# Dirac semimetal in three dimensions

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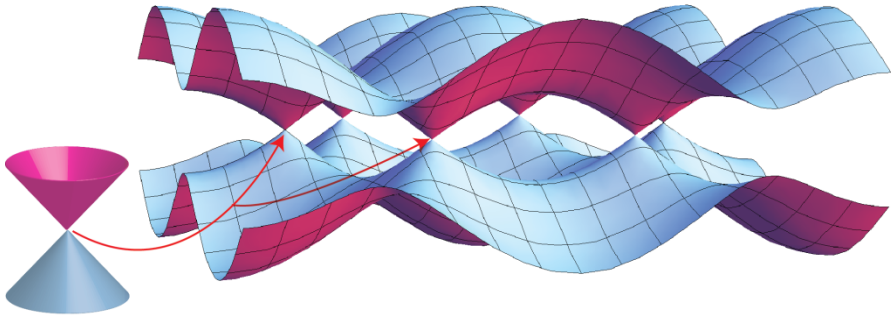
# Dirac points in Graphene



Without spin-orbit coupling

- At the Fermi level, two bands intersect at *K* and *K'*
- Dirac points in 2D; opposite chirality
- Dirac Hamiltonian:

$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\sigma_x + k_y\sigma_y\right)$$

- $\sigma_i$ are the Pauli matrices that describe electron pseudospin

What kind of perturbations will split these point-like two-fold degeneracies?

# 2D Dirac points lead to 2D topological phases

$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\sigma_x + k_y\sigma_y\right)$$

- Dirac Points in 2D are *not* robust
- Perturbations $\hat{H}' \propto \sigma_z$ split the Dirac points in graphene
- Haldane[1]: *T*-breaking $\hat{H}' \propto \sigma_z$ gaps the system into a quantum Hall insulator

- Including spin brings an additional index (Pauli matrices $\tau_i$)
- With spin, Dirac point has *four* degenerate states
- Must also include spin-orbit effects
- Kane & Mele[2]: spin-orbit $\propto \sigma_z\tau_z$ gaps the system into a topological insulator
- C atom is light so spin-orbit is negligible
- Effectively, four bands are point-like degenerate at *K* and *K'*


1. Haldane, F. D. M. Phys. Rev. Lett. **61**, 2015-2018 (1988).
2. Kane, C.L. and Mele, E.J. Phys. Rev. Lett. **95**, 226801 (2005).

# What about 3D?

- In 3D, the analogous 2-band Hamiltonian will be

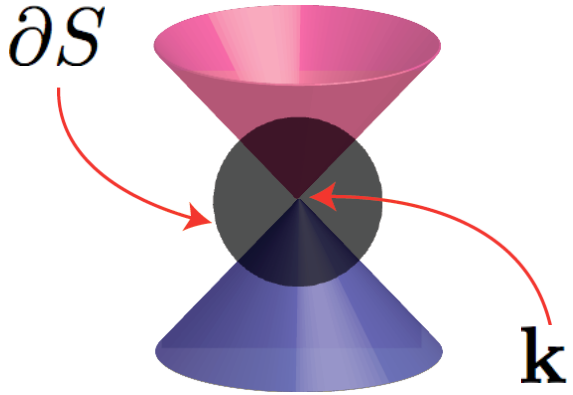
$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\sigma_x + k_y\sigma_y + k_z\sigma_z\right)$$

- 2-component spinor with this $\hat{H}_{\text{eff}}$ is called a Weyl fermion
- $\hat{H}_{\text{eff}}$ uses all 3 $\sigma_i$ so Weyl points are robust against perturbations

Does the Weyl Hamiltonian
have any topological content?

# Chern number of Weyl point

- Indeed, the first Chern number of the Weyl Hamiltonian is ±1



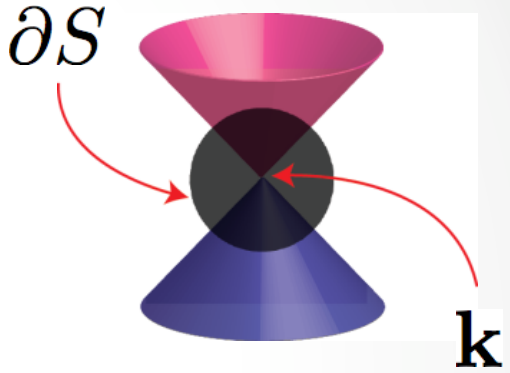

$n_{\mathbf{k}} = \pm 1$

- The first Chern number of a point $\mathbf{k}$ is given by

$$n = \frac{1}{2\pi i}\int_{\partial S} d\mathbf{a}\cdot\nabla\times\langle\psi_v(\mathbf{k})|\nabla|\psi_v(\mathbf{k})\rangle$$
$$= \frac{1}{\pi}\int_{\partial S} d\theta d\phi\ \mathrm{Im}\langle\partial_\theta\psi_v(\mathbf{k})|\partial_\phi\psi_v(\mathbf{k})\rangle$$

# 3D Weyl points

$$n = \frac{1}{2\pi i}\int_{\partial S} d\mathbf{a}\cdot\nabla\times\langle\psi_v(\mathbf{k})|\nabla|\psi_v(\mathbf{k})\rangle$$
$$= \frac{1}{\pi}\int_{\partial S} d\theta d\phi\ \mathrm{Im}\langle\partial_\theta\psi_v(\mathbf{k})|\partial_\phi\psi_v(\mathbf{k})\rangle$$




- Under **k** to –**k** (such as inversion or time reversal), the orientation of $d\mathbf{a}$ reverses as does $\nabla$.
- Under inversion, Chern number at **k**, $n_{\mathbf{k}} = -n_{-\mathbf{k}}$
- But time reversal is antiunitary ($i \rightarrow -i$), so $n_{\mathbf{k}} = +n_{-\mathbf{k}}$

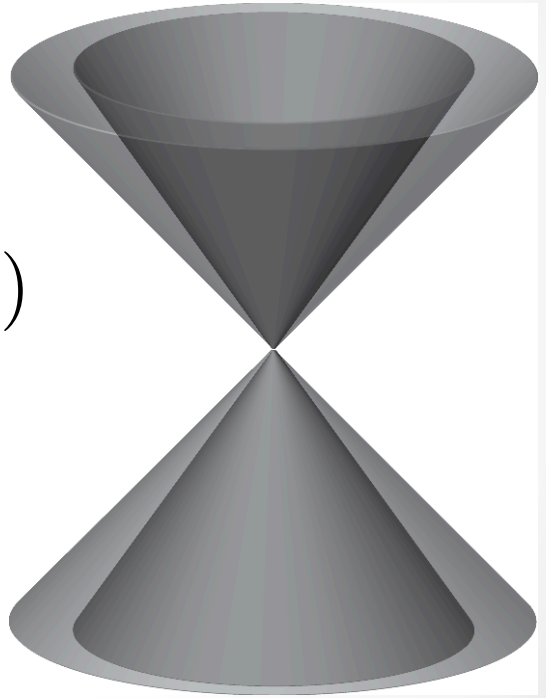
Under both time reversal and inversion, there must be two Weyl points at **k** with opposite Chern number and two more at **-k**

# 3D Dirac points

- When two Weyl points with opposite Chern number are on top of each other, the $\hat{H}_{\text{eff}}$ will be a 4 × 4 matrix linear in momentum **k**

$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\gamma_x + k_y\gamma_y + k_z\gamma_z\right)$$

- $\gamma_i$ are 4 × 4 Dirac matrices
- $\hat{H}_{\text{eff}}$ is called Dirac Hamiltonian
- Total Chern number of a Dirac point is 0



Therefore 3D Dirac points are *not* robust.
Can perturb Dirac point to access insulators!

# Weyl *vs.* Dirac semimetals

- Weyl semimetal: point-like degeneracy at the Fermi level between *one* conduction and *one* valence band

$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\sigma_x + k_y\sigma_y + k_z\sigma_z\right)$$

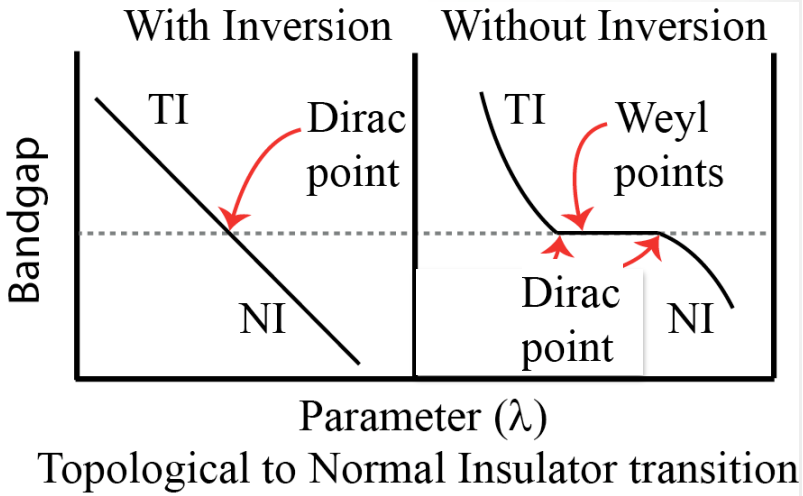
- Dirac semimetal: pointlike degeneracy at the Fermi level between *two* conduction and *two* valence bands

$$\hat{H}_{\text{eff}}(\mathbf{k}) = v\left(k_x\gamma_x + k_y\gamma_y + k_z\gamma_z\right)$$

- In both cases, the bands disperse linearly in all directions in $\mathbf{k}$

# One way to realize Dirac/Weyl semimetals

- The intermediate phase between a topological and a normal insulator is a Dirac/ Weyl semimetal[1]
- Breaking inversion or time reversal splits a Dirac point into Weyl points[2]
- Right before gap opening, Weyl points come together to form a Dirac point
- To realize a Weyl semimetal in 3D, one must start with a parent Dirac semimetal!



