Spherical description of photon fields: application to RET

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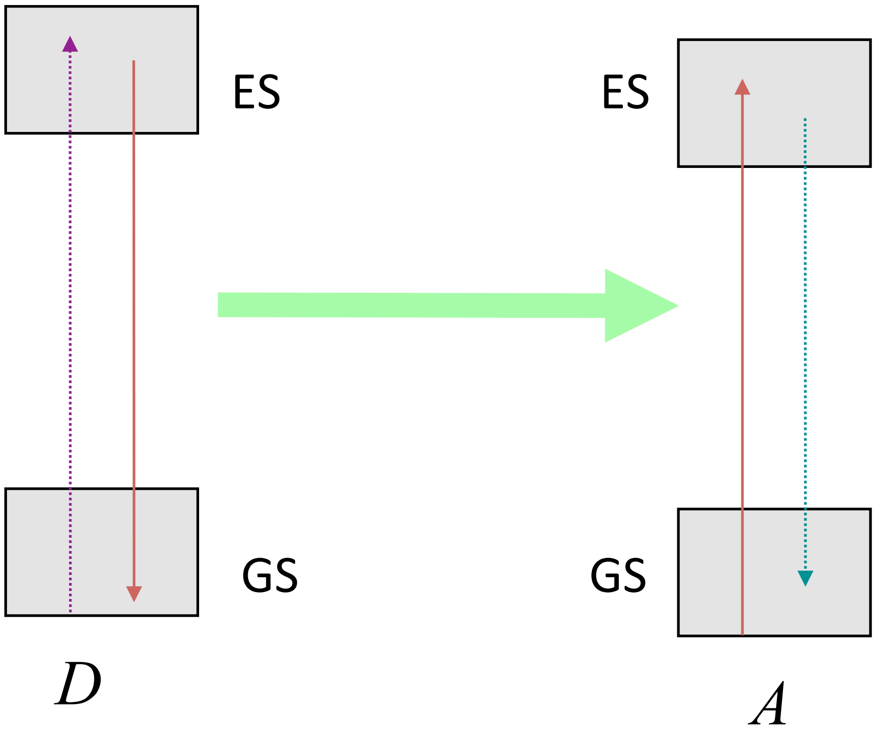
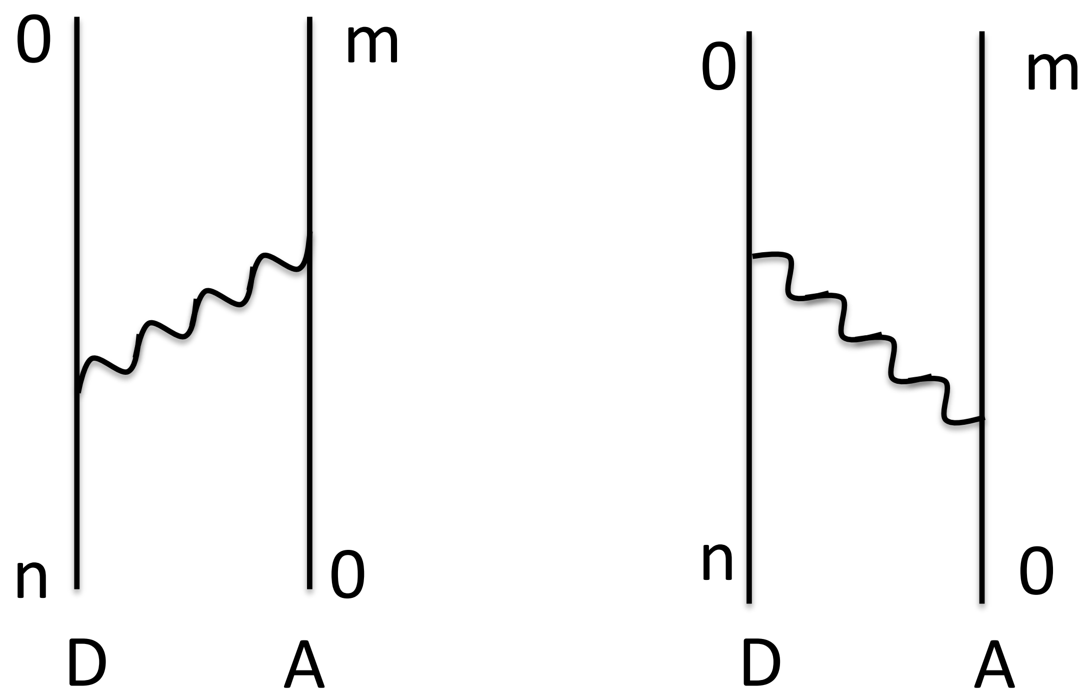
Electronic energy transfer

