STRONGLY CORRELATED COLLECTIVE EXCITATIONS IN QUASI-2D NANOSTRUCTURES OF METALS AND SEMICONDUCTORS

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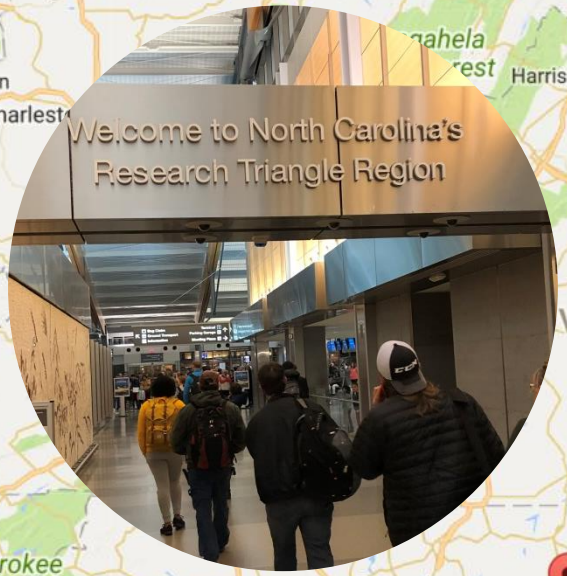
US National Science Foundation – DMR-1830874
US Department of Energy – DE-SC0007117
UNC-GA ROI grant (NCSU-NCCU-UNC-Chapel Hill)



North Carolina's Research Triangle Region:
NCSU, UNC-CH, NCCU, DUKE Univ., RTI, Cisco, IBM, SAS, other HiTech companies

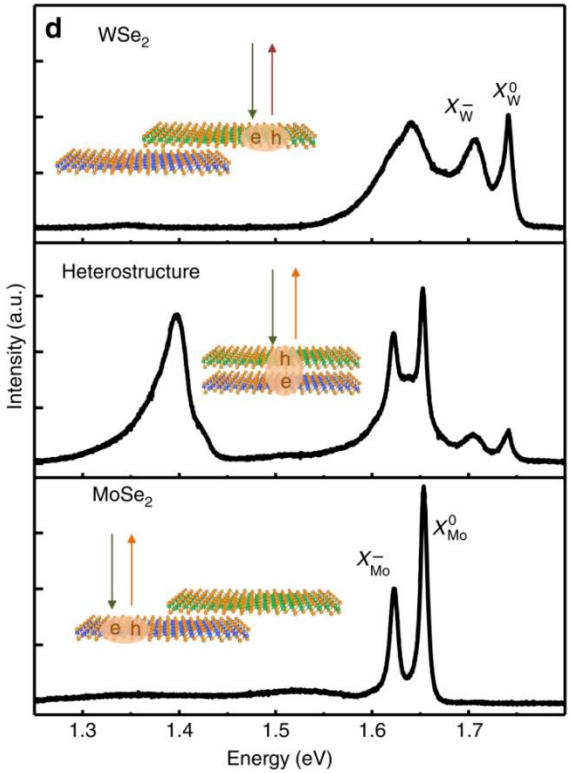
OUTLINE

- **Biexcitons and Trions Formed by Indirect Excitons in Layered Semiconductors: Binding Energies within the Configuration Space (Landau-Herring) Approach**
- **Organic Molecular Semiconductor Crystals with *Two* Isolated Frenkel Exciton States: Frenkel-Charge-Transfer Exciton Intermixing**
- **Ultrathin Plasmonic Films of Finite Thickness: Plasma Frequency Spatial Dispersion and Magneto-Optical Response**
- **Summary**

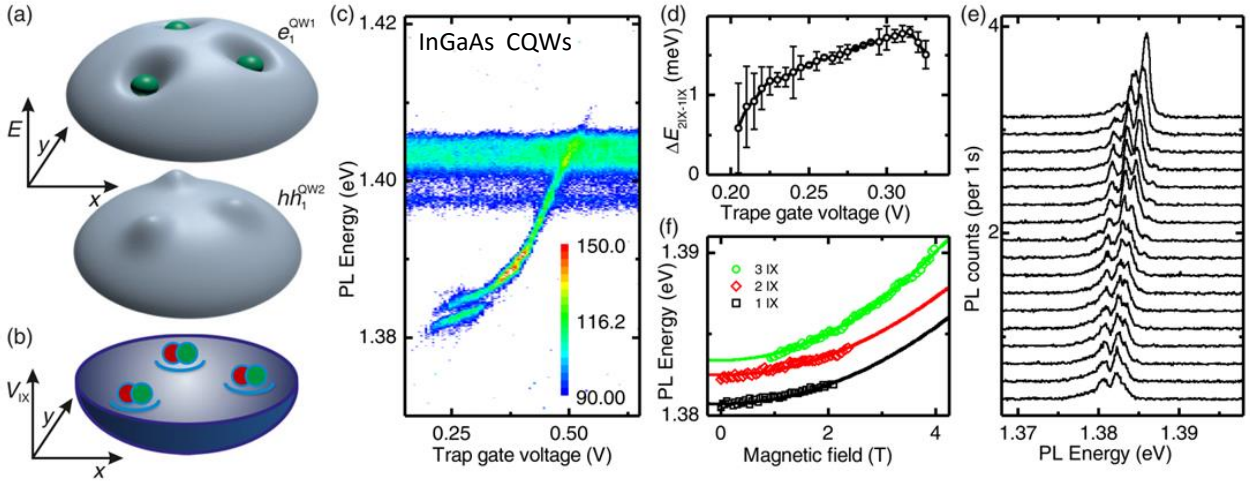
RECENT EXPERIMENTS

with Direct and Indirect Excitons in Coupled Quantum Wells (CQWs) and quasi-2D Layered van der Waals Heterostructures

P.Rivera, *et al*, Nature Commun. 6, 6242 (2015)



G.J.Schinner, et al, Phys. Rev. Lett. 110, 127403 (2013)



(1) K.Sivalertporn, L.Mouchliadis, A.L.Ivanov, R.Philp, & E.A.Muljarov, Phys. Rev. B 85, 045207 (2012)
(2) G.J.Schinner, J.Repp, E.Schubert, A.K.Rai, D.Reuter, A.D.Wieck, A.O.Govorov, A.W.Holleitner, & J.P.Kotthaus, Phys. Rev. Lett. 110, 127403 (2013)
(3) M.M.Fogler, L.V. Butov, & K.S.Novoselov, Nature Commun. 5, 4555 (2014)
(4) F.Ceballos, M.Z.Bellus, H.-Y.Chiu, & H.Zhao, ACS Nano 8, 12717 (2014)
(5) P.Rivera, J.R.Schaibley, A.M.Jones, J.S.Ross, S.Wu, G.Aivazian, P.Klement, K.Seyler, G.Clark, N.J.Ghimire, J.Yan, D.G.Mandrus, W.Yao, & X.Xu, Nature Commun. 6, 6242 (2015)
(6) L.V.Butov, JETP 122, 434 (2016)
(7) K.F.Mak & J.Shan, Nature Photonics 10, 216 (2016)
(8) Y.Y.Kuznetsova, C.J.Dorow, E.V.Calman, L.V.Butov, J.Wilkes, E.A.Muljarov, K.L.Campman, & A.C.Gossard, Phys. Rev. B 95, 125304 (2017)
(9) J.S.Ross, P.Rivera, J.Schaibley, E.Lee-Wong, H.Yu, T.Taniguchi, K.Watanabe, J.Yan, D.Mandrus, D.Cobden, W.Yao, & X.Xu, Nano Lett. 17, 638 (2017)
(10) M.Baranowski, A.Surrente, L.Klopotowski, J.M.Urban, N.Zhang, D.K.Maude, K.Wiwatowski, S.Mackowski, Y.C.Kung, D.Dumcenco, A.Kis, & P.Plochocka, Nano Lett. 17, 6360 (2017)
(11) J.I.A.Li, T.Taniguchi, K.Watanabe, J.Hone, & C.R.Dean, Nature Physics 13, 751 (2017)
(12) I.V.Bondarev & M.R.Vladimirova, Phys. Rev. B 97, 165419 (2018)
(13) C.Choi, J.Huang, H.-C.Cheng, H.Kim, A.K.Vinod, S.-H.Bae, V. O.Özçelik, R.Grassi, J.Chae, S.-W.Huang, X.Duan, K.Kaasbjerg, T.Low & C.W.Wong, npj 2D Materials and Applications (2018) 30
(14) S.Ovesen, S.Brem, C.Linderälv, M.Kuisma, T.Korn, P.Erhart, M.Selig & E.Malic, Commun. Phys. (2019) 2:23
(15) L.A.Jauregui, A.Y.Joe, K.Pistunova, D.S.Wild, A.A.High, Y.Zhou, G.Scuri, K.De Greve, A.Sushko, C.-H.Yu, T.Taniguchi, K.Watanabe, D.J.Needleman, M.D.Lukin, H.Park, & P.Kim, arXiv:1812.08691

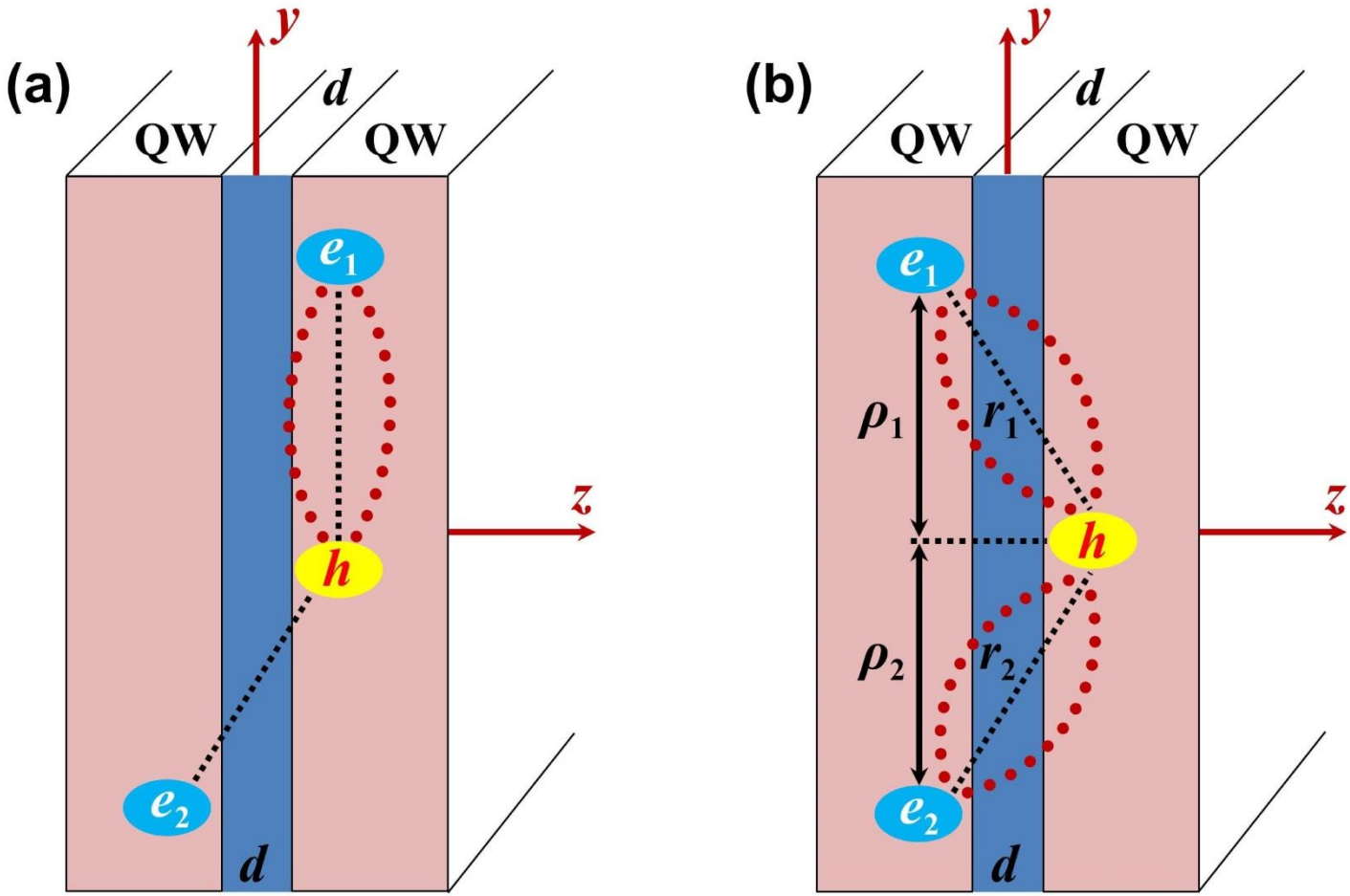
INDIRECT EXCITONS:

- ***Janina Maultzsch NT19 talk***
- ***Tony Heinz NT19 talk***
- ***Significant Binding Energies***
- ***Long Lifetimes***
- ***High-T BEC & Superfluidity***
- ***Wigner Crystallization***
- ***… more ??? …***

