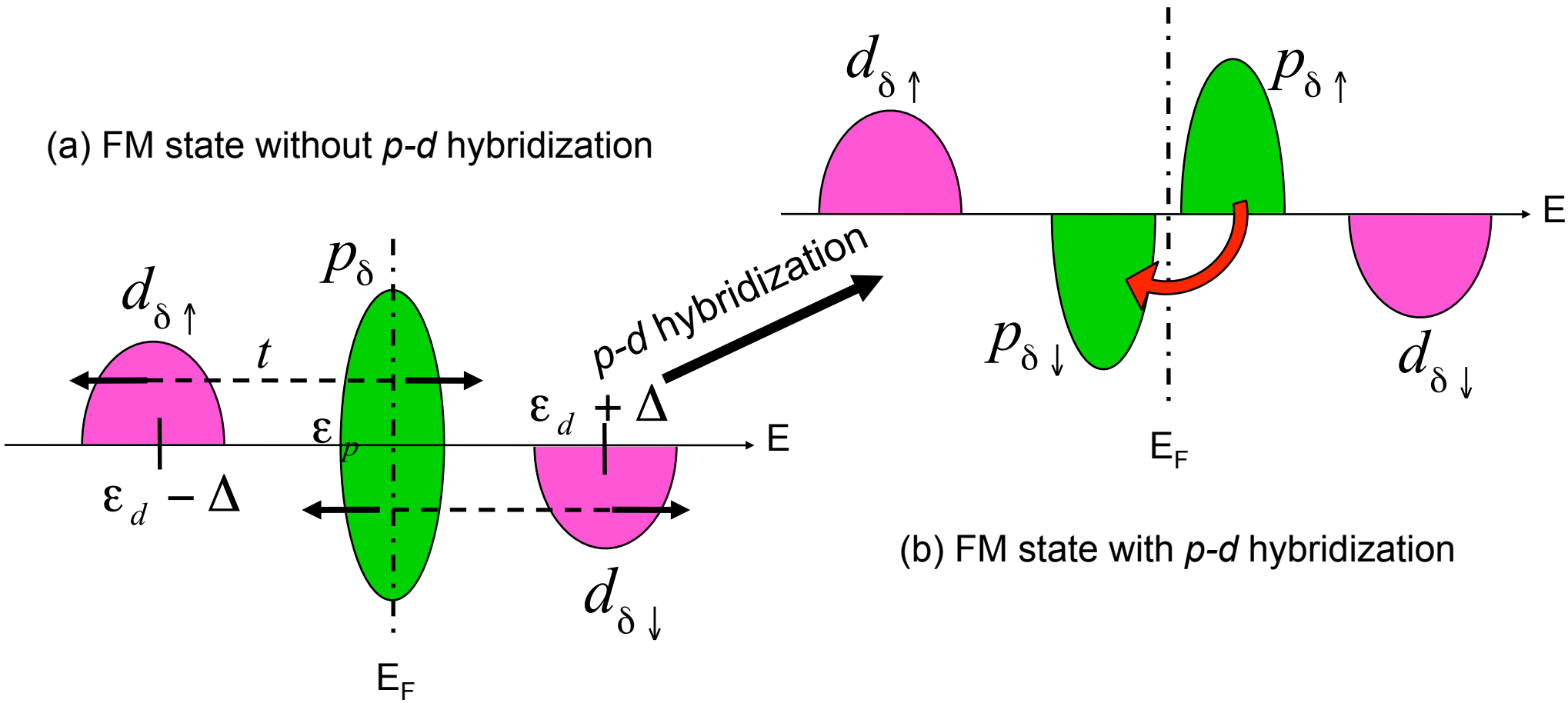
HOMO-2 -8.61 eV (a_{2u}) ———

Vanadium Benzene Chain



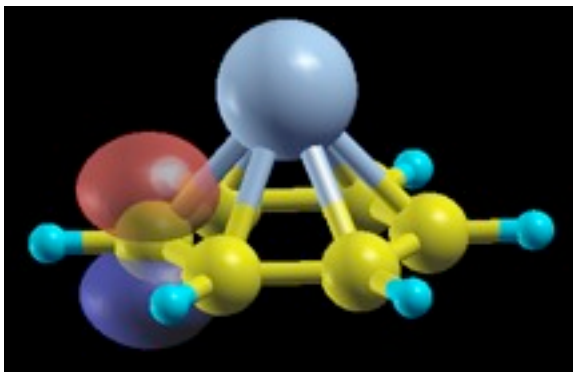
Model of V-Bz electronic structure

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

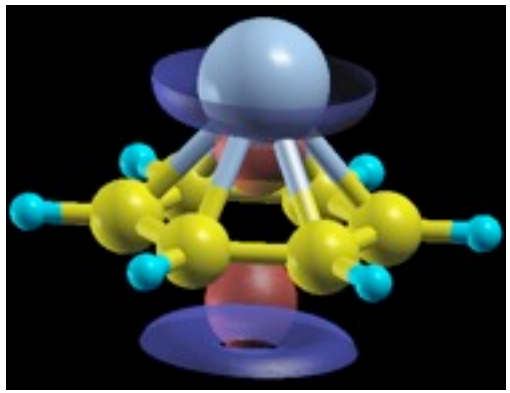


VBz Chain FM GGA MLWF

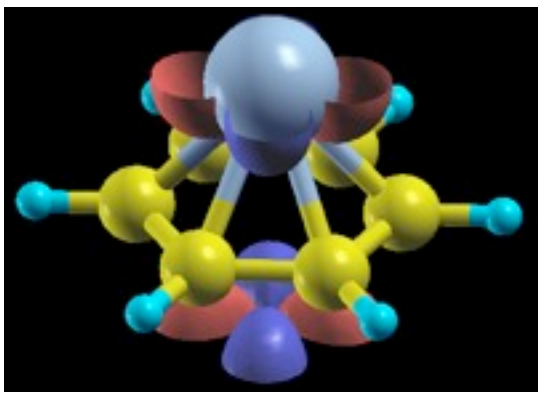
Initial guess: pz orbital on each C atom and 5d on V atom

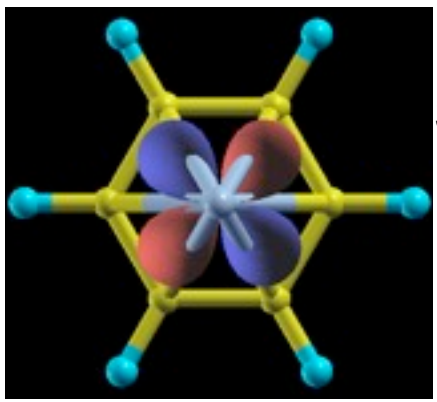