$$D^* + A \rightarrow D + A^*$$



QED of electronic energy transfer



$$\langle F|\hat{T}^{(2)}|I\rangle = \frac{\langle F|\hat{H}_{\text{int}}|I_1(\mathbf{k},\lambda)\rangle\langle I_1(\mathbf{k},\lambda)|\hat{H}_{\text{int}}|I\rangle}{cK - ck + is} + \frac{\langle F|\hat{H}_{\text{int}}|I_2(\mathbf{k},\lambda)\rangle\langle I_2(\mathbf{k},\lambda)|\hat{H}_{\text{int}}|I\rangle}{-cK - ck + is}$$

Multipolar Hamiltonian

$$H = H_{\mathrm{mol}}(D) + H_{\mathrm{mol}}(A) + H_{\mathrm{rad}} + H_{\mathrm{int}}(D) + H_{\mathrm{int}}(A)$$

$H_{\mathrm{mol}}(X);\ X = D,\ A$ (Molecular Hamiltonian)

$H_{\mathrm{rad}} = \sum_{\mathbf{k},\lambda} a^{(\lambda)\dagger}(\vec{k})\, a^{(\lambda)}(\vec{k})\, \hbar c k + e_{\mathrm{vac}}$ (EM radiation Hamiltonian)

$H_{\mathrm{int}}(\xi) = -\varepsilon_0^{-1} \int \vec{p}^{\perp}(\xi,\vec{r}) \cdot \hat{d}^{\perp}(\vec{r})\, \mathrm{d}^3\vec{r}$ (Interaction Hamiltonian)

Interaction Hamiltonian

$$H_{\text{int}}\left(\xi\right)=-\varepsilon_0^{-1}\int\vec{p}^{\perp}\left(\xi,\vec{r}\right)\cdot\hat{d}^{\perp}\left(\vec{r}\right)\mathrm{d}^3\vec{r}$$

$$\vec{p}\left(\vec{r}\right)=\sum_{\alpha}e_{\alpha}\left(\vec{q}_{\alpha}-\vec{R}\right)\int_0^1\left[1-\left\{\lambda\left(\vec{q}_{\alpha}-\vec{R}\right)\nabla\right\}+\frac{1}{2!}\left\{\lambda\left(\vec{q}_{\alpha}-\vec{R}\right)\nabla\right\}^2-\cdots\right]\delta\left(r-R\right)\mathrm{d}\lambda$$

$$d^{\perp}\left(R\right)=i\sum_{k,\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{\frac{1}{2}}e^{(\lambda)}\left(\vec{k}\right)\left\{a^{(\lambda)}\left(\vec{k}\right)\mathrm{e}^{i\vec{k}\cdot\vec{R}}-a^{(\lambda)\dagger}\left(\vec{k}\right)\mathrm{e}^{-i\vec{k}\cdot\vec{R}}\right\}$$

Theory of RET

Matrix element

$$\langle F | T^{(2)} | I \rangle \longrightarrow \mu_{A_l}^{full} \theta_{lj}^{vac} \mu_{D_j}^{full}$$

$$\theta_{lj}^{vac}\left(k,\hat{\mathbf{R}}\right) = \frac{k^3 e^{iKR}}{4\pi\varepsilon_0}\left[\left(\delta_{lj} - 3\hat{R}_l\hat{R}_j\right)\left(\frac{1}{k^3R^3} - \frac{i}{k^2R^2}\right) - \left(\delta_{lj} - R_lR_j\right)\frac{1}{kR}\right]$$