TRION COMPLEXES

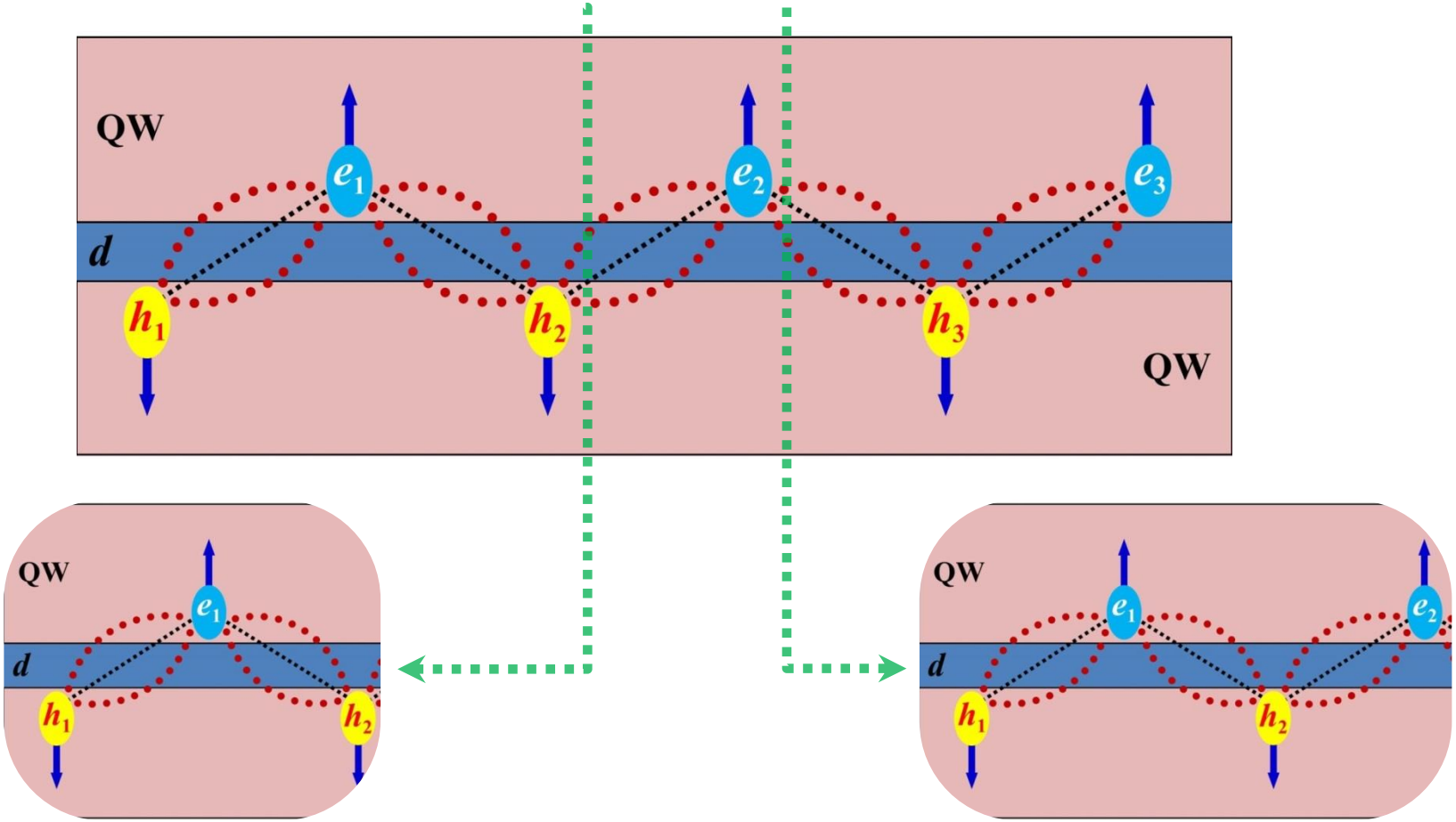
formed by direct **(a)** *and indirect* **(b)** *excitons in CQWs*

I.V.Bondarev, Mod. Phys. Lett. B 30, 1630006 (2016)



SCHEMATIC VIEW

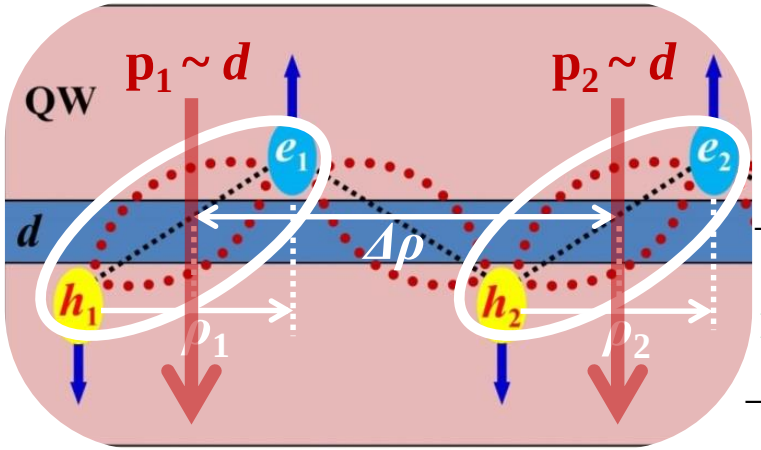
*of the charge-neutral spin-aligned Wigner crystal structure of two trions (also can be viewed as **triexciton** – three indirect singlet excitons)*



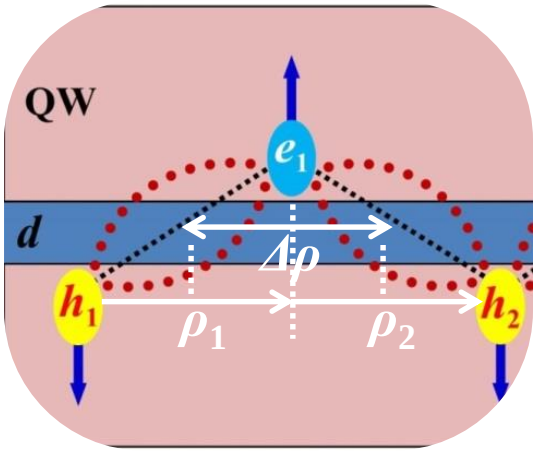
INDIRECT EXCITONS, TRIONS, and BIEXCITONS formed by indirect excitons are those building blocks that control the formation of more complex Wigner-like electron-hole crystal structures in quasi-2D layered van der Waals bound semiconductor heterostructures

BIEXCITON AND TRION FORMED BY INDIRECT EXCITONS

Theoretical Description of the Ground State within the Configuration Space Approach (atomic units)



$$V_{p_1p_2} \sim d^2/\Delta\rho^3$$



$$\hat{H}(\rho_1,\rho_2,\Delta\rho,d) = -\frac{1}{\rho_1}\frac{\partial}{\partial\rho_1}\rho_1\frac{\partial}{\partial\rho_1} - \frac{1}{\rho_2}\frac{\partial}{\partial\rho_2}\rho_2\frac{\partial}{\partial\rho_2}$$

$$- \frac{1}{\sqrt{\rho_1^2+d^2}} - \frac{1}{\sqrt{\rho_2^2+d^2}} - \frac{1}{\sqrt{(\rho_1-\Delta\rho)^2+d^2}} - \frac{1}{\sqrt{(\rho_2+\Delta\rho)^2+d^2}}$$

Exact solution available: *R.P.Leavitt & J.W.Little, PRB 42, 11774 (1990)*

$$- \frac{2\ e_1\text{-}h_2}{\sqrt{[(\rho_1+\sigma\rho_2)/\lambda-\Delta\rho]^2+d^2}} - \frac{2\ e_2\text{-}h_1}{\sqrt{[(\sigma\rho_1+\rho_2)/\lambda+\Delta\rho]^2+d^2}}$$

$$+ \frac{2\ h_1\text{-}h_2}{|\sigma(\rho_1-\rho_2)/\lambda+\Delta\rho|} + \frac{2\ e_1\text{-}e_2}{|(\rho_1-\rho_2)/\lambda-\Delta\rho|}$$

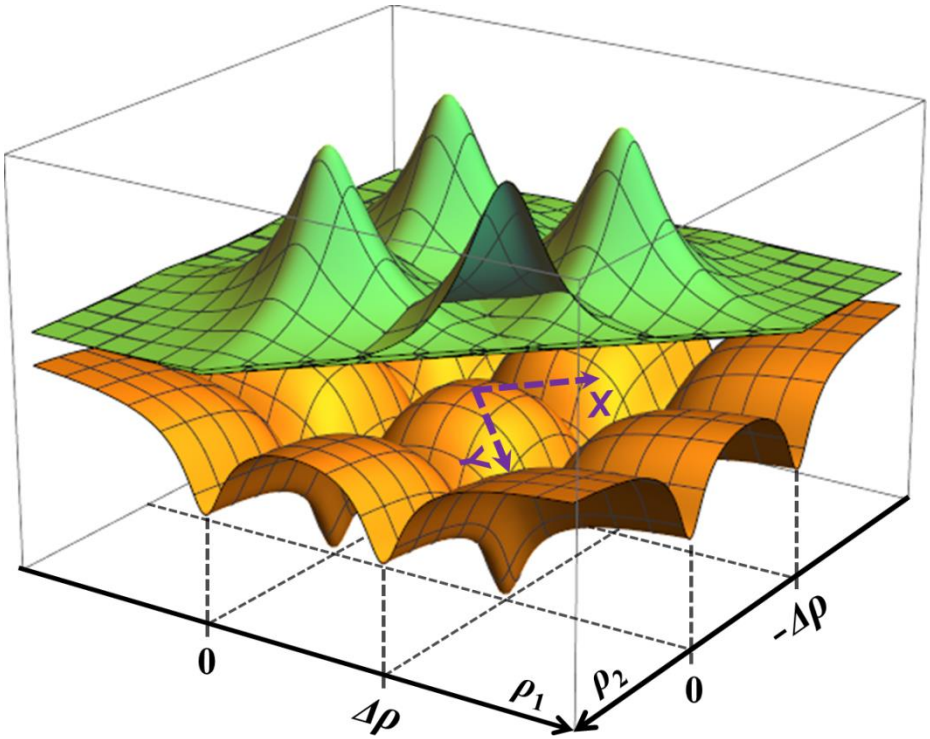
positive trion ***negative trion***

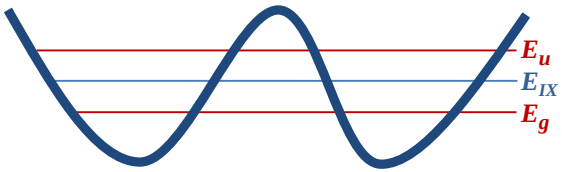
$$\lambda = 1+\sigma; \quad \sigma = m_e/m_h \to 1$$

due to the mass reversal effect

$$Ry^* = \frac{\hbar^2}{2\mu a_B^{*2}} = \frac{\mu(\text{in } m_0)}{\varepsilon^2}13.6\text{ eV}; \quad a_B^* = \frac{\varepsilon}{\mu}0.529\,\text{Å}$$

SCHEMATIC VIEW
of the Tunnel Exchange Coupling Configuration for Two Ground-State Indirect Excitons to Form the Trion or Biexciton Complex





Trion Binding Energy

$$E_{X^*} = E_g - 2E_X = -J_{X^*}(\Delta\rho_0)$$

$$J_{X^*}(\Delta\rho) = \int_{-\Delta\rho/\sqrt{2}}^{\Delta\rho/\sqrt{2}} \left| \psi_{X^*}(x,y) \frac{\partial \psi_{X^*}(x,y)}{\partial x} \right|_{x=0} dy$$

$$\psi_{X^*}(x,y) = \psi_{IX}(\rho_1(x,y),d)\,\psi_{IX}(\rho_2(x,y),d)\,exp(-S_{X^*}(x,y))$$

Biexciton Binding Energy

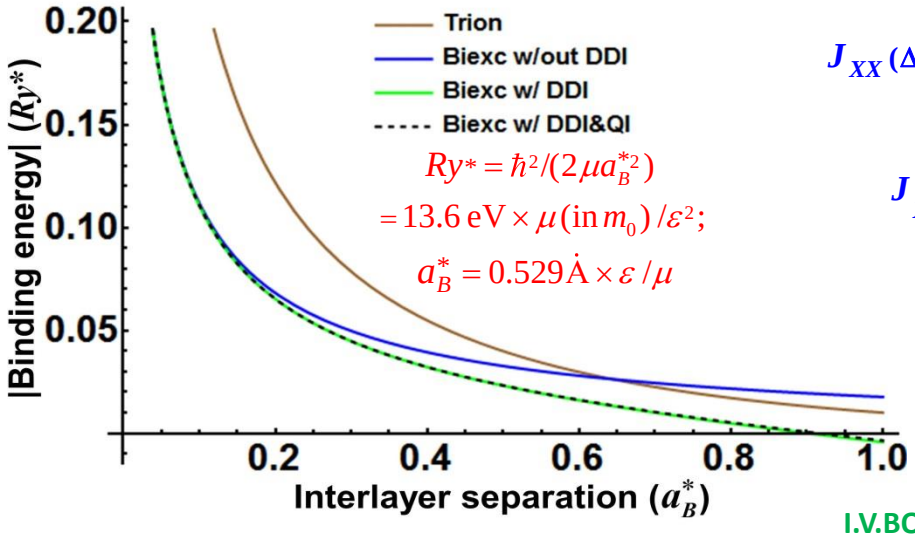
$$E_{XX} = E_g - 2E_X = -J_{XX}(\Delta\rho_0)$$

$$J_{XX}(\Delta\rho) = \frac{2}{3!} \int_{-\Delta\rho/\sqrt{2}}^{\Delta\rho/\sqrt{2}} \left| \psi_{XX}(x,y) \frac{\partial \psi_{XX}(x,y)}{\partial x} \right|_{x=0} dy$$

I.V.Bondarev, Mod. Phys. Lett. B 30, 1630006 (2016);
PRB 90, 245430 (2014); PRB 83, 153409 (2011)