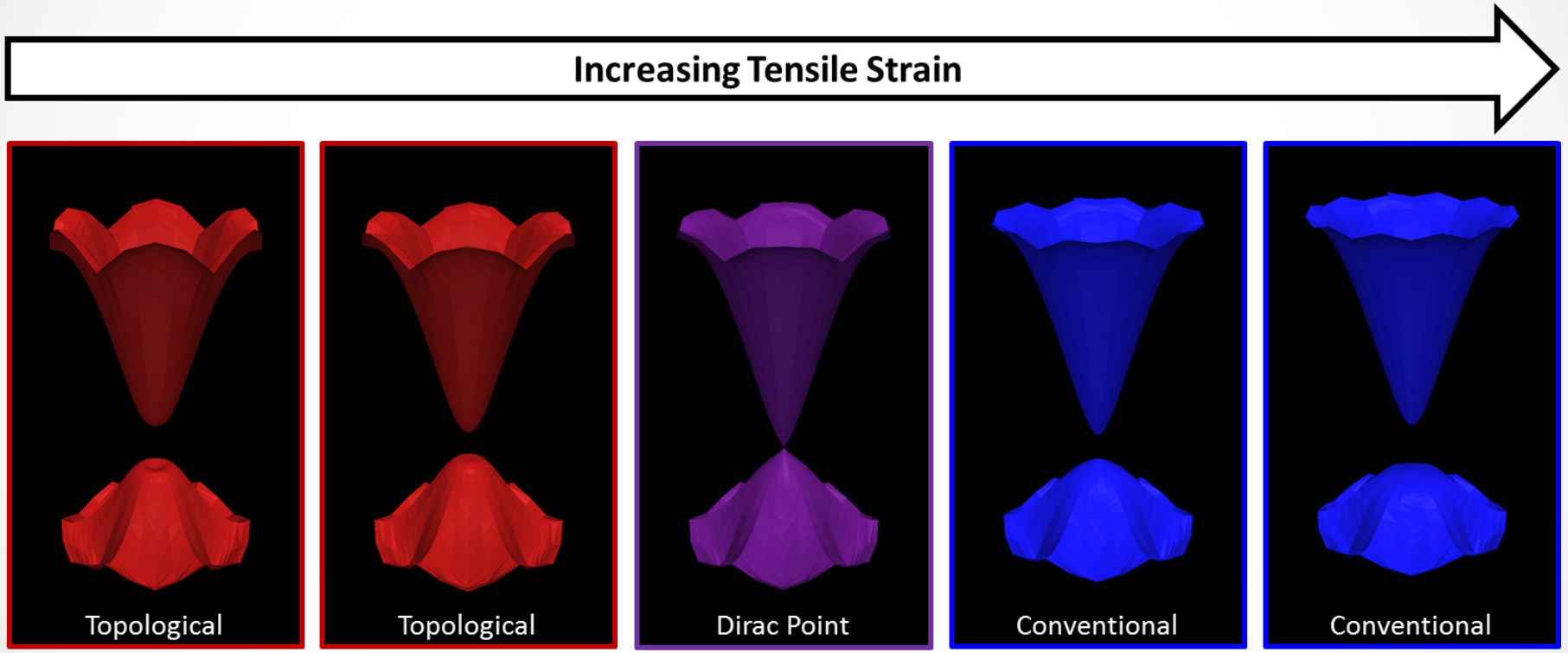

Such Dirac points are topologically protected but not necessarily symmetry protected


1. Murakami, S. New Journ. of Phys. **9**, 356 (2007).
2. Burkov, A.A. and Balents, L. Phys. Rev. Lett. **107**(12), 127205 (2011).

# Recent work on Weyl semimetals

- *"Topological nodal semimetals"*
  Burkov, Hook and Balents, PRB 84, 235126 (2011).
- *"Charge Transport in Weyl Semimetals"*
  Hosur, Parameswaran and Vishwanath, PRL 108, 046602 (2012).
- *"Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates"*
  Wan, Turner, Vishwanath, Savrasov, PRB 83, 205101 (2011).
- *"Quantum Hall effects in a Weyl Semi-Metal: possible application in pyrochlore Iridates"*
  Yang, Lu, Ran PRB 84, 075129 (2011).
- *"Double-Weyl Topological Metals Stabilized by Point Group Symmetry"*
  Fang, Gilbert, Dai, Bernevig, arXiv:1111.7309v1 (2011)

# Dirac point in $Bi_2Se_3$ TI/NI phase transition

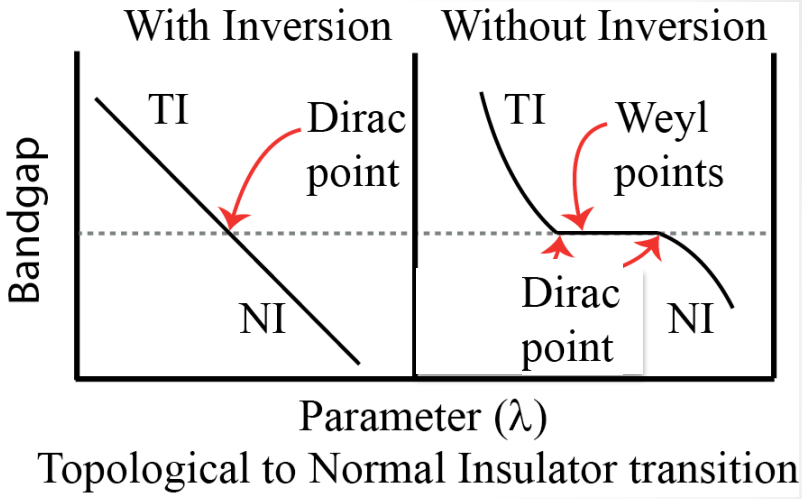



The valence and conduction energy bands of $Bi_2Se_3$ in the (111) plane during the phase transition from topological insulator to conventional insulator. With increasing strain the topological band gap closes, forming a Dirac point, and then reopens as conventional band gap.

- Young S. M. et al. Phys. Rev. B **84**, 085106 (2011).

# 3D Dirac semimetals

- There are proposals for a TI/ NI multilayer heterostructure which realizes a phase transition between a normal and a topological insulator
- With either inversion or time reversal symmetry breaking, a range of parameters realizes Weyl points[1,2]
- In general, topological phase transitions are hard to engineer



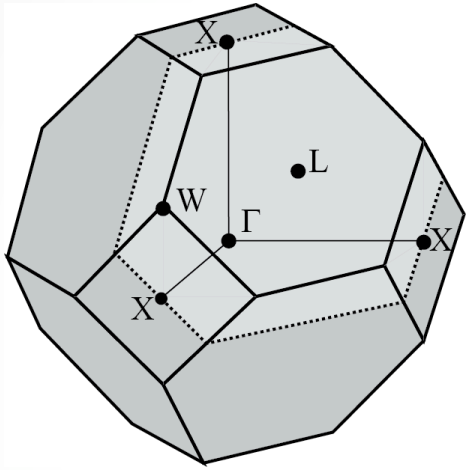
Topological to Normal Insulator transition

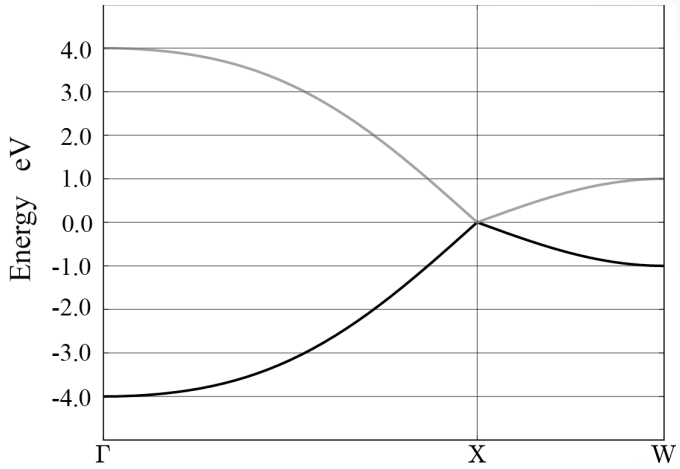
*Main point of talk:* Is it possible to prevent two Weyl points of opposite Chern number from annihilating due to the presence of (another) crystallographic symmetry?

Yes!


1. Burkov, A.A. and Balents, L. Phys. Rev. Lett. **107**(12), 127205 (2011).
2. Halász, G.B. and Balents, L. arXiv:1109.6137[cond-mat.mes-hall] (2011).

# *s*-states on a diamond lattice




- Tight-binding model of *s*-states on the diamond lattice (Fu, Kane, and Mele)[1]
- The point *X* in the Brillouin zone, realizes a symmetry-protected Dirac point
- Why space group 227?
- Why the *X* point?
- Is there a realistic material that can have a Dirac point at the Fermi level?

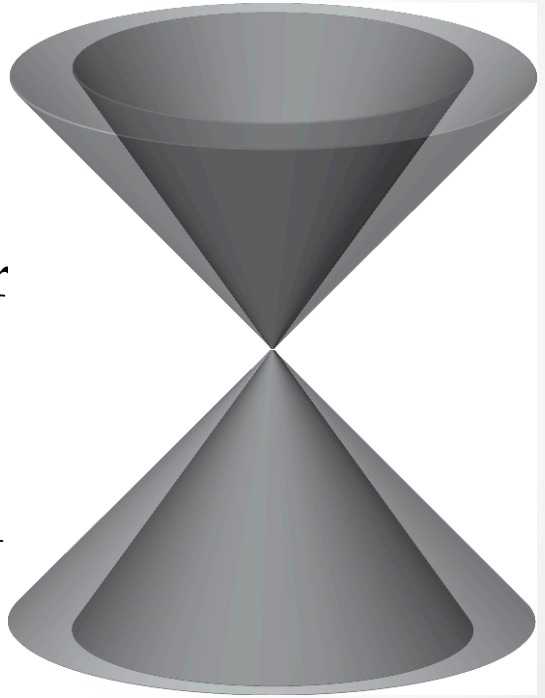
1. Fu, L., Kane, C.L. and Mele, E.J. Phys. Rev. Lett. **98**, 106803-1-4 (2007).