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- A. Salam, *J. Chem. Phys.*, 122, 044112, **2005**.
- R. Grinter and G. A. Jones, *J. Chem. Phys.*, *145*, 074107, **2016**

Zones of EET

$$\theta_{lj}^{vac}\left(k,\hat{\mathbf{R}}\right)=\frac{k^{3}e^{iKR}}{4\pi\varepsilon_{0}}\left[\left(\delta_{lj}-3\hat{R}_{l}\hat{R}_{j}\right)\left(\frac{1}{k^{3}R^{3}}-\frac{i}{k^{2}R^{2}}\right)-\left(\delta_{lj}-R_{l}R_{j}\right)\frac{1}{kR}\right]$$

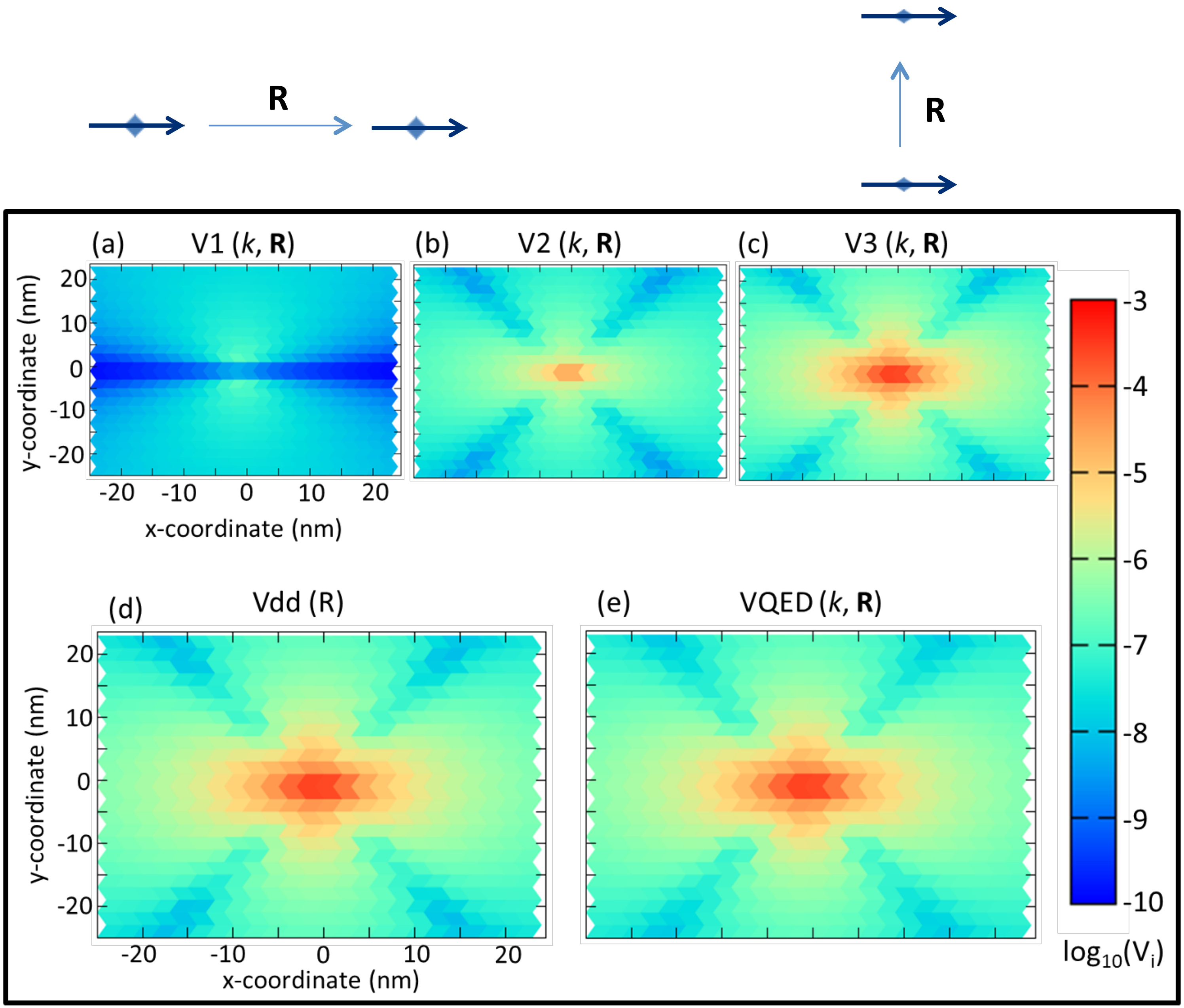
Near-zone	Intermediate Zone	Far Zone
$kR << 1$	$kR \sim 1$	$kR >> 1$
$R << ƛ$	$R \sim ƛ$	$R >> ƛ$

