**TAILORING TWO-PHOTON SPONTANEOUS EMISSION USING ATOMICALLY THIN PLASMONIC NANOSTRUCTURES**

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# A brief introduction about spontaneous emission

SPONTANEOUS EMISSION (SE)

 An **excited atom**, even when isolated, **decays** to its fundamental state.



- Phenomenon induced by **quantum vacuum fluctuations**.
- Quantum electrodynamics (QED): excited atom + zero photons is not a stationary state of the atom-field system.

# **SE** Most of the light we see is from SE.







#### PURCELL EFFECT

- E.M. **Purcell** (**1946**): Bodies in the vicinities of an emitter change its SE rate.
- Reason: The presence of the bodies affects the **boundary conditions** (BC) on the electromagnetic field.



$$
\Gamma(\mathbf{R})=\frac{\pi}{\epsilon_o\hbar}\sum_{\mathbf{k}p}\omega_k|\mathbf{d}_{eg}\cdot\mathbf{A}_{\mathbf{k}p}(\mathbf{R})|^2\delta(\omega_k-\omega_{eg})
$$

o It can be shown that the SE rate is proportional to the local density of states (**LDOS**) of the electromagnetic field.

**L. Novotny** and **B. Hecht**, *Principles of nano-optics*. Cambridge university press, 2012.

#### PURCELL EFFECT ON THE ONE-PHOTON SE



# TWO-PHOTON SPONTANEOUS EMISSION (TPSE)

- **Second order process** in perturbation theory (**Göppert-Mayer**, **1931**).
- Relevant process when the one-photon SE is forbidden, for instance, due to **selection rules**.
- **o** Ex: 2s 1s transition in **H**(Breit, Teller, 1940).  $\tau \approx 1/7s$
- **o Broadband** spectrum of emission.
- Explains the emission spectrum of planetary nebulae. **L. Spitzer and J. L. Greenstein**, The Astrophysical Journal, vol. **114**, p. **407 (1951)**.

# PURCELL EFFECT ON THE TPSE

**Not widely discussed** in the literature.

- The progress in **near-field optics, plasmonics,** and **materials science** in general has improved our **control** over **radiation-matter interactions**.
- In some situations the TPSE can even dominate conventionally fast transitions!

**N. Rivera** *et al*, "*Making two-photon processes dominate one-photon processes using mid-ir phonon polaritons*", PNAS, p. **201713538** (**2017**)

 TPSE is a rich phenomenon, with very much to be explored yet.



#### AN EMITTER BETWEEN TWO PERFECT MIRRORS  $(s \rightarrow s)$



Abrupt changes in the spectral density due to discontinuities in the LDOS.

#### AN EMITTER BETWEEN TWO PERFECT MIRRORS  $(s \rightarrow s)$



RELATION BETWEEN TPSE AND ONE-PHOTON SE **o** It is possible to show that

$$
\Gamma(\mathbf{R}_e) = \int_0^{\omega_t} d\omega \gamma_0(\omega) \sum_{a,b} t_{ab}(\omega) P_a(\mathbf{R}_e, \omega) P_b(\mathbf{R}_e, \omega_t - \omega)
$$

$$
t_{ab}(\omega) = |\mathbb{D}_{ab}(\omega, \omega_t - \omega)|^2 / |\mathbb{D}(\omega, \omega_t - \omega)|^2
$$

 $P_a(\mathbf{R}_e,\omega)$ 



 Once we know the **one-photon S**E rate of an emitter we can obtain immediately the **TPSE spectral density**!

# TPSE near plasmonic nanostructures

# PLASMONICS

#### What is a plasmon?



# PLASMONICS

What is plasmonics?

"You just have Maxwell's equations, some material properties and some boundary conditions, all classical stuff - what's new about that?''

> **S. A. Maier***, Plasmonics: fundamentals and applications*.

#### **Physics!**

- $\bullet$  Strong light confinement  $\rightarrow$  beyond the diffraction limit.
- Extreme enhancement of the electromagnetic field intensity  $\rightarrow$  surface physics and **non-linear optics**.