# Finding 3D Dirac points

- Which space groups:  crystallographic symmetry
- Which k-points:  projective representations of little groups
- Presence at Fermi level:  chemical and electronic

# Dirac point: search criteria

- A Dirac point has *four* degenerate eigenstates: must find double space groups with four-dimensional irreducible representations: 4DIR
- Each band disperses linearly in **k** around the Dirac point: must ensure nonzero linear coeffs
- Want Dirac point(s) as only Fermi surface: the total Chern number of the *two* occupied states must be zero
- Dirac points can also exist accidentally as in the TI/NI transition; our methods cannot identify accidentally occurring Dirac points

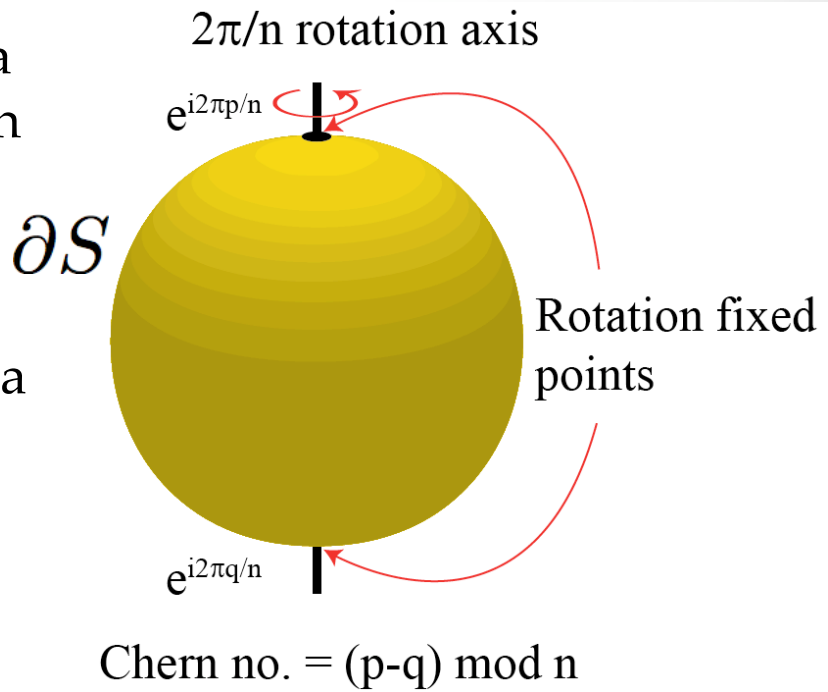


# First test: Chern number=0

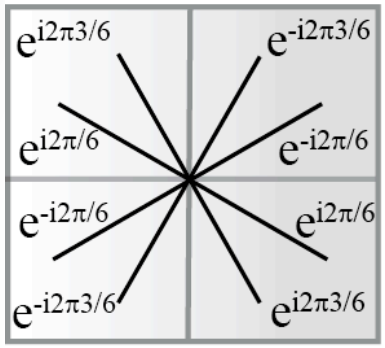
- The Chern number can be determined up to an integer when a rotation symmetry is present
- If a Dirac point is protected by 3-fold rotation symmetry, its Chern number cannot be made to vanish
- For 2-fold and 4-fold rotation symmetry, the Chern number can be made to vanish
- This rules out all 4DIRs that arise in groups containing 3-fold rotation symmetry

# Calculating Chern number

- In the presence of an $n$-fold rotation symmetry, the Chern number mod $n$ at a point **k** can be determined using rotation eigenvalues of filled states at the fixed points
- The difference of eigenvalues from one pole to the other signals the presence of a singularity inside $\partial S$
- A point-like crossing of bands is exactly that singularity!
- This singularity is quantified by the Chern number which gives the winding around $\partial S$ of the gauge transformation required to match states at the two poles



# Chern number under 3-fold rotations

| | | | |
|---|---|---|---|
| $q = 3/2$ |  | $p = -3/2$ | $p-q = 3 = 0$ |
| $q = 1/2$ | | $p = -1/2$ | $p-q = -1$ |
| $q = -1/2$ | | $p = 1/2$ | $p-q = 1$ |
| $q = -3/2$ | | $p = 3/2$ | $p-q = 3 = 0$ |



$(4 = 1) \bmod 3$

- A 4DIR is spanned by $p^{3/2}$ states, also denoted ${}^2P_{3/2}$
- Along a 3-fold rotation axis, such a 4DIR has 4 eigenvalues shown above
- The Chern numbers of the 2 filled bands do not sum to zero!

For symmorphic space groups: even if they have a 4DIR at a **k**-point, if there is a 3-fold axis in the little group at that point, there cannot be a symmetry-protected Dirac point there!

# Why focus on 3-fold rotations?

- In all the symmorphic space groups (73 out of 230), 4DIRs occur at points **k** which have cubic symmetry
- All cubic point groups (5 of 32 total) have three-fold rotations!
- The rest of the 27 point groups do not carry four dimensional representations
- Linearly dispersing bands along axes of $n$-fold rotations for $n = 2, 4$ can adjust so that the Chern number vanishes

Is it possible to find 4DIRs for groups without three-fold symmetry?

# Second test: 4 dimensional representations

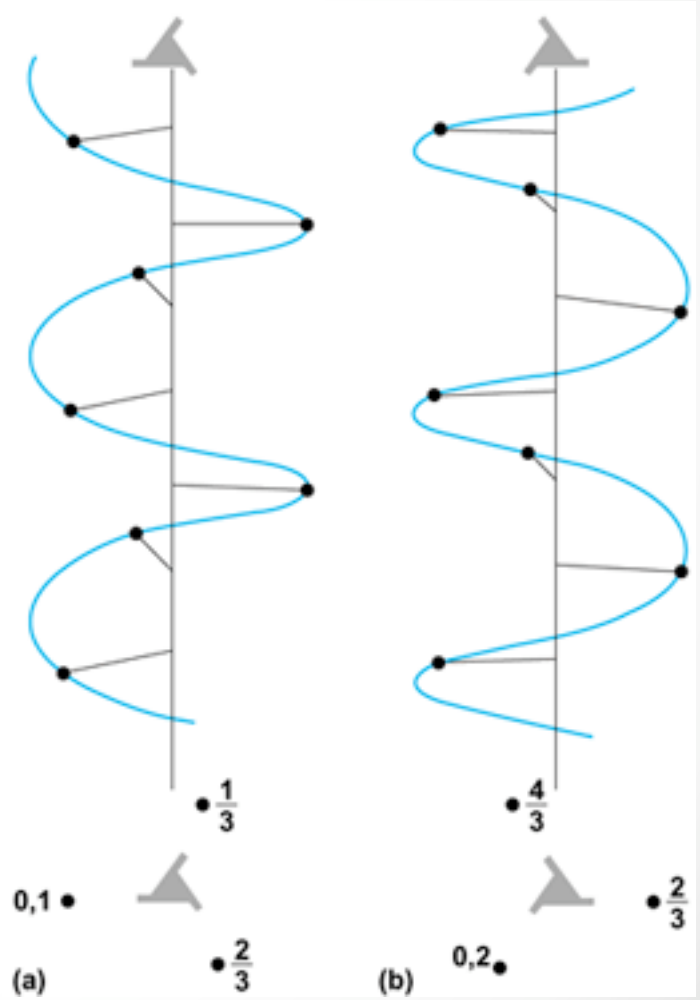
- Non-symmorphic (double) space groups (157 out of 230) can carry 4DIRs even though most of them lack three-fold symmetry
- What are non-symmorphic space-groups? Those that have screw axis or glide plane—operations that combine a point group operation with a non-primitive lattice translation
- Examples

a) DNA

b) Diamond lattice (2 interpenetrating FCC lattices)

# Non-symmorphic symmetry operations

- Rotation of the helix is not a symmetry
- To return the helix to its original configuration, we need to translate the lattice by a small vector **t** which is not a multiple of any of the lattice vectors
- Therefore the symmetry operator is $\{R|\mathbf{t}\}$: rotation followed by translation **t**…a "screw axis".



# What happens in the Brillouin zone?

- A non-symmorphic symmetry operation carries translation in *real space*. In reciprocal space, the point group operation carries a phase factor, not translation.

