Multiexcitons and correlation effects in perovskite nanocrystals

Journées Pérovskites Halogénées

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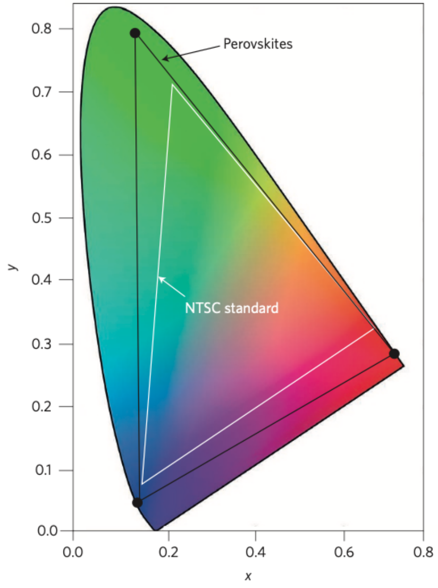
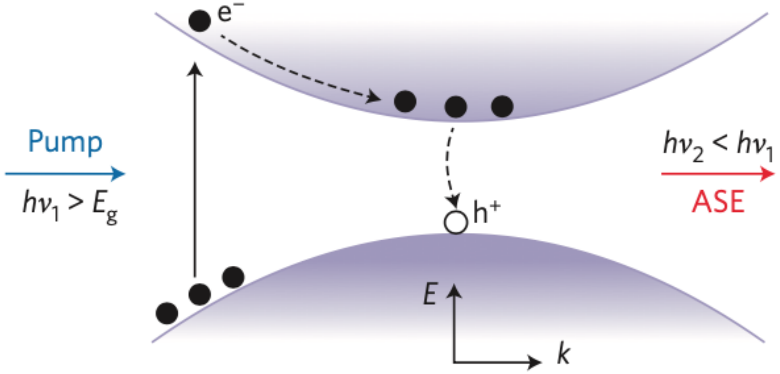
CEA, CNRS, IRIG, SyMMES

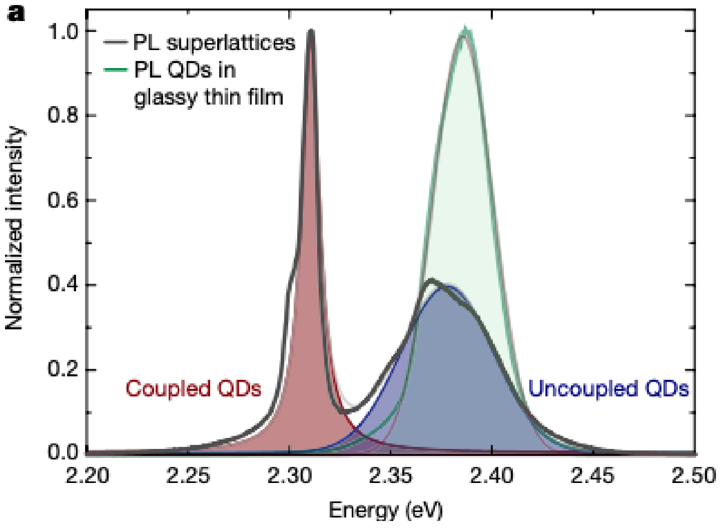
Light emitting devices

Diverse lighting applications

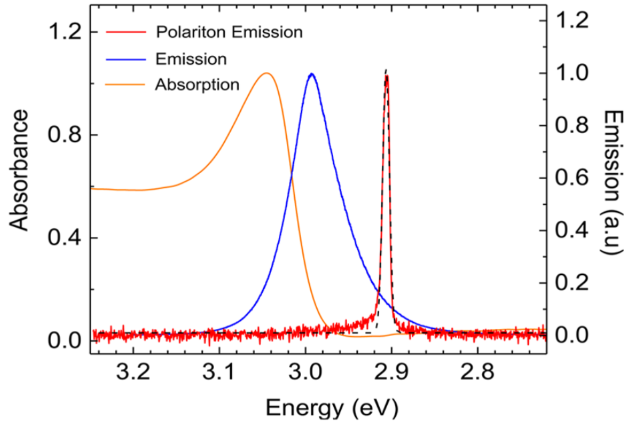
colour gamut







Thin-film Fabry–Pérot cavity



Motivations

◊ System of interest:
+ nano-cubes
+ nanoplatelets

◊ Emission properties:
+ size-dependent energy
+ lifetime, line width

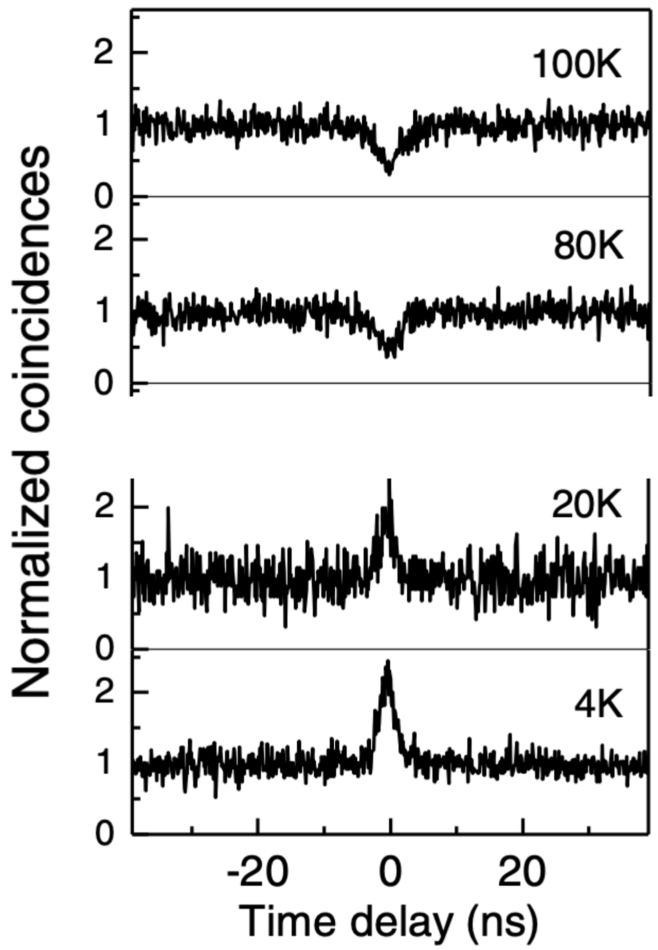
◊ Multiexcitons under high fluence:
+ emission energy, lifetime
+ carrier-carrier interaction