# Spatially resolved optical sensing in the infrared PLASMONICS IN 2D SYSTEMS - GRAPHENE



•ACS Photonics 2017, 4, 1831−1838 •*ACS Photonics* 2018, 5, 8, 3282-3290

Ultrafast radiative heat transfer



Nature Communications**, 8**, 2 (2017)

# (QUASI-)2D NOBLE METALS

Wide range of frequencies (visible and near-infrared)

Recent fabrication of quasi-2D metal films.



•ACS NANO,**13**, 7 (2019) •Nature Photonics, **8**, 328- 333 (2019)

# SYSTEM UNDER STUDY

 An emitter near a 2D plasmonic nanostructure of arbitrary geometry.



#### PLASMONS IN 2D NANOSTRUCTURES

Plasmon Wave Function (**PWF**) formalism:

$$
\rho_{2D}(\mathbf{r},\omega) = \frac{4\pi\epsilon_0}{D} \sum_j \frac{c_j}{1/\eta_j - 1/\eta(\omega)} v_j(\mathbf{u}) \longrightarrow Plasmon \ Wave \ Function \ j
$$

o Resonance frequencies:

 $\eta(\omega) = i\sigma(\omega)/4\pi\epsilon_0\omega D$  $\text{Re}[1/\eta_{i} - 1/\eta(\omega_{i})] = 0$ 



## PLASMONS IN 2D NANOSTRUCTURES

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$$

o Resonance frequencies:

 $\eta(\omega) = i\sigma(\omega)/4\pi\epsilon_0\omega D$  $\text{Re}[1/\eta_i - 1/\eta(\omega_i)] = 0$ Excelent agreement with numerical calculations.



# PURCELL FACTORS

 The Purcell factors are numerically equal to the ratio between the power dissipated by an electric dipole near the nanostructure with respect to its free-space radiation rate.

 $P_a(\mathbf{R}_e,\omega) = W_a(\mathbf{R}_e,\omega)/W_0(\omega)$ 

# PURCELL FACTORS

 The Purcell factors are numerically equal to the ratio between the power dissipated by an electric dipole near the nanostructure with respect to its free-space radiation rate.

$$
P_a(\mathbf{R}_e,\omega) = W_a(\mathbf{R}_e,\omega)/W_0(\omega)
$$

$$
P_a(\mathbf{R}_e, \omega) = P_{a, nr}(\mathbf{R}_e, \omega) + P_{a, r}(\mathbf{R}_e, \omega)
$$

Absorption (**plasmon emission**):

$$
P_{a,nr}(\mathbf{R}_e,\omega) = \frac{6\pi\epsilon_0 c^3}{\omega^4 |\mathbf{d}_a|^2} \int d^3\mathbf{R}' \text{Re}\{\mathbf{J}^*(\mathbf{R}',\omega) \cdot \mathbf{E}(\mathbf{R}',\omega)\}
$$

Far-field radiation (**photon emission**):

 $P_{a,r}(\mathbf{R}_e,\omega)=\frac{6\pi\epsilon_0c^3}{\omega^4|\mathbf{d}_e|^2}\int_{\mathbf{R}'}d\mathbf{A'}\cdot\mathrm{Re}\{\mathbf{E}(\mathbf{R'},\omega)\times\mathbf{H}^*(\mathbf{R'},\omega)\}\,$ 

# TPSE DECAY CHANNELS



$$
\gamma(\mathbf{R}_e, \omega) = \gamma_0(\omega) \sum_{a,b} t_{ab}(\omega) P_a(\mathbf{R}_e, \omega) P_b(\mathbf{R}_e, \omega_t - \omega)
$$

$$
P_a(\mathbf{R}_e, \omega) = P_{a,nr}(\mathbf{R}_e, \omega) + P_{a,r}(\mathbf{R}_e, \omega)
$$

 Photon-photon, photon-plasmon and plasmon-plasmon states.