BIEXCITON AND TRION FORMED BY INDIRECT EXCITONS

Ground State Binding Energies Calculated using the Configuration Space (Landau-Herring) Method



$$Ry^* = \hbar^2/(2\mu a_B^{*2}) = 13.6\,\text{eV} \times \mu(\text{in}\,m_0)/\varepsilon^2;$$

$$a_B^* = 0.529\,\text{Å} \times \varepsilon/\mu$$

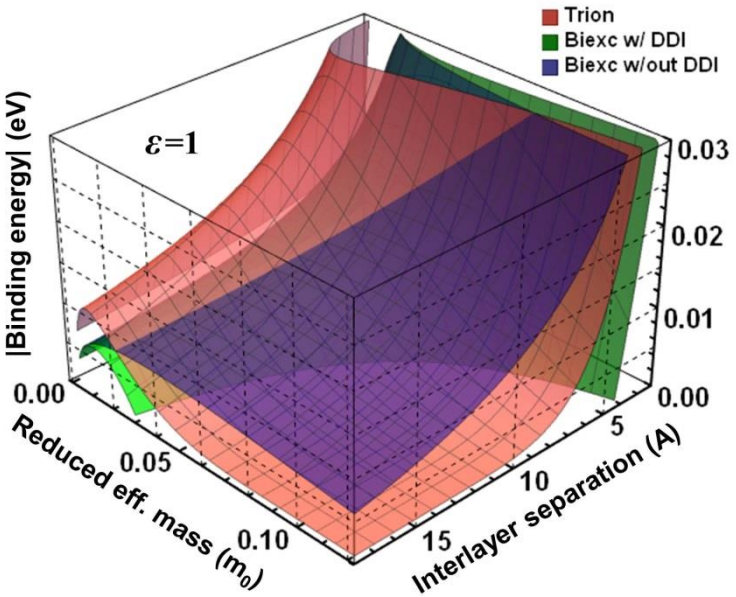
$$J_{XX}(\Delta\rho,d) = \frac{2N^4\Delta\rho}{3}\left(\frac{\alpha\Delta\rho}{\sqrt{\Delta\rho^2+4d^2}} + \frac{1}{3(\alpha\Delta\rho-1)}\right)\left(\frac{e}{3}\right)^{\frac{2\Delta\rho}{\alpha\Delta\rho-1}} e^{-2\alpha\left(\sqrt{\Delta\rho^2+4d^2}-2d\right)} - \frac{2d^2}{\Delta\rho^3}$$

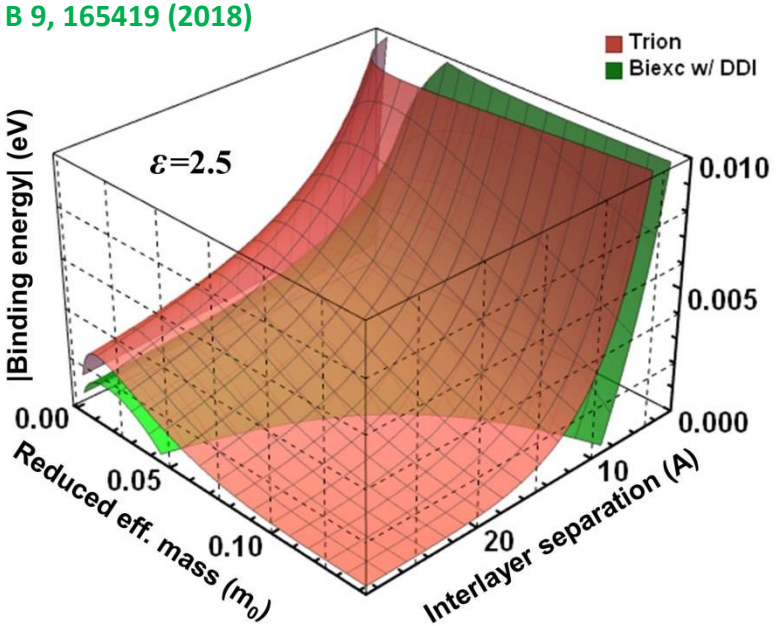
$$J_{X^*}(\Delta\rho,d) = 2N^4\Delta\rho\left(\frac{\alpha\Delta\rho}{\sqrt{\Delta\rho^2+4d^2}} + \frac{1}{\alpha\Delta\rho-1}\right)\left(\frac{1}{2}\right)^{\frac{2\Delta\rho}{\alpha\Delta\rho-1}} e^{-2\alpha\left(\sqrt{\Delta\rho^2+4d^2}-2d\right)}$$

$$N = \frac{4}{\sqrt{1+4\sqrt{d}+8d\left(1+\sqrt{d}\right)}};\quad \alpha = \frac{2}{1+\sqrt{d}};\quad \Delta\rho >> 2d$$

$$\Delta\rho_0^{XX} = \frac{7\alpha - 2/3}{2\alpha^2},\qquad \Delta\rho_0^{X^*} = \frac{7\alpha-2}{2\alpha^2}$$

I.V.BONDAREV & M.R.VLADIMIROVA,
Phys. Rev. B 9, 165419 (2018)





PHYSICAL REVIEW B **97**, 165419 (2018)

Complexes of dipolar excitons in layered quasi-two-dimensional nanostructures

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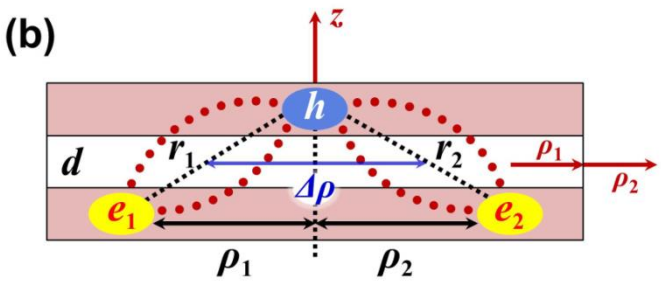
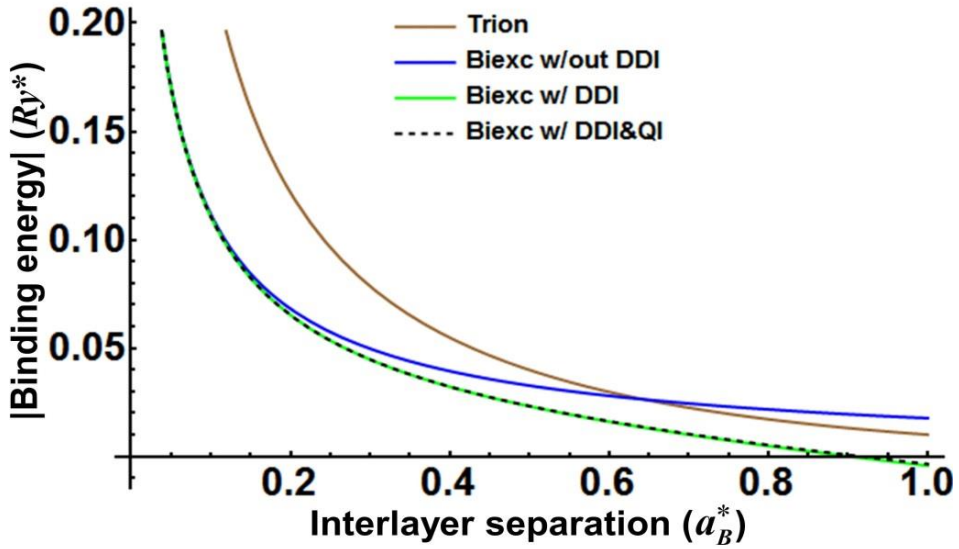
(Received 25 December 2017; revised manuscript received 19 March 2018; published 16 April 2018)





PHYSICAL REVIEW B **97**, 075424 (2018)

Stability of trions in coupled quantum wells modeled by two-dimensional bilayers

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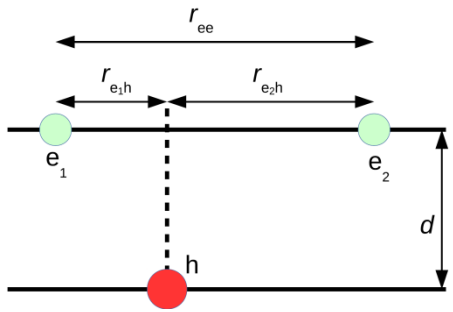
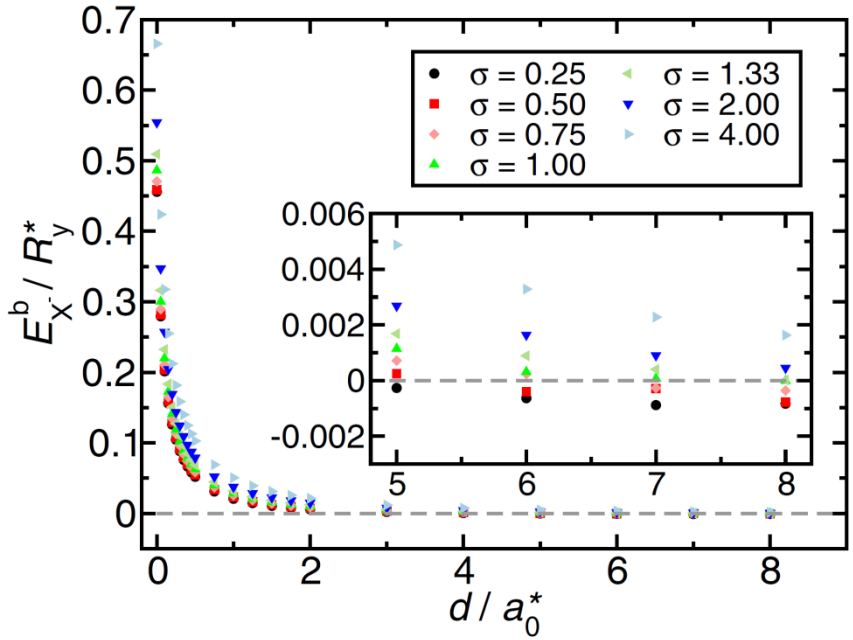
[2]*Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom*

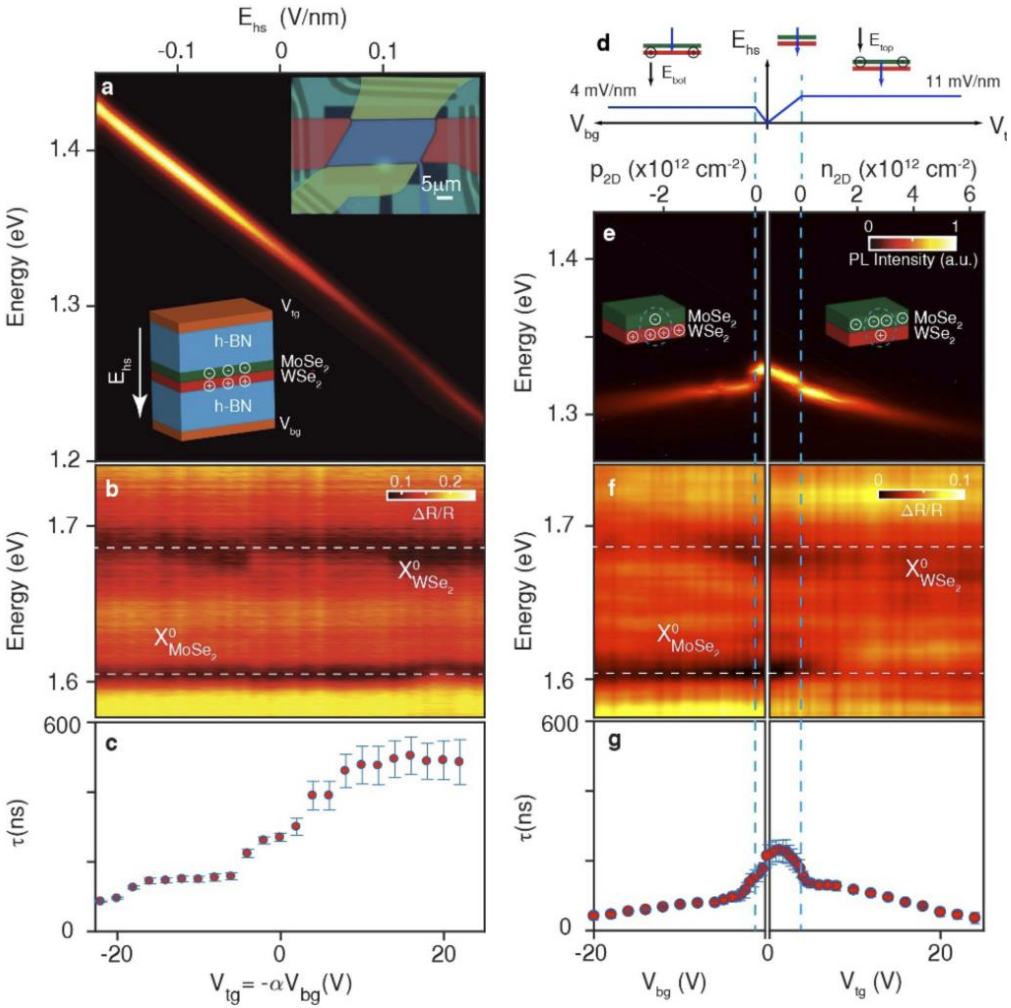
(Received 28 July 2017; published 20 February 2018)



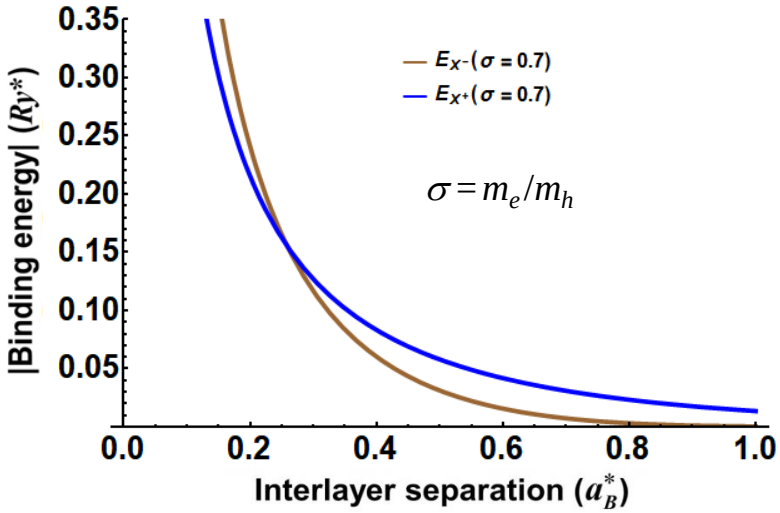


TRIONS FORMED BY INDIRECT EXCITONS
Latest Experiments @ HARVARD

L.A.Jauregui, A.Y.Joe, K.Pistunova, D.S.Wild, A.A.High, Y.Zhou, G.Scuri, K.De Greve, A.Sushko, C.-H.Yu, T.Taniguchi, K.Watanabe, D.J.Needleman, M.D.Lukin, H.Park, & P.Kim, arXiv:1812.08691



Our measurements in the doped regime can be explained by the formation of charged IEs (CIEs) (*21*). As shown in the normalized reflection measured with the same gating scheme, we can identify the *p*/intrinsic, intrinsic/intrinsic, intrinsic/*n* regions by the disappearance of the absorption dips for intralayer excitons in $MoSe_2$ and WSe_2 (*22*), which are well aligned with the sudden red shift observed in IE PL (vertical dashed lines). Thus, this jump in energy can be related to the CIE. We note that charged excitons can be referred to trions (*23-26*), three-body bound states, or alternatively, attractive polarons, excitonic states dressed by a polarized fermionic sea (*27, 28*), similar in monolayer TMDs. The value of the observed jump ≈ 10 meV (15 meV) for positive (negative) CIEs is in good agreement with the calculated binding energy of CIEs (*21*). The lifetime of CIEs is ≈ 100 ns near the band edge, decreasing with increasing doping presumably due to additional decay channels enabled by scattering with free carriers (Figure 1g).



