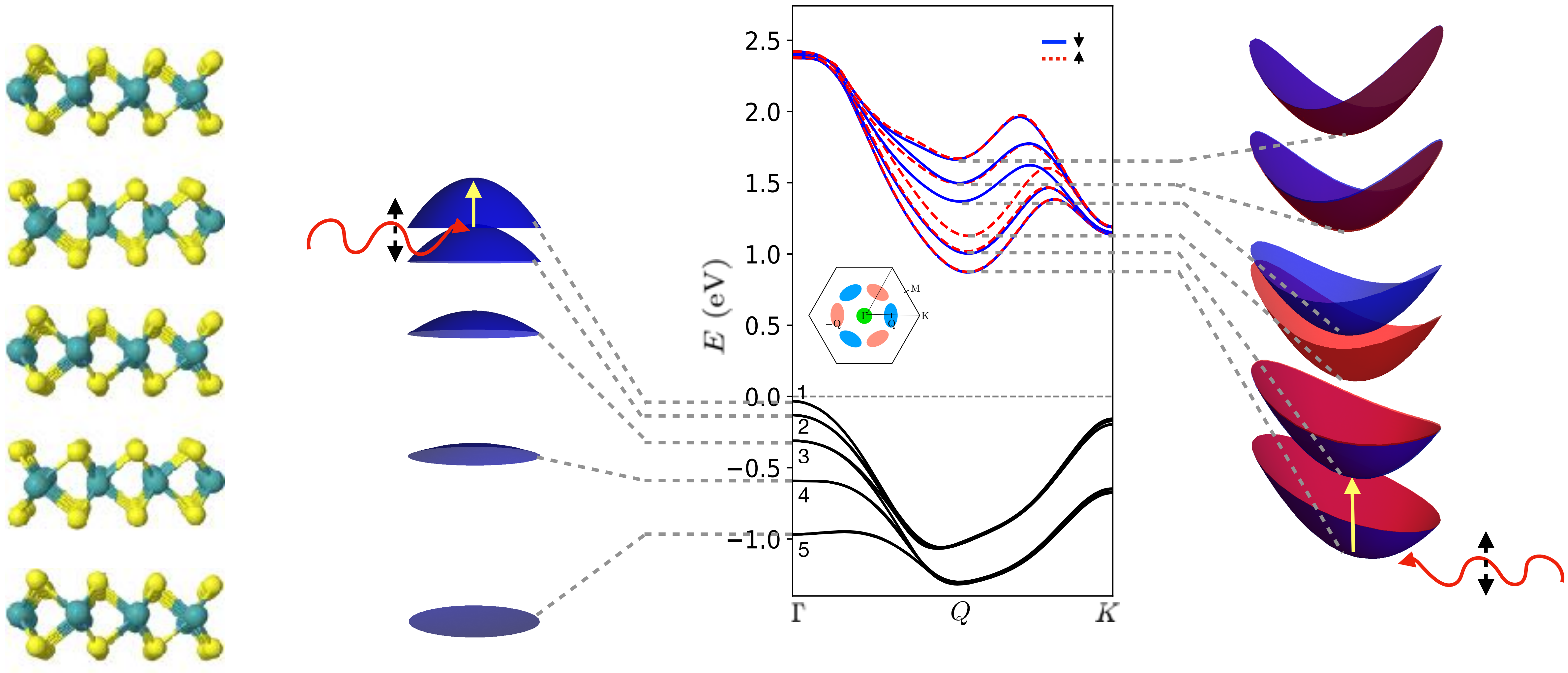
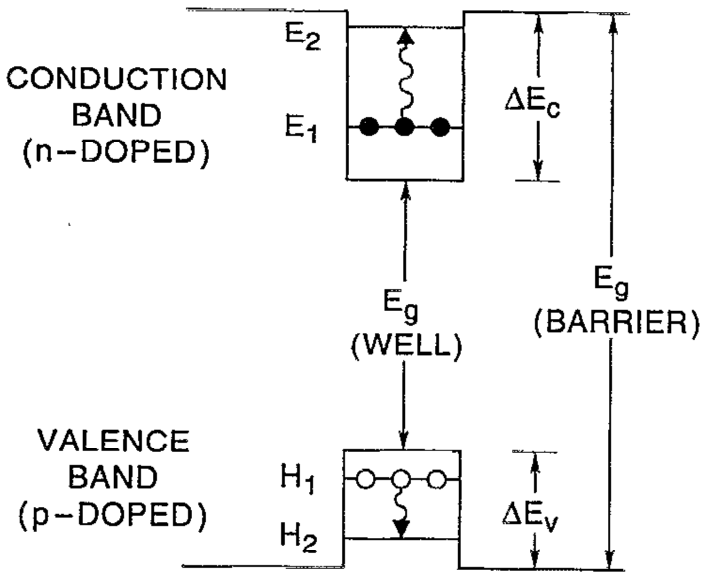
Intersubband optics in few-layer transition metal dichalcogenides

$2\mathrm{H} - \mathrm{MX}_2$



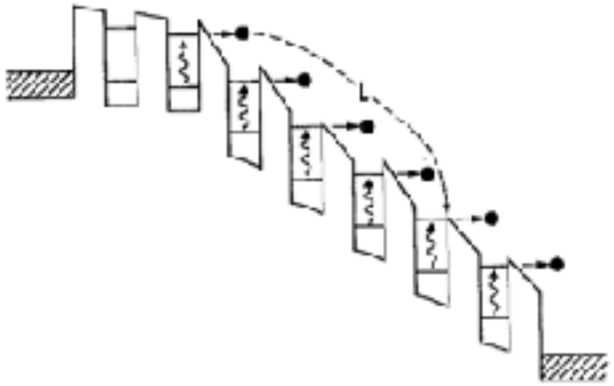
M. Danovich, D. Ruiz-Tijerina, C. Yelgel, V. Zólyomi, V. Fal'ko

Motivation

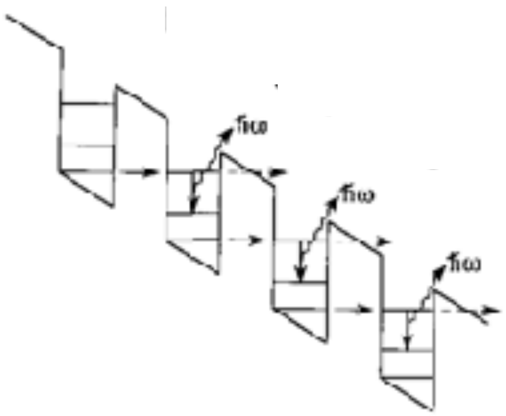


Levine, B. F. (1993). Quantum-well infrared photodetectors. *Journal of Applied Physics*, *74*(8), R1–R81. http://doi.org/10.1063/1.354252

IR photodetectors



IR Quantum cascade lasers



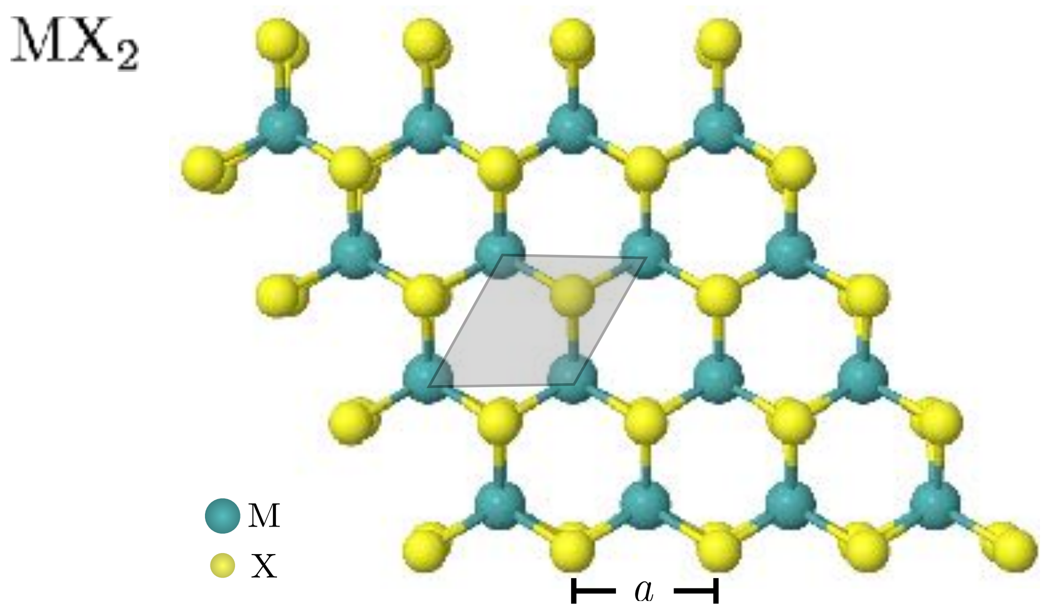
Rui Q.Yang, Infrared laser based on intersubband transitions in quantum wells, Superlattices and Microstructures, 17, 1 (1995)

IR/MIR/FIR optoelectronic devices have multiple applications in: Medicine, Security, Military, Telecommunication, etc.

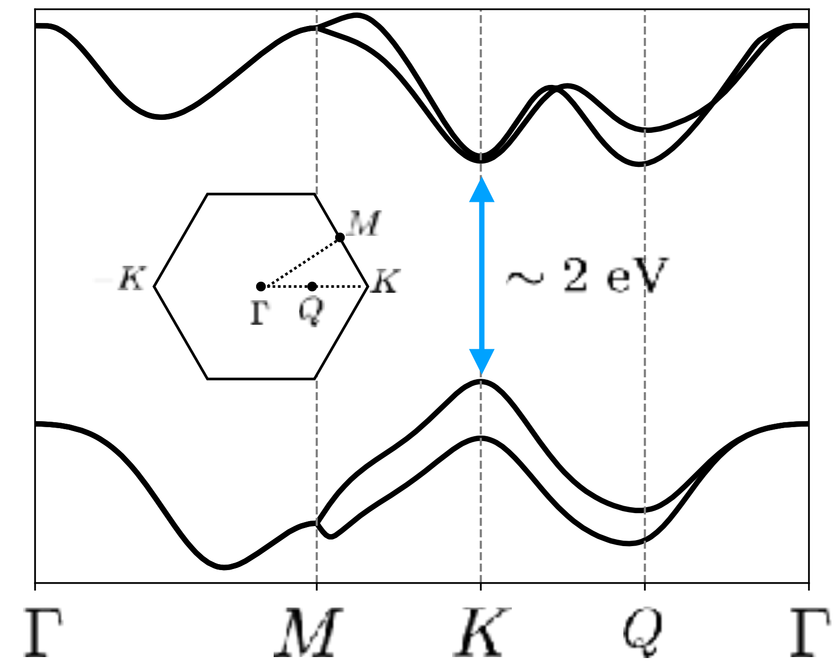
Why 2D materials?

- Thin
- Natural Van der Waals Quantum wells in the form of heterostructures
- Versatile, wide range of materials: MX2, GaSe, InSe (S. Magorrian, V. Zólyomi, V. Fal'ko (2018))

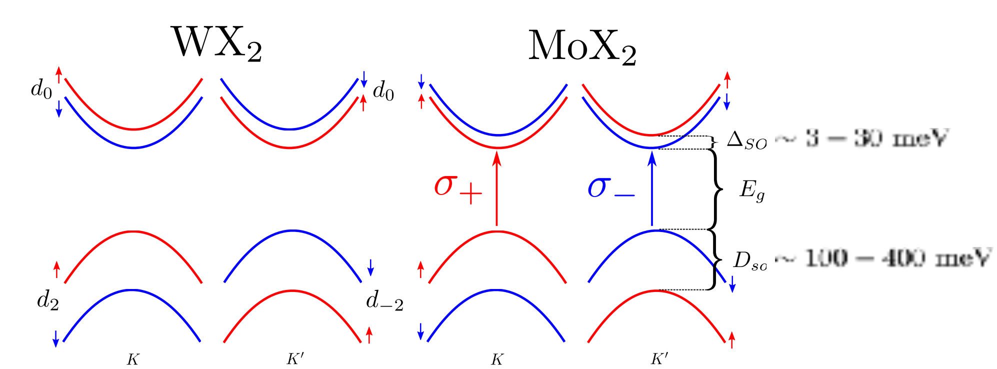
Monolayer TMDs

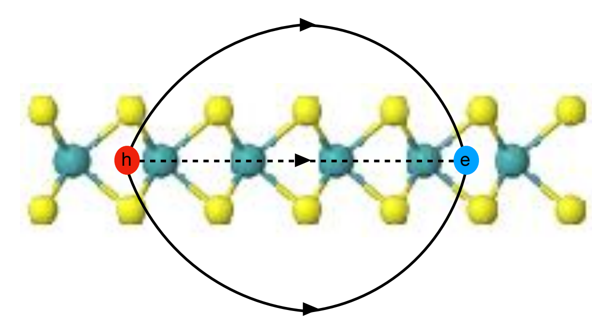


$\mathrm{M = Mo, W;\ \ X = S, Se}$



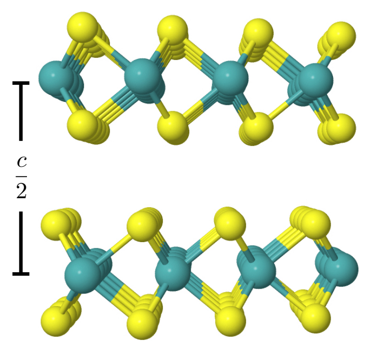
- Direct band gap at the K/K’ points
- Large spin-orbit splitting, spin-valley locking, circular dichroism
- Enhanced Coulomb interaction, strongly bound complexes: excitons, trions