#### APPROXIMATED PURCELL FACTORS: DRUDE MODEL

$$
P_{a,nr}(\mathbf{R}_e,\omega) \simeq \sum_{q=1}^N \frac{A_{a,q}}{\omega^2} \frac{1/2\tau}{(\omega - \omega_q)^2 + (1/2\tau)^2}
$$

Plasmonic contribution **Lorentzian resonances**

#### APPROXIMATED PURCELL FACTORS: DRUDE MODEL

$$
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$$

Plasmonic contribution **Lorentzian resonances**

$$
P_{a,r}(\omega) \simeq \sum_{q=1}^{N} \frac{B_{a,q}(1/2\tau)^2 + (\omega - \omega_q + f_{a,q}/2\tau)^2}{(\omega - \omega_q)^2 + (1/2\tau)^2} - (N-1)
$$

Photonic contribution  $\rightarrow$  **Fano**  $+$  **Lorentzian resonances** 

# APPROXIMATED RESULTS: DRUDE MODEL



 $\omega$ 

#### A METALLIC NANODISK CLOSE TO AN ON-AXIS QUANTUM EMITTER: RESONANT MODES



can be **tuned** by changing the **size** of the nanodisk.



A METALLIC NANODISK CLOSE TO AN ON-AXIS QUANTUM EMITTER: TPSE SPECTRUM

 **Crossings** between **Bright-Bright** or **Dark-Dark** modes produce **extreme enhancements**.



A METALLIC NANODISK CLOSE TO AN ON-AXIS QUANTUM EMITTER: DECAY CHANNELS

 Spectral line-shapes serve as **fingerprints** of the three **decay channels**. $10<sup>3</sup>$ 



#### DYNAMICAL CONTROL OF TPSE WITH A GRAPHENE NANODISK

 **Enhanced selective spectral emission** compared to the typical broadband spectrum of monolayers.



#### DYNAMICAL CONTROL OF TPSE WITH A GRAPHENE NANODISK

$$
QY^{1q}(\omega) = \frac{\gamma_{ph}^{1q}(\omega)}{\gamma^{1q}(\omega)}, \quad QY^{TPSE}(\omega) = \frac{\gamma_{ph,ph}(\omega) + \gamma_{ph,pl}(\omega)}{\gamma(\omega)}
$$
\n
$$
I_{\text{D1}} \quad \text{QY^{TPSE}} \quad \text{D2Y^{TPSE}}
$$
\n
$$
I_{\text{D3}} \quad \text{D3Y^{TPSE}} \quad \text{D4Y^{1q}}
$$
\n
$$
I_{\text{D4Y^{1q}}} \quad \text{D5Y^{1q}}
$$
\n
$$
I_{\text{D5Y^{1q}}} \quad \text{D6Y^{1q}}
$$
\n
$$
I_{\text{D6Y}} \quad \text{D7Y^{1q}}
$$
\n
$$
I_{\text{D7Y^{1q}}} \quad \text{D8Y^{1q}}
$$
\n
$$
I_{\text{D8Y^{1q}}} \quad \text{D9Y^{1q}}
$$
\n
$$
I_{\text{D9Y^{1q}}} \quad \text{D1Y^{1q}}
$$
\n
$$
I_{\text{D1Y^{1q}}} \quad \text{D2Y^{1q}}
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\n
$$
I_{\text{D2Y^{1q}}}
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I_{\text{D3Y^{1q}}} \quad \text{D1Y^{1q}}
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$$
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$$
I_{\text{D1Y^{1q}}}
$$
\n
$$
I_{\text{D2Y
$$

 Single photon creation via a two-quanta process can be much more efficient than standard one-photon emission.



$$
QE = \Gamma_{4s \to 3s} / (\Gamma_{4s \to 3s} + \gamma_{4s \to 3p}^{1q} + \gamma_{4s \to 2p}^{1q})
$$

 For any disk diameter the quantum efficiency can be optimized by tuning the Fermi energy so that  $\omega_{B_1} = \omega_t/2$ .



$$
\mu = 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}
$$

Numbers near curves: **ph-ph Purcell factors**

# **CONCLUSIONS**

- It is possible to pre-select the frequencies of emission by tuning the size and doping of the nanostructure.
- 2D plasmonic nanostructures allow enhanced TPSE rate with **generation of photons**, not only plasmons.
- Surprisingly, **TPSE** can be a **single photon source** orders of magnitude more efficient than one-photon SE.
- **Finite-sized** plasmonic systems have many **advantages** over **extended** ones.