Orientational Factors

$$\theta_{lj}^{vac}\left(k,\hat{\mathbf{R}}\right)=\frac{k^{3}e^{iKR}}{4\pi\varepsilon_{0}}\left[\left(\delta_{lj}-3\hat{R}_{l}\hat{R}_{j}\right)\left(\frac{1}{k^{3}R^{3}}-\frac{i}{k^{2}R^{2}}\right)-\left(\delta_{lj}-R_{l}R_{j}\right)\frac{1}{kR}\right]$$

- Orientational factor for near- and intermediate-transfer
- This couples molecules via both longitudinal and transverse fields

- Orientational factor for free space transfer
- This couples molecules via transverse fields only


R
R
(a) V1 (k, R)
(b) V2 (k, R)
(c) V3 (k, R)
(d) Vdd (R)
(e) VQED (k, R)
y-coordinate (nm)
x-coordinate (nm)
20
10
0
-10
-20
-3
-4
-5
-6
-7
-8
-9
-10
log10(Vi)

The photon field

- The character of the field will change significantly as we move from near to far zone.
- In the near-zone both longitudinal and transverse components are involved in coupling
- In the far zone, only transverse components of the field are relevant
- We are particularly interested in orientational characteristics of the field as we move from near to the far zone

Plane wave description of photon fields

$$e^{ik\cdot r} = \sum_l \frac{\left(i\vec{k}\cdot\vec{r}\right)}{l!} = 1 + i\left(\vec{k}\cdot\vec{r}\right) - \frac{\left(\vec{k}\cdot\vec{r}\right)^2}{2} - \frac{i\left(k\cdot r\right)^3}{6} + \cdots$$

- This expression invites one to interpret the multipolar contributions with respect to the field of the photon.
- The first term relates to the transition dipole moment, the second to the magnetic dipole or the transition quadrupole moment, etc.,…
- Only the full expression defines the complete field

z propagation in terms of spherical waves

$$e^{i\vec{k}\cdot\vec{z}} = \sum_J \sum_l i^l \left[4\pi(2l+1)\right]^{\frac{1}{2}} j_l(kr)\langle l10n|Jn\rangle Y_{J\ln}(\vartheta,\varphi)$$

$j_l(kr)$ Radial part Bessel functions of half order

$\langle l10n|Jn\rangle$ Clebsch-Gordon Coefficients

$$Y_{J\ln}(\vartheta,\varphi) = \sum_n \sum_m \langle l1\mathrm{mn}|JM\rangle Y_{lm} e_{1n}$$ Vector Spherical Harmonics

Angular Momentum; Brink and Satchler, Oxford Publishing, (1963, Third Ed. 1993)

Vector Spherical Harmonics and light

$$Y_{J\,l\,n}(\vartheta,\varphi)=\sum_{n}\sum_{m}\langle l1\mathrm{mn}|JM\rangle Y_{lm}e_{1n}$$

$e_{1\,-1}, e_{1\,0}, e_{1\,+1}$ Polarization unit vectors

The laws of addition of angular momentum say;

For $l\neq 0 \rightarrow J=l+1,\ l,\ l-1$

From any SSH Y_{lm} there are only three possible VSH $Y_{l+1\ l\ M}, Y_{l\ l\ M}, Y_{l-1\ l\ M}$