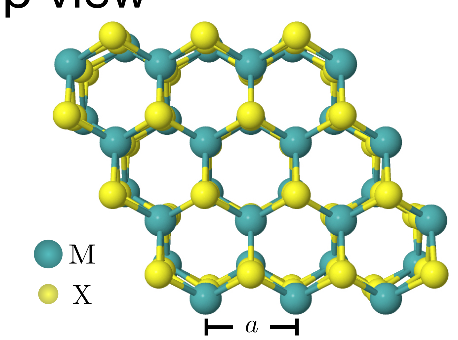


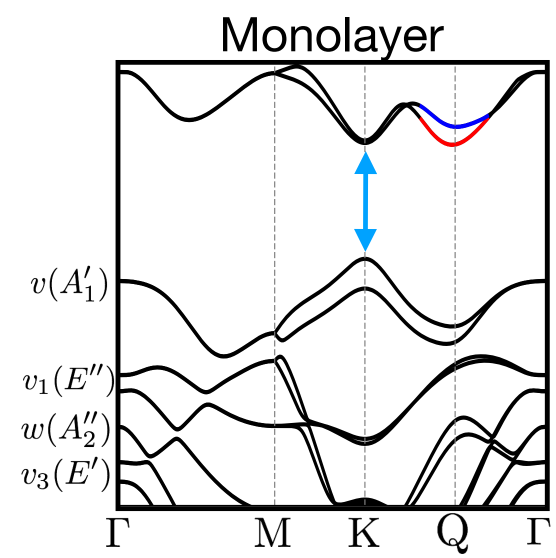
Symmetry: monolayer and few layers

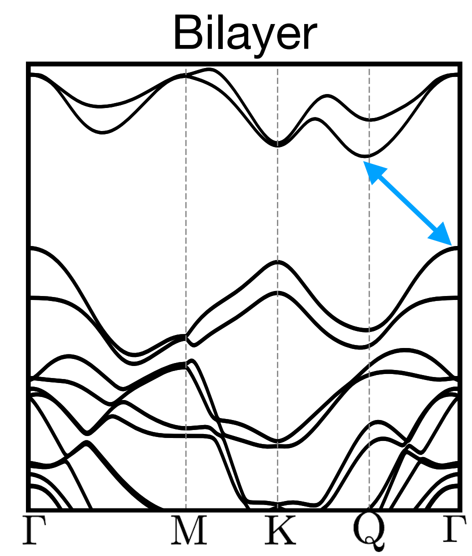
side view

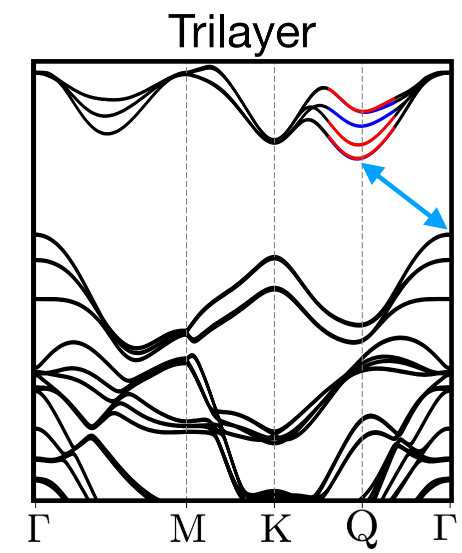


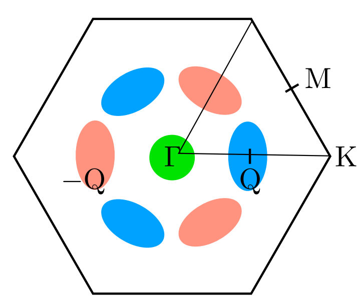
top view











	$\hat{C}_3,$	$\hat{\sigma}_v(x \to -x),$	$\hat{\sigma}_h(z \to -z),$	$\hat{I}(\mathbf{r} \to -\mathbf{r})$
Monolayer (D_{3h}):	✓	✓	✓	×
Even N-layers (D_{3d}):	✓	✓	×	✓
Odd N-layers (D_{3h}):	✓	✓	✓	×

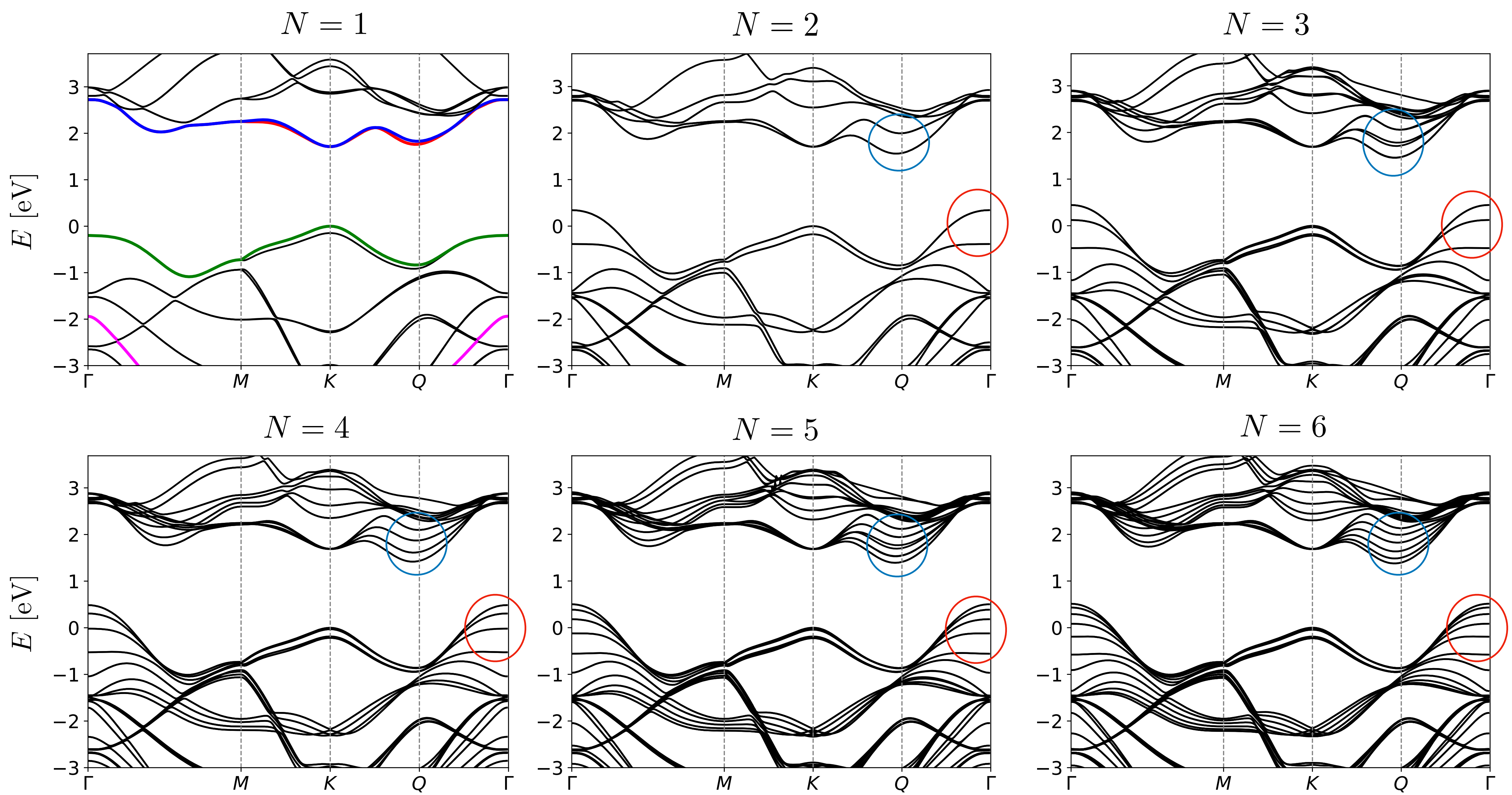
$$[\hat{H}, \hat{S}_z] = 0$$

$$E_{s_z}(\mathbf{k}) = E_{-s_z}(\mathbf{k})$$

$$[\hat{H}, \hat{S}_z] = 0$$

$$E_{s_z}(\mathbf{k}) = E_{-s_z}(-\mathbf{k})$$ (Time reversal)

DFT band structures N=1-6 (MoS2)



Hybrid k·p - tight binding model

$$\mathrm{VB} - \Gamma$$

Monolayer dispersions:

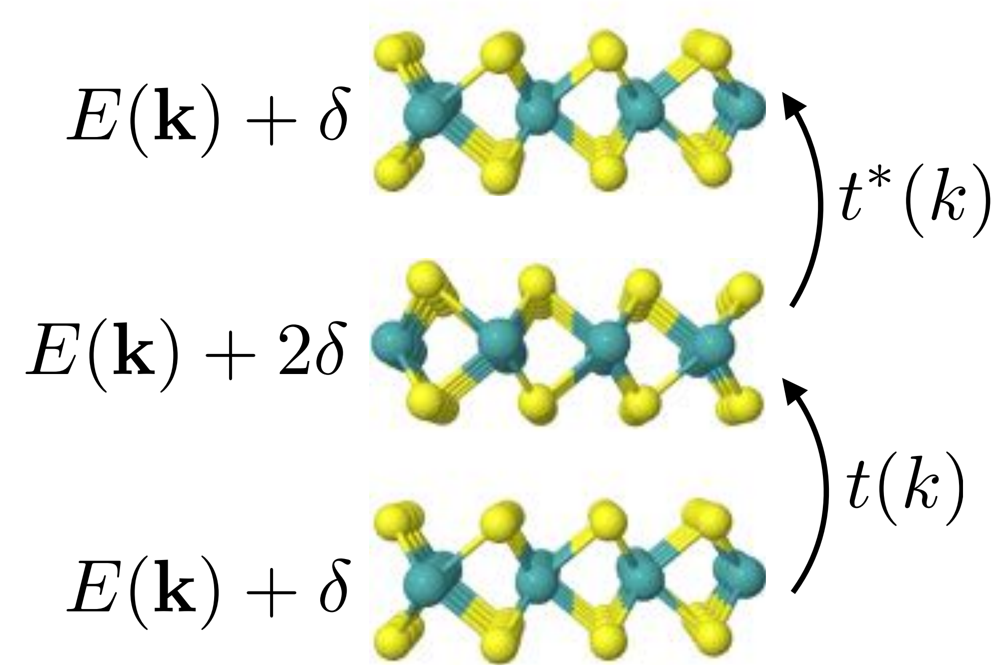
$$E_\sigma(\mathbf{k}) = E_\sigma^0 - \frac{\hbar^2 k^2}{2m_\sigma}$$

$$\sigma = v, w$$

Interlayer hoppings:

$$t_\sigma(\mathbf{k}) = t_\sigma^{(0)} + t_\sigma^{(2)} k^2$$

$$t_{vw}(\mathbf{k}) = t_{vw}^{(0)} + t_{vw}^{(2)} k^2$$



$$\hat{H}_{SO} \propto L_z S_z + L_+ S_- + L_- S_+ \qquad \delta_\sigma = \sum_i \frac{\langle \sigma | L_\pm S_\mp | v_i \rangle|^2}{\Delta E}$$

$$\hat{H}'_{SO} \propto \frac{\partial V}{\partial z} (\mathbf{k} \times \mathbf{S})_z \qquad \mu_\sigma(k) = \sum_i \frac{|\langle \sigma | S_\mp k_\pm | v_i \rangle|^2}{\Delta E} = \mu_\sigma k^2$$