# Representations of non-symmorphic operations I

- Even though a non-symmorphic operation like $\{m|\mathbf{t}\}$ in graphene acts like a point group operation in the Brillouin zone, its representation for a non-symmorphic lattice is different from a symmorphic lattice
- Recall that any translation $\{E|\mathbf{t}\}$ of the crystal implements a phase $e^{-i\mathbf{k}\cdot\mathbf{t}}$ on bloch states $\Psi_{\mathbf{k}}$
- Therefore non-symmorphic operations like $\{m|\mathbf{t}\}$ act as $e^{-i\mathbf{k}\cdot\mathbf{t}}U_{\mathbf{k}}(m)$, where $U_{\mathbf{k}}(m)$ is a unitary operator that implements the mirror operation

# Representations of non-symmorphic operations II

- Recall how space-group operations multiply:

$$\{R_1|\mathbf{t}_1\}\{R_2|\mathbf{t}_2\} = \{R_1R_2|\mathbf{t}_1 + R_1\mathbf{t}_2\}$$

- The representatives follow as,

$$e^{-i\mathbf{k}\cdot\mathbf{t_1}}U_{\mathbf{k}}(R_1)e^{-i\mathbf{k}\cdot\mathbf{t_2}}U_{\mathbf{k}}(R_2)e^{-i\mathbf{k}\cdot(\mathbf{t_1}+R_1\mathbf{t_2})}U_{\mathbf{k}}(R_1R_2)$$

$$U_{\mathbf{k}}(R_1)U_{\mathbf{k}}(R_2) = e^{-i(R_1^{-1}\mathbf{k}-\mathbf{k})\cdot\mathbf{t_2}}U_{\mathbf{k}}(R_1R_2)$$

- If $\mathbf{k}$ is an internal point of the Brillouin zone, $R_1^{-1}\mathbf{k} = \mathbf{k}$ since all the $\{R|\mathbf{t}\}$ under consideration belong to the little space group at $\mathbf{k}$
- If $\mathbf{k}$ is on the surface of the Brillouin zone, $R_1^{-1}\mathbf{k} = \mathbf{k} + \mathbf{g}_i$ where $\mathbf{g}_i$ is a reciprocal lattice vector:

$$U_{\mathbf{k}}(R_1)U_{\mathbf{k}}(R_2) = e^{-i\mathbf{g}_i\cdot\mathbf{t_2}}U_{\mathbf{k}}(R_1R_2)$$

# Representations of non-symmorphic operations III

- The matrices $U_k$ form a representation of the point group consisting of all rotations $R_i$ with the following multiplication rule:

$$U_{\mathbf{k}}(R_1)U_{\mathbf{k}}(R_2) = e^{-i\mathbf{g}_i\cdot\mathbf{t_2}}U_{\mathbf{k}}(R_1R_2)$$

- The phase $\exp(-i\mathbf{g}_i.\mathbf{t}_2) = 1$ if and only if either $\mathbf{g}_i = 0$, or $\mathbf{t}_2$ is a real-space lattice vector
- For non-symmorphic operations, $\mathbf{t}_2$ is non-primitive, so the unitary matrices $U_k$ form a projective representation with some lattice-specific factor system
- Projective representations of point groups without 3-fold rotation symmetry can be 4DIRs
- In 3D crystals, all candidate Dirac points belong to a projective representation of one of the 32 crystal point groups

Ref: Bradley, C.J. and Cracknell, A.P. *The Mathematical Theory of Symmetry in Solids* (Oxford, 1972).

# Third test: Splitting of the representation

- We can use $\mathbf{k}\cdot\mathbf{p}$ perturbation theory to determine whether the effective Hamiltonian at a 4DIR has linear dispersion in all directions
- For a general spin-orbit coupled system, the Schrodinger equation reads,

$$\left[\frac{\mathbf{p}^2}{2m} + V + \frac{\hbar}{4m^2c^2}(\nabla V \times \mathbf{p}).\sigma\right]\psi_{\mathbf{k}} = E_{\mathbf{k}}\psi_{\mathbf{k}} \quad \text{where } \psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}$$

$$\left[\frac{\mathbf{p}^2 + 2\hbar\mathbf{k}\cdot\mathbf{p}}{2m} + V + \frac{\hbar}{4m^2c^2}\nabla V \times (\mathbf{p} + \hbar\mathbf{k}).\sigma\right]u_{\mathbf{k}} = \left(E_{\mathbf{k}} - \frac{\hbar^2k^2}{2m}\right)u_{\mathbf{k}}$$

# k.p perturbation theory I

- Suppose there is a four dimensional representation at X
- At X+**k** the Schrodinger equation for $u_{X+\mathbf{k}}$ gets modified accordingly
- $E_{X+k}$ can be written as

$$\mathbf{k} \rightarrow X + \mathbf{k} \quad E_{X+\mathbf{k}} = E_X + \langle \psi_X | \hat{H}' | \psi_X \rangle + \ldots$$

$$\text{where } \hat{H}' = \hbar \mathbf{k} \cdot \left( \frac{\mathbf{p}}{m} + \frac{\hbar}{4m^2c^2} \sigma \times \nabla V \right) = \mathbf{k} \cdot \mathbf{R}$$

- If all $\langle \psi_X^i | \mathbf{R} | \psi_X^j \rangle$ are identically zero, none of the bands degenerate at X can disperse linearly in **k** in its vicinity

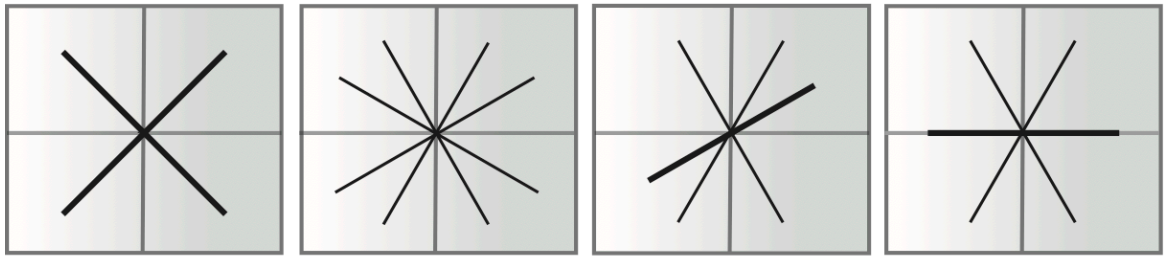
Ref: Dresselhaus, G. Phys. Rev. **100**, 580-586 (1955).

# k.p perturbation theory II

- $\Psi_X^i$ span the four dimensional representation $\Gamma$ at X
- **R** is a vector, so it belongs to the vector representation $\Gamma^V$ of the little space-group at X
- If $\Gamma \times \Gamma^V \times \Gamma$ contains the identity representation of the group, some of the matrix elements $\langle \psi_X^i | \mathbf{R} | \psi_X^j \rangle$ are guaranteed to be non-vanishing
- Alternatively, we can check if the symmetric kronecker product $[\Gamma \times \Gamma]$ contains the vector representation $\Gamma^V$

# Splitting of the representation

- What are the possible ways in which a four dimensional can split up to linear order in **k**




- Symmetry determines how the 4-fold degeneracy splits:

a) 2+2 dimensional representations
b) 1+1+1+1 dimensional representations
c) 1+2+1 dimensional representations
d) 1+2+1 dimensional representations with identical energy spectra on both sides

# Summary of the criteria

- Is there a point **k** in the Brillouin zone such that its little space group carries a four dimensional irreducible representation (4DIR) Γ?
- Does Γ carry a Chern number of zero?
- Does the symmetric kronecker product [Γ × Γ] contain the vector representation of the little space group at **k**?
- How does Γ split along high-symmetry lines away from **k**? In a way that avoids zero slope?
- If the answer to all of these questions is yes, then **k** is a candidate for hosting a Dirac point

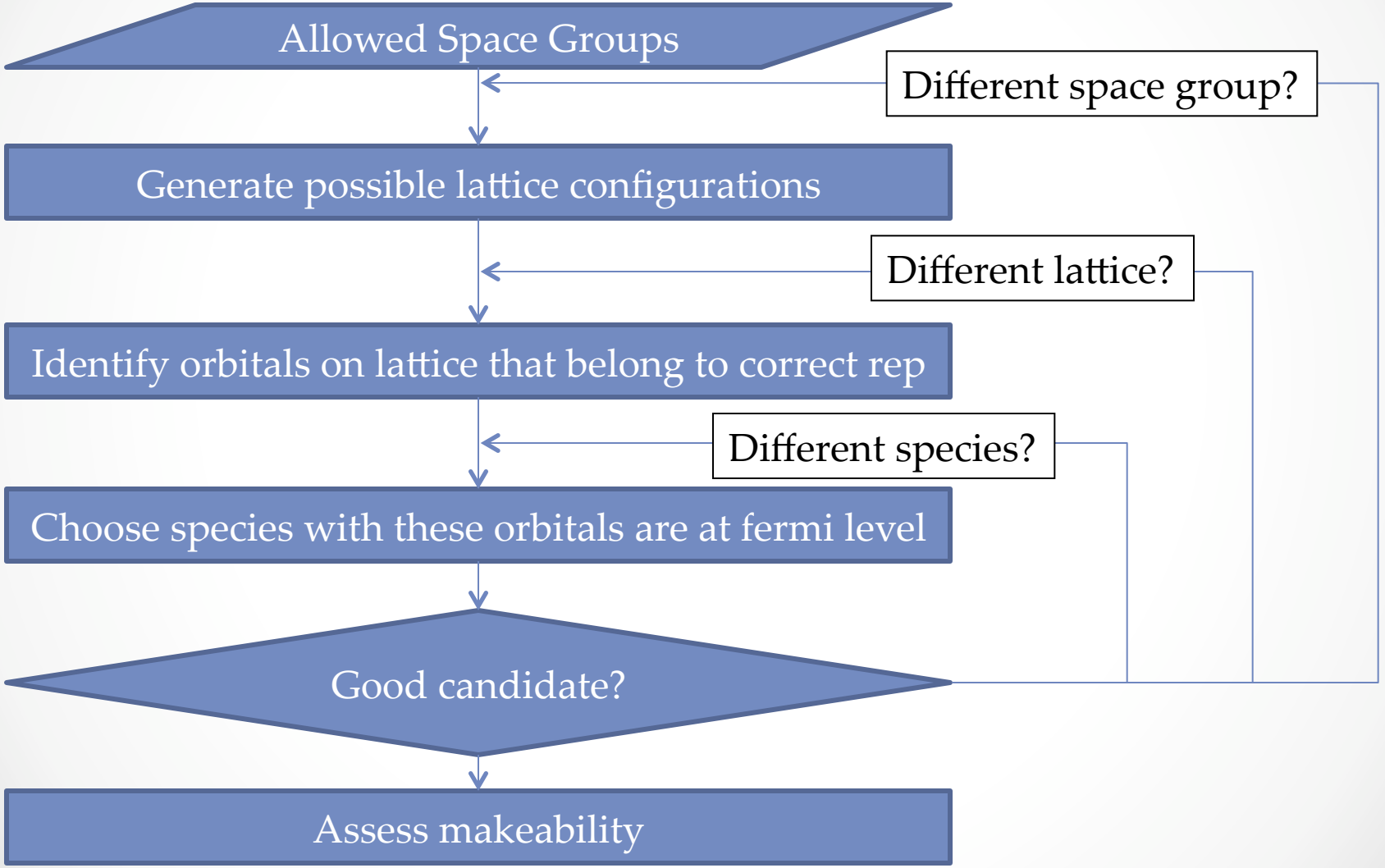
This leaves about two dozen "good" candidate space groups

# Beyond Symmetry

- Symmetry guarantees:
  - Four-fold degeneracy
  - Linear dispersion in neighborhood of high symmetry point
- Does not answer:
  - Is the degeneracy at the Fermi level?
  - Is it the only Fermi surface?
  - Does the linearity persist over a useful energy range?