Usually these are written in terms of *J*

$$Y_{J\ J\text{-}1\ M}, Y_{J\ J\ M}, Y_{J\ J+1\ M}$$

Properties Vector Spherical Harmonics

$$\hat{J}^2 \left| J \ ,l \ ,M \right\rangle = \left[J \left(J+1 \right) \right]^{1/2} \hbar \left| J,\, l,\, M \right\rangle$$

$$\hat{J}_z \left| J \ ,l \ ,M \right\rangle = M\hbar \left| J,\, l,\, M \right\rangle$$

$$\left\langle J,\, l,\, M \middle| J' \ ,l' \ ,M' \right\rangle = \delta_{J,J'} \delta_{l,l'} \delta_{M,M'}$$

With

$$\left\langle J,\, l,\, M \right| = \left| J,\, l,\, M \right\rangle^* = \left(-1 \right)^{l+J+M+1} \left| J \ ,l \ ,-M \right\rangle$$

Multipole radiation from VSH

$$l = J \rightarrow Y_{JJM}$$

This is perpendicular to *k* and represents the magnetic 2^J-pole

$$\Xi_{J,J\pm1,M} = \sqrt{\frac{J}{2J+1}}\, Y_{J,J+1,M} + \sqrt{\frac{J+1}{2J+1}}\, Y_{J,J-1,M}$$

This the electric 2^J-pole radiation and is orthogonal to both *k* and Y_{JJM}

Note that this combination ensures cancellation of longitudinal fields at large distances.

Electric dipole radiation: E1 transitions

$$J = 1,\ l = J - 1 = 0$$

$$Y_{10+1} = Y_{00} \cdot e_{1\ +1}$$

Left circularly polarized light

$$Y_{100} = Y_{00} \cdot e_{1\ 0}$$

Longitudinal fields

$$Y_{10-1} = Y_{00} \cdot e_{1\ -1}$$

Right circularly polarized light

R. Grinter, J. Phys. B: At., Mol. Opt. Phys. 41, 095001 (2008).

Electric dipole radiation: E1 transitions

$$J = 1,\ l = J + 1 = 2$$

$$Y_{12+1} = \frac{1}{\sqrt{10}}\left\{\sqrt{6}Y_{2+2} \cdot e_{1-1} - \sqrt{3}Y_{2+1} \cdot e_{10} + Y_{20} \cdot e_{1+1}\right\}$$

$$Y_{120} = \frac{1}{\sqrt{10}}\left\{\sqrt{3}Y_{2+1} \cdot e_{1-1} - \sqrt{2}Y_{20} \cdot e_{10} + \sqrt{3}Y_{2-1} \cdot e_{1+1}\right\}$$

$$Y_{12-1} = \frac{1}{\sqrt{10}}\left\{Y_{20} \cdot e_{1-1} - \sqrt{3}Y_{2-1} \cdot e_{10} + \sqrt{6}Y_{2-2} \cdot e_{1+1}\right\}$$

Magnetic dipole radiation

$J=1,\ l=J=1:\mathrm{M1\ transitions}$

$$Y_{11+1}=\frac{1}{\sqrt{2}}\left\{Y_{1\ +1}\cdot e_{1\ 0}-Y_{1\ 0}\cdot e_{1\ +1}\right\}$$

$$Y_{110}=\frac{1}{\sqrt{2}}\left\{Y_{1\ +1}\cdot e_{1\ -1}-Y_{1\ -1}\cdot e_{1\ +1}\right\}$$

$$Y_{11-1}=\frac{1}{\sqrt{2}}\left\{Y_{10}\cdot e_{1\ -1}-Y_{1\ -1}\cdot e_{1\ 0}\right\}$$