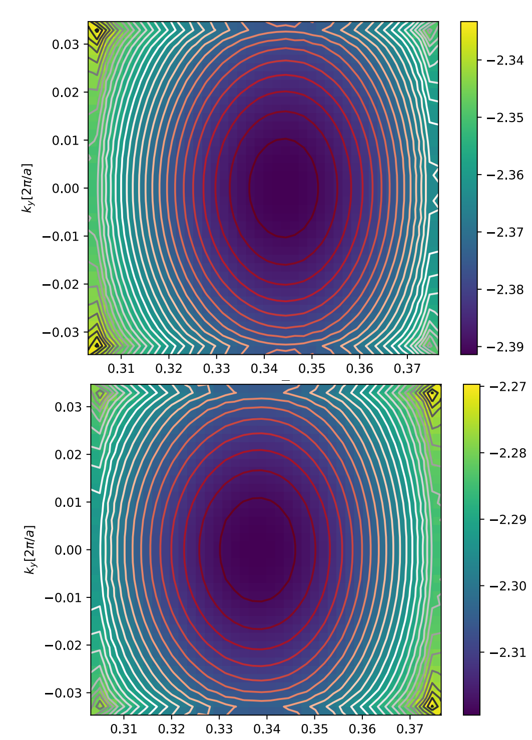
$$\mathrm{CB} - Q$$

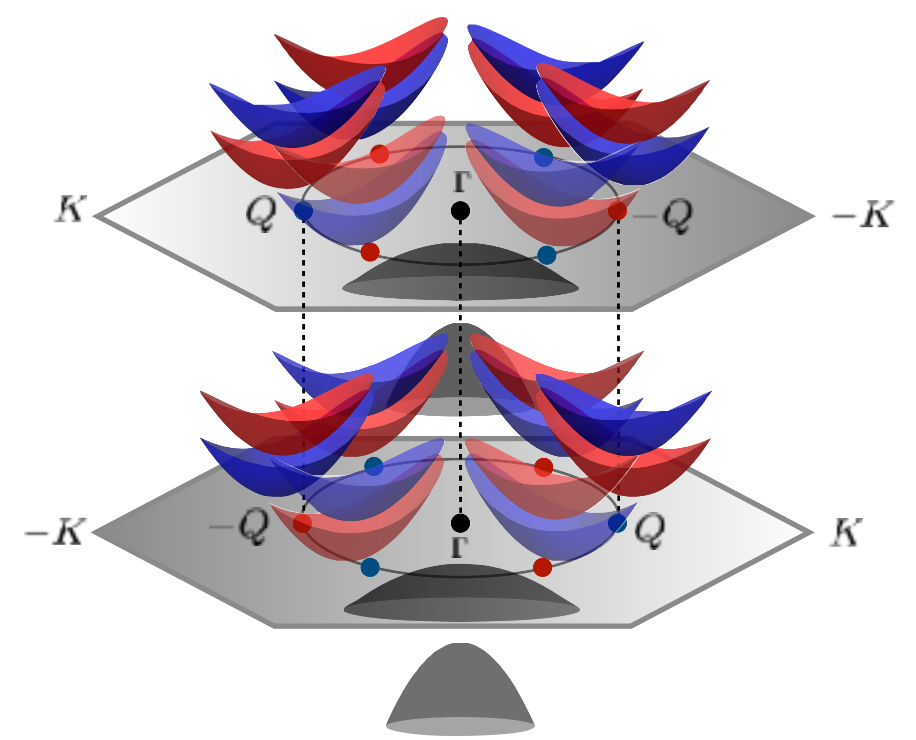
Monolayer dispersion:

$$E_s^\tau(\mathbf{k}) = \frac{\hbar^2 (k_x - q_s^\tau)^2}{2m_{x,s}^\tau} + \frac{\hbar^2 k_y^2}{2m_{y,s}^\tau} + E_{0s}^\tau$$

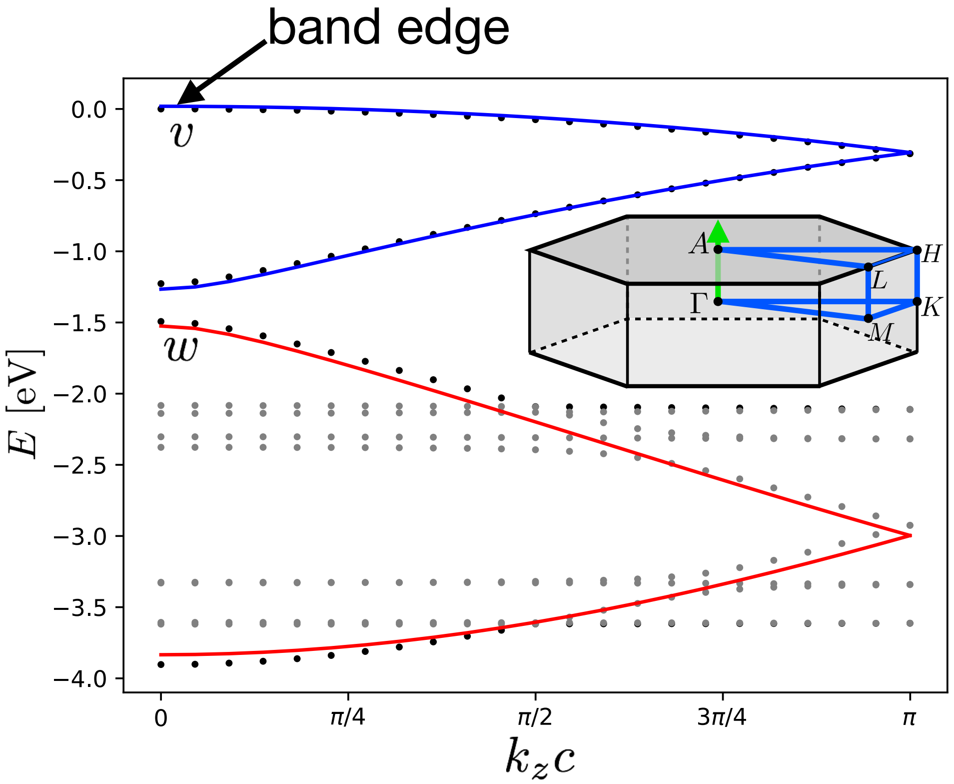
Interlayer hoppings:

$$t_\tau(\mathbf{k}) = t_0 + \tau t_1 k_x + i u_1 k_y + t_2 k_x^2 + u_2 k_y^2,$$





Bulk Crystals (VB)



Bulk Hamiltonian:

$$H_\Gamma(\mathbf{k},k_z) = \begin{pmatrix} E_v(\mathbf{k})+2\delta_v+2\mu_v(\mathbf{k}) & 0 & 2t_v(\mathbf{k})\cos\left(\frac{k_z c}{2}\right) & 2it_{vw}(\mathbf{k})\sin\left(\frac{k_z c}{2}\right) \\ 0 & E_w(\mathbf{k})+2\delta_w+2\mu_w(\mathbf{k}) & -2it_{vw}(\mathbf{k})\sin\left(\frac{k_z c}{2}\right) & 2t_w(\mathbf{k})\cos\left(\frac{k_z c}{2}\right) \\ 2t_v(\mathbf{k})\cos\left(\frac{k_z c}{2}\right) & 2it_{vw}(\mathbf{k})\sin\left(\frac{k_z c}{2}\right) & E_v(\mathbf{k})+2\delta_v+2\mu_v(\mathbf{k}) & 0 \\ -2it_{vw}(\mathbf{k})\sin\left(\frac{k_z c}{2}\right) & 2t_w(\mathbf{k})\cos\left(\frac{k_z c}{2}\right) & 0 & E_w(\mathbf{k})+2\delta_w+2\mu_w(\mathbf{k}) \end{pmatrix}$$

Band edge dispersion:

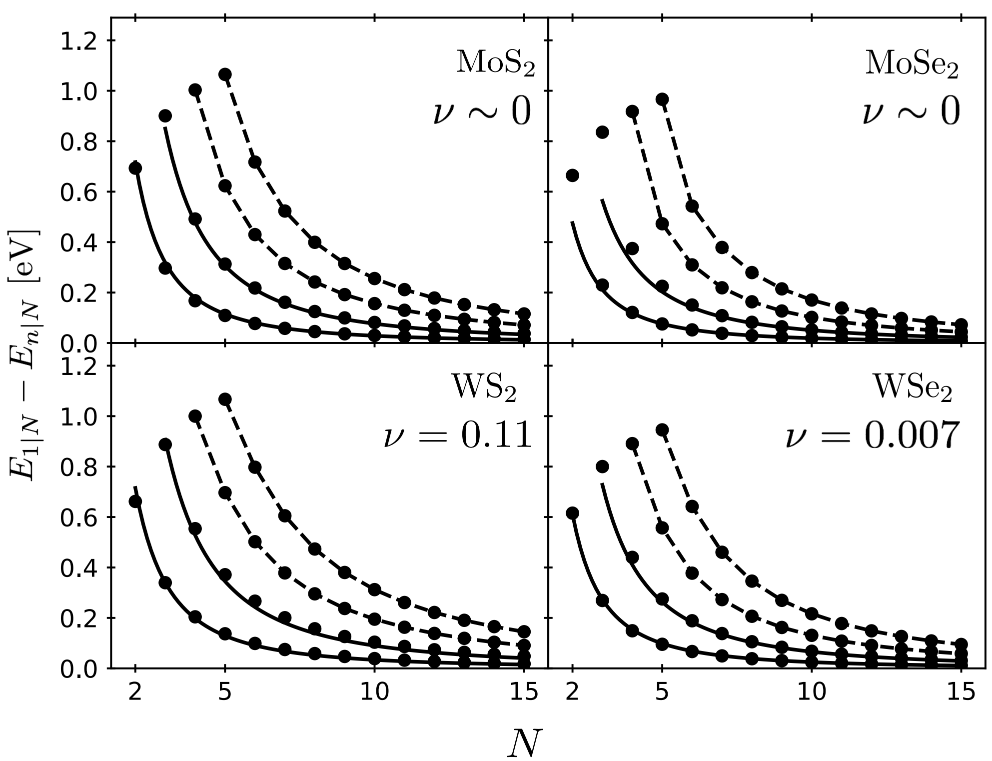
$$E_\Gamma(k_z,\mathbf{k}) \approx -\frac{\hbar^2 k_z^2}{2m_{v,z}} - \frac{\hbar^2 k^2}{2m_{v,xy}}\left(1+\zeta k_z^2\right)$$

Finite crystal, boundary conditions: $\left[\pm\nu d\partial_z\psi(z)+\psi(z)\right]_{z=\pm\frac{L}{2}} = 0$

Travelling waves solution (1D): $\psi(z) = ve^{ik_z z} + ue^{-ik_z z}$

Quantization condition: $Lk_z + 2\arctan(\nu d k_z) = \pi n \implies k_z = \dfrac{\pi n}{d(N+2\nu)}$

$$k_z \sim \frac{1}{L} \ll \frac{1}{d}$$



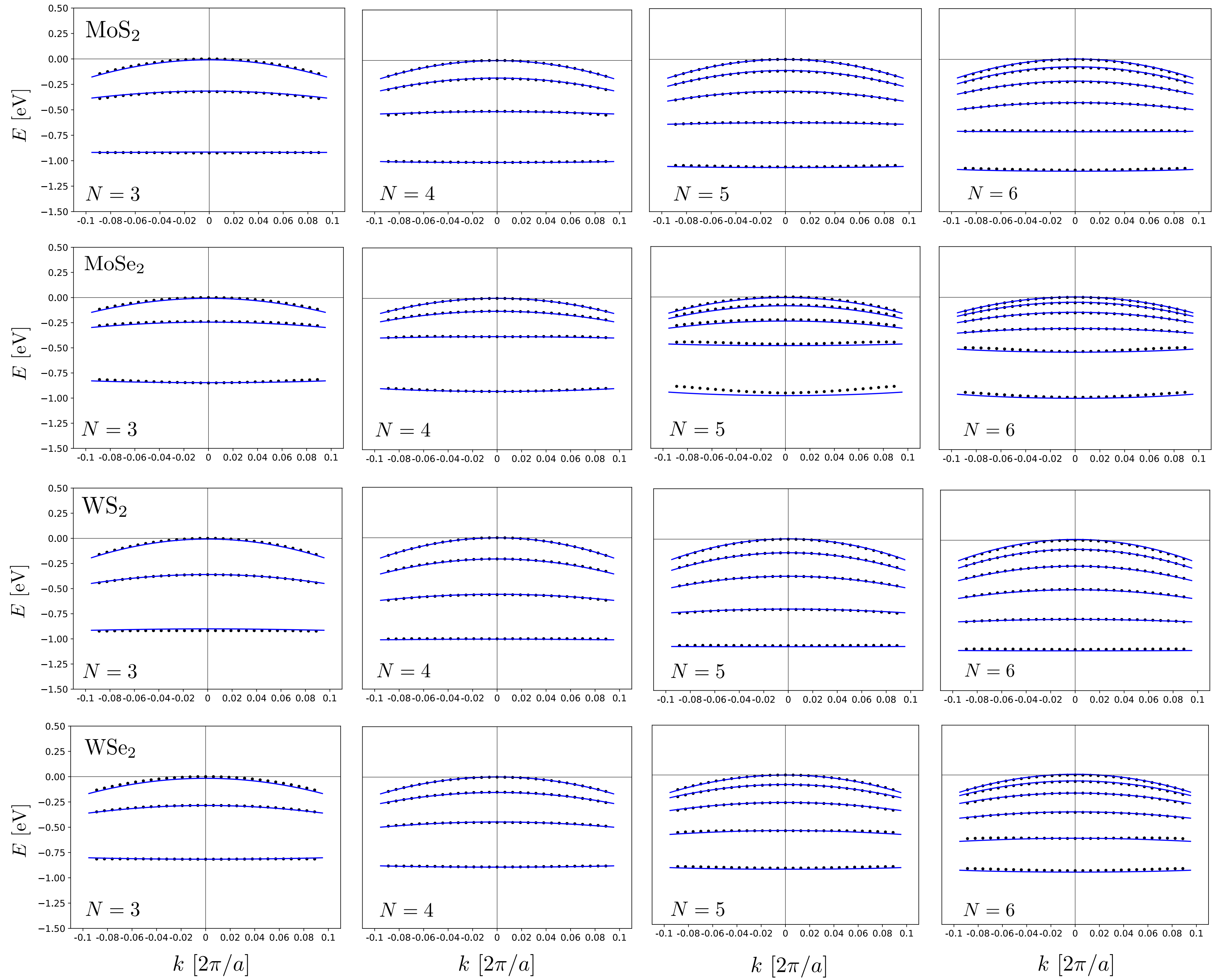
Intersubband energy spacings:

$$E_{1|N} - E_{2|N} = \frac{3\pi^2\hbar^2}{2m_{v,z}d^2(N+2\nu)^2}$$

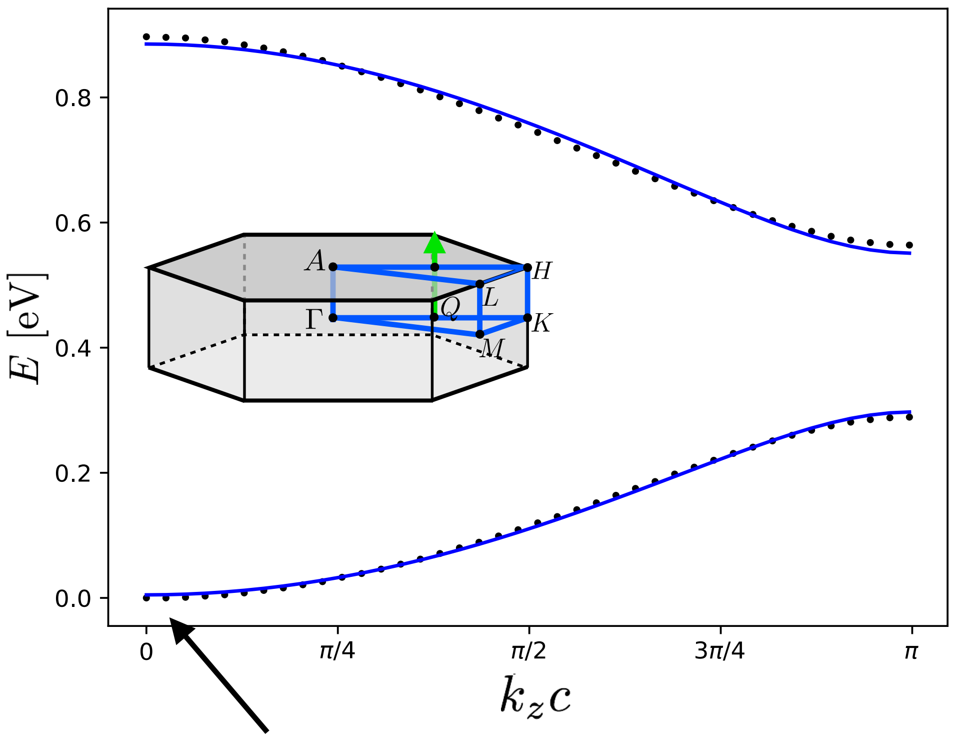
Subband effective masses:

$$m_{n|N} = m_{v,xy}\left[1+\frac{\zeta\pi^2 n^2}{d^2(N+2\nu)^2}\right]^{-1}$$

VB few-layer model-DFT comparison



Bulk Crystals (CB)



band edge

Bulk Hamiltonian:

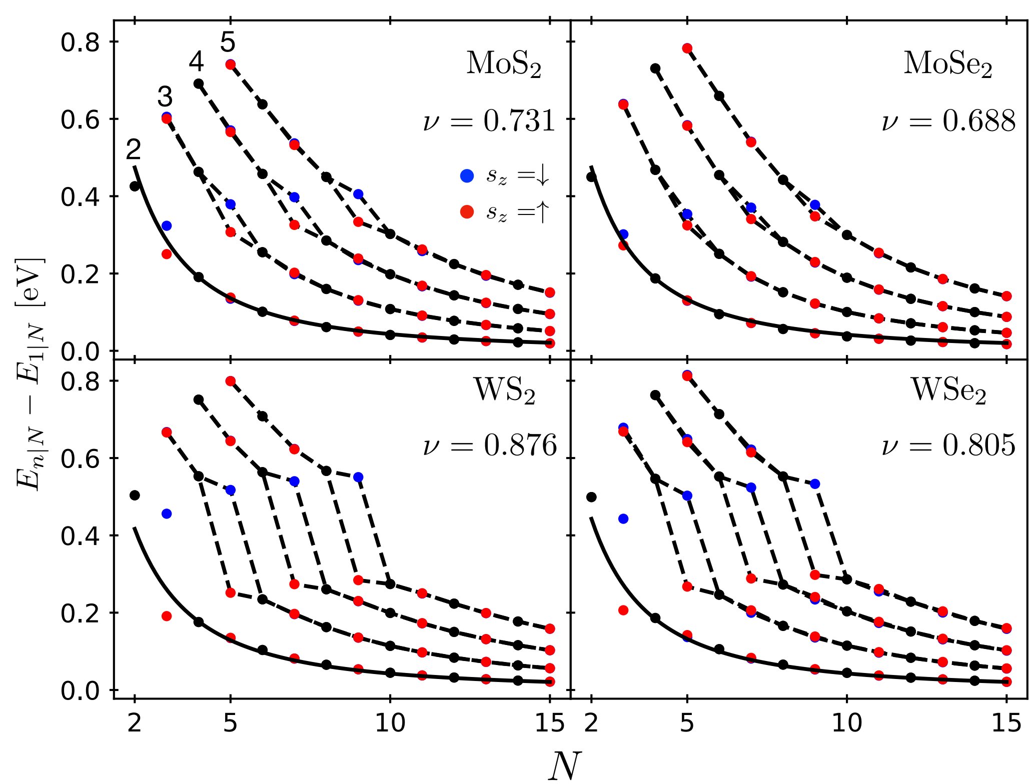
$$H_Q^{s,\tau}(\mathbf{k}, k_z) = \begin{pmatrix} \frac{E_\uparrow^\tau(\mathbf{k}) + E_\downarrow^\tau(\mathbf{k})}{2} + s_z \tau \Delta(\mathbf{k}) + 2t' \cos(k_z c) & 2t_\tau(\mathbf{k}) \cos\left(\frac{k_z c}{2}\right) \\ 2t_\tau^*(\mathbf{k}) \cos\left(\frac{k_z c}{2}\right) & \frac{E_\uparrow^\tau(\mathbf{k}) + E_\downarrow^\tau(\mathbf{k})}{2} - s_z \tau \Delta(\mathbf{k}) + 2t' \cos(k_z c) \end{pmatrix}$$

$$\Delta(\mathbf{k}) = \frac{E_\uparrow^\tau(\mathbf{k}) - E_\downarrow^\tau(\mathbf{k})}{2}$$

Band edge dispersion:

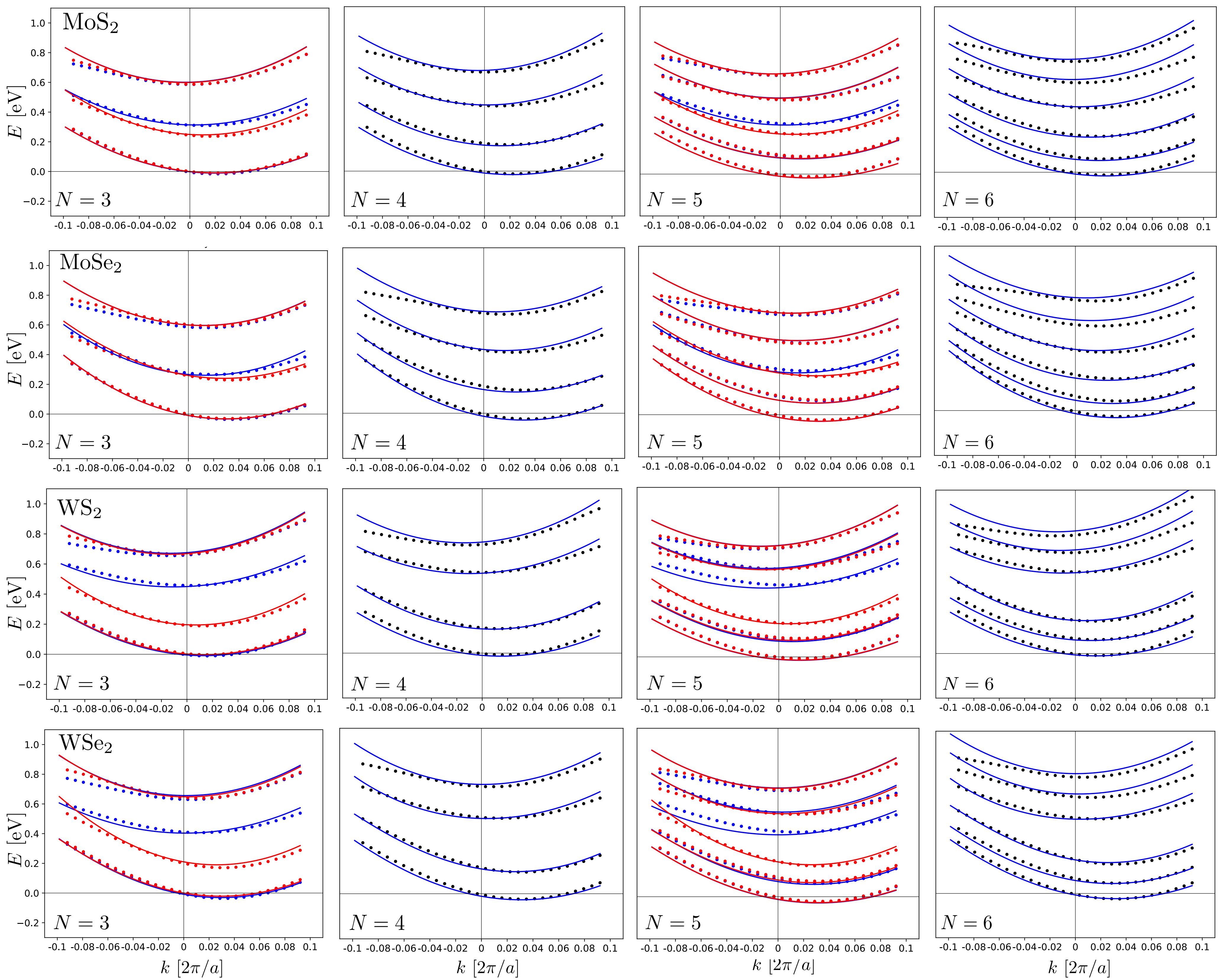
$$E_Q(\mathbf{k}, k_z) \approx \frac{\hbar^2 k_z^2}{2m_{c,z}} + \frac{\hbar^2}{2m_{c,x}} (k_x - [\kappa_0 + \kappa_2 k_z^2])^2 \left(1 + \zeta_x k_z^2\right) + \frac{\hbar^2 k_y^2}{2m_{c,y}} \left(1 + \zeta_y k_z^2\right)$$