# THANK YOU!



A METALLIC NANODISK CLOSE TO AN ON-AXIS QUANTUM EMITTER: PH-PH DECAY CHANNEL

 **Finite size** is critical to accomplish **giant photonphoton production**.



# DYNAMICAL CONTROL OF TPSE WITH A GRAPHENE NANODISK

 Graphene nanostructures disrupt the usual unbalance between one- and two-quanta emission.

$$
QE = \Gamma_{4s \to 3s} / (\Gamma_{4s \to 3s} + \gamma_{4s \to 3p}^{1q} + \gamma_{4s \to 2p}^{1q})
$$



#### PURCELL EFFECT

- E.M. **Purcell** (**1946**): bodies in the vicinities of an emitter change its SE rate.
- **o** Reason: the presence of the bodies affects the **boundary conditions** (BC) on the electromagnetic field.

$$
\Gamma(\mathbf{R}) = \frac{\pi}{\epsilon_o \hbar} \sum_{\mathbf{k}p} \omega_k |\mathbf{d}_{eg} \cdot \mathbf{A}_{\mathbf{k}p}(\mathbf{R})|^2 \delta(\omega_k - \omega_{eg}).
$$
  

$$
\frac{\Gamma}{\Gamma_o} = \frac{6\pi c}{\omega_{eg}} \mathbf{\hat{n}}_{eg}^* \cdot [\text{Im}\mathbb{G}(\mathbf{R}, \mathbf{R}, \omega_{eg})] \cdot \mathbf{\hat{n}}_{eg},
$$
  

$$
\nabla \times \nabla \times \mathbb{G}(\mathbf{r}, \mathbf{r}', \omega) - \frac{\omega^2}{c^2} \mathbb{G}(\mathbf{r}, \mathbf{r}', \omega) = \mathbb{I}\delta(\mathbf{r} - \mathbf{r}').
$$

**L. Novotny** and **B. Hecht**, *Principles of nano-optics*. Cambridge university press, 2012.



# GREEN'S FUNCTION METHOD

 The imaginary part of the Green's function can be written in terms of the field modes as

Im
$$
\mathbb{G}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\pi c^2}{2\omega} \sum_{\mathbf{k}p} \mathbf{A}_{\mathbf{k}p}^*(\mathbf{r}') \mathbf{A}_{\mathbf{k}p}(\mathbf{r}) \delta(\omega - \omega_k).
$$

 Using the previous identity, we recover the well known expression for the TPSE rate, namely

$$
\Gamma = \frac{\mu_0^2}{\pi \hbar^2} \int_0^{\omega_{eg}} d\omega \omega^2 (\omega_{eg} - \omega)^2 \text{Im} \mathbb{G}_{il}(\omega) \text{Im} \mathbb{G}_{jn}(\omega_{eg} - \omega) \mathbb{D}_{ij}(\omega, \omega_{eg} - \omega) \mathbb{D}_{ln}^*(\omega, \omega_{eg} - \omega).
$$

**N. Rivera** et al., Science, vol. **353**, no. **6296**, pp. **263–269** (**2016**).

 This constitutes an **alternative demonstration** of this formula!

# THE PURCELL FACTORS RELATION

 Choosing the basis which diagonalizes the Green's function we have

$$
\gamma(\omega) = \frac{\mu_0^2}{\pi \hbar^2} \omega^2 (\omega_{eg} - \omega)^2 \sum_{i,j} \text{Im} \mathbb{G}_{ii}(\omega) \text{Im} \mathbb{G}_{jj} (\omega_{eg} - \omega) |\mathbb{D}_{ij}(\omega, \omega_{eg} - \omega)|^2.
$$

We define the **Purcell factors** as

$$
P_i(\mathbf{R},\omega) := \frac{6\pi c}{\omega} \text{Im}\mathbb{G}_{ii}(\mathbf{R},\mathbf{R},\omega).
$$

o In this way, we can write

$$
\frac{\gamma(\omega)}{\gamma_o(\omega)} = \sum_{i,j} \frac{|\mathbb{D}_{ij}(\omega, \omega_{eg} - \omega)|^2}{|\mathbb{D}(\omega, \omega_{eg} - \omega)|^2} P_i(\omega) P_j(\omega_{eg} - \omega).
$$

 The **TPSE** rate **dependence** on the **local density of states** (LDOS) was made explicit!