Electric quadrupole radiation

$J = 2,\ l = J - 1 = 1$: E2 transitions

Note there is also a set for $l = J + 1$

$$Y_{21+2} = Y_{1\ +1} \cdot e_{1\ +1}$$

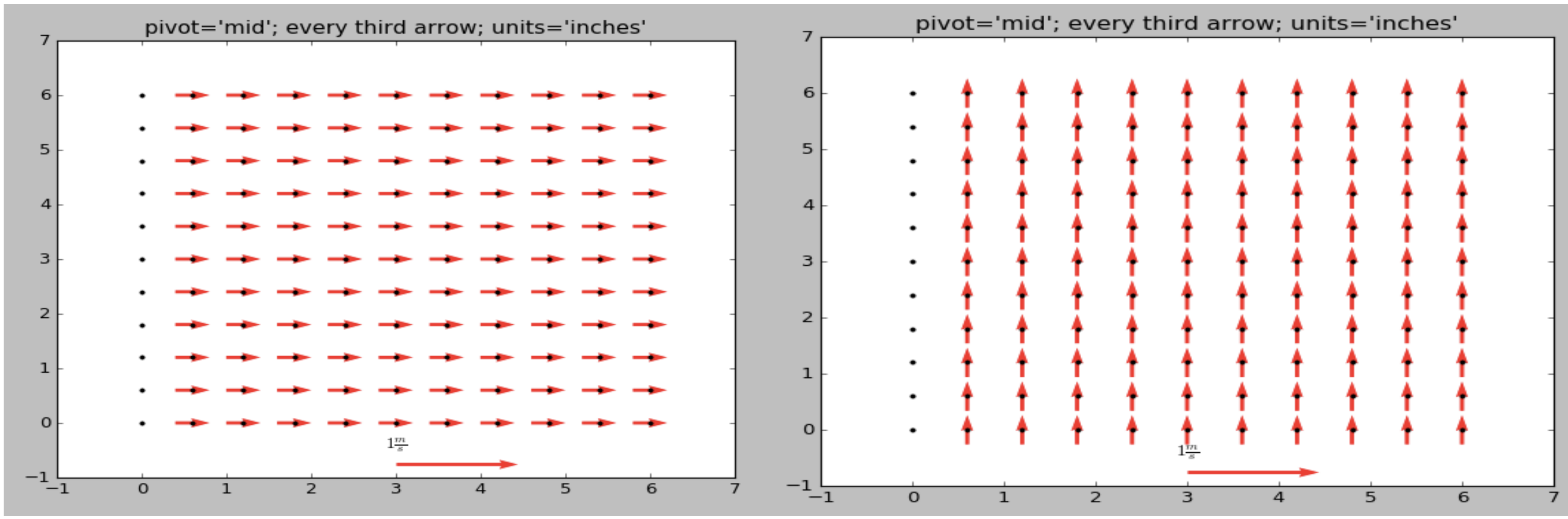
$$Y_{21-1} = \frac{1}{\sqrt{2}} \left\{ Y_{1\,0} \cdot e_{1\ -1} + Y_{1\ -1} \cdot e_{1\,0} \right\}$$

$$Y_{21+1} = \frac{1}{\sqrt{2}} \left\{ Y_{1\ +1} \cdot e_{1\ 0} + Y_{1\ 0} \cdot e_{1\ +1} \right\}$$

$$Y_{21-2} = Y_{1\ -1} \cdot e_{1\ -1}$$

$$Y_{210} = \frac{1}{\sqrt{6}} \left\{ Y_{1\ +1} \cdot e_{1\ -1} + 2Y_{1\,0} \cdot e_{1\,0} + Y_{1\ -1} e_{1\ +1} \right\}$$