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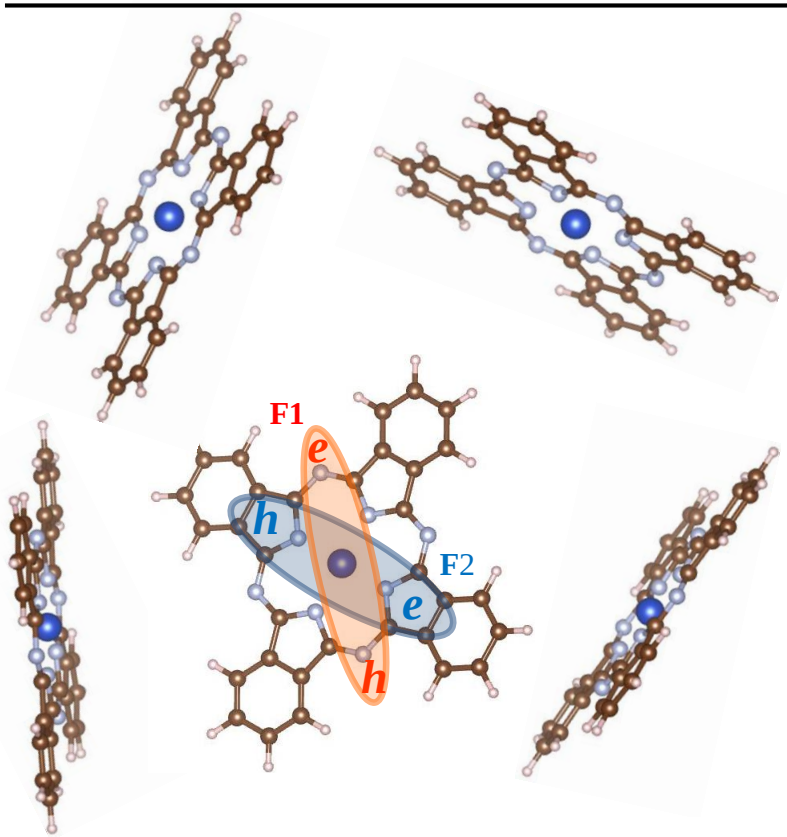
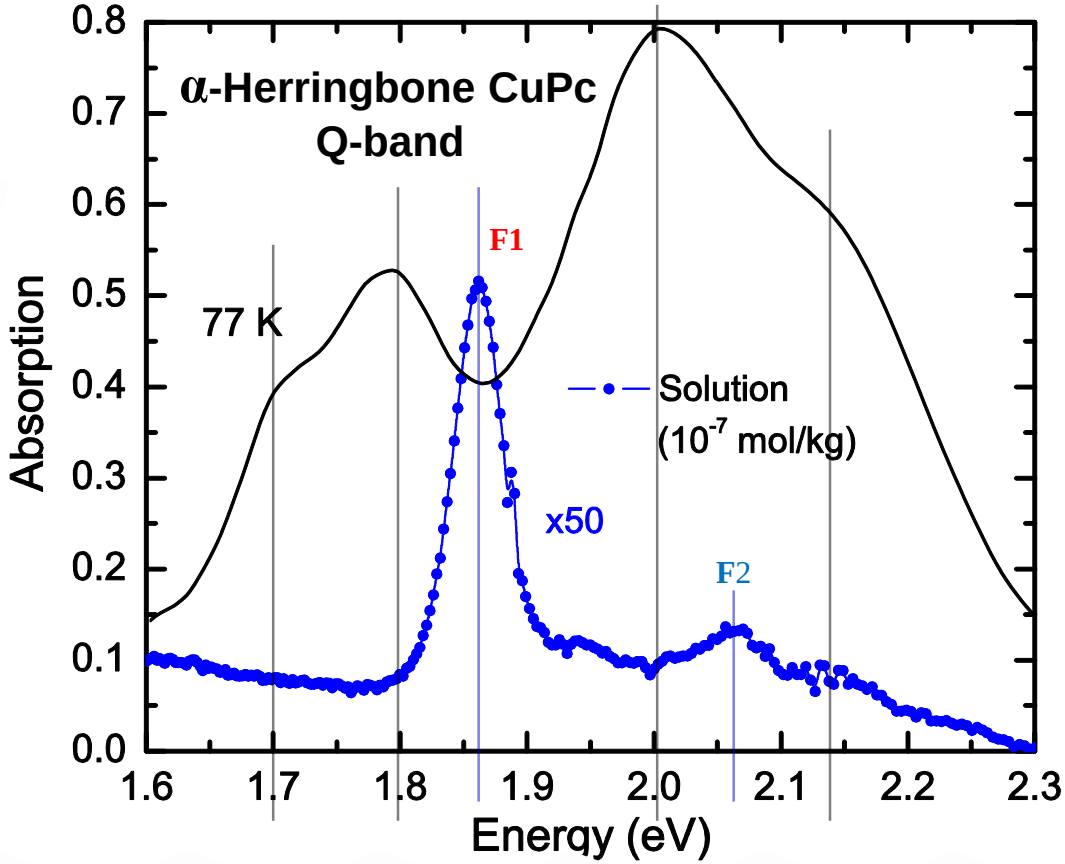
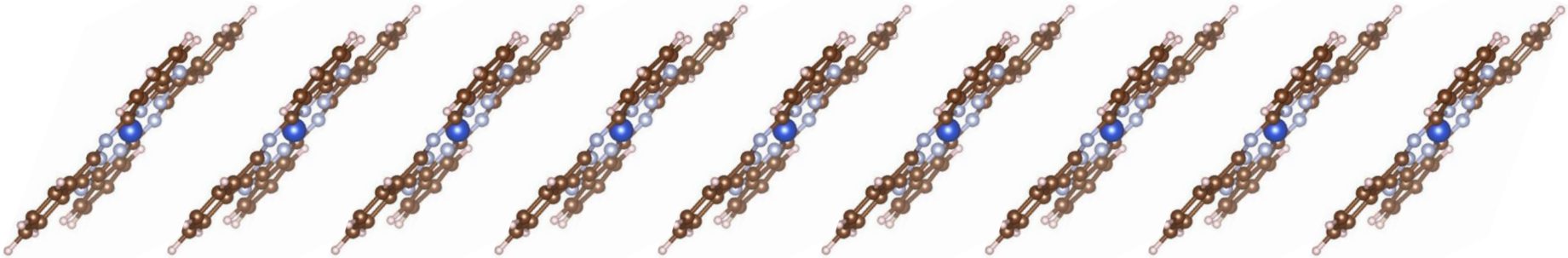
- **Summary**

Experimental Data I

Crystalline CuPc on a glass substrate vs CuPc in solution (NCSU data)



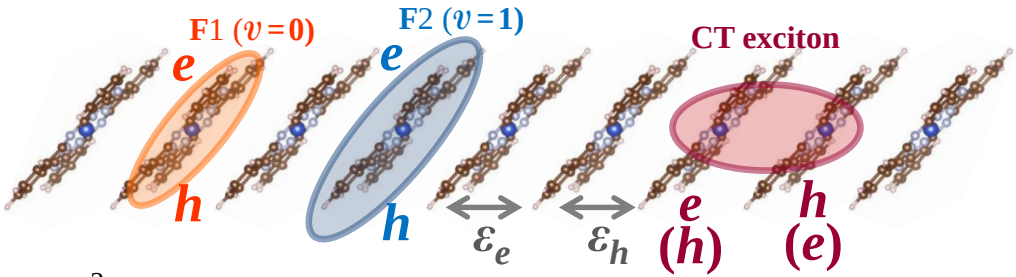




Quantum Theory of the Frenkel-CT Exciton Intermixing

Solving the Eigen-Value Problem for the Hamiltonian of the Two Frenkel Excitons Coupled Individually to the CT exciton

$$\hat{H}\{k\text{-space}\} = \sum_k \left(\hat{H}_k^F + \hat{H}_k^{FF} + \hat{H}_k^C + \hat{H}_k^{FC} \right),$$



$$\hat{H}_k^F = \sum_{v=0,1} \Delta_F^v B_{kv}^\dagger B_{kv}, \quad H_k^{FF} = \sum_{v=0,1} L_k^{vv'} B_{kv}^\dagger B_{kv'},$$

$$L_k^{vv'} \approx 2M\, s_v s_{v'} \cos k, \quad s_v = \left\langle \chi_n^{1v} \middle| \chi_n^{00} \right\rangle, \quad s_v^2 = F_{0v} = \frac{g^{2v}}{v!} e^{-g^2} \; (if \;\; g \approx 1, \; then \;\; s_0 \approx s_1 \approx 0.6 = s)$$

$$\hat{H}_k^C = \Delta_{CT} \left(\tilde{C}_{kg}^\dagger \tilde{C}_{kg} + \tilde{C}_{ku}^\dagger \tilde{C}_{ku} \right), \quad H_k^{FC} = \sum_{v=0,1} \sqrt{2} \varepsilon_k s_v B_{kv}^\dagger \tilde{C}_{kg} + h.c., \quad \varepsilon_k = \sqrt{\varepsilon_+^2 \cos^2 \frac{k}{2} + \varepsilon_-^2 \sin^2 \frac{k}{2}}, \quad \varepsilon_\pm = \varepsilon_e \pm \varepsilon_h$$

$$\xi_{v\mu}(k) = u_{v\mu}^*(k) B_{kv} + c_v^*(k) \tilde{C}_{kg}, \; v = 0,1; \; \mu = 1,2$$

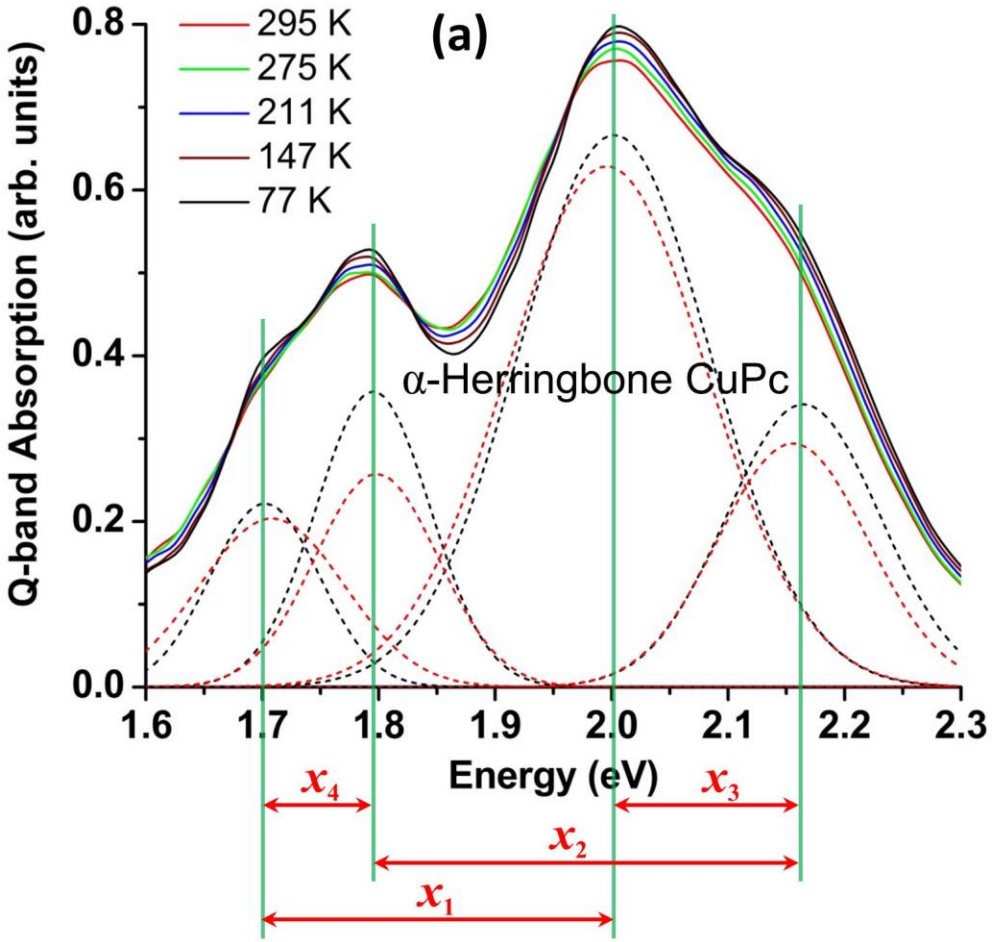
$$\hat{H} = \sum_{\mu=1,2} \sum_{v=0,1} \sum_k \hbar \omega_{v\mu}(k) \xi_{v\mu}^\dagger(k) \xi_{v\mu}(k) + E_0$$