Intersubband energy spacings

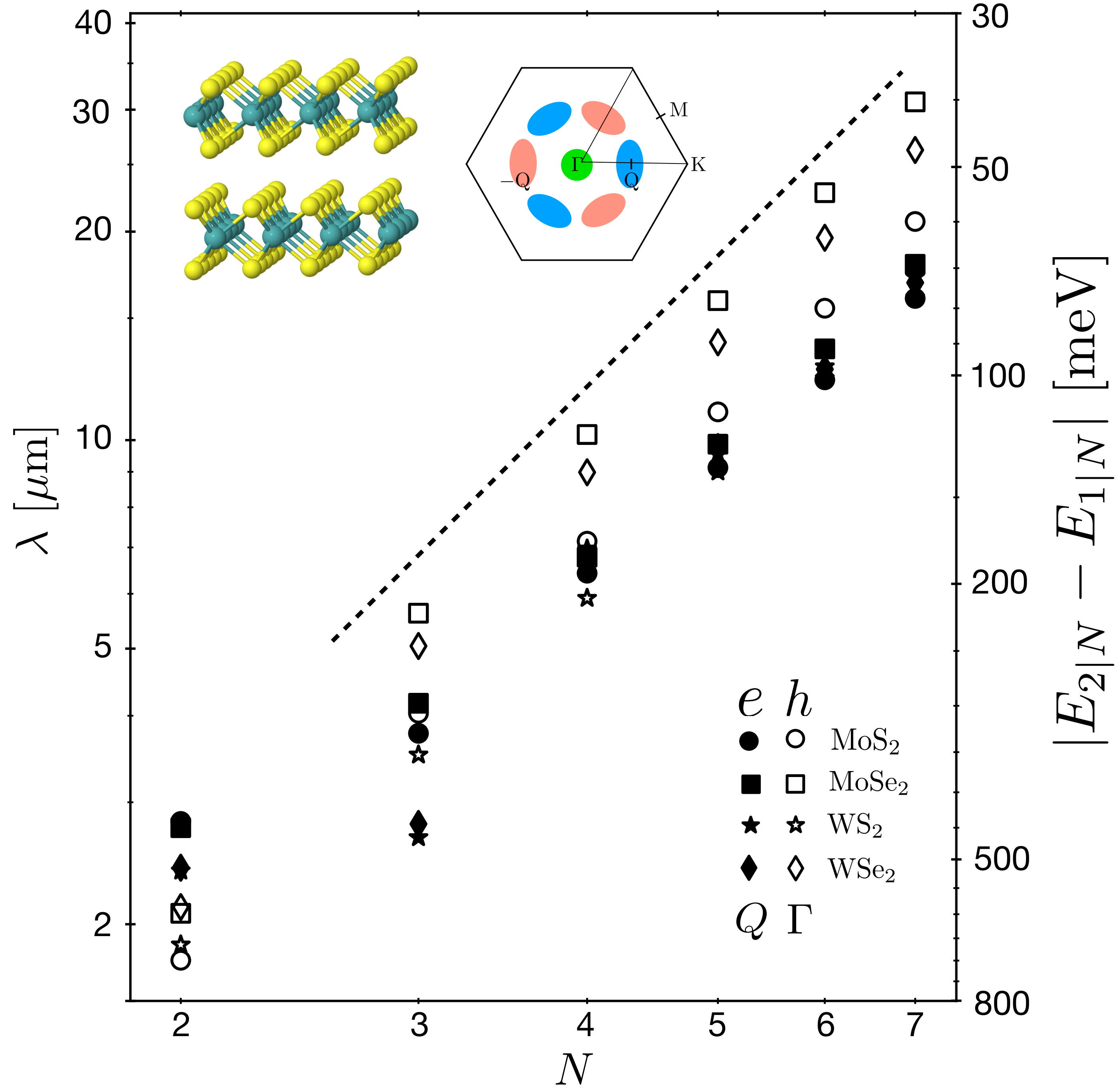


$$E_{2|N} - E_{1|N} = \frac{3\pi^2 \hbar^2}{2m_{c,z} d^2 (N + 2\nu)^2}$$

CB few-layer model-DFT comparison

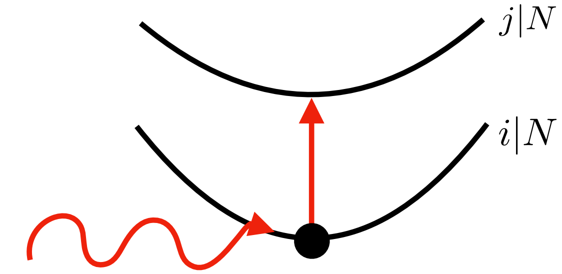


Intersubband transition energies



Optical intersubband transitions

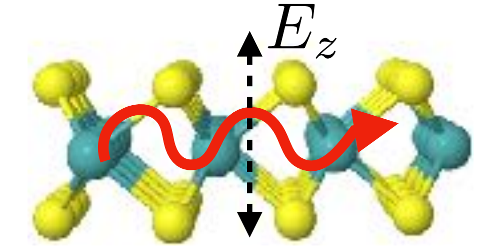
Light matter interaction (dipole approximation): $H' = e\mathbf{E}\cdot\mathbf{r}$



Subbands have alternating parity: $\langle j|H'|i\rangle \neq 0 \quad \Rightarrow \quad H' = eE_z z$

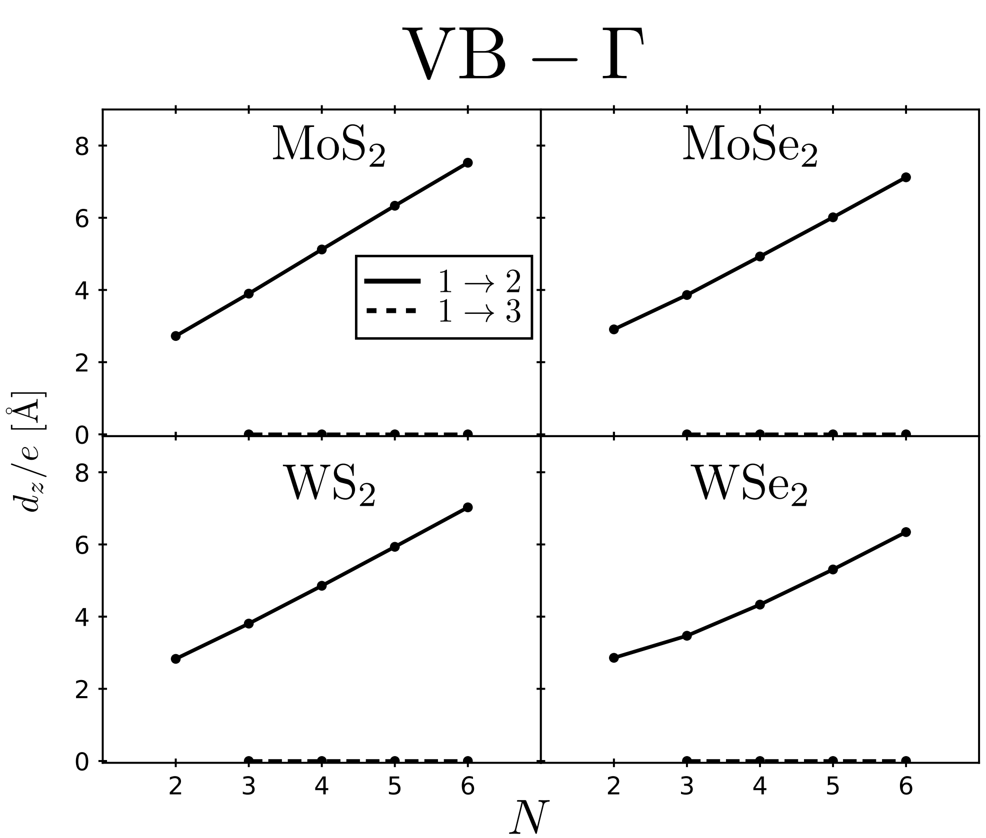
odd even

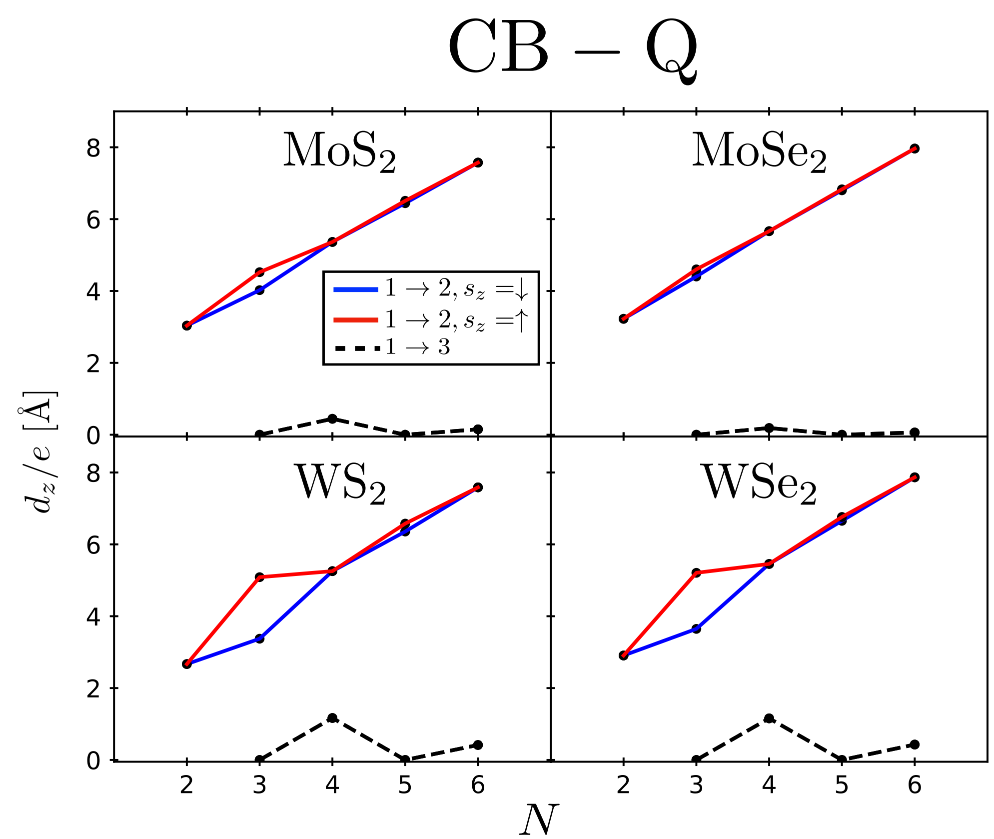
Out-of-plane polarised light



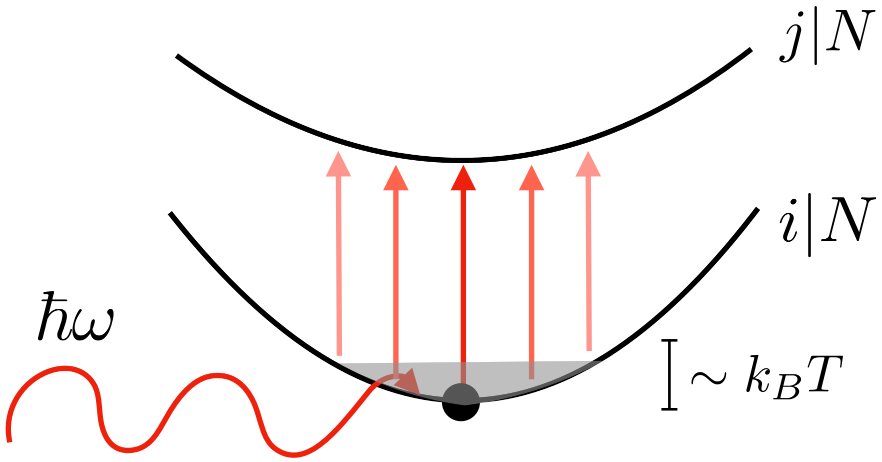
dipole moment matrix element

$$d_z^{ij}(\mathbf{k}) = e\langle j,\mathbf{k}|z|i,\mathbf{k}\rangle = e\sum_{n=1}^{N} z_n c_{j,n}^*(\mathbf{k})c_{i,n}(\mathbf{k}),$$





Optical intersubband transitions - dispersion broadening



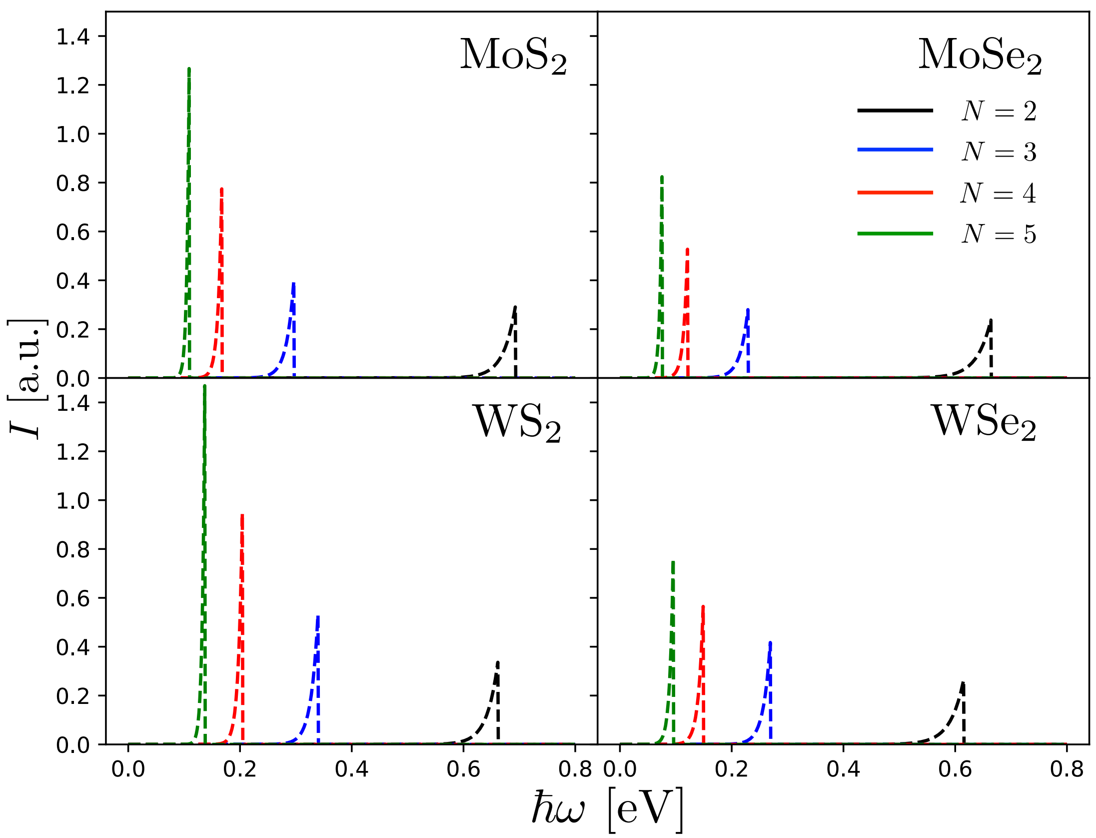
Intersubband transition rate:

$$\tau_{i,j}^{-1}(\hbar\omega) = \frac{2\pi}{\hbar} g_s g_v |E_z(\hbar\omega)|^2 |d_z^{ij}|^2 \sum_{\mathbf{k}} f(\mathbf{k}) \delta(E_j(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega)$$

For valence subbands:

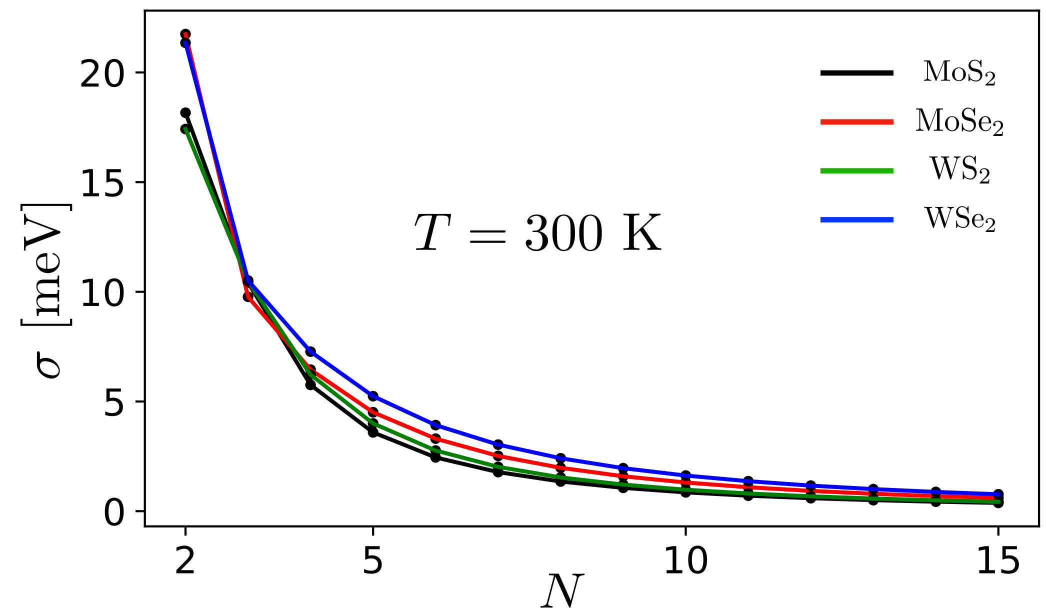
$$I(\hbar\omega) \propto \frac{4\pi}{\hbar} \frac{\hbar^2 n_h}{m_{1|N} k_B T} |E_z d_z|^2 \frac{\mu}{\hbar^2} e^{-\frac{\mu}{m_{1|N} k_B T}(E_{2|N} - E_{1|N} - \hbar\omega)} \Theta(E_{2|N} - E_{1|N} - \hbar\omega)$$

$$\frac{1}{\mu} = \frac{1}{m_{1|N}} - \frac{1}{m_{2|N}}$$

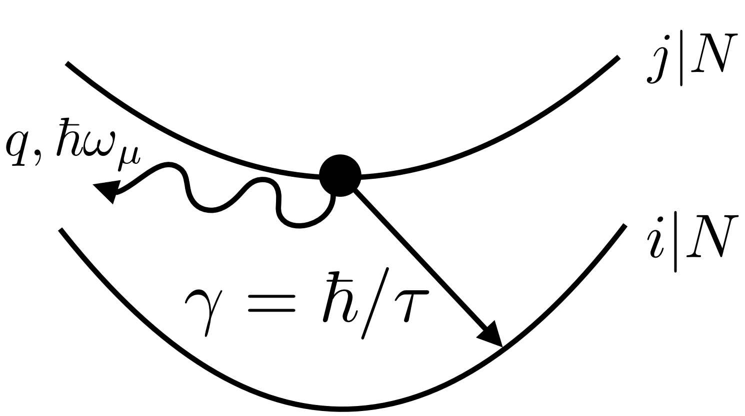


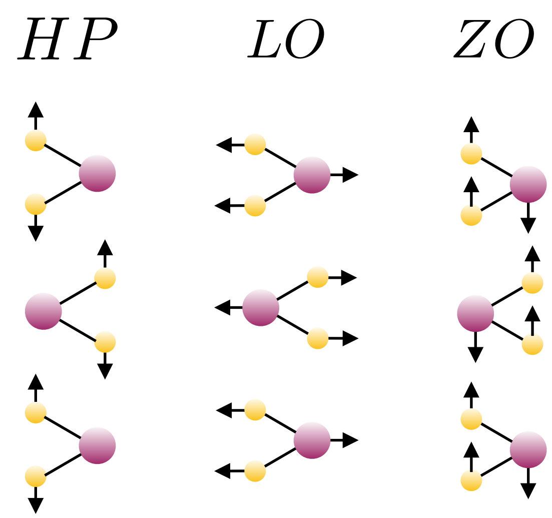
FWHM

$$\sigma = \left(1 - \frac{m_{1|N}}{m_{2|N}}\right) k_B T \log 2$$



Intersubband optical phonon relaxation





Phonon modes μ

broadening

$$\gamma = 2\pi[1 + n(\hbar\omega_\mu)] \sum_{\mathbf{q},\mu,\nu} |M_{i,j}^{\mu,\nu}(\mathbf{k}, \mathbf{k} - \mathbf{q})|^2$$

$$\times \, \delta[E_i(\mathbf{k}) - E_j(\mathbf{k} + \mathbf{q}) - \hbar\omega_\mu]$$

electron-phonon matrix element

$$M_{\mu,\nu}^{i,j}(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \sum_n g_{\mu,n}^{\nu}(\mathbf{q}) c_{j,n}^*(\mathbf{k} + \mathbf{q}) c_{i,n}(\mathbf{k})$$

Basis for N multilayer phonon modes

$\nu = 0, .., N-1$

$$f_\nu = \frac{1}{\sqrt{N}} [e^{\frac{2\pi i k}{N}\nu}]_{k=0}^{N-1}$$

HP phonon

$$g_{\mathrm{HP},n}^{\nu} = f_\nu(n) \sqrt{\frac{\hbar}{2\rho\omega_{\mathrm{HP}}}} D$$

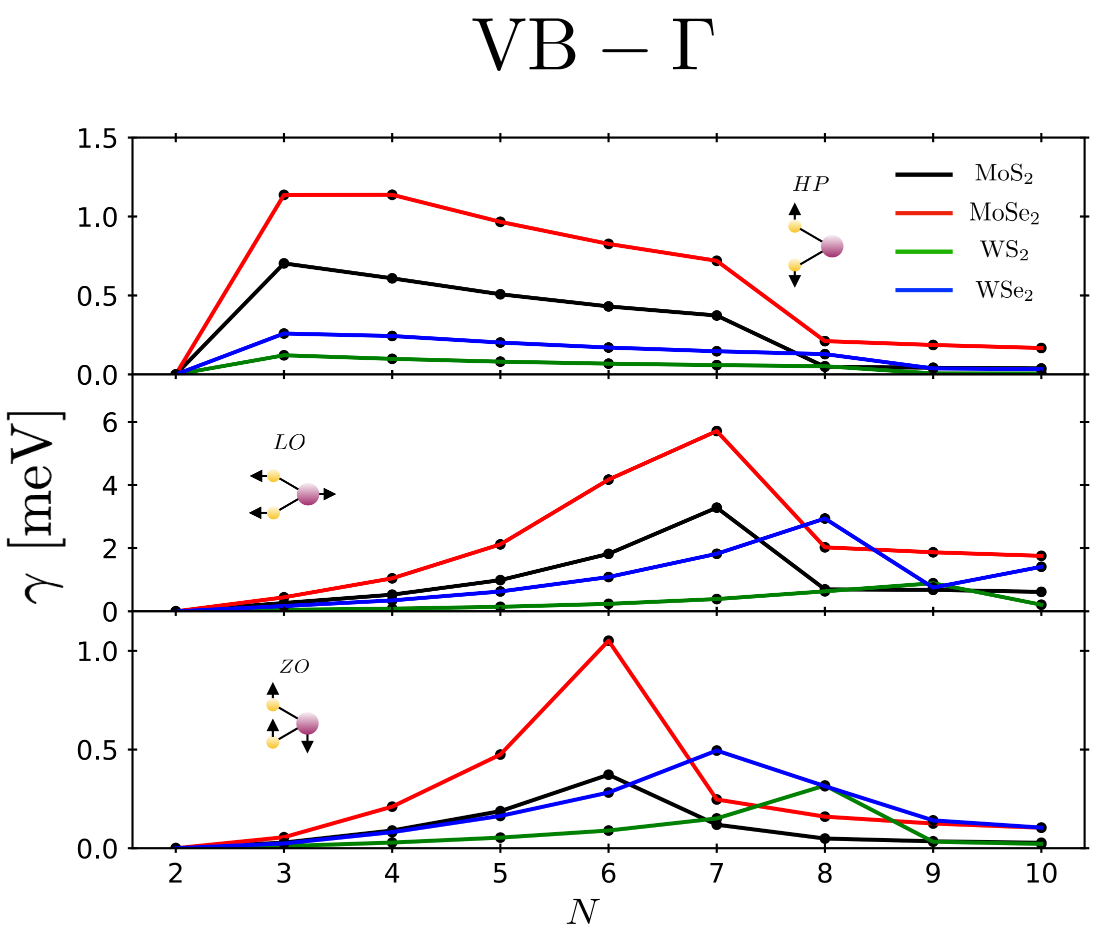
LO phonon

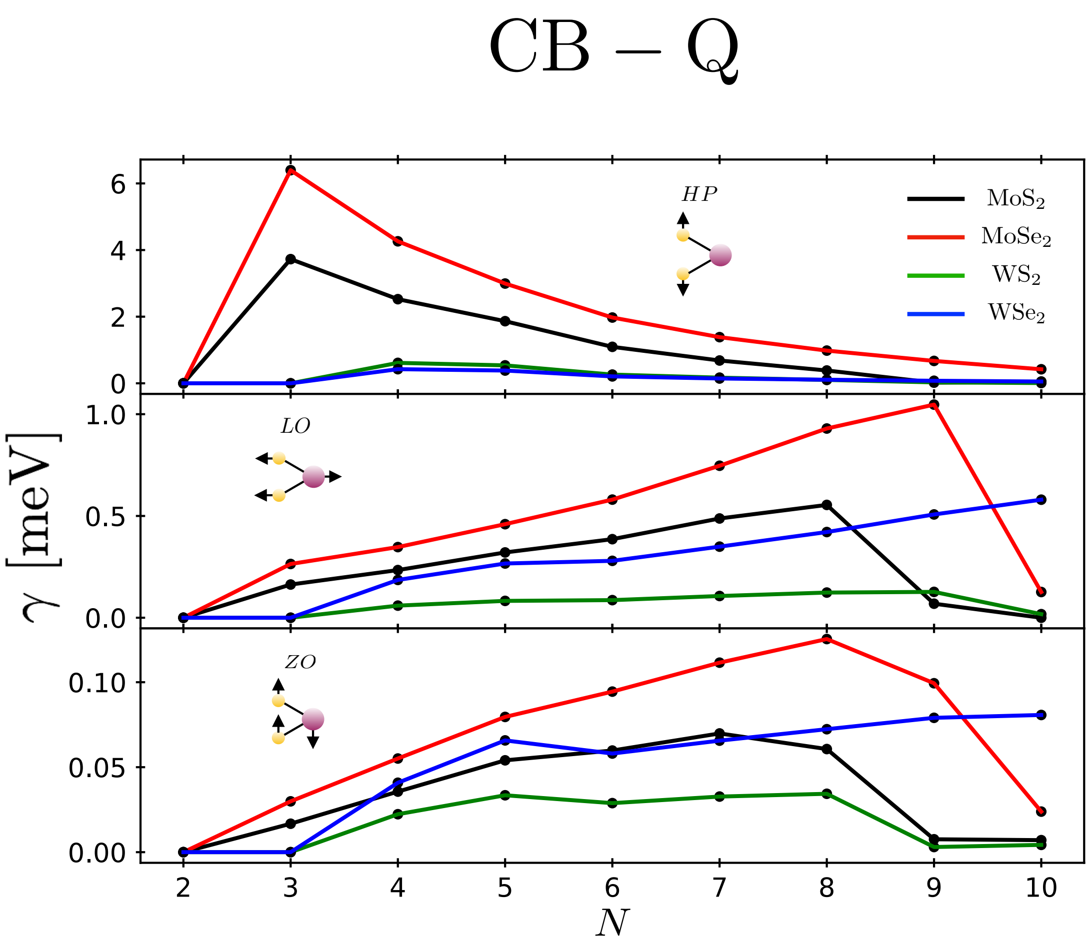
$$g_{\mathrm{LO},n}^{\nu}(q) = \frac{2\pi i e^2 Z}{A(1 + r_* q)} \sqrt{\frac{\hbar}{2\rho M_r/M\omega_{\mathrm{LO}}}} \sum_m f_\nu(m) e^{-qd|n-m|}(-1)^m$$

ZO phonon

$$g_{\mathrm{ZO},n}^{\nu} = \frac{2\pi e^2 Z_z}{A} \sqrt{\frac{\hbar}{2\rho M_r/M\omega_{\mathrm{ZO}}}} \sum_m{}' f_\nu(m) e^{-qd|n-m|} \frac{n-m}{|n-m|}$$