Visualization of VSH



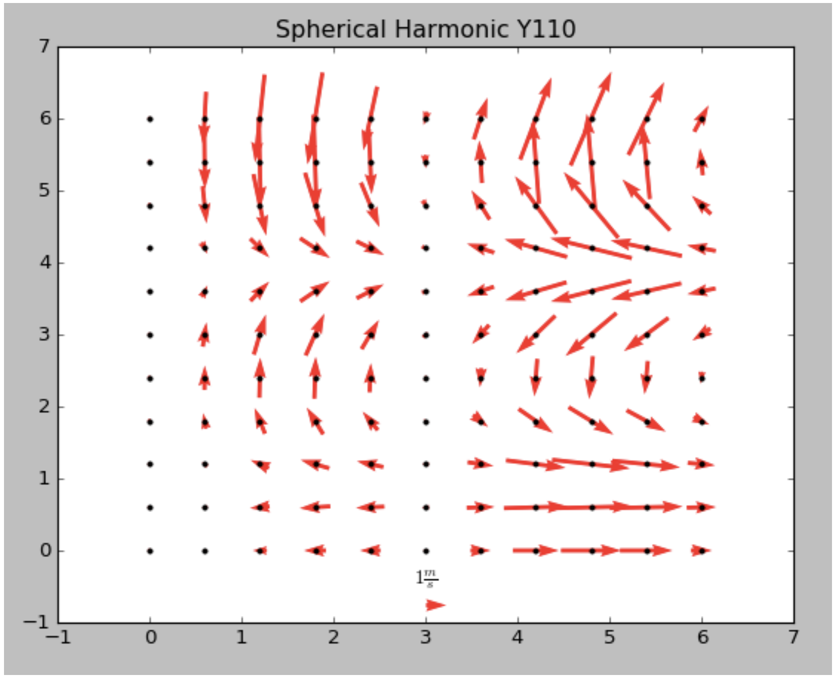
$$Y_{10-1} = Y_0^0 \cdot e_{1-1}$$

Right polarised light

$$Y_{10+1} = Y_0^0 \cdot e_{1+1}$$

Left polarised light

Y_{110} Magnetic multipole transition



$$Y_{110} = \left(1/\sqrt{2}\right)\left(Y_{1+1} \cdot e_{1+1} - Y_{1-1} \cdot e_{1+1}\right)$$

Back to Resonance Energy Transfer

R. Grinter and G. A. Jones, *J. Chem. Phys*. 145, 074107, (2016).

Using spherical polar basis vectors

$$Y_{J,l,M} = \Theta_{J,l,M}\hat{\Theta} + \Phi_{J,l,M}\hat{\Phi} + R_{J,l,M}\hat{R}$$

$$e_{1-1} = \frac{e^{-i\varphi}}{\sqrt{2}}\left\{+\cos\vartheta\hat{\Theta} - i\hat{\Phi} + \sin\vartheta\hat{R}\right\}$$

$$e_{10} = -\sin\vartheta\hat{\Theta} + \cos\vartheta\hat{R}$$

$$e_{1+1} = \frac{e^{+i\varphi}}{\sqrt{2}}\left\{-\cos\vartheta\hat{\Theta} - i\hat{\Phi} - \sin\vartheta\hat{R}\right\}$$

The electric field via VSH

The VSH theory requires that the electric field associated with any particular transition is described by a combination of two VSHs both of which have the same *J* and *M* but different *l* numbers;

$$l = J - 1,\ l = J + 1$$

We can write the overall electric field of a photon as

$$\vec{E} = A_J^E e^{iM\varphi} \Big\{ a_{J-1} h_{J-1}^{(1)}(kr) \Big[\Theta_{J,\,J-1,\,M} \hat{\Theta} + \Phi_{J,\,J-1,\,M} \hat{\Phi} + R_{J,\,J-1,\,M} \hat{R} \Big]$$
$$+ a_{J+1} h_{J+1}^{(1)}(kr) \Big[\Theta_{J,\,J+1,\,M} \hat{\Theta} + \Phi_{J,\,J+1,\,M} \hat{\Phi} + R_{J,\,J+1,\,M} \hat{R} \Big] \Big\}$$