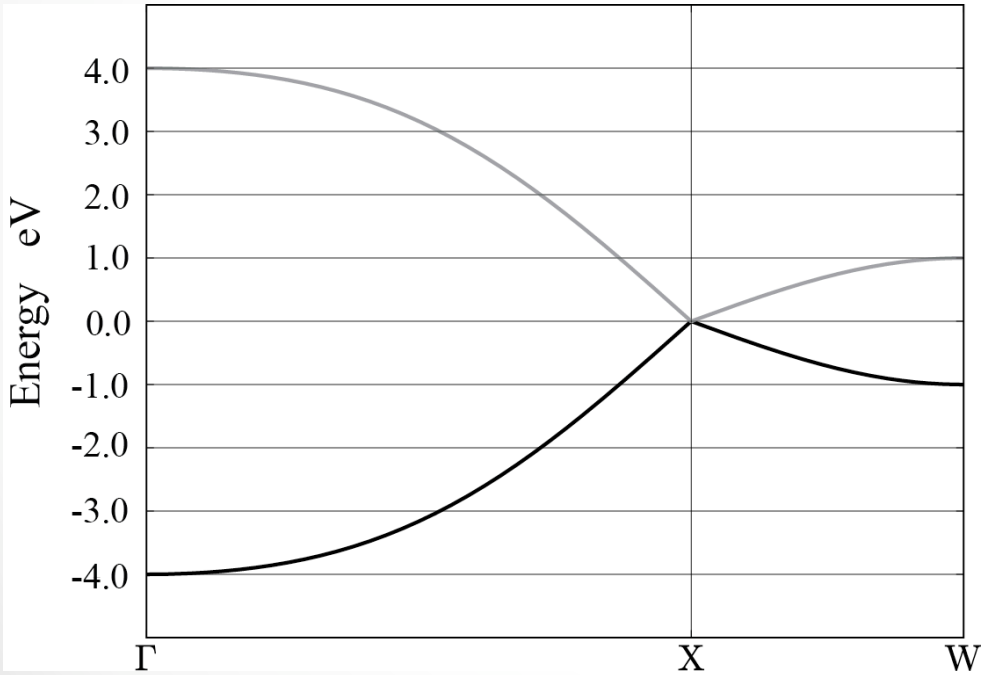
These are questions that chemistry must answer!

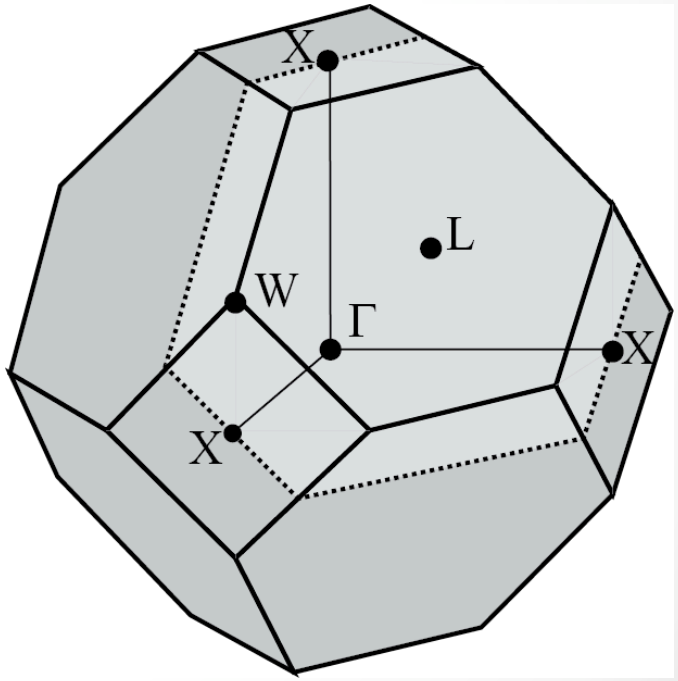
# Design Strategy



# Example: Space Group 227

- We already know that a diamond lattice of *s*-orbitals will give us a Dirac point at *X*

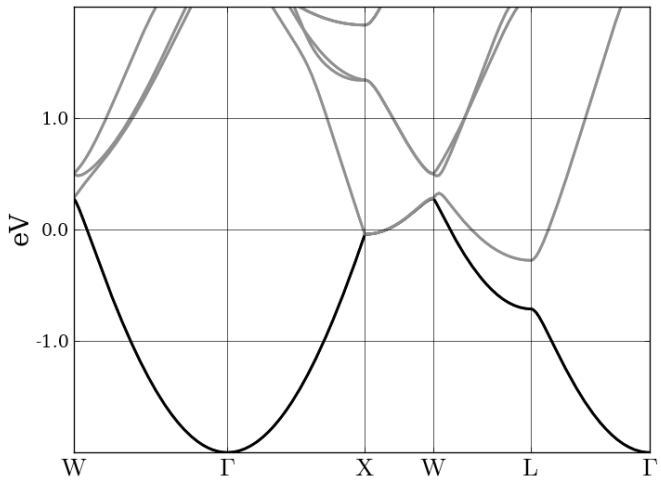


# Example: Space Group 227

- Put $s_1$ species on diamond lattice
- Results:
  - Too much Fermi surface
  - Dirac point is overwhelmed
  - Almost certainly un-makeable

K

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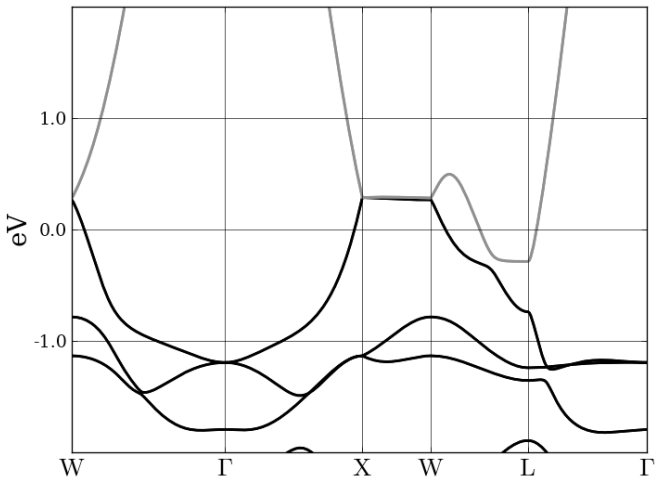
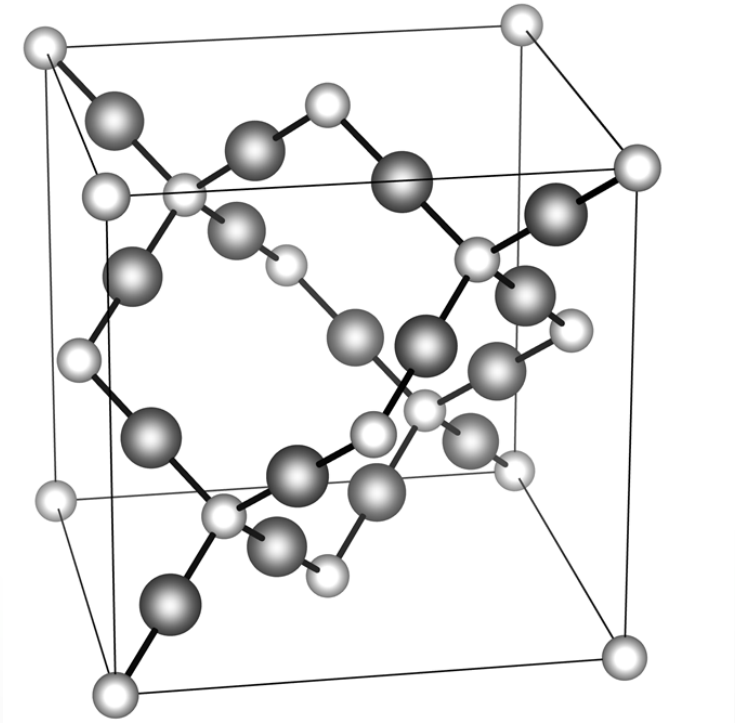
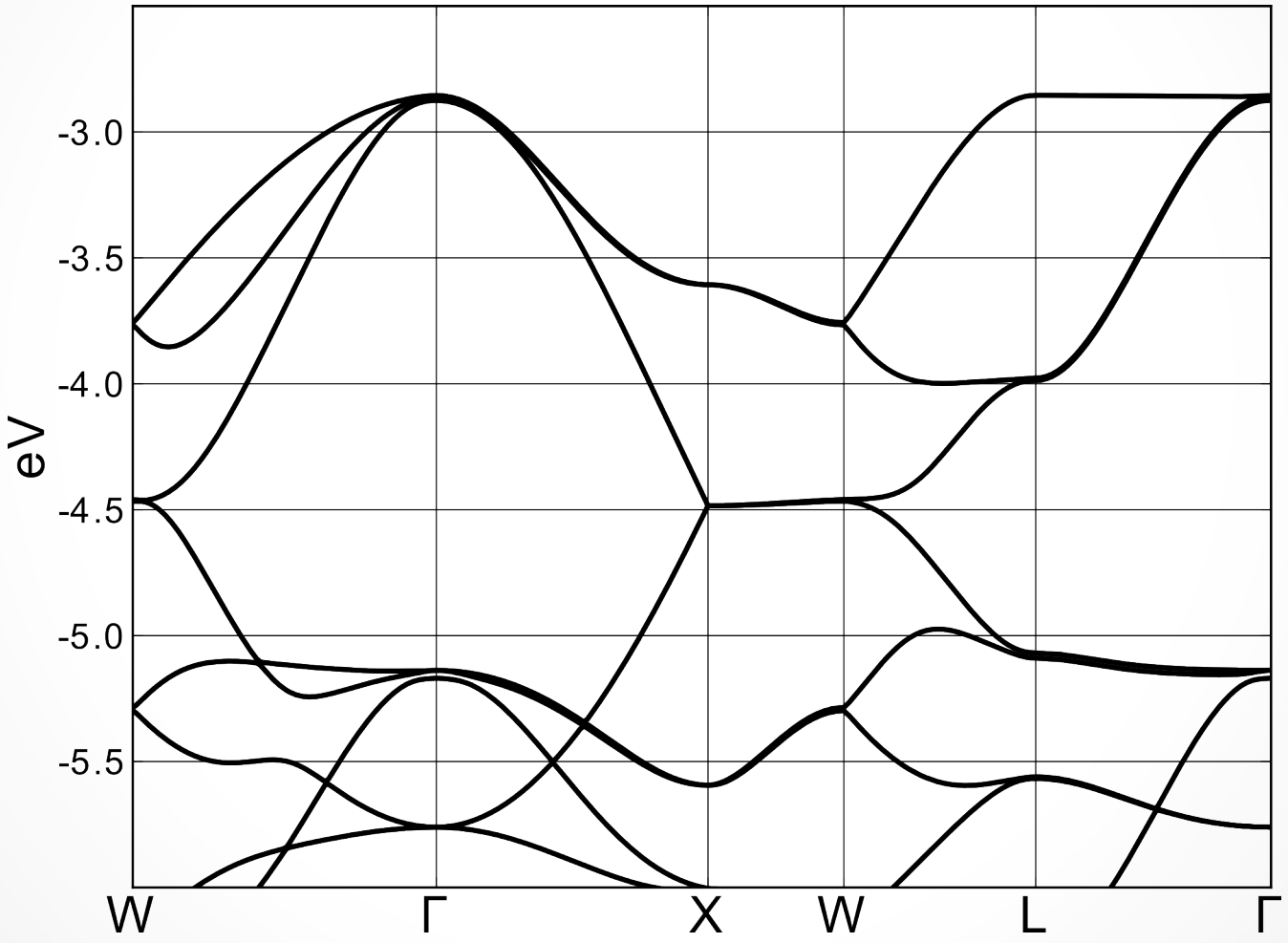