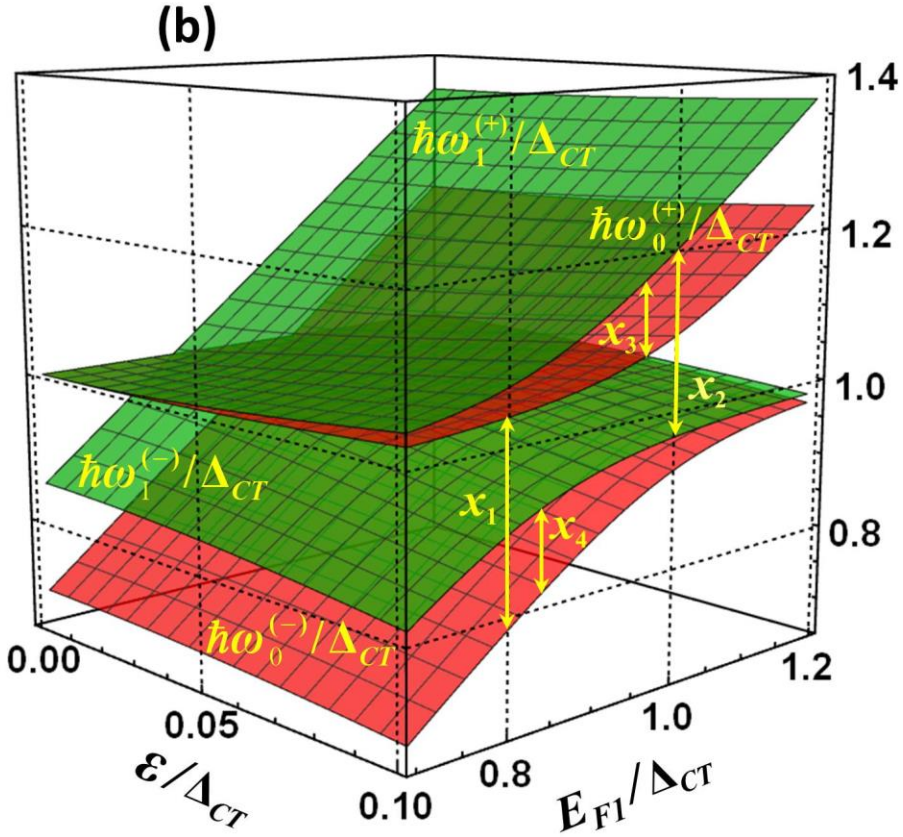
$$\hbar \omega_{v\mu}(k) = \hbar \omega_{v1,2}(k) = \hbar \omega_v^{(\pm)}(k) = \frac{1}{2} \left(D_k^{vv} + \Delta_{CT} \pm \sqrt{(D_k^{vv} - \Delta_{CT})^2 + 8(s_v \varepsilon_k)^2} \right),$$

$$D_k^{vv'} = \Delta_F^v \delta_{vv'} + 2M\, s_v s_{v'} \cos k$$

$$E_{F1} = D_0^{00}, \quad E_{F2} = D_0^{11}, \quad E_v^{(\pm)} = \hbar \omega_v^{(\pm)}(0), \; v = 0,1$$

Comparison of the Theory with the Experiment





From the experimental graph:

$x_1 = 2.0 - 1.7 = 0.3$ eV,

$x_2 = 2.16 - 1.8 = 0.36$ eV,

$x_3 = 2.16 - 2.0 = 0.16$ eV,

$x_4 = 1.8 - 1.7 = 0.1$ eV $\Rightarrow$

From the k = 0 dispersion equation:

$$\Delta = E_{F2} - E_{F1} = x_3 + x_4; \quad x_1 + x_3 = x_2 + x_4$$

$$x_2^2 + x_1^2 = 2(E_{F1} - \Delta_{CT})^2 + \Delta[\Delta + 2(E_{F1} - \Delta_{CT})] + 16s^2\varepsilon^2$$

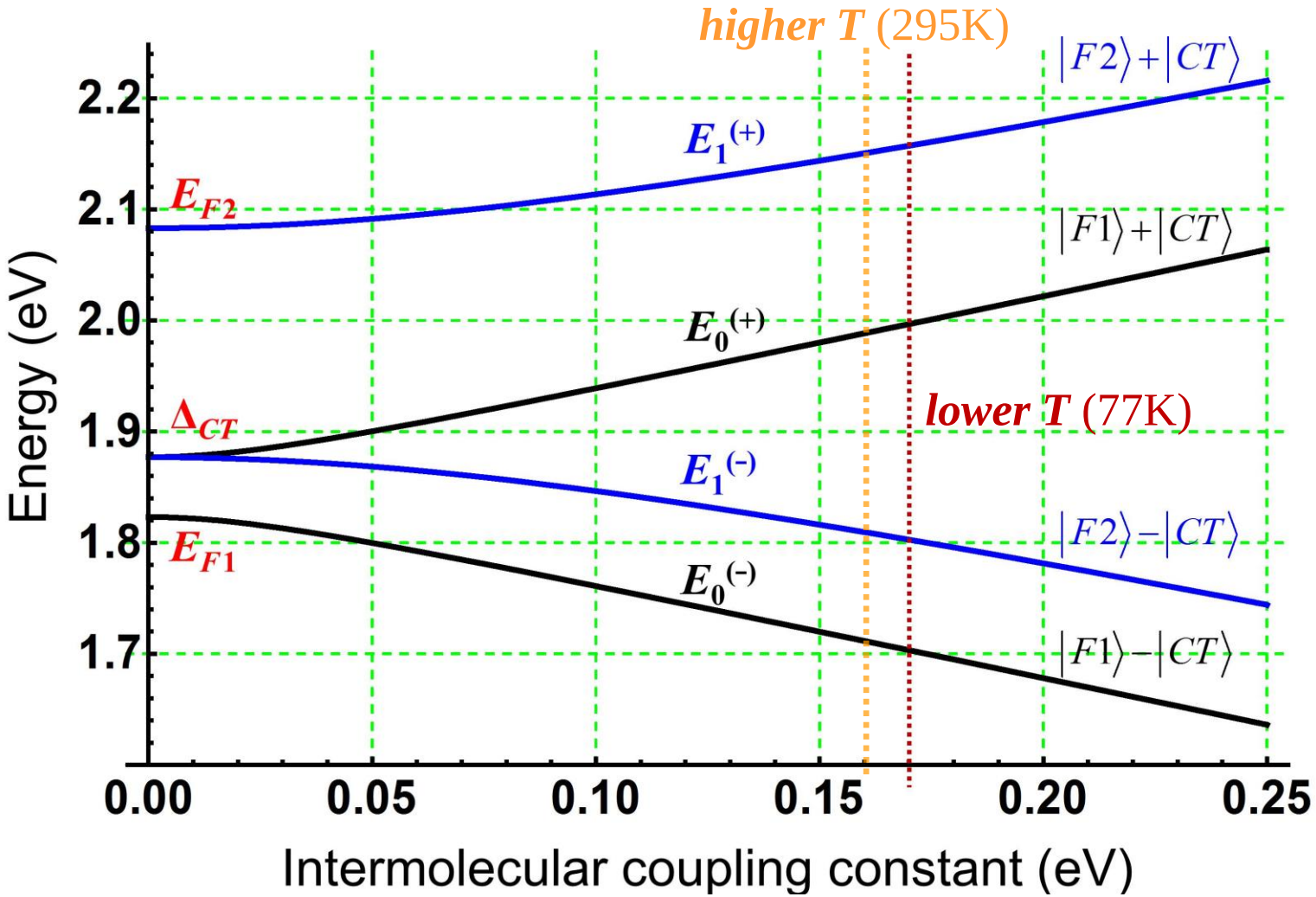
$$x_2^2 - x_1^2 = \Delta[\Delta + 2(E_{F1} - \Delta_{CT})]$$

$$\Downarrow$$

$$E_{F1} = 1.82\,\text{eV},\ E_{F2} = 2.08\,\text{eV},\ \Delta_{CT} = 1.88\,\text{eV},\ \varepsilon = 0.17\,\text{eV}$$

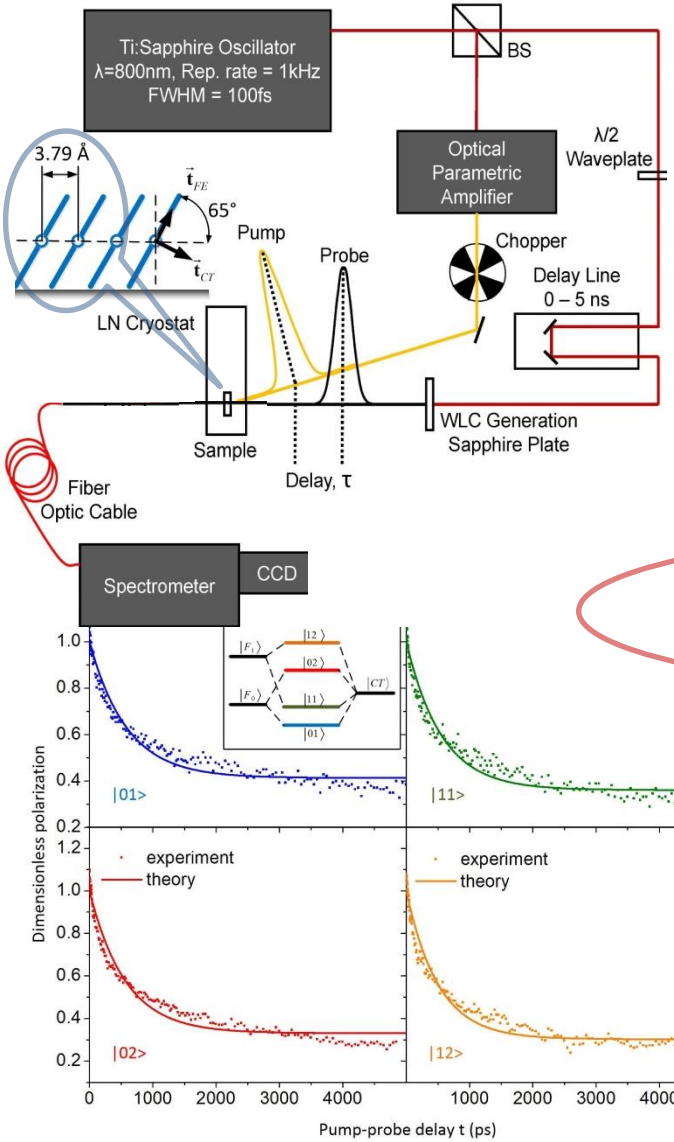
Calculated Frenkel-CT Exciton Splitting and Intermixing

as a function of the Intermolecular Coupling Constant

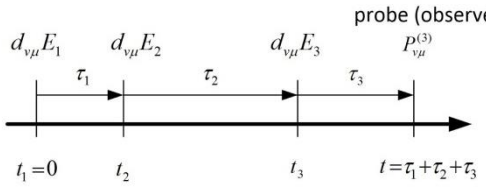


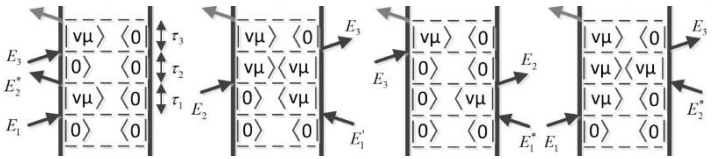
I.V.Bondarev, A.Popescu, R.A.Younts, B.Hoffman, T.McAfee, D.B.Dougherty, K.Gundogdu, and H.W.Ade, Appl. Phys. Lett. 109, 213302 (2016)

Monitoring Charge Separation Processes in Crystalline Organic Molecular Semiconductor Thin Films (CuPc)



$$P^{(3)}_{v\mu}(t) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \, P_{v\mu}(\tau_3,\tau_2,\tau_1)\, E_1(t-\tau_3-\tau_2-\tau_1) E_2(t-\tau_3-\tau_2) E_3(t-\tau_3)$$





$$P_{v\mu}(t) = 8\frac{i}{\hbar^3} d^4_{v\mu} e^{-t/\tau_{v\mu}} \qquad 0 \le t \le \tau_2$$

$$\vec{P}_{v\mu}(t) = \langle v\mu|\hat{\vec{\mathcal{P}}}(t)|0\rangle \qquad \vec{P}_{v\mu}(t) = P^{\mathrm{FE}}_{v\mu}(t)\vec{\mathbf{t}}_{\mathrm{FE}} + P^{\mathrm{CT}}_{v\mu}(t)\vec{\mathbf{t}}_{\mathrm{CT}} \qquad v = 0,\ 1; \qquad \mu = 1,\ 2$$

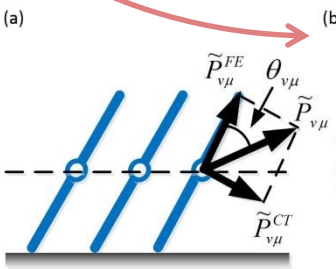
$$\tilde{P}^{\mathrm{FE}}_{v\mu}(t) = [1 - \tilde{P}^{\mathrm{FE}}_{v\mu}(\tau_2)]e^{-t/\tau_{v\mu}} + \tilde{P}^{\mathrm{FE}}_{v\mu}(\tau_2)$$

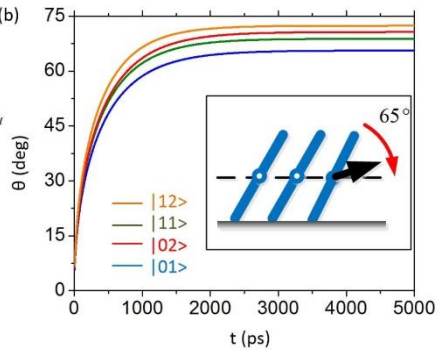
$$\theta_{v\mu}(t) = \tan^{-1}\left[\frac{\tilde{P}^{\mathrm{CT}}_{v\mu}(t)}{\tilde{P}^{\mathrm{FE}}_{v\mu}(t)}\right] = \tan^{-1}\frac{\sqrt{1-\tilde{P}^{\mathrm{FE}}_{v\mu}(t)^2}}{\tilde{P}^{\mathrm{FE}}_{v\mu}(t)}$$

$$\tilde{P}^{\mathrm{FE}}_{v\mu}(t) = P^{\mathrm{FE}}_{v\mu}(t)/P^{\mathrm{FE}}_{v\mu}(0)$$

$$\tilde{P}^{\mathrm{CT}}_{v\mu}(t) = P^{\mathrm{CT}}_{v\mu}(t)/P^{\mathrm{FE}}_{v\mu}(0)$$

A.Popescu, R.A.Younts, B.Hoffman, T.McAfee, D.B.Dougherty, H.W.Ade, K.Gundogdu, and I.V.Bondarev, Nano Letters 17, 6056 (2017)