$h_n^{(1)} = j_n + i n_n$ Hankel function for travelling waves

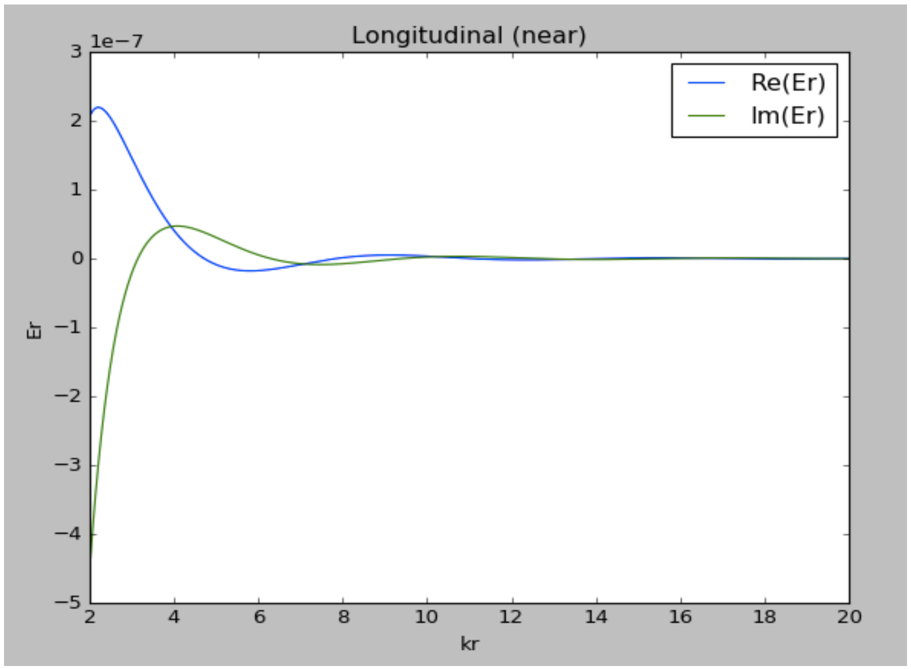
Electric field in the *z* - direction

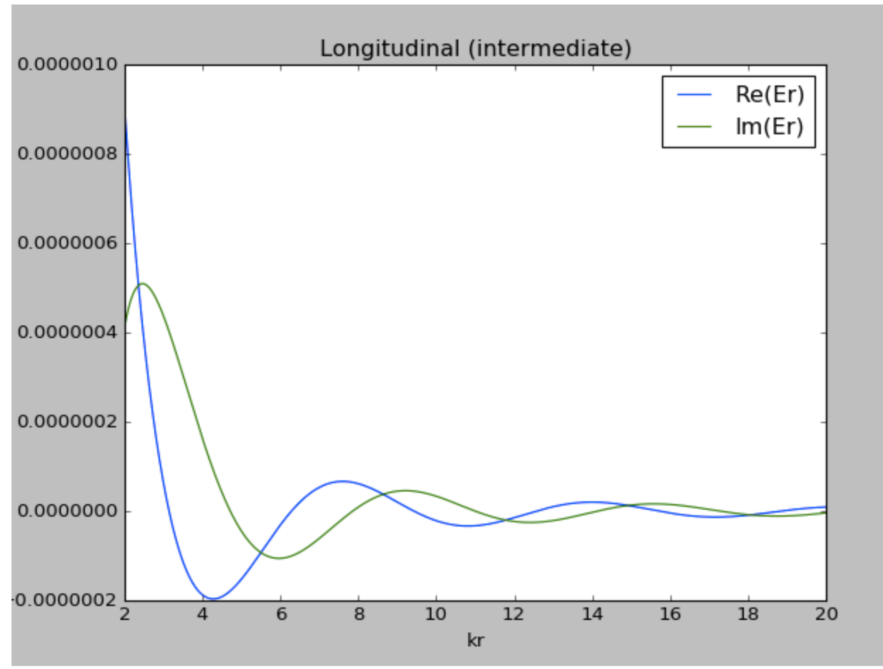
$$\vec{E} = E_R \hat{R} + E_\Theta \hat{\Theta}$$

$$E_R \equiv E_{\parallel} = \frac{2\vec{\mu}k^3}{4\pi\varepsilon_0} \exp(ikR) \left[-\frac{i}{(kR)^2} + \frac{1}{(kR)^3} \right] \cos\vartheta$$

$$E_\Theta \equiv E_{\perp} = \frac{\vec{\mu}k^3}{4\pi\varepsilon_0} \exp(ikR) \left[-\frac{1}{kR} - \frac{i}{(kR)^2} + \frac{1}{(kR)^3} \right] \sin\vartheta$$

Longitudinal components