PLASMONS IN 2D NANOESTRUCTURES

Plasmon Wave Function (**PWF**) formalism:

$$
\rho_{2D}(\mathbf{r},\omega) = \frac{4\pi\epsilon_0}{D} \sum_j \frac{c_j}{1/\eta_j - 1/\eta(\omega)} v_j(\mathbf{u}),
$$

 $v_i(\mathbf{u}) = \nabla_{\mathbf{u}} \cdot \sqrt{f(\mathbf{u}) \mathbf{V}_i(\mathbf{u}) + P}$  *Plasmon Wave Functions*  $\int d^2\mathbf{u}' \, \mathbb{M}(\mathbf{u},\mathbf{u}') \cdot \mathbf{V}_j(\mathbf{u}') = \frac{1}{\eta_j} \mathbf{V}_j(\mathbf{u}) \, .$  $\mathbb{M}(\mathbf{u}, \mathbf{u}') = \sqrt{f(\mathbf{u})f(\mathbf{u}')}\nabla_{\mathbf{u}}\nabla_{\mathbf{u}'}|\mathbf{u} - \mathbf{u}'|^{-1}$ 

**o** Resonance frequencies:

 $\eta(\omega) = i\sigma(\omega)/4\pi\epsilon_0\omega D$  $\text{Re}[1/\eta_i - 1/\eta(\omega_i)] = 0$ 

External field dependence:

$$
c_j = \int d^2 \mathbf{u} \, \mathbf{V}_j^*(\mathbf{u}) \cdot \mathbf{\mathcal{E}}^{ext}(\mathbf{u}, \omega)
$$

•ACS Photonics 2017, 4, 3106−3114 •*Faraday Discussions* 2015, 178, 87-107

# POWER DISSIPATED BY ABSORPTION

$$
\mathbf{J}(\mathbf{R}', \omega) = \mathbf{K}(\mathbf{r}', \omega)\delta(z') = \sigma(\omega)f(\mathbf{r}')\mathbf{E}_{\parallel}(\mathbf{r}', \omega)\delta(z')
$$
  
\n
$$
\mathbf{F}(\mathbf{u}, \omega) = \sum_{\alpha} \frac{c_{\alpha}}{1 - \eta(\omega)/\eta_{\alpha}} \mathbf{V}_{\alpha}(\mathbf{u}), c_{\alpha} = \int d^{2} \mathbf{u} \mathbf{V}_{\alpha}^{*}(\mathbf{u}) \cdot \mathbf{E}^{ext}(\mathbf{u}, \omega)
$$
  
\n
$$
\mathbf{E}^{ext}(\mathbf{R}', \omega) = \frac{1}{4\pi\epsilon_{0}} \nabla d_{a} \cdot \nabla |\mathbf{R} - \mathbf{R}'|^{-1}
$$
  
\n
$$
\mathbf{F}_{d}^{2} \mathbf{u} \mathbf{V}_{\alpha}^{*}(\mathbf{u}) \cdot \mathbf{V}_{\alpha'}(\mathbf{u}) = \delta_{\alpha\alpha'}.
$$
  
\n
$$
P_{a,nr}(\mathbf{R}_{e}, \omega) = \frac{3c^{3}}{2D^{3}\omega^{3}} \text{Im} \sum_{\alpha} \hat{\mathbf{e}}_{a} \cdot \frac{\mathbf{F}_{\alpha}(\mathbf{R}_{e}) \otimes \mathbf{F}_{\alpha}^{*}(\mathbf{R}_{e})}{1/\eta(\omega) - 1/\eta_{\alpha}} \cdot \hat{\mathbf{e}}_{a}.
$$
  
\n
$$
\mathbf{F}_{\alpha}(\mathbf{R}_{e}) = \int d^{2} \mathbf{u}' \frac{v_{\alpha}(\mathbf{u}')(\mathbf{R}_{e}/D - \mathbf{u}')}{|\mathbf{R}_{e}/D - \mathbf{u}'|^{3}}
$$