Frenkel (single-molecule) exciton states spread over time towards CT (inter-molecular) states to turn the overall polarization along the 1D crystal axis – ***We monitor the process of the charge separation in a real time !!!***

OUTLINE

- **Biexcitons and Trions Formed by Indirect Excitons in Layered Semiconductors: Binding Energies within the Configuration Space (Landau-Herring) Approach**
- **Organic Molecular Semiconductor Crystals with *Two* Isolated Frenkel Exciton States: Frenkel-Charge-Transfer Exciton Intermixing**
- **Ultrathin Plasmonic Films of Finite Thickness: Plasma Frequency Spatial Dispersion and Magneto-Optical Response**
- **Summary**

ULTRATHIN PLASMONIC FILMS OF FINITE THICKNESS. EFFECTS OF QUANTUM CONFINEMENT

Keldysh-Rytova Potential

Coulomb interaction in thin semiconductor and semimetal films

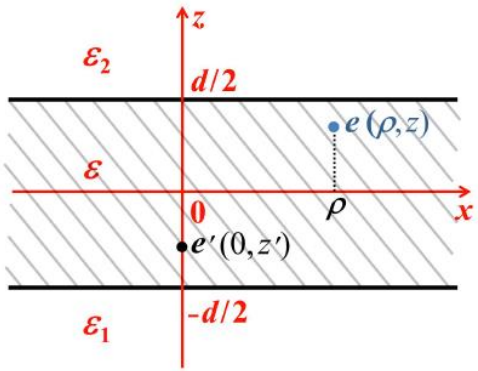
L. V. Keldysh
P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted 28 April 1979)

L.V.Keldysh, JETP Lett. 29, 658 (1980)
N.S.Rytova, Moscow State University Physics Bulletin 3, 30 (1967)

$$V(\vec{\rho}, z, z') = \frac{4\pi e e'}{\epsilon} \int \frac{d^2k}{(2\pi)^2} e^{2k\vec{\rho}} \frac{\mathrm{ch}\left[|k|\left(\frac{d}{2} - z\right) + \eta_2\right] \mathrm{ch}\left[|k|\left(\frac{d}{2} + z'\right) + \eta_1\right]}{|k|\,\mathrm{sh}[|k|\,d + \eta_1 + \eta_2]}$$

$$\eta_{1,2} = \frac{1}{2} \ln \frac{\epsilon + \epsilon_{1,2}}{\epsilon - \epsilon_{1,2}} .$$



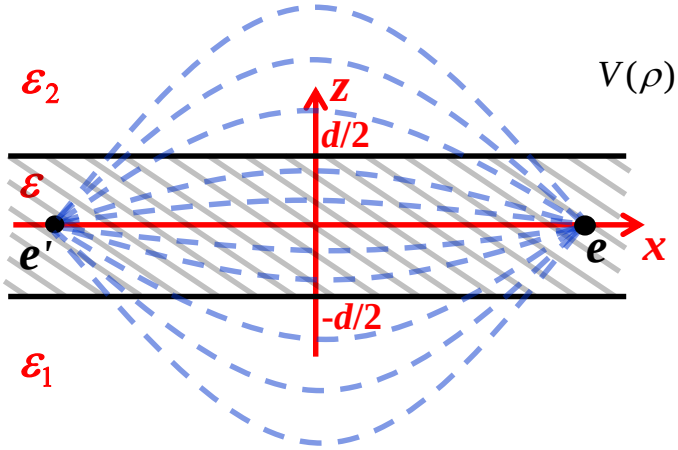
$$V(\vec{\rho}) = \frac{2ee'}{\epsilon d} \int_0^\infty \frac{J_0(t)\,dt}{t + \frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{\rho}{d}}$$

$d \ll \rho$

$$= \frac{\pi e e'}{\epsilon d} \left[\mathcal{H}_0\left(\frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{\rho}{d}\right) - N_0\left(\frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{\rho}{d}\right) \right],$$

PLASMA FREQUENCY SPATIAL DISPERSION AND NONLOCAL OPTICAL RESPONSE OF ULTRATHIN PLASMONIC FILMS

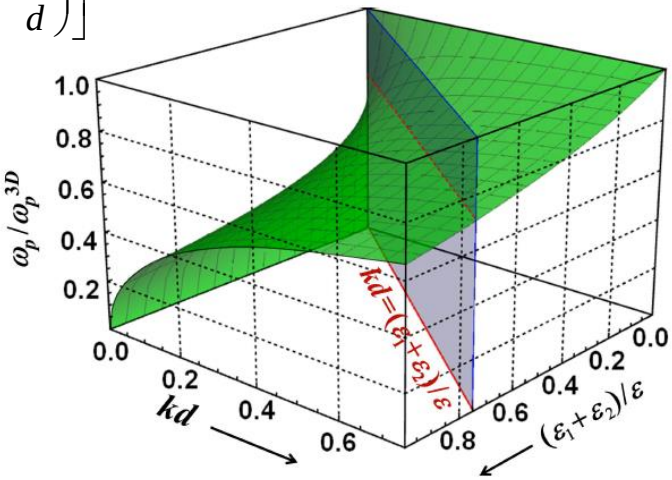
Momentum Space



$$V(\rho)=\frac{\pi ee'}{\varepsilon d}\left[H_0\left(\frac{\varepsilon_1+\varepsilon_2}{\varepsilon}\frac{\rho}{d}\right)-N_0\left(\frac{\varepsilon_1+\varepsilon_2}{\varepsilon}\frac{\rho}{d}\right)\right]$$

$$V(k)\neq\frac{4\pi ee'}{k^2}$$

$$V(k)=\frac{4\pi ee'}{k\left(kd+\dfrac{\varepsilon_1+\varepsilon_2}{\varepsilon}\right)}$$



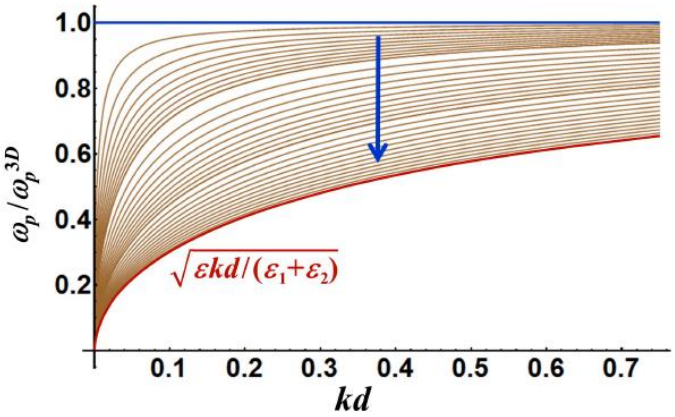
For thin enough plasmonic films, one has $N_{3D}d = N_{2D}$, so that Eq. (9) can be written as

$$\omega_p=\omega_p(k)=\frac{\omega_p^{3D}}{\sqrt{1+(\varepsilon_1+\varepsilon_2)/\varepsilon kd}}. \qquad (11)$$

If $(\varepsilon_1+\varepsilon_2)/\varepsilon kd \ll 1$ (relatively thick film), then $\omega_p=\omega_p^{3D}$ of Eq. (10), whereas one has

$$\omega_p=\omega_p^{2D}(k)=\sqrt{\frac{4\pi e^2 N_{2D}k}{(\varepsilon_1+\varepsilon_2)m^*}} \qquad (12)$$

if $(\varepsilon_1+\varepsilon_2)/\varepsilon kd \gg 1$ (ultrathin film), which agrees precisely with the plasma frequency spatial dispersion of the 2D electron gas in air (see, e.g., Ref. [33]), but does show the explicit dependence on bottom (ε_1) and top (ε_2) surrounding materials.



$$\frac{\varepsilon(k,\omega)}{\varepsilon}=1-\frac{\omega_p^2}{\omega(\omega+i\gamma)}$$

Optical Response Nonlocality

I.V.Bondarev and V.M.Shalaev, Opt. Mater. Express 7, 3731 (2017)

PLASMA FREQUENCY SPATIAL DISPERSION AND NONLOCAL OPTICAL RESPONSE OF ULTRATHIN PLASMONIC FILMS

Coordinate Space

$$\frac{\varepsilon(k,\omega)}{\varepsilon}=1-\left(\frac{\omega_p^{3D}}{\sqrt{1+(\varepsilon_1+\varepsilon_2)/\varepsilon kd}}\right)^2\frac{1}{\omega(\omega+i\gamma)}$$

$$\Downarrow$$

(per unit area)

$$\Downarrow$$

$$\frac{\varepsilon(\boldsymbol{\rho},\boldsymbol{\rho}',\omega)}{\varepsilon}=\delta(|\boldsymbol{\rho}-\boldsymbol{\rho}'|)-\frac{1}{(2\pi)^2}\int_{2\pi/L}^{k}dk\,k\int_0^{2\pi}d\varphi\left(\frac{\omega_p^{3D}}{\sqrt{1+(\varepsilon_1+\varepsilon_2)/\varepsilon kd}}\right)^2\frac{e^{ik|\boldsymbol{\rho}-\boldsymbol{\rho}'|\cos\varphi}}{\omega(\omega+i\gamma)}$$

$$\Downarrow \qquad\qquad \Downarrow$$

$(\varepsilon_1+\varepsilon_2)L/2\pi\varepsilon d<<1$ $\qquad$ $L\to\infty,\ (\varepsilon_1+\varepsilon_2)/\varepsilon k_c d>>1,\ k_c|\boldsymbol{\rho}-\boldsymbol{\rho}'|>>1$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\frac{\varepsilon(\boldsymbol{\rho},\boldsymbol{\rho}',\omega)}{\varepsilon}=\left(1-\frac{\left(\omega_p^{3D}\right)^2}{\omega(\omega+i\gamma)}\right)\delta(|\boldsymbol{\rho}-\boldsymbol{\rho}'|)$$

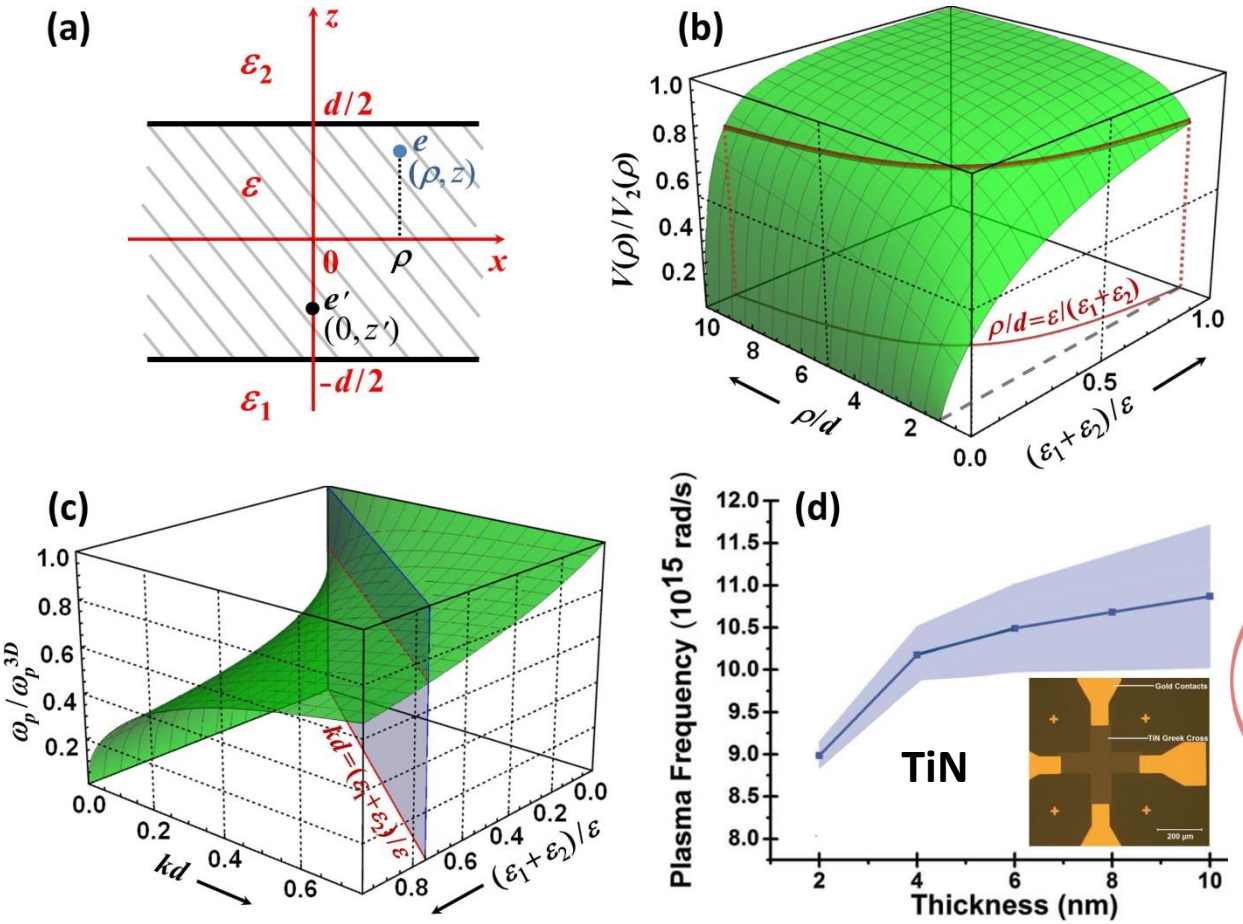
$$\frac{\varepsilon(\boldsymbol{\rho},\boldsymbol{\rho}',\omega)}{\varepsilon}\approx\left(1-\frac{\varepsilon k_c d}{\varepsilon_1+\varepsilon_2}\cdot\frac{\left(\omega_p^{3D}\right)^2}{\omega(\omega+i\gamma)}\right)\delta(|\boldsymbol{\rho}-\boldsymbol{\rho}'|)$$

$$+\frac{\varepsilon k_c d}{\varepsilon_1+\varepsilon_2}\cdot\frac{\left(\omega_p^{3D}\right)^2}{\omega(\omega+i\gamma)}\cdot\frac{\cos\left(k_c|\boldsymbol{\rho}-\boldsymbol{\rho}'|+3\pi/4\right)}{\sqrt{2\pi^3 k_c}\,|\boldsymbol{\rho}-\boldsymbol{\rho}'|^{5/2}}$$

Optical Response Nonlocality in coordinate space

ULTRATHIN PLASMONIC FILMS OF FINITE THICKNESS. EFFECTS OF QUANTUM CONFINEMENT

Comparison with Experiments



Same effect in topological insulator thin films:
T.P.Ginley & S.Law, Adv. Optical Mater. 1800113 (2018)

(a,b) Schematic of the confined thin film geometry (a) and the normalized Coulomb interaction potential (b) for ultrathin finite thickness plasmonic films. **(c)** Thin film plasma frequency normalized by the bulk plasma frequency derived theoretically in Ref.[1]. **(d)** Plasma frequency extracted from the ellipsometry measurements done on ultrathin TiN films of controlled variable thickness fabricated at Purdue University [2].