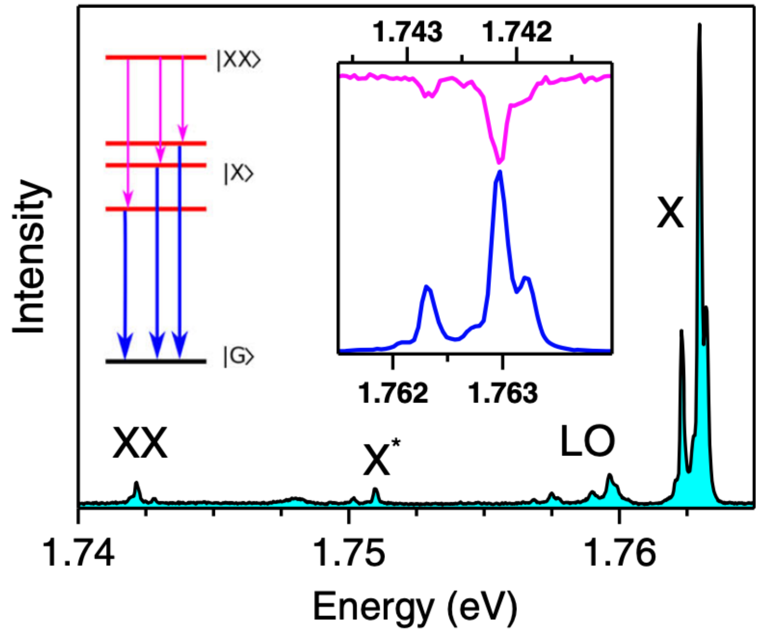
→Theoretical approach(es)?

Sutherland and Sargent, Nature Photonics 10, 295–302 (2016)
Raino et al., Nature 563, 671−675 (2018)
Su et al., Nano Lett. 2017, 17, 3982-2988

Light emitting devices

Novel lighting sources





Tamarat et al., Nature Comm. 11, 6001 (2020)

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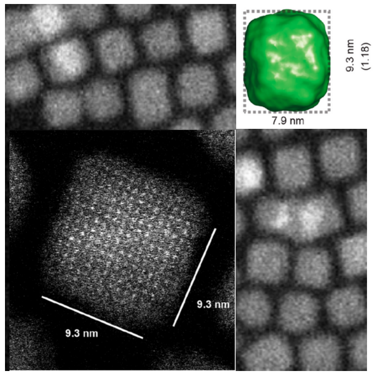
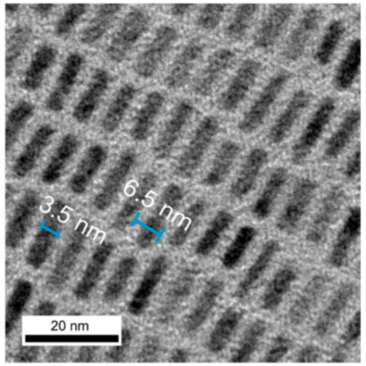
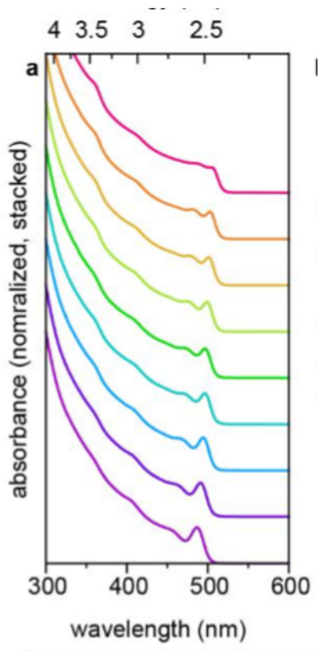
Perovskite cuboids and nanoplatelets

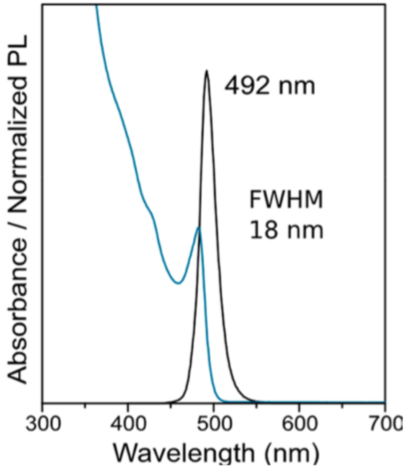




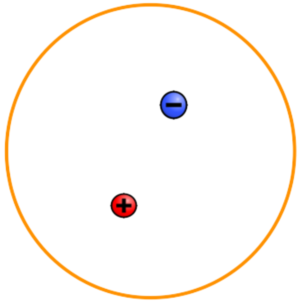
Cuboids
2.5–15.0nm

Nanoplatelets
n-monolayer thick





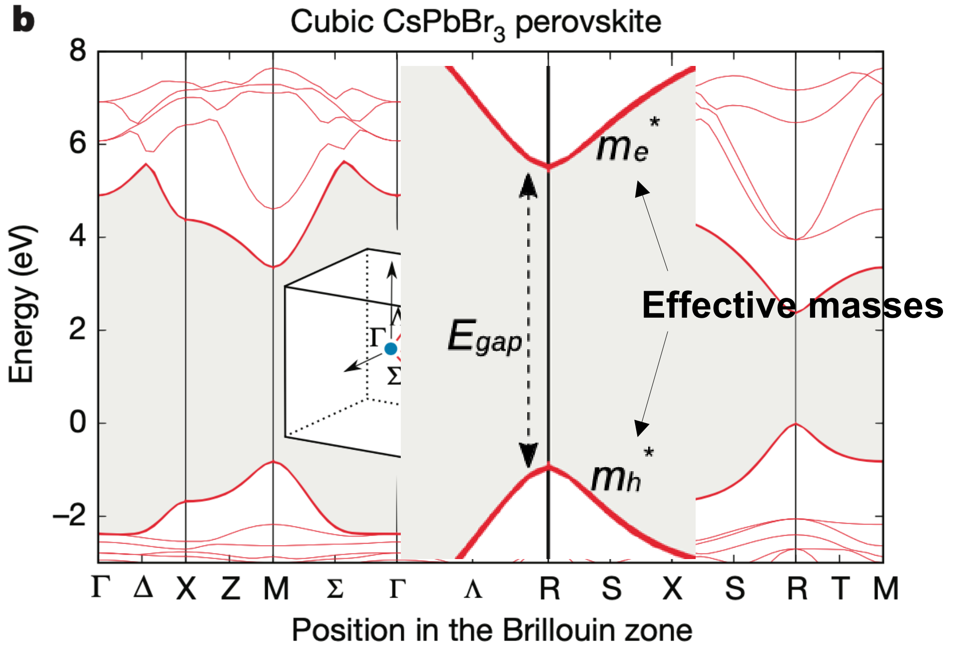
Spherical model



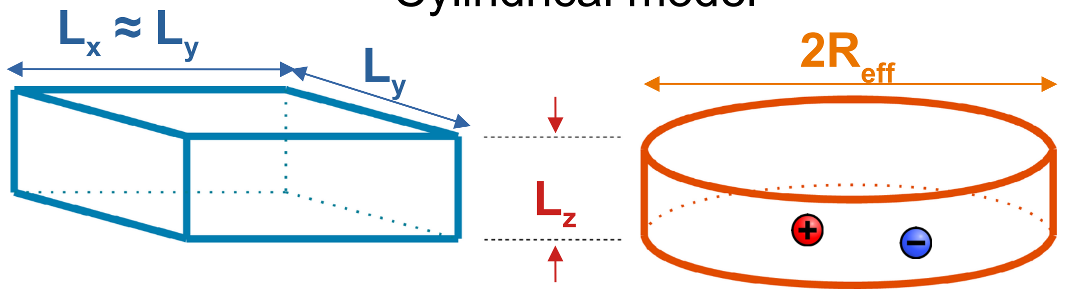
◊ **Empirical** models

◊ **Symmetry** (shape)

◊ Screened Coulomb interaction
"effective" dielectric constant ε_{eff}

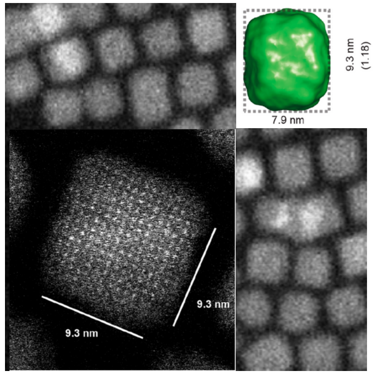


Cylindrical model



Krieg et al., J. Am. Chem. Soc. 2019, 141,19839-19849
Krieg et al., ACS Cent. Sci. 2021, 7, 135−144
Bertolotti et al., ACS Nano 2019, 13, 14294−14307
Becker et al., Nature 553, 189-193 (2018)

Perovskite cuboids and nanoplatelets



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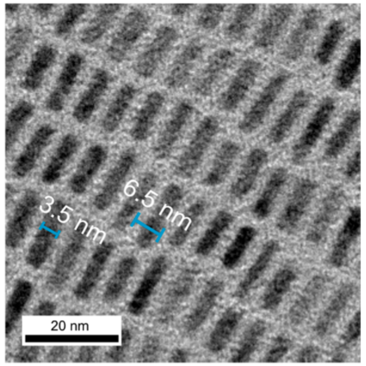

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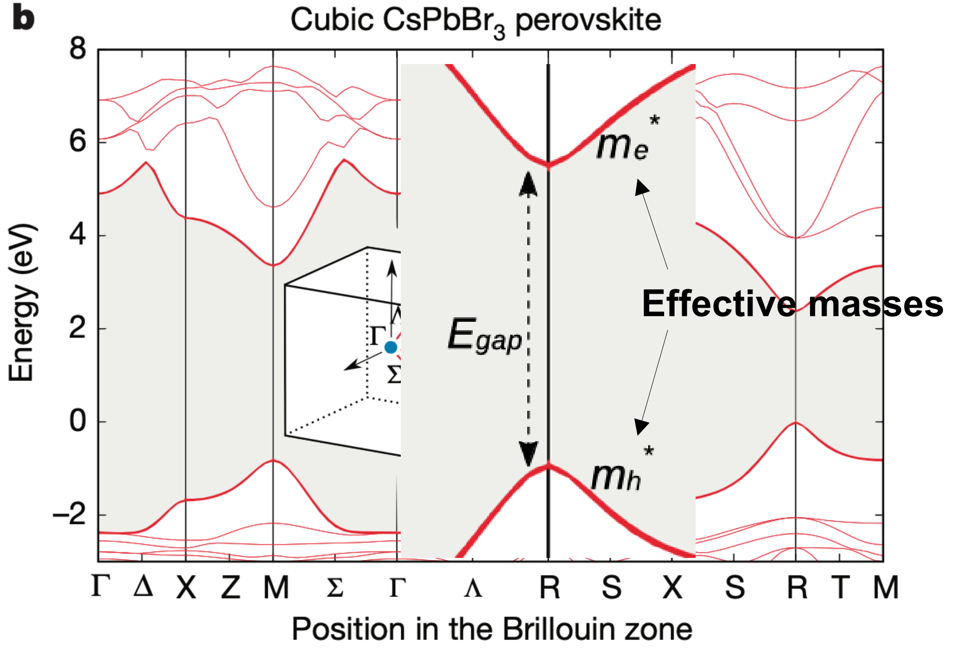

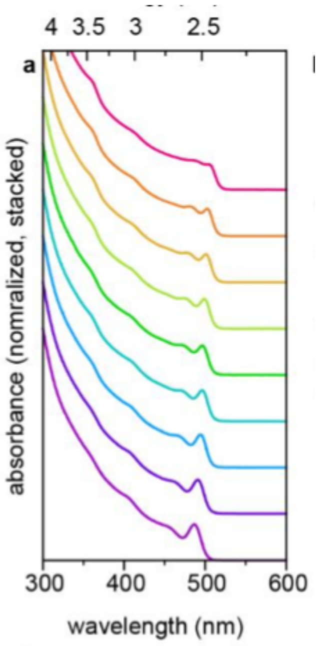

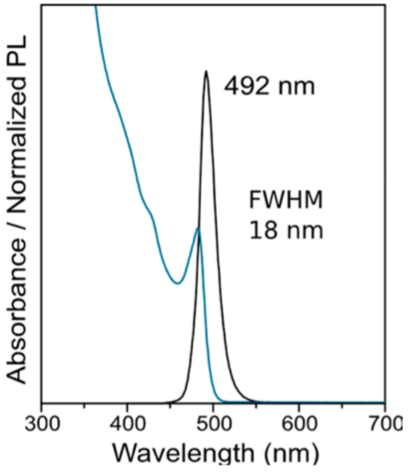

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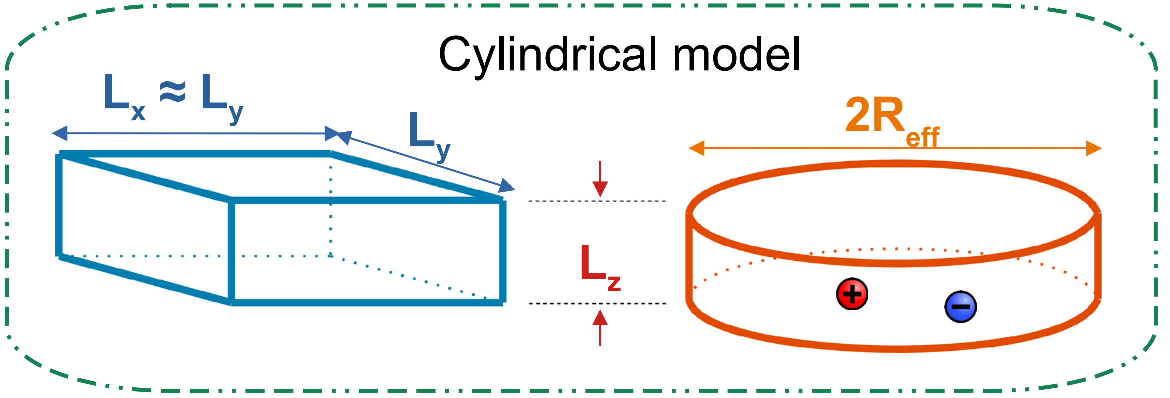

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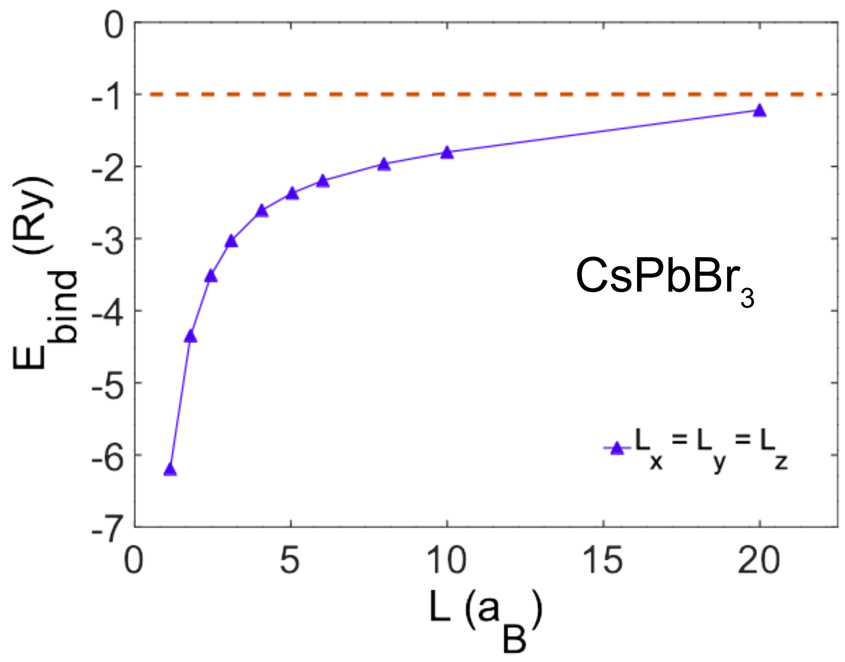


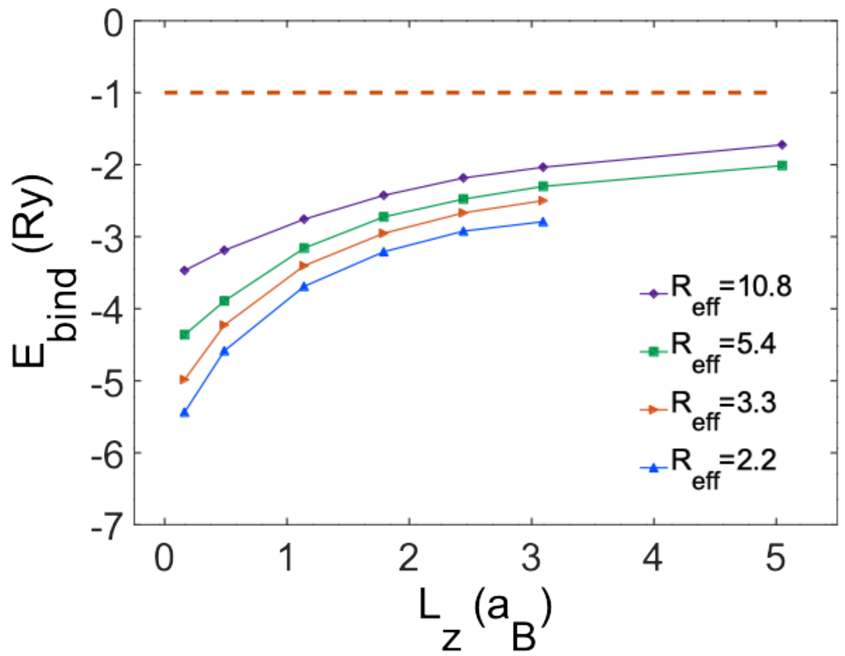
◊ *Isotropic* nanocrystals
$L_x = L_y = L_z = L$

◊ *Correlation* effects ($L>a_B$)
→binding energy E_{bind} for ground state single exciton
a_B – effective Bohr radius
Ry – exciton Rydberg

◊ *Anisotropic* effects
$L_x = L_y \neq L_z$

◊ Thickness:
Monolayer → several a_B

◊ R_{eff} – effective radius



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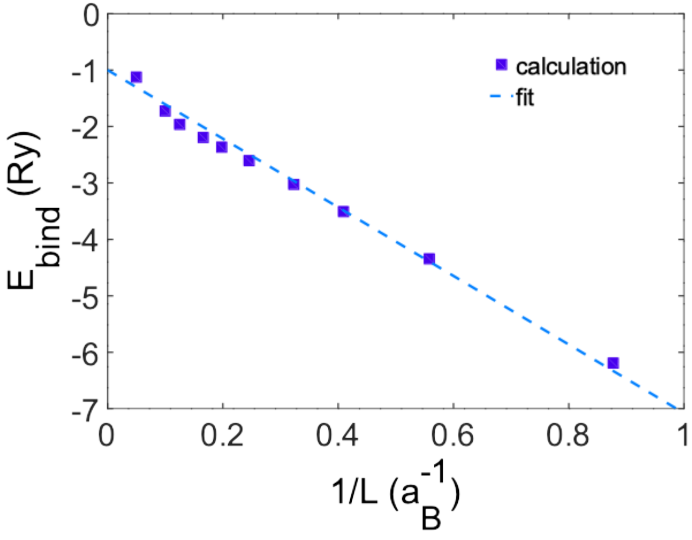

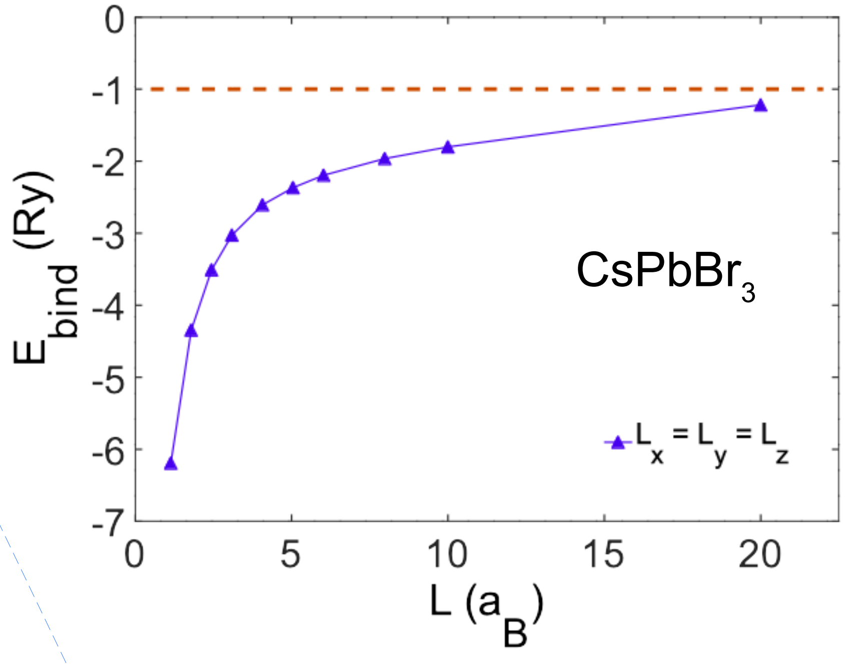

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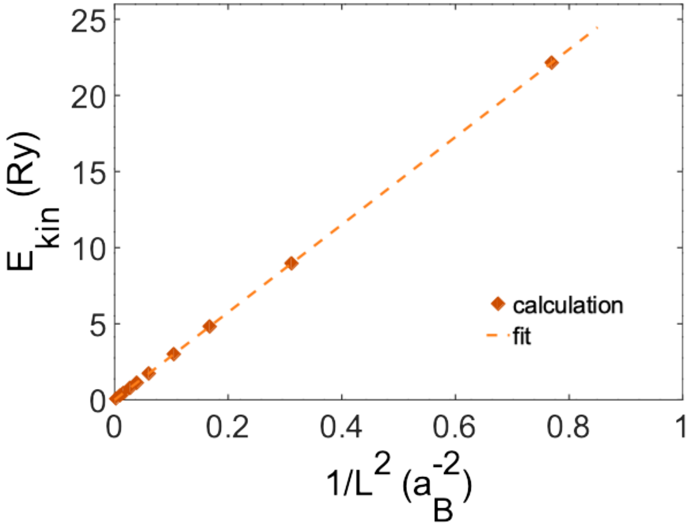


Energy-size relation (fit)

$E_{gap} + E_{bind} + E_{kin} = \mathbf{E_{exc}}$

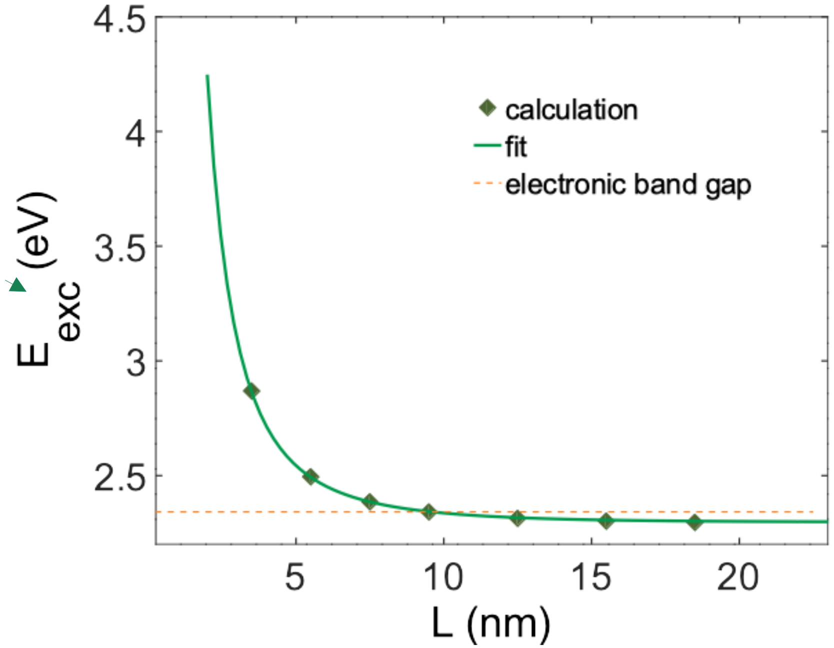
◊ E_{bind} (Ry) = -6.1/L - 1.0

◊ E_{kin} (Ry) = $28.8/L^2$

$L(a_B)$

$CsPbBr_3$: 1 a_B = 3.1 nm

1 Ry = 33 meV



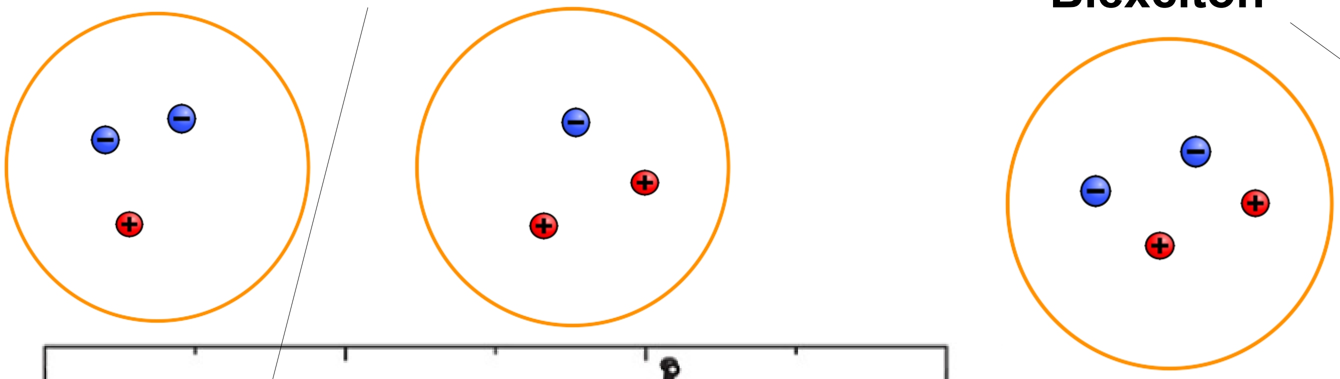
Correlated excitonic systems

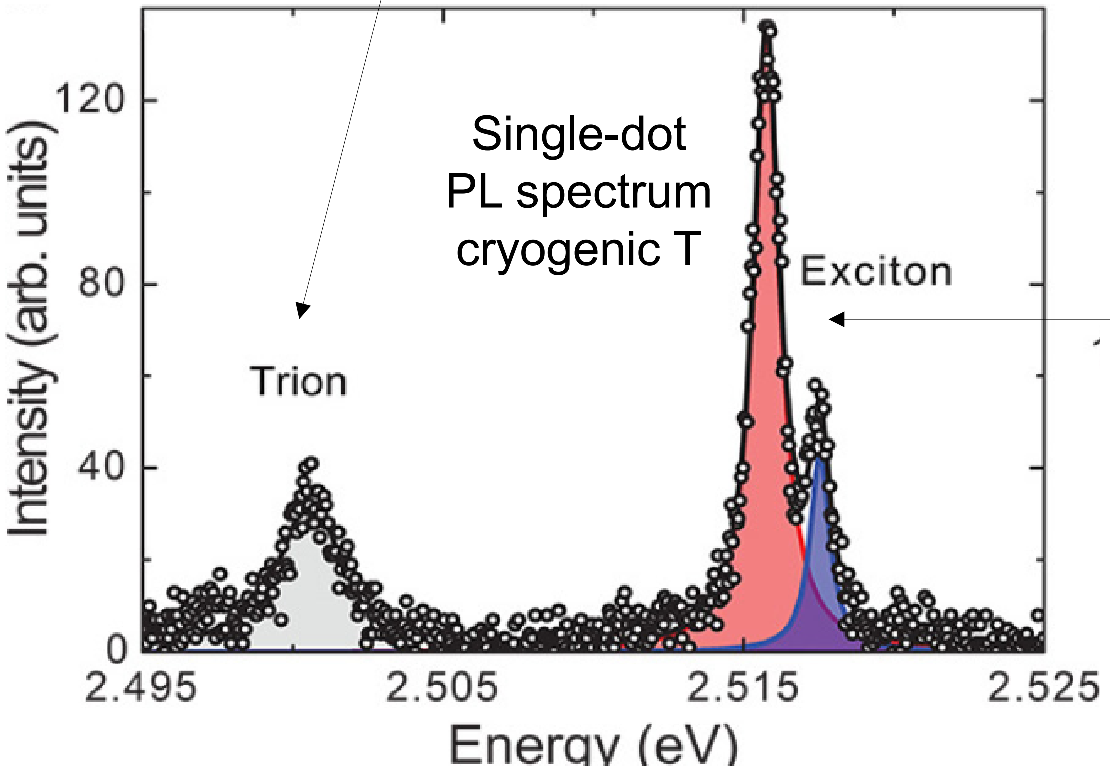
PoLLoC

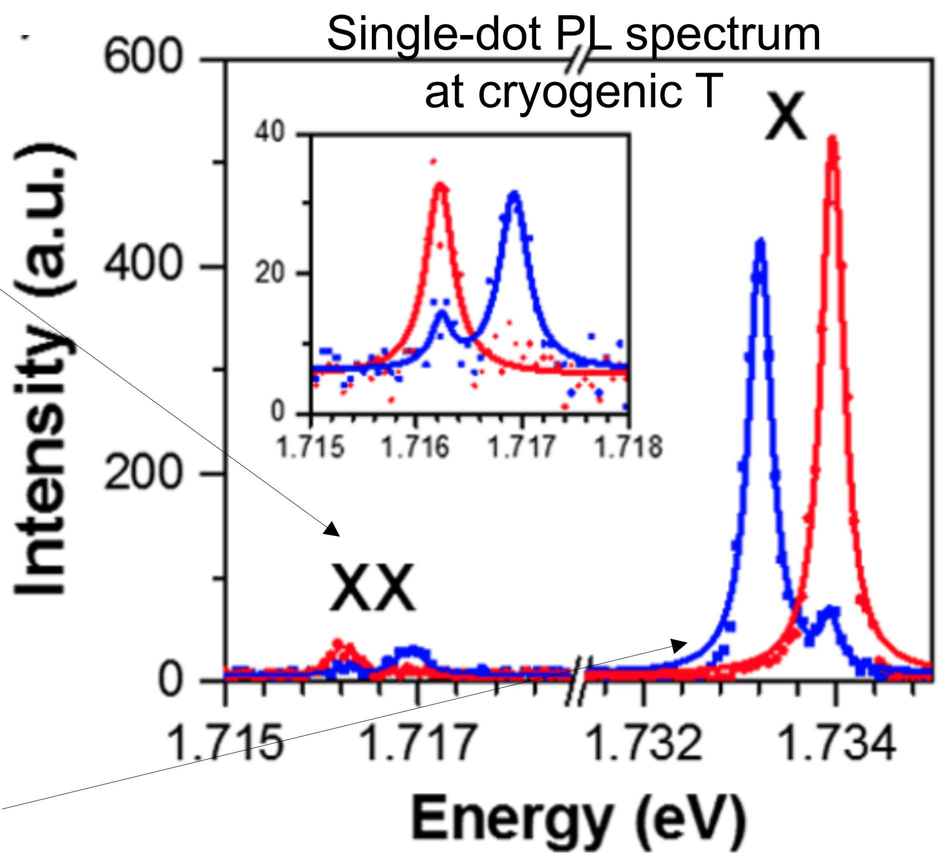
Spherical model

Negative/positive trion

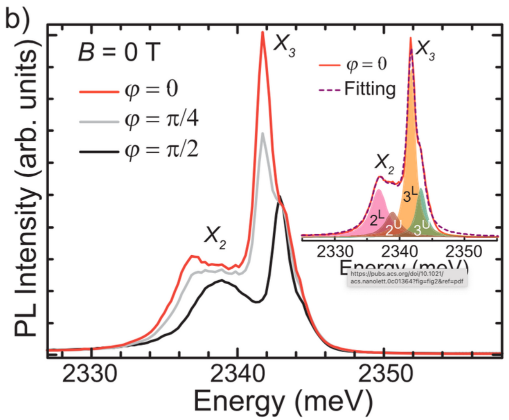
Biexciton







Exciton fine-structure



Yin et al., PRL 119, 026401 (2017)
Becker et al., Nature 553, 189-193 (2018)
Do et al., Nano Lett. 2020, 20, 5141-5148

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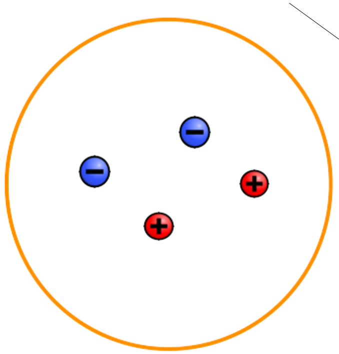

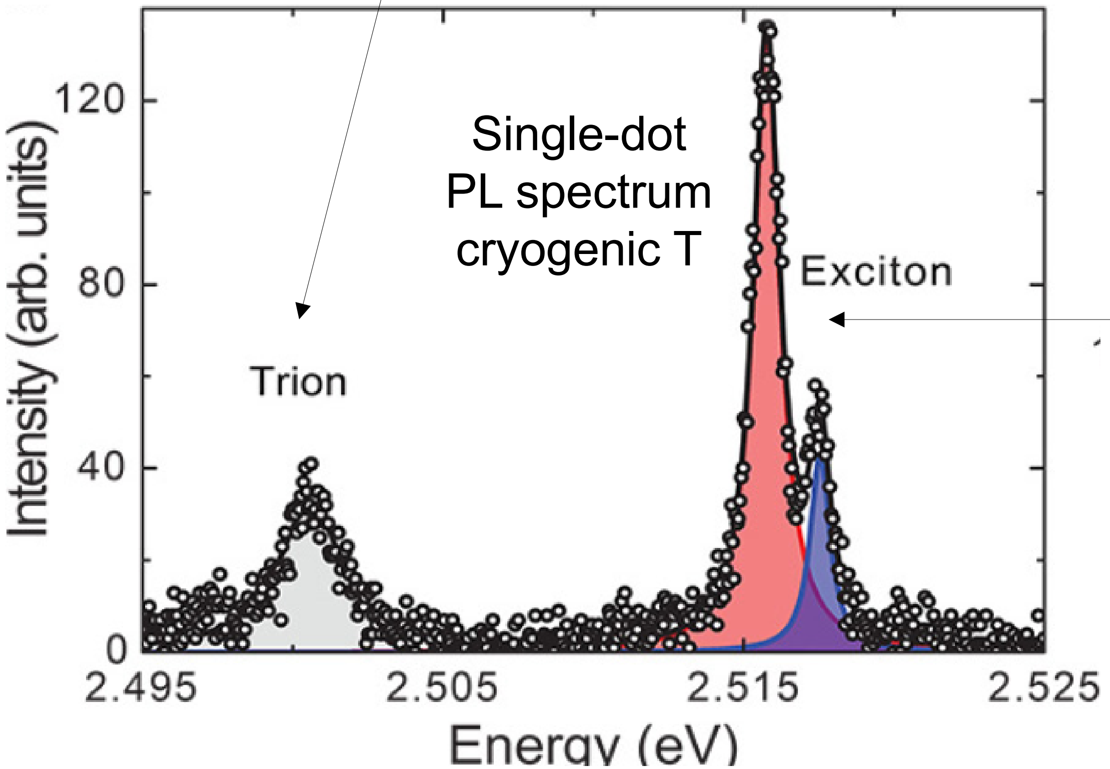

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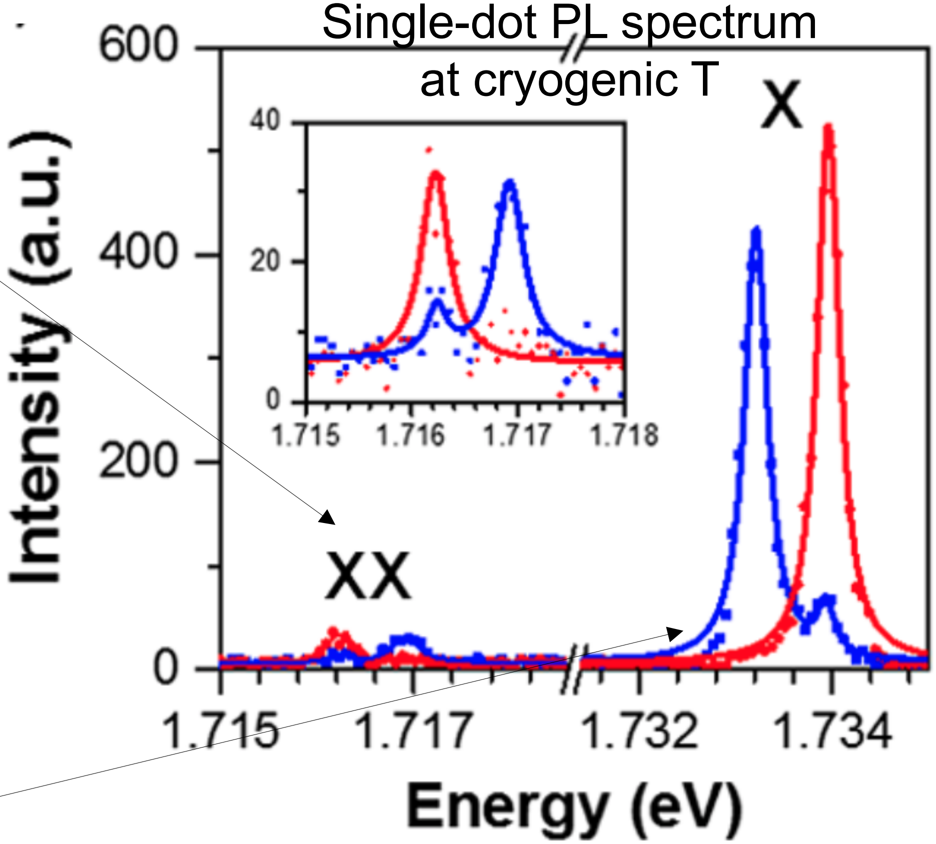
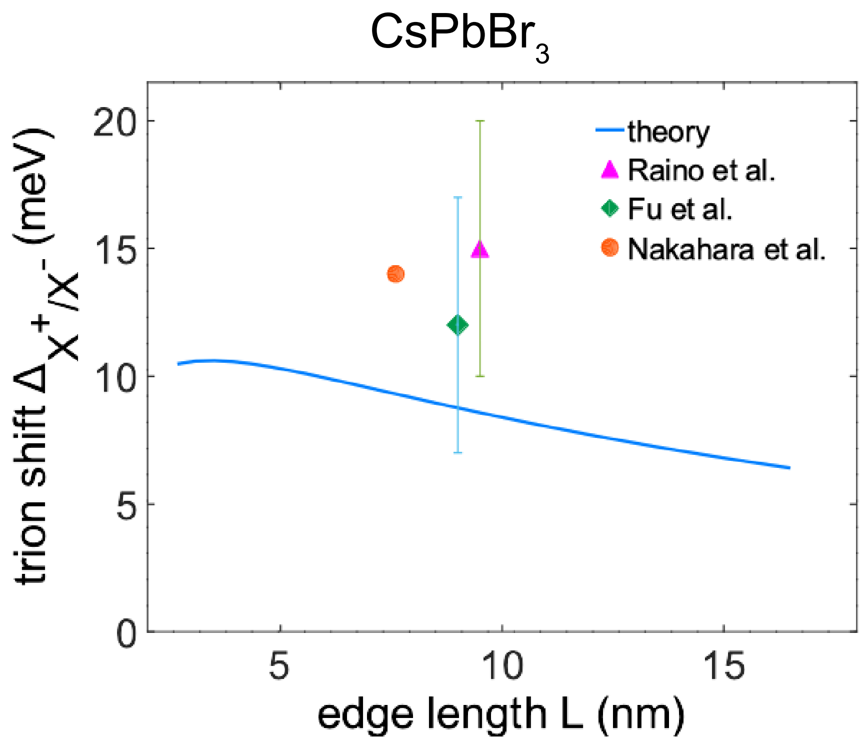


Correlation effects

(beyond mean-field level)

Yin et al., PRL 119, 026401 (2017)
Becker et al., Nature 553, 189-193 (2018)
Do et al., Nano Lett. 2020, 20, 5141-5148
Shumway et al., PRB 63, 155316 (2001)

Second-order perturbation theory



$$\Delta_{X^+} = (E_X + E_h) - E_{X^+}$$
$$\Delta_{X^-} = (E_X + E_e) - E_{X^-}$$

◊ No biexciton/trion shift at mean-field level

◊ **Correlation** effects in multiexcitons

◊ **Red shifts** (exp.) for 2.5-15 nm size range

◊ Second-order level = lowest order correlation
→ qualitative explanation

◊ **Higher-order correlation**
→ **more quantitative** prediction

Nguyen, Blundell, et al., PRB 101, 125424 (2020)
T. P. T. Nguyen, Phd Thesis 2020

Raino et al., ACS Nano, 10(2), 2485–2490 (2016)
Fu et al., Nano Lett. 17(5), 2895–2901 (2017)
Nakahara et al., J. Phys. Chem. C 2018, 122, 38, 22188–22193

Conclusion and outlook

Take home message

◊ **Correlation** contributions: exciton **binding energy**, **fine structure**

◊ Role of correlation in **multiexciton**ic systems

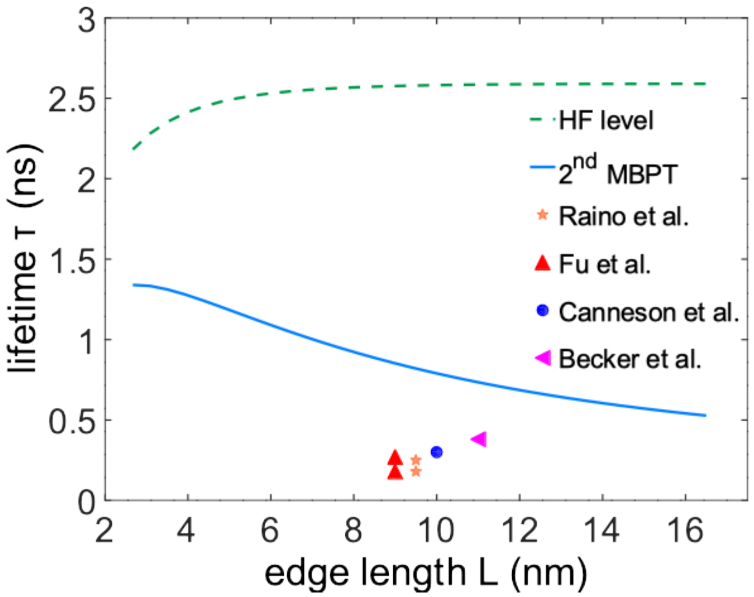
◊ Effect of shape **anisotropy** on single-exciton binding energy

Future directions

◊ More complete description of carrier-carrier interaction (beyond second-order perturbation)
→biexciton, trions

◊ Radiative lifetime of multi-carrier systems

Nguyen, Blundell, et al., PRB 101, 195414 (2020)
Raino et al., ACS Nano, 10(2), 2485–2490 (2016)
Fu et al., Nano Lett. 17(5), 2895–2901 (2017)
Becker et al., Nature 553, 189-193 (2018)
Canneson et al., Nano Lett. 17(10), 6177-6183 (2017)



◊ Anisotropy in multiexcitons

Acknowledgements

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THANK YOU FOR YOUR ATTENTION!