# POWER DISSIPATED BY RADIATION

 The system is spatially localized, therefore we can make a multipole expansion. The first contribution to the power radiated by the system is

$$
P_{a,r}(\mathbf{R}_e, \omega) \simeq \frac{|\mathbf{d}_a + \mathbf{d}_{a,ind}(\mathbf{R}_e, \omega)|^2}{|\mathbf{d}_a|^2}
$$

$$
\mathbf{d}_{a,ind}(\mathbf{R}_e, \omega) = \int d^2 \mathbf{r} \, \mathbf{r} \rho_{2D}(\mathbf{r}, \omega)
$$

$$
\rho_{2D}(\mathbf{r}, \omega) = \frac{4\pi\epsilon_0}{D} \sum_{\alpha} \frac{c_{\alpha}}{1/\eta_{\alpha} - 1/\eta(\omega)} v_{\alpha}(\mathbf{u})
$$

$$
P_{a,r}(\mathbf{R}_e, \omega) = \left| \hat{\mathbf{e}}_a + \sum_{\alpha} \frac{\zeta_{\alpha} \otimes \mathbf{F}_{\alpha}^*(\mathbf{R}_e)}{1/\eta_{\alpha} - 1/\eta(\omega)} \cdot \hat{\mathbf{e}}_a \right|^2. \quad \zeta_{\alpha} = \int d^2 \mathbf{u} \, \mathbf{u} v_{\alpha}(\mathbf{u})
$$

# APPROXIMATED RESULTS: DRUDE MODEL

$$
P_{a,nr}(\mathbf{R}_e, \omega) \simeq \sum_{q=1}^N \frac{A_{a,q}}{\omega^2} \frac{1/2\tau}{(\omega - \omega_q)^2 + (1/2\tau)^2}
$$

$$
A_{a,q} = \frac{3c^3 \omega_p^2 t}{16\pi D^4 \omega_q^2} \sum_{j=1}^{g_q} |\hat{\mathbf{e}}_a \cdot \mathbf{F}_{q,j}(\mathbf{R}_e)|^2.
$$

$$
P_{a,r}(\omega) \simeq \sum_{q=1}^{N} \frac{B_{a,q}(1/2\tau)^{2} + (\omega - \omega_{q} + f_{a,q}/2\tau)^{2}}{(\omega - \omega_{q})^{2} + (1/2\tau)^{2}} - (N-1)
$$
  

$$
f_{a,q} = \frac{\omega_{p}^{2} \tau t}{4\pi D \omega_{q}} \sum_{j=1}^{g_{q}} \text{Re}\left[\hat{\mathbf{e}}_{a} \cdot \mathbf{F}_{q,j}^{*}(\mathbf{R}_{e}) \zeta_{a;q,j}^{\parallel}\right]
$$

PLASMONS IN 2D NANOSTRUCTURES

How do we obtain the PWFs?



# PLASMONS IN A NANODISK

#### Analytical solution!

PWFs = 
$$
R_{ln}(u)e^{il\phi}
$$
.  $R_{ln}(u) = (2u)^{|l|} \sum_{m'} a_{m'}^{ln} P_{m'}^{(|l|,0)} (1 - 8u^2)$ 

$$
\mathbb{G}^l \mathbf{a}^{ln} = -4\pi \eta_{ln} \mathbb{K}^l \mathbf{a}^{ln},
$$

$$
\mathbb{K}_{mm'}^l = \frac{(-1)^{m-m'+1}}{\pi[4(m-m')^2 - 1] (|l| + m + m' + 1/2)(|l| + m + m' + 3/2)}, \quad m, m' = 0, 1, 2, 3...
$$

$$
\mathbb{G}_{mm'}^{l} = \frac{\delta_{m0}\delta_{m'0}}{8|l|(|l|+1)^2} + \frac{\delta_{mm'}}{4(|l|+2m')(|l|+2m'+1)(|l|+2m'+2)} + \frac{\delta_{m+1,m'}}{8(|l|+2m+1)(|l|+2m+2)(|l|+2m+3)} + \frac{\delta_{m,m'+1}}{8(|l|+2m'+1)(|l|+2m'+2)(|l|+2m'+3)}, \quad m, m' = 0, 1, 2, 3...
$$

•PRB 1986, **33,** 5221 •PRB 2016, **93,** 035426