[1] I.V.Bondarev and V.M.Shalaev, Opt. Mater. Express 7, 3731 (2017); [2] D.Shah, *et al.*, Adv. Opt. Mater. 1700065 (2017)

PLASMA FREQUENCY SPATIAL DISPERSION & MAGNETO-OPTICAL RESPONSE OF ULTRATHIN PLASMONIC FILMS OF FINITE THICKNESS

L.D.Landau & E.M.Lifshitz, *Electrodynamics of Continuous Media*, 2nd edn., 1984

When spatial dispersion is present, the permittivity is a tensor, not a scalar, even in an isotropic medium: a distinctive direction is generated by the wave vector. If the medium not only is isotropic but also has a centre of symmetry, the tensor ε_{ik} must be constructed from the components of the vector $\mathbf{k}$ and the unit tensor δ_{ik} (in the absence of a centre of symmetry, there may also be a term containing the antisymmetric unit tensor e_{ikl}; see §104). The general form of such a tensor may be written as

$$\varepsilon_{ik}(\omega, \mathbf{k}) = \varepsilon_t(\omega, k)(\delta_{ik} - k_i k_k/k^2) + \varepsilon_l(\omega, k) k_i k_k/k^2, \qquad (103.12)$$

where ε_t and ε_l depend only on the magnitude of the wave vector (and on ω). If $\mathbf{E}$ is parallel to the wave vector, then $\mathbf{D} = \varepsilon_l \mathbf{E}$; if $\mathbf{E} \perp \mathbf{k}$, then $\mathbf{D} = \varepsilon_t \mathbf{E}$. The quantities ε_l and ε_t are accordingly called the *longitudinal* and *transverse permittivities*. When $\mathbf{k} \to 0$, the expression (103.12) should tend to $\varepsilon(\omega)\delta_{ik}$, which does not depend on the direction of $\mathbf{k}$; it is therefore clear that

$$\varepsilon_l(\omega, 0) = \varepsilon_t(\omega, 0) = \varepsilon(\omega). \qquad (103.13)$$

The description of the electromagnetic properties of an isotropic medium by means of the permittivities ε_l and ε_t corresponds to Maxwell's equations written in the form (103.3) and (103.4). On the other hand, as $\mathbf{k} \to 0$ and the spatial dispersion disappears, we can revert to the description by means of ε and μ. There is consequently a certain relation between these quantities (see Problem 1).

PLASMA FREQUENCY SPATIAL DISPERSION & MAGNETO-OPTICAL RESPONSE OF ULTRATHIN PLASMONIC FILMS OF FINITE THICKNESS

L.D.Landau & E.M.Lifshitz, *Electrodynamics of Continuous Media*, 2nd edn., 1984

PROBLEM 1. Find the relation between the functions $\varepsilon(\omega)$, $\mu(\omega)$ and the limiting values of $\varepsilon_l(\omega, k)$ and $\varepsilon_t(\omega, k)$ as $k \to 0$.

SOLUTION. We compare the expressions for the averaged microscopic current $\overline{\rho \mathbf{v}}$ in the forms (103.5) and (79.3). For a monochromatic field, we have in the first case

$$\overline{\rho v_i} = -i\omega[\varepsilon_{ik}(\omega, \mathbf{k}) - \delta_{ik}] E_k/4\pi,$$

and in the second case

$$\overline{\rho \mathbf{v}} = -i\omega[\varepsilon(\omega) - 1]\mathbf{E}/4\pi + ic[\mu(\omega) - 1]\mathbf{k} \times \mathbf{H}/4\pi.$$

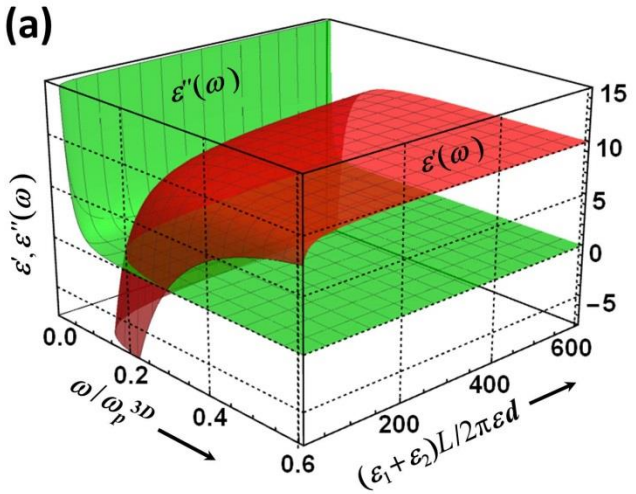
Substituting in the first $\varepsilon_{ik}(\omega, \mathbf{k})$ from (103.12), and in the second $\mathbf{H} = c\mathbf{k} \times \mathbf{E}/\omega\mu$ in accordance with Maxwell's equation, and equating the two expressions (for $k \to 0$), we find

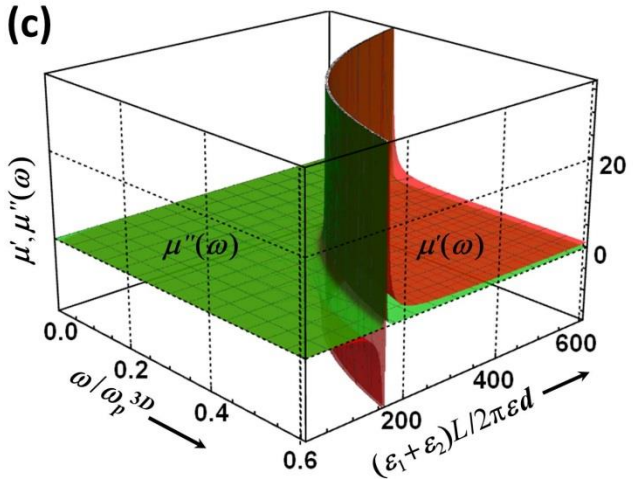
$$1 - \frac{1}{\mu(\omega)} = \frac{\omega^2}{c^2} \lim_{k \to 0} \frac{\varepsilon_t(\omega, k) - \varepsilon_l(\omega, k)}{k^2}$$

by comparing the terms in $\mathbf{k}(\mathbf{k} \cdot \mathbf{E})$. Together with (101.13), this gives the required relation

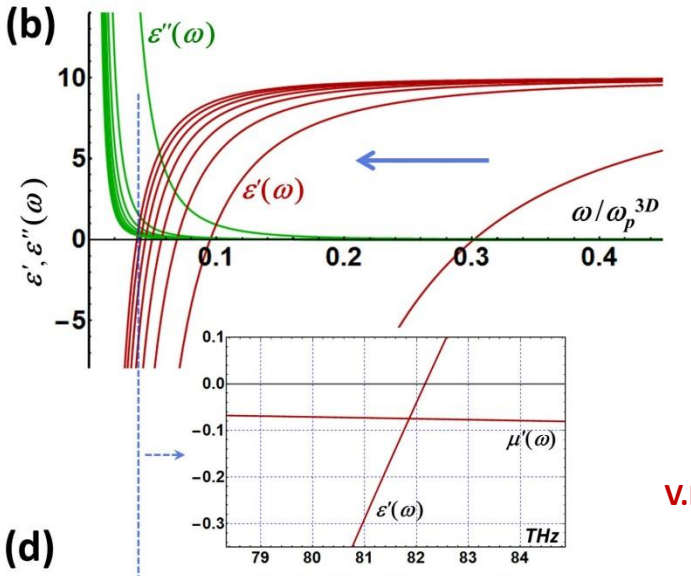
MAGNETO-OPTICAL RESPONSE OF ULTRATHIN PLASMONIC FILMS OF FINITE THICKNESS

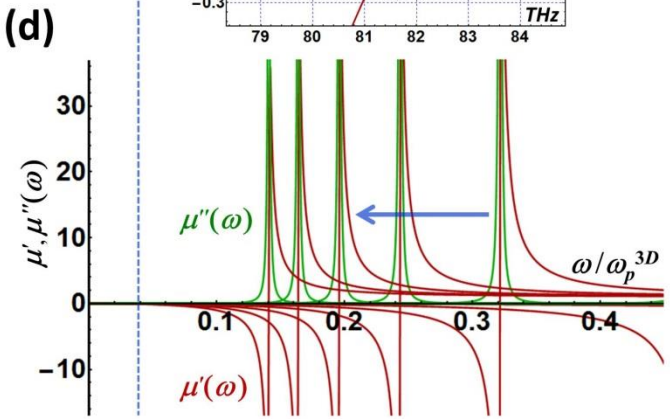
Possibility for Negative Refraction





$$\gamma/\omega_p^{3D} = 0.001, \quad L/\lambda_p^{3D} = 100$$





$$\gamma \ll \omega < \omega_p^{3D}\sqrt{\frac{2\pi\varepsilon d}{(\varepsilon_1+\varepsilon_2)L}}$$

$$\varepsilon'(\omega)|\mu(\omega)| + \mu'(\omega)|\varepsilon(\omega)| < 0$$

$$\Downarrow$$

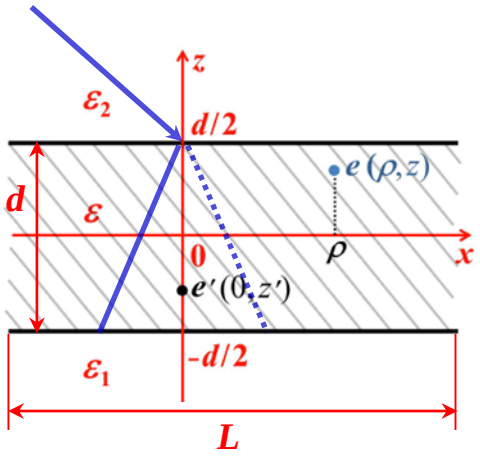
$$\varepsilon'(\omega) \,\&\, \mu'(\omega) < 0$$

$$\Updownarrow$$

Negative Refraction :

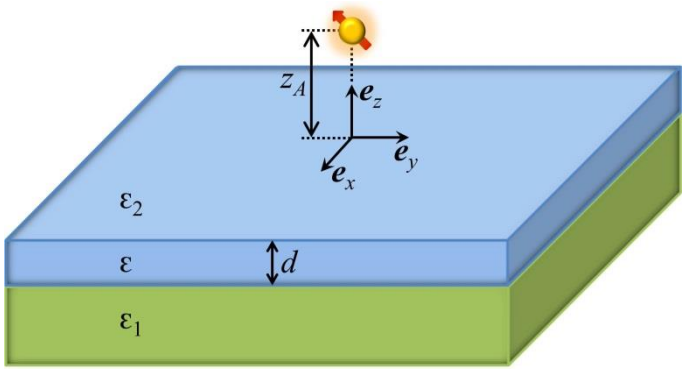
$$\sqrt{n(\omega)} = \sqrt{\varepsilon(\omega)\mu(\omega)} < 0$$

V.M.Shalaev, Nature Photonics 1, 41 (2007)



I.V.Bondarev, H.Mousavi & V.M.Shalaev, MRS Commun. 8, 1092 (2018)

QED EFFECT *example – Dipolar Spontaneous Decay*



$$\hat{E}_\alpha(\mathbf{r},\omega) = i\frac{4\pi\omega^2}{c^2}\int d\mathbf{r}' \sum_{\lambda=x,y,z} G_{\alpha\lambda}(\mathbf{r},\mathbf{r}',\omega)\hat{J}_\lambda(\mathbf{r}',\omega) + \text{h.c.},$$

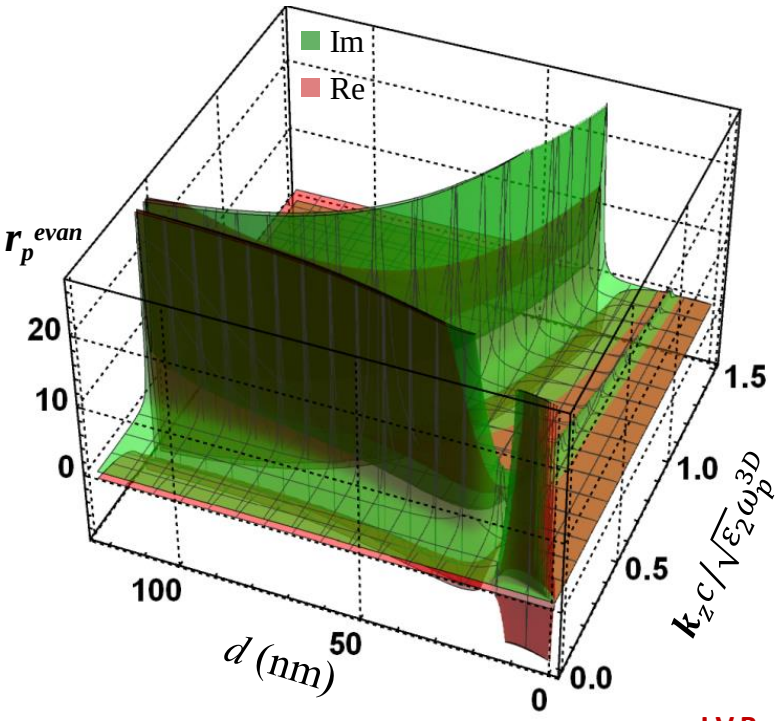
$$\hat{J}_\lambda(\mathbf{r},\omega) = \sqrt{\text{Im}\,\varepsilon_{\lambda\lambda}(\mathbf{r},\omega)/\pi}\ \hat{f}_\lambda(\mathbf{r},\omega)$$

$$[\hat{f}_\lambda(\mathbf{r},\omega), \hat{f}^\dagger_{\lambda'}(\mathbf{r}',\omega')] = \delta_{\lambda\lambda'}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(\omega-\omega')$$

$$\Gamma(\mathbf{r}_A,\omega) = \frac{8\pi\omega^2}{\hbar c^2}\sum_{\alpha,\lambda=x,y,z}\left\langle \hat{d}_\alpha \hat{d}^\dagger_\lambda \right\rangle \text{Im}\,G_{\alpha\lambda}(\mathbf{r}_A,\mathbf{r}_A,\omega) \sim \boldsymbol{r}^{prop}_{s,p} \ \&\ \boldsymbol{r}^{evan}_{s,p}$$

$$\sum_{\beta=x,y,z}\left(\nabla\times\nabla\times - \omega^2\hat{\varepsilon}(\mathbf{r},\omega)/c^2\right)_{\alpha\beta} G_{\beta\lambda}(\mathbf{r},\mathbf{r}',\omega) = \delta_{\alpha\lambda}(\mathbf{r}-\mathbf{r}')$$