# β-Cristobalite

- High temperature form of $SiO_2$
- Si on a diamond lattice with O bridging the bonds
- p-orbitals of O belong to correct rep!



# β-Cristobalite



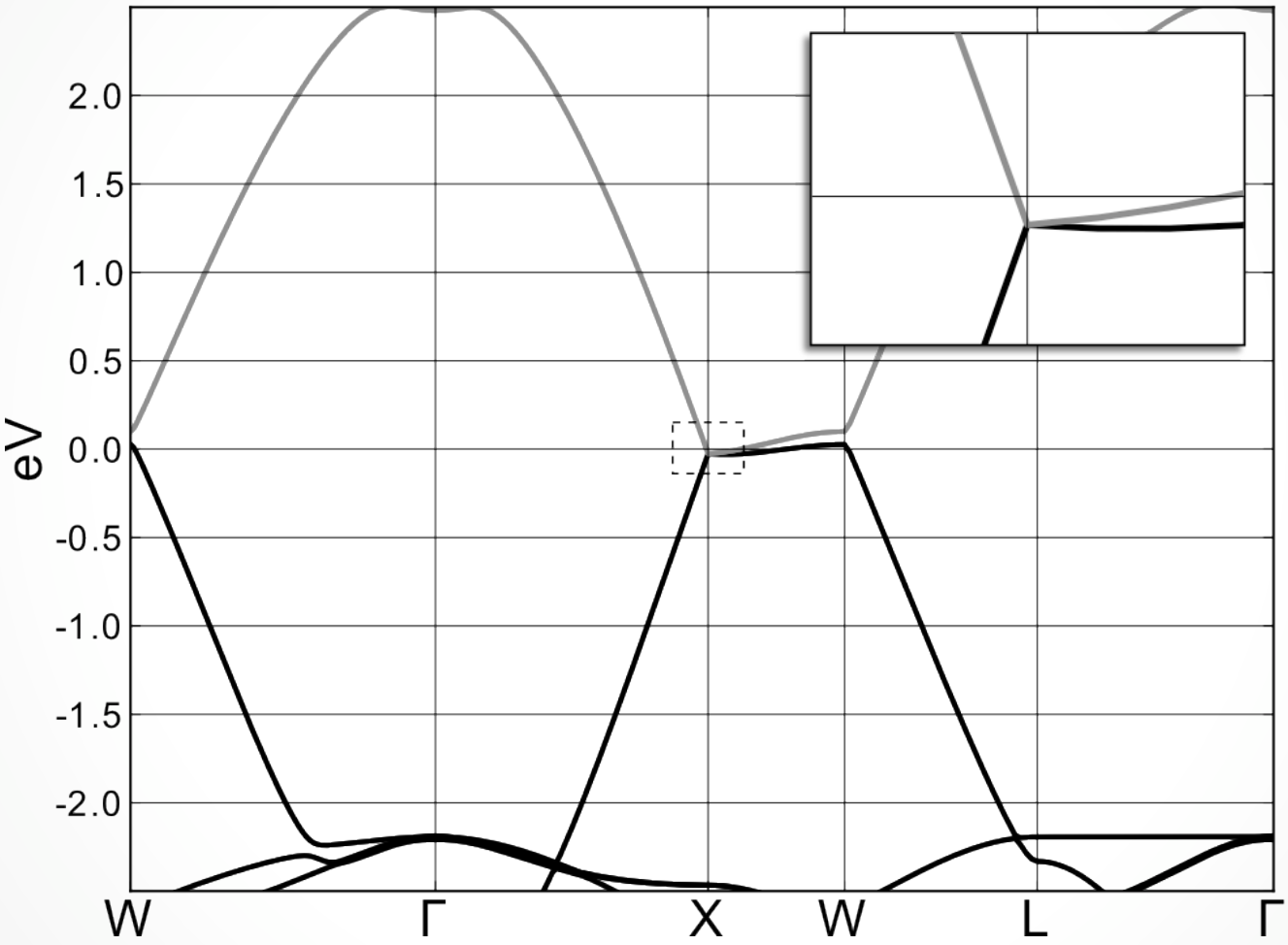
# β-Cristobalite

- Degeneracy not at Fermi energy
- Along the X-W line, bands nearly degenerate
  - Single group representation is doubly degenerate along X-W

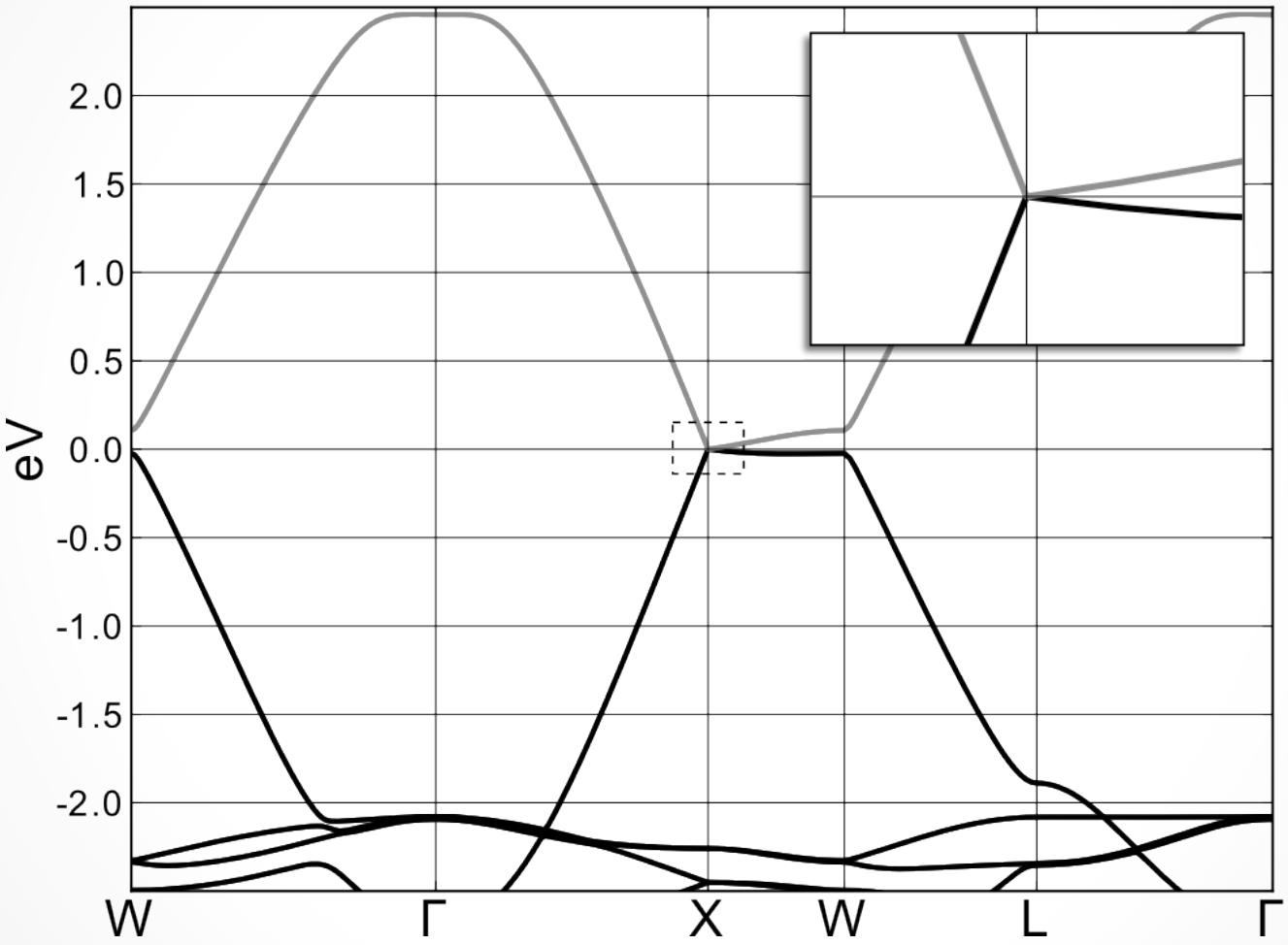
Substitutions for Si:

- Can we split the bands better?
  - Heavier atoms for more spin orbit coupling
- Can we move the Fermi level?
  - Atoms with different numbers of valence electrons and different energy ordering

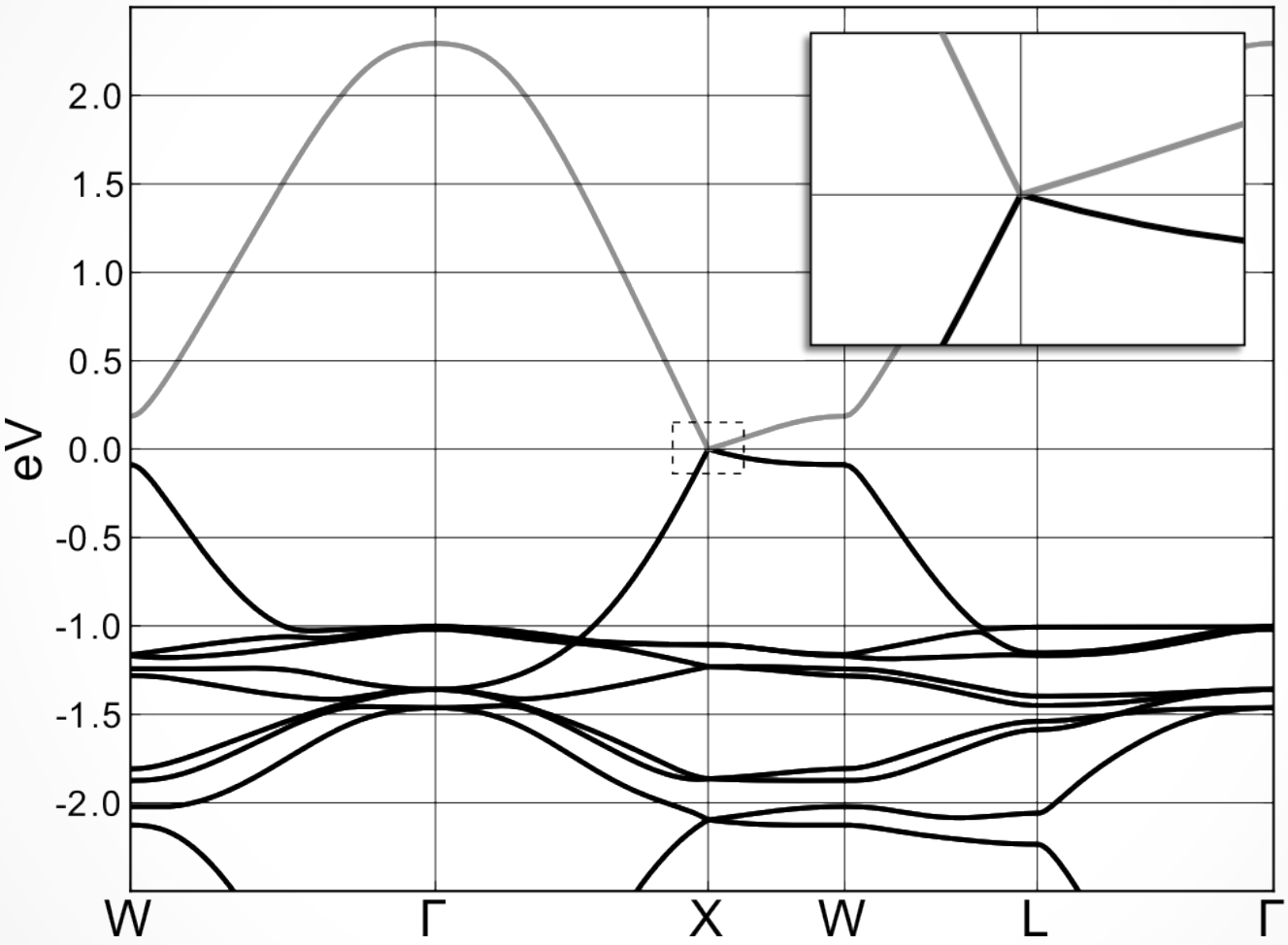
# $AsO_2$



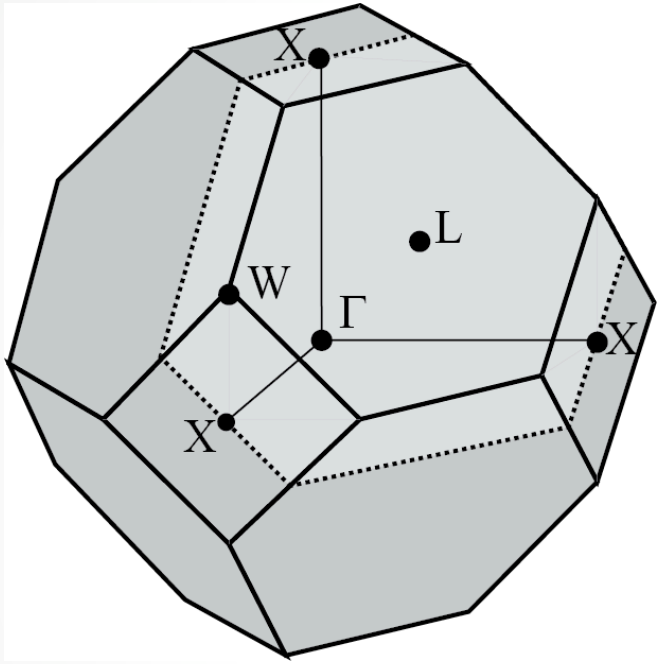
# $SbO_2$

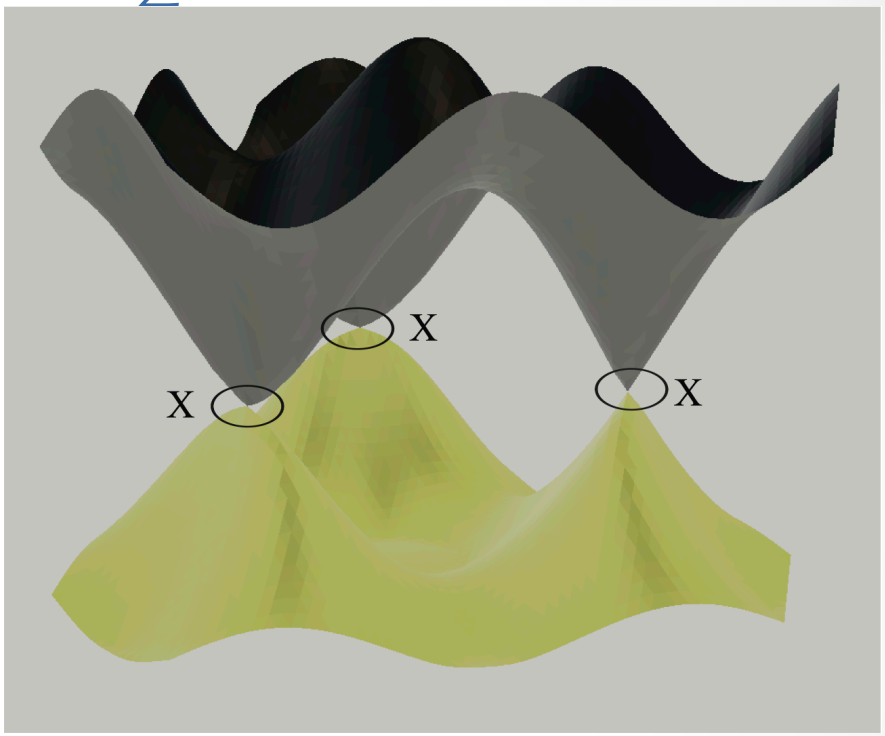


# $BiO_2$



# $BiO_2$




- Fermi surface at Dirac point
- Wide energy range where linear
- Meta-stable!