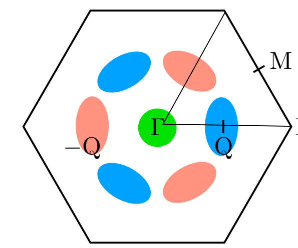
Intersubband phonon relaxation



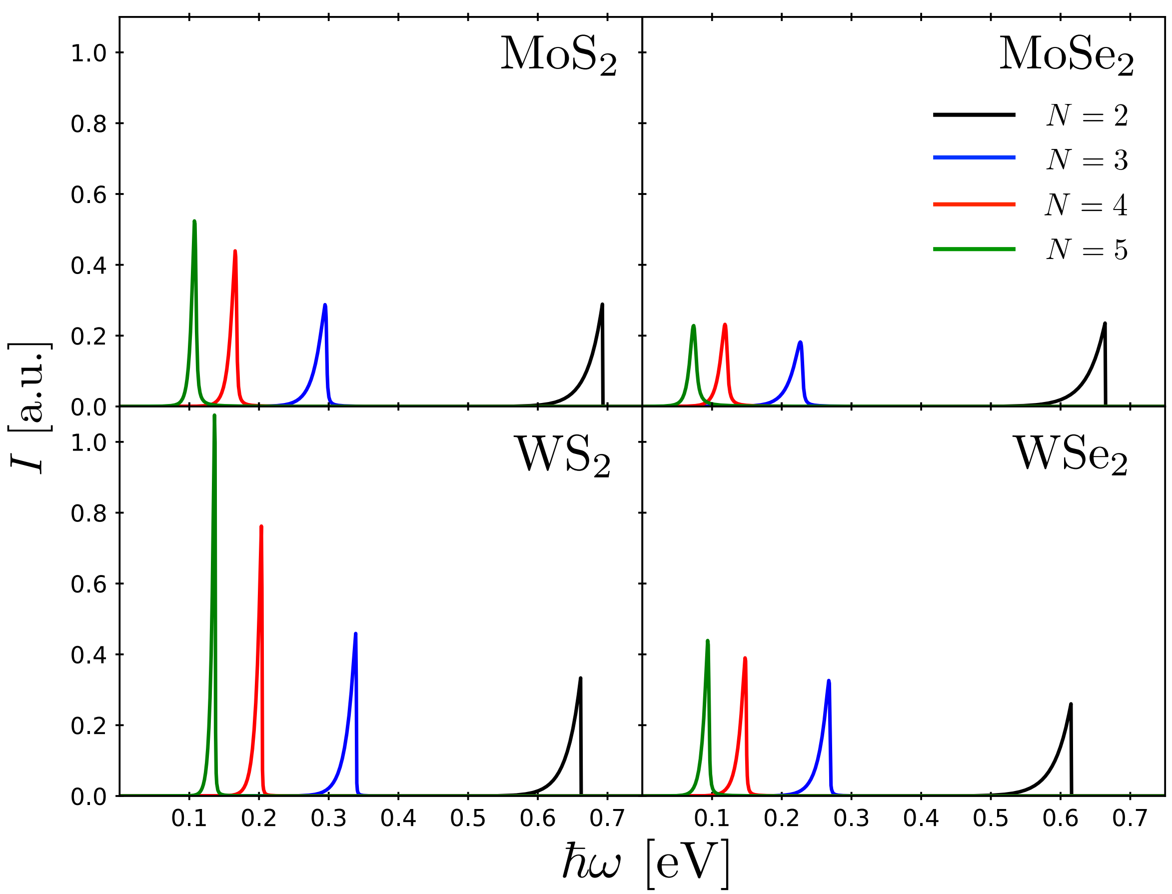


Intersubband absorption spectrum (T=300K)

$$\tau_{i,j}^{-1}(\hbar\omega) = \frac{2\pi}{\hbar} g_s g_v |E_z(\hbar\omega)|^2 \sum_{\mathbf{k}} |d_z^{ij}(\mathbf{k})|^2 f(\mathbf{k}) \frac{\gamma/\pi}{(E_j(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega)^2 + \gamma^2}$$



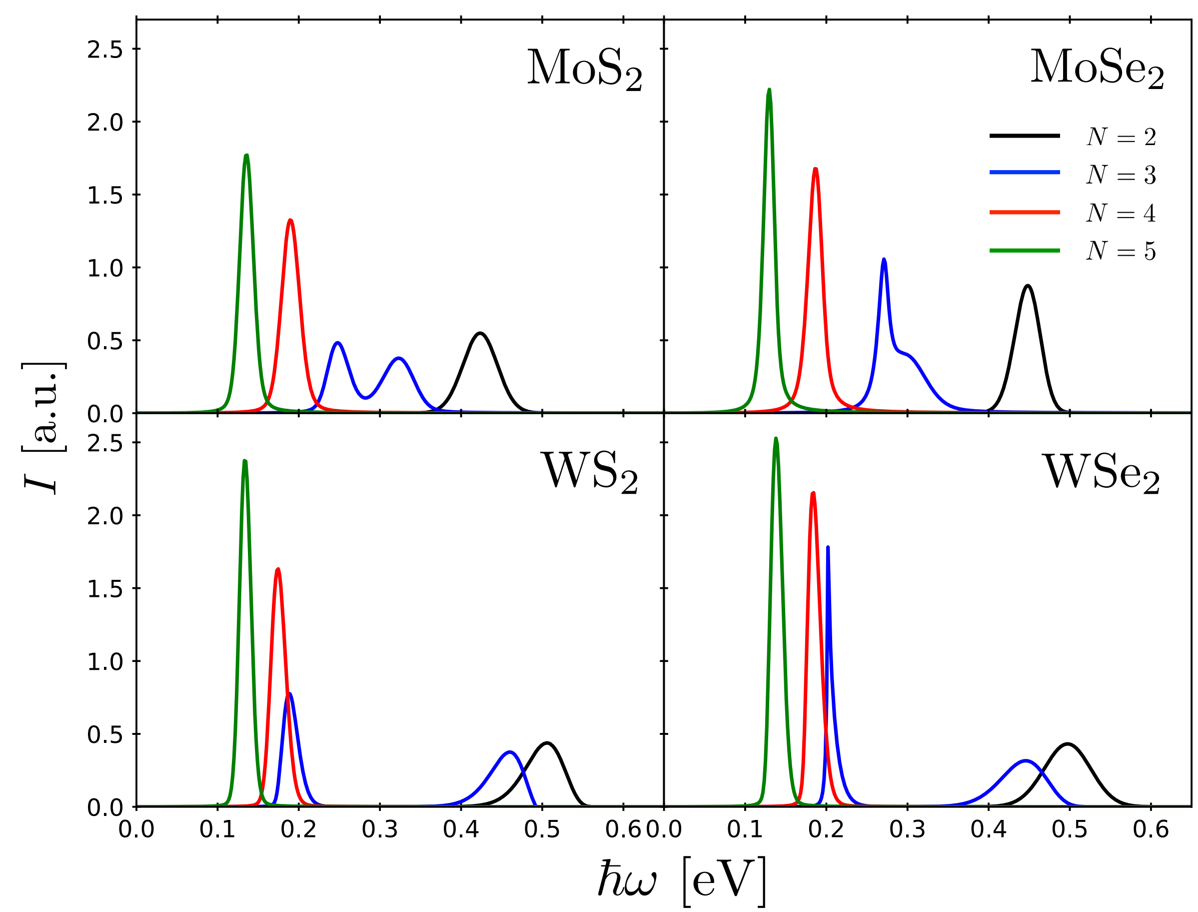
$\mathrm{VB} - \Gamma$ $\quad g_s = 2, g_v = 1$



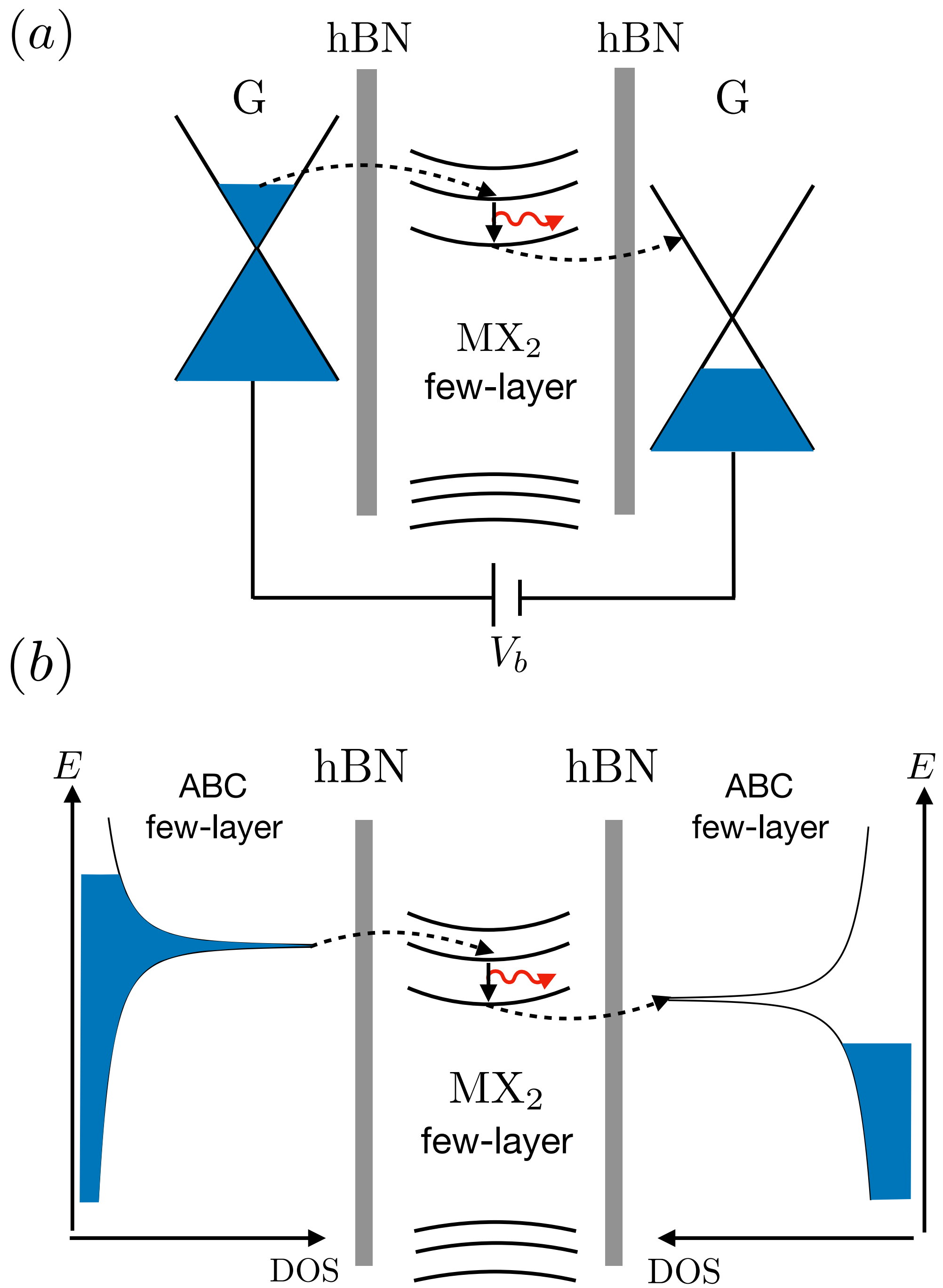
$\mathrm{CB} - \mathrm{Q}$

$g_s = 1, g_v = 6$ (N odd)

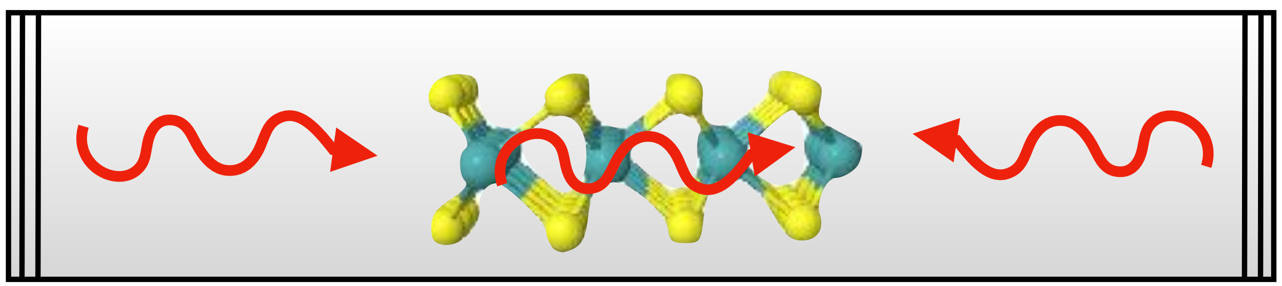
$g_s = 2, g_v = 6$ (N even)