Spread 1.200



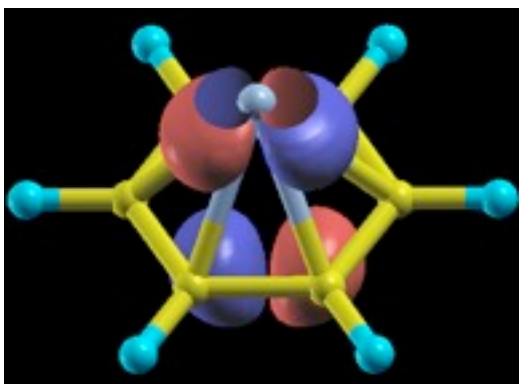
Spread 1.235

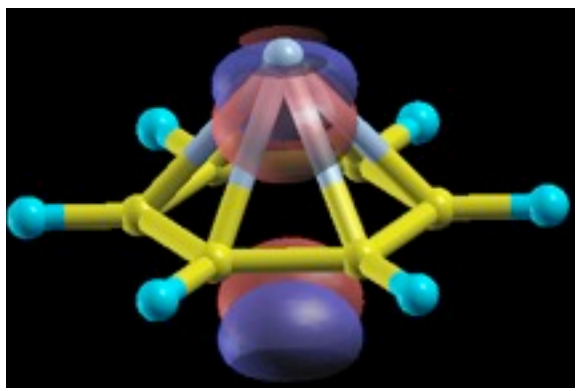




Spread 0.857

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

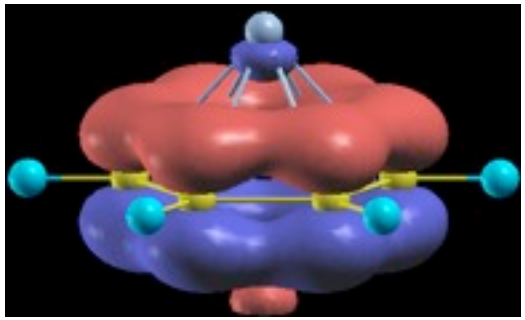




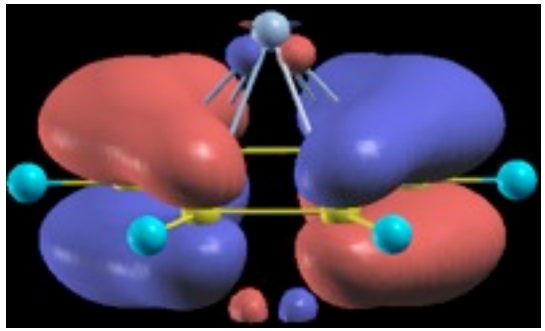
Spread 1.122

VBz Chain FM GGA MLWF

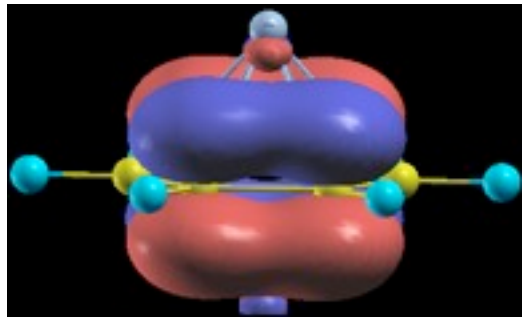
Initial guess: Benzene molecular orbitals and 5d on V atom



2.831 σ



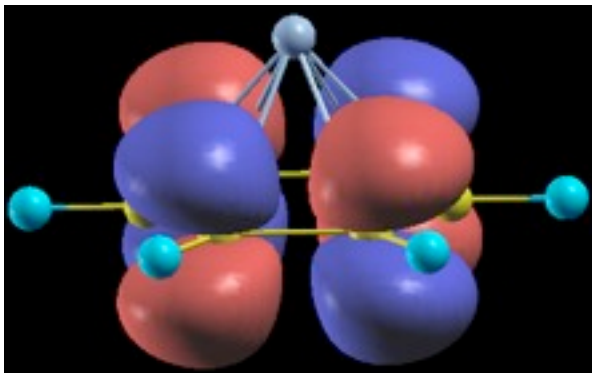
3.391 π



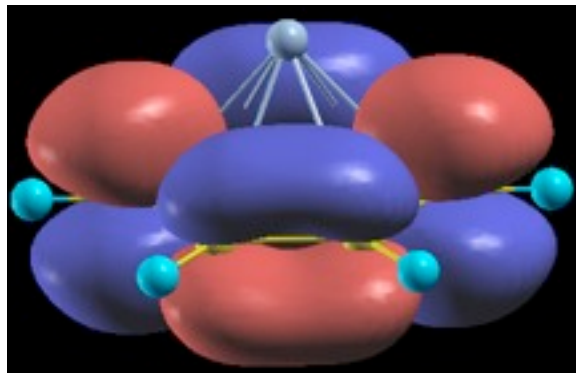
3.390 π

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

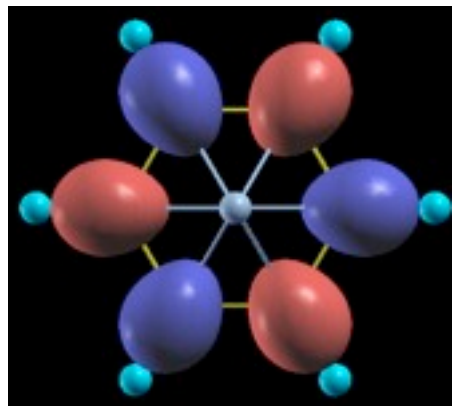
3.622 δ



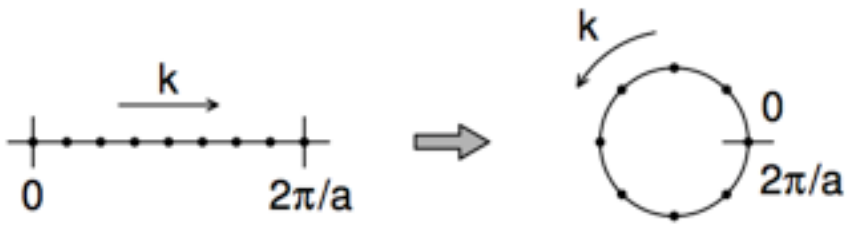
3.616 δ



3.920



Berry Phase and Wannier function



1D hybrid WF : $|w_0\rangle = \frac{a}{2\pi}\int dk\, e^{ikx}\,|u_k\rangle$

$$x_0 = \langle w_0|x|w_0\rangle$$

$$x|w_0\rangle = \frac{a}{2\pi}\int dk\,(-i\partial_k e^{ikx})\,|u_k\rangle = \frac{a}{2\pi}\int dk\, e^{ikx}\, i\,|\partial_k u_k\rangle$$

$$x_0 = -\frac{a}{2\pi}\,\mathrm{Im}\int_0^{2\pi/a} dk\,\langle u_k|\partial_k|u_k\rangle$$

$$x_0 = \frac{a\phi}{2\pi}$$

that is, *the Berry phase ϕ introduced earlier is nothing other than a measure of the location of the Wannier center in the unit cell.* The fact that ϕ was

ref: David Vanderbilt, Raffaele Resta: Quantum electrostatics of insulators – Polarization, Wannier functions, and electric fields

Thank you for your attention!

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Next lecture on the Berry phase based Band Topology Theory and its application on Topological Materials.