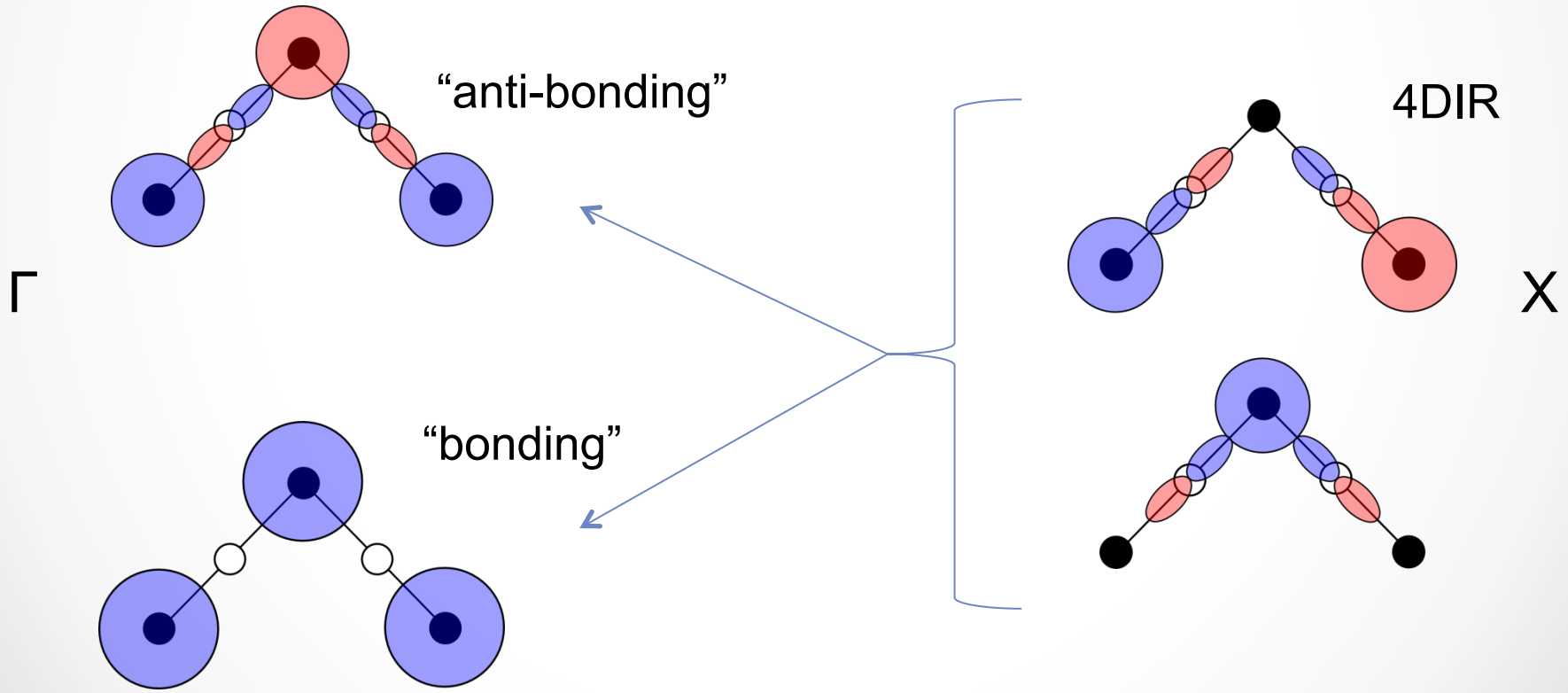
# $BiO_2$

- The 4DIR at X is the only allowed double-valued representation at X
- Why aren't there more Dirac-like crossings in the band structure
- There actually are, but they are of low quality

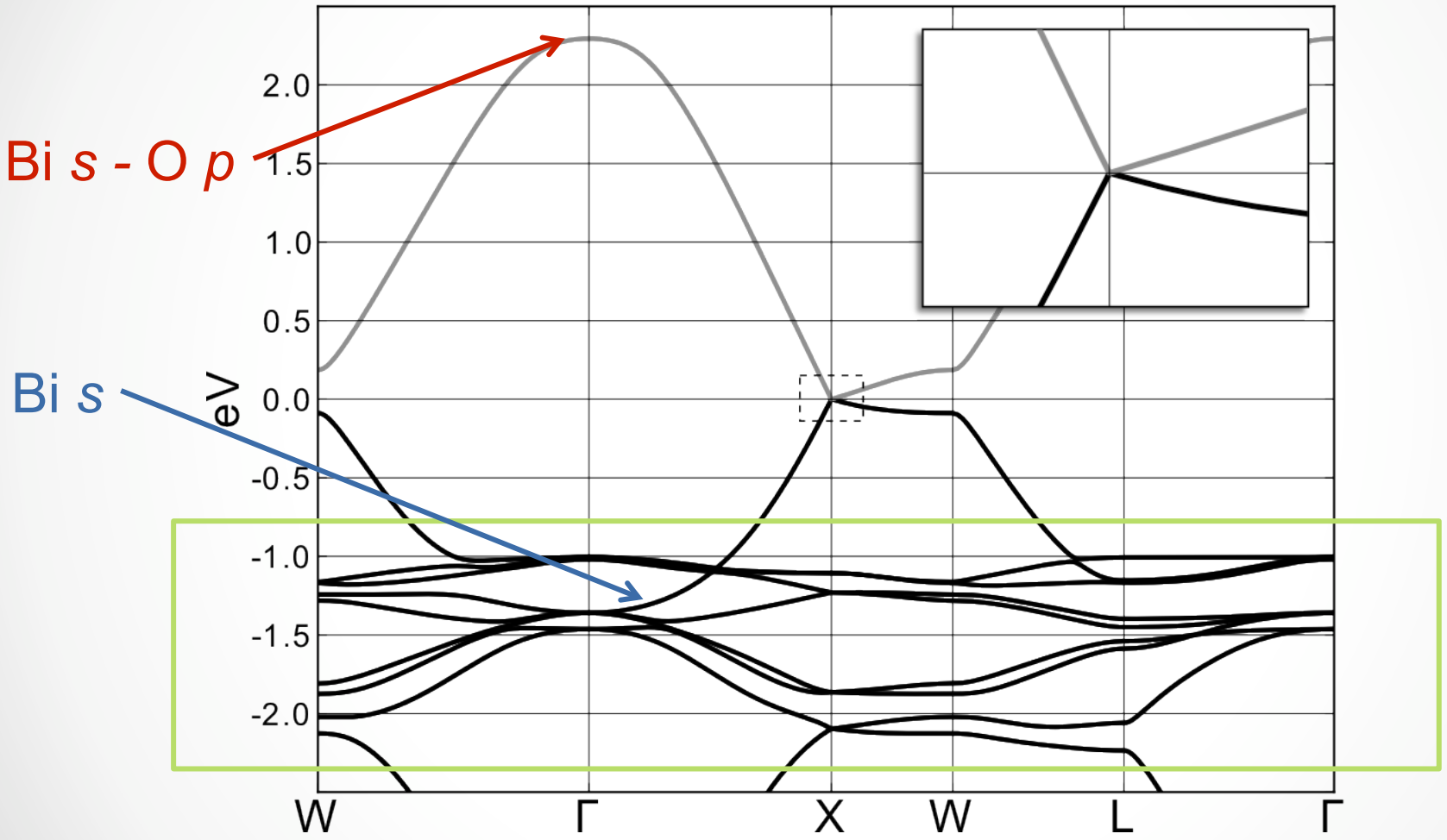
Why is the one at the Fermi energy so good?

# $BiO_2$

- The bands of the Dirac point are composed of Bi s and O p states, with splitting into bonding- and antibonding-like states.



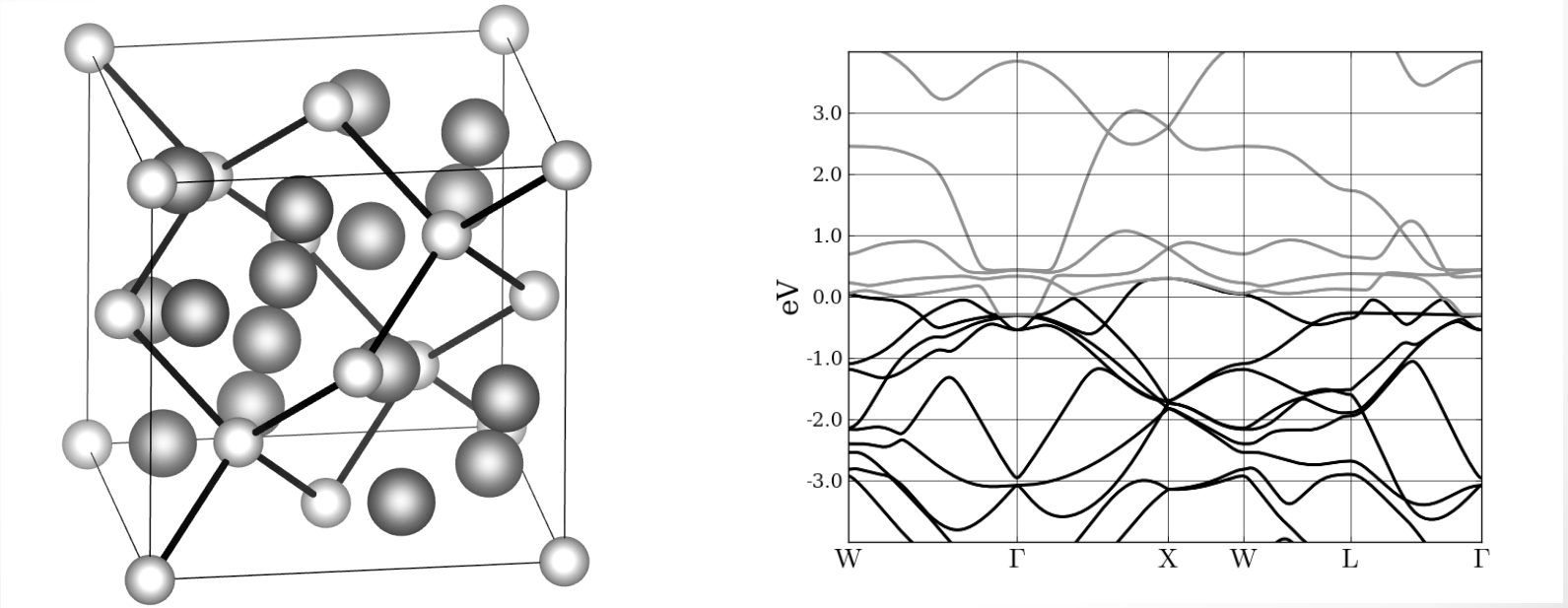
# $BiO_2$




Dirac point involves states
with strong bonding interactions

# Counter Example: Laves Structure

- Belongs to 227, but structure is more closely packed
- No distinct bonding states arise
- Structure is metallic; band structure is messy



# Conclusions

- Identified symmetry criteria to look for candidate space-groups that will allow 3D Dirac points
- Identified chemical and physical criteria required to elevate said Dirac points to the Fermi level
- Proposed a realistic metastable material that realizes three symmetry protected Dirac points at the BZ

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