Device application

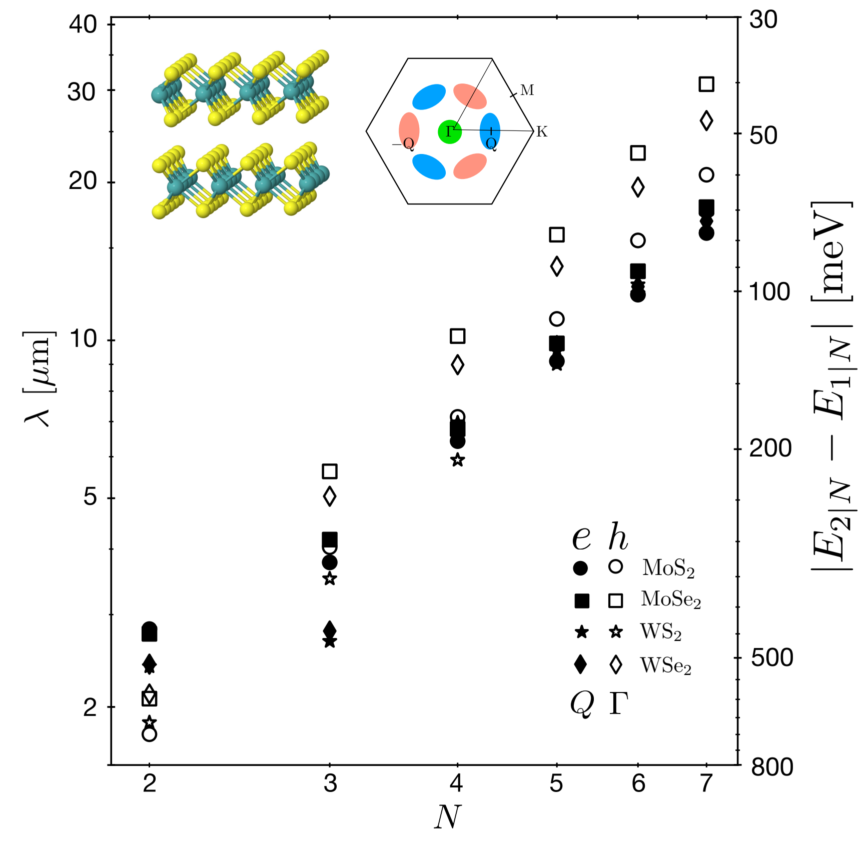


Bragg resonator

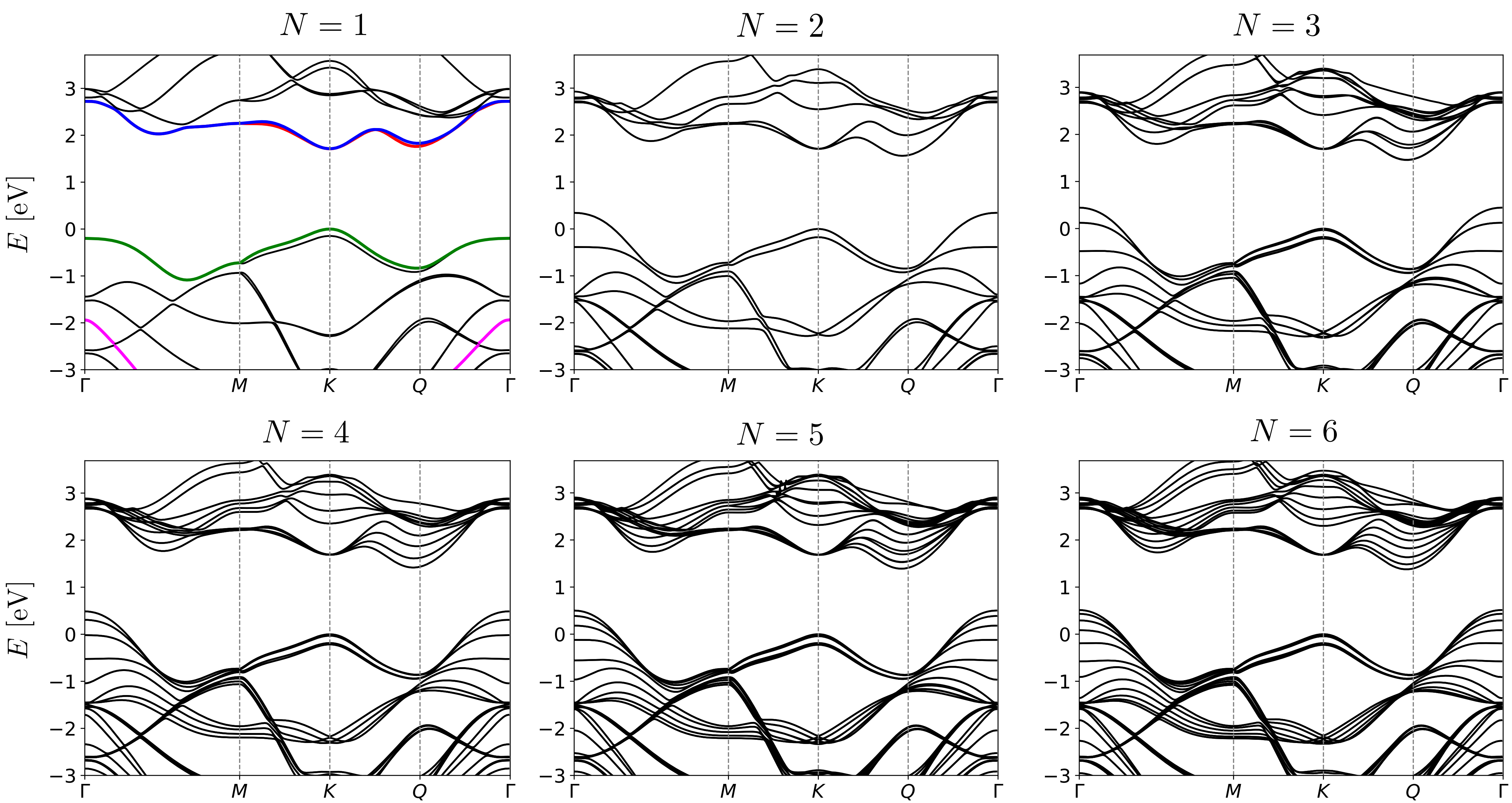


Summary

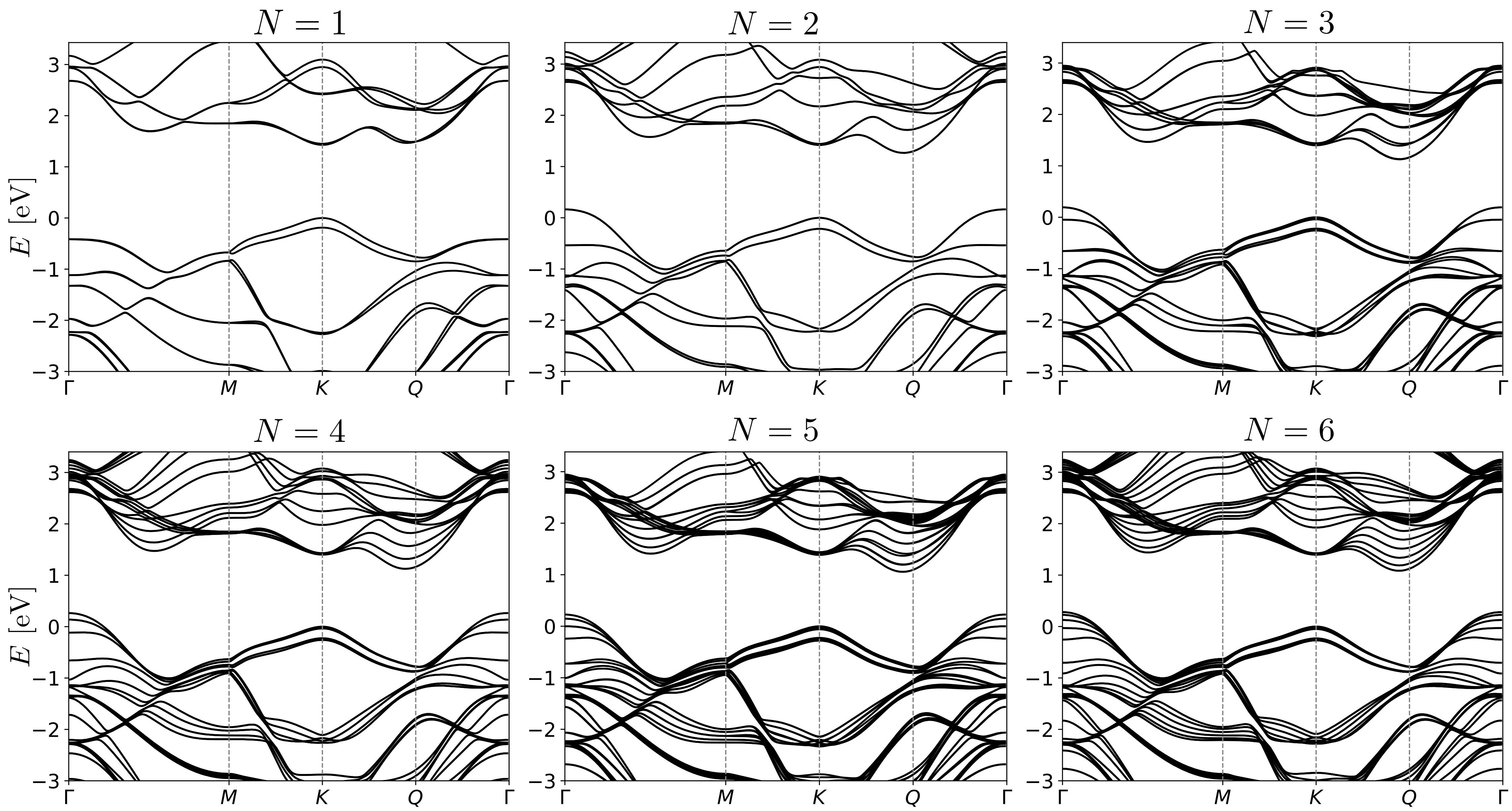
- Multilayer 2H-stacked TMDs show a rich subband structure both in the valence and conduction bands, which can be modelled by our Hybrid k.p-tight binding model.
- The four main TMDs cover densely the spectrum range of interest to many industries and applications (IR/FIR).
- The intersubband absorption of out-of-plane polarised light show dispersion broadening, and weaker phonon induced broadening as compared to conventional quantum wells.



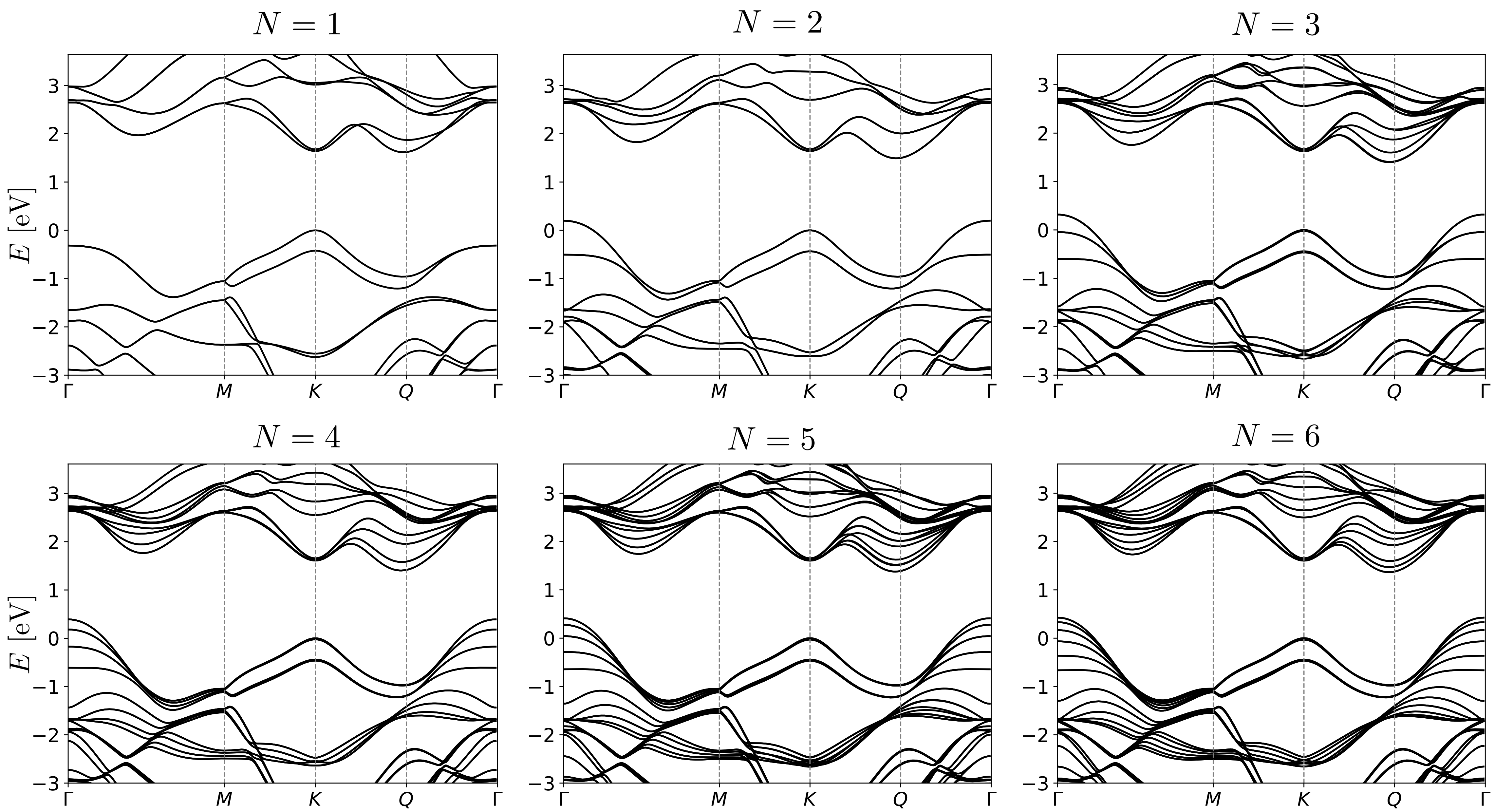
MoS2



MoSe2



WS2



WSe2