Green Tensor of Planar Multilayers:
M.S.Thomas, PRA 51, 2545 (1995)



$\omega_p^{3D} = 2.79$ **eV**

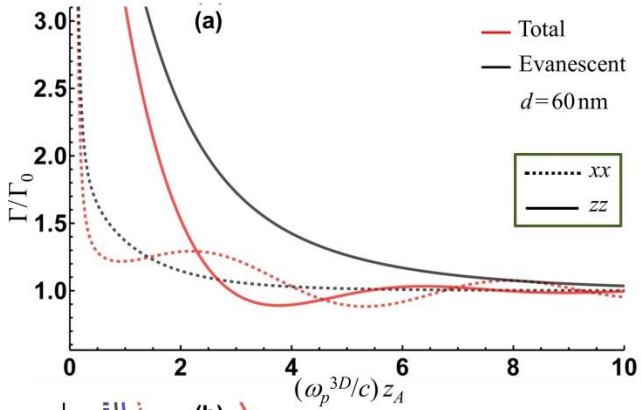
$\varepsilon = 7.8$

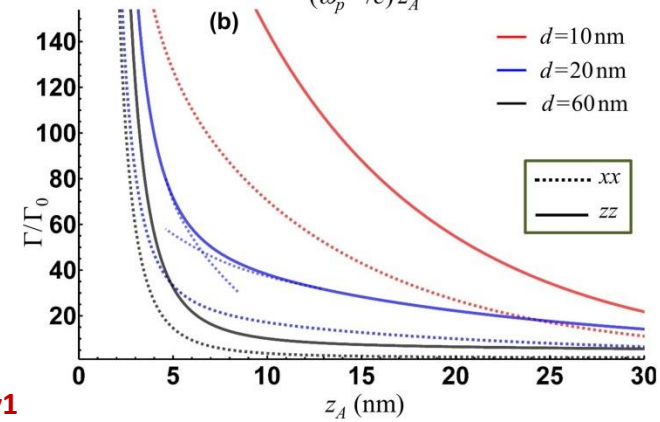
$\varepsilon_2 = \varepsilon_1 = 1$

$\omega = 0.65\,\omega_p^{3D}$;

$\gamma = 0.01\,\omega_p^{3D}$

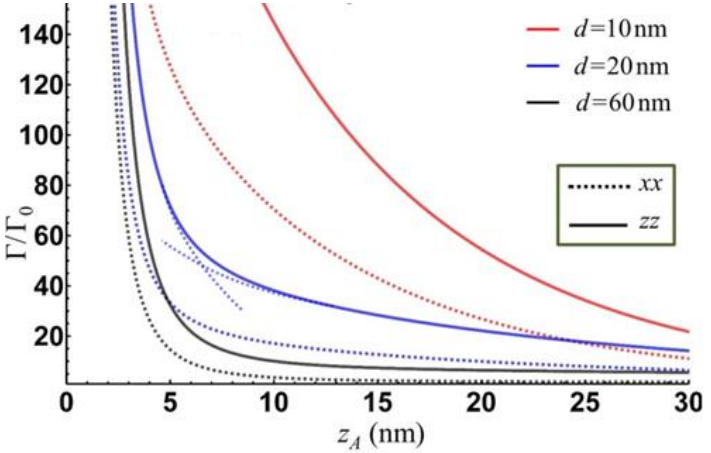
TiN & NV-center





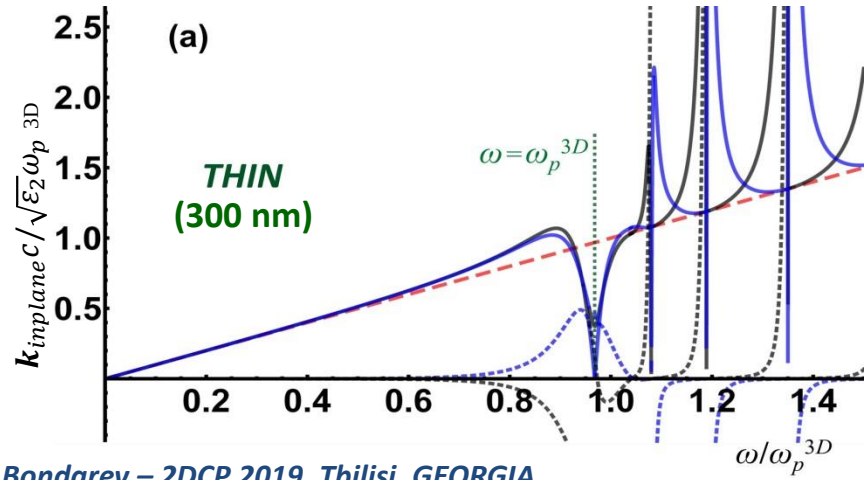
I.V.Bondarev, H.Mousavi
& V.M.Shalaev, arXiv1908.00640v1

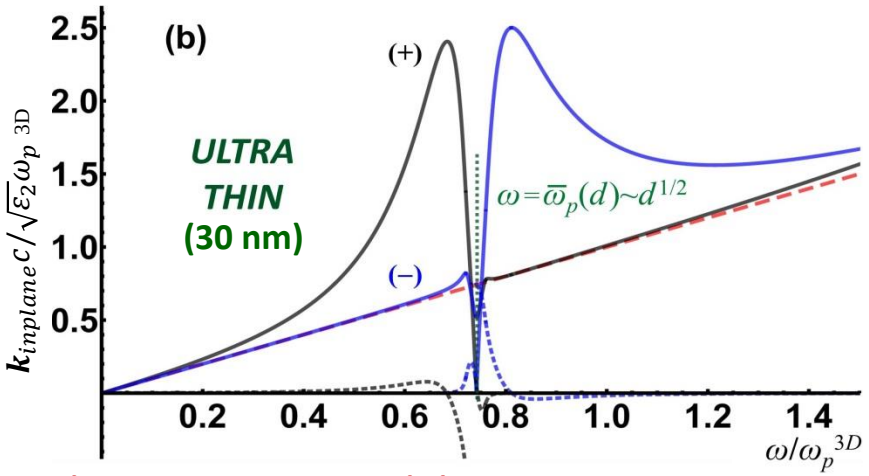
A WAY TO UNDERSTAND WHAT WE OBTAIN



$$V_{dd}^{\perp} = 2V_{dd}^{\parallel} \sim -\frac{2d^2}{\varepsilon R^3} \Leftarrow V_{dd} = \frac{\mathbf{d}_1\cdot\mathbf{d}_2 - 3(\mathbf{d}_1\cdot\mathbf{n})(\mathbf{d}_2\cdot\mathbf{n})}{R^3} \Rightarrow V_{dd}^{\perp} = 2V_{dd}^{\parallel} \sim -\frac{2d^2}{R^3}$$

Surface Plasmon Mode Dispersion

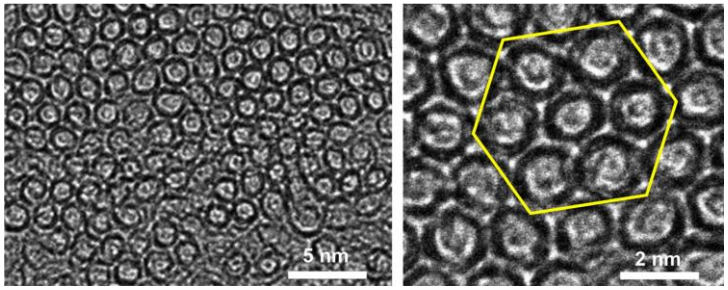




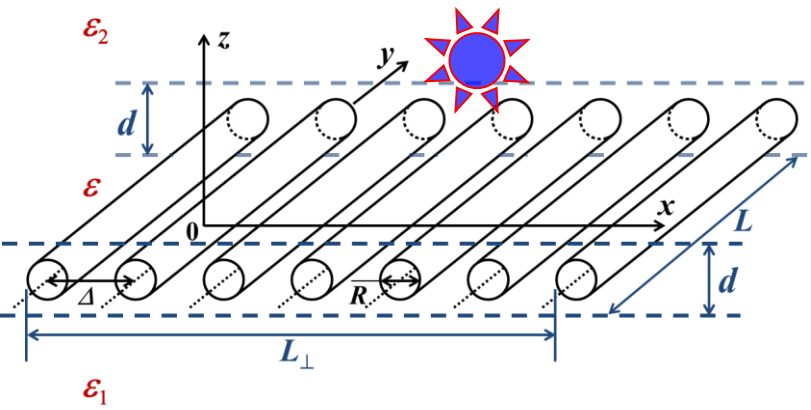
I.V.Bondarev, H.Mousavi & V.M.Shalaev, arXiv1908.00640v1

EXPLORING EFFECTS OF ANISOTROPY

Finite-Thickness Effects in Plasmonic Films with Cylindrical Anisotropy



Aligned Carbon Nanotube Films (cross-sectional view): Jun Kono group @ Rice; Abram Falk @ IBM; Jon Fan group @ Stanford; see, e.g., Nano Lett. 19, 3131 (2019)



$$\hat{\varepsilon}(\omega,q)=\begin{bmatrix}\varepsilon_\perp & 0\\ 0 & \varepsilon_\parallel(\omega,q)\end{bmatrix},\quad \varepsilon_\perp=\varepsilon\,,$$

$$\varepsilon_\parallel(\omega,q)=\varepsilon\left(1-\frac{\omega_p^2(q)}{\omega^2+i\gamma\omega}\right)$$

$$\omega_p(k)=\omega_p(q,k_\perp)=\sqrt{\frac{8\pi e^2N_{2D}\,qRI_0(qR)K_0(qR)}{\varepsilon m^*d\,[1+(\varepsilon_1+\varepsilon_2)/\varepsilon kd]}}$$

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One can see that $\omega_p(0,k_\perp)=\omega_p(k_\perp)=0$ due to the properties of the modified cylindrical Bessel functions, while $\omega_p(q,0)=\omega_p(q)\neq 0$ and is strongly thickness dependent. No plasma oscillations occur and the film behaves as a dielectric in the direction perpendicular to the cylinder alignment (x-direction in Fig. 1). There are plasma oscillations in the cylinder alignment direction (y-direction in Fig. 1), in which case the plasma frequency takes the form

$$\omega_p(q)=\omega_p^{3D}\sqrt{\frac{2qRI_0(qR)K_0(qR)}{1+(\varepsilon_1+\varepsilon_2)/\varepsilon qd}}\,, \tag{7}$$

where $\omega_p^{3D}=\sqrt{4\pi e^2N_{3D}/\varepsilon m^*}$ is the *effective* bulk plasma frequency of the film material ($N_{3D}=N_{2D}/d$ being the *volumetric* electron density), whereby the film behaves as a spatially dispersive metal with the dispersion character controlled by the thickness d and by the relative dielectric constant $(\varepsilon_1+\varepsilon_2)/\varepsilon$ of the film. Specifically, if $(\varepsilon_1+\varepsilon_2)/\varepsilon qd\ll 1$ (relatively thick film), then

$$\omega_p(q)=\omega_p^{3D}\sqrt{2qRI_0(qR)K_0(qR)}\,, \tag{8}$$

whereas one has

$$\omega_p(q)=\omega_p^{2D}(q)=q\sqrt{\frac{8\pi e^2N_{2D}RI_0(qR)K_0(qR)}{(\varepsilon_1+\varepsilon_2)m^*}} \tag{9}$$

if $(\varepsilon_1+\varepsilon_2)/\varepsilon qd\gg 1$ (ultrathin film), whose q-dependence is different, independent of the material of the film and does show the explicit dependence on the substrate and superstrate

Thickness Controlled

Unidirectional

Spontaneous Emission Enhancement

SUMMARY

- **TOPIC I: Biexcitons and Trions Formed by Indirect Excitons in Layered Semiconductors**
  - **The configuration space (Landau-Herring) method to evaluate the ground-state binding energies of the neutral and charged exciton complexes (biexciton and trion)**
  - **Trion and biexicton binding energies can be significant, up to a few tens of meV, with the trion always having a greater binding energy than the biexciton**
  - **Important for non-linear optics and spin-optronics applications**
- **TOPIC II: Organic Molecular Semiconductor Crystals with Two Frenkel Exciton States**
  - **Frenkel-Charge-Transfer intermixing theory to explain optical spectroscopy data**
  - **Important for the proper interpretation of optical properties of crystalline transition metal phthalocyanines — organic semiconductors for advanced optoelectronics**
- **TOPIC III: Transdimentional Effects in Ultrathin Metallic Films of Finite Thickness**
  - **Plasma frequency spatial dispersion to result in nonlocal dielectric response**
  - **Negative refraction, resonance magnetic response, and novel QED effects (biexponential spontaneous decay)**
  - **Important for the field of plasmonics and optical metasurfaces**

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ACKNOWLEDGEMENTS: Mikhail Lapine (UT-Sydney, Australia), Hamze Moussavi (NCCU), Adrian Popescu (USF-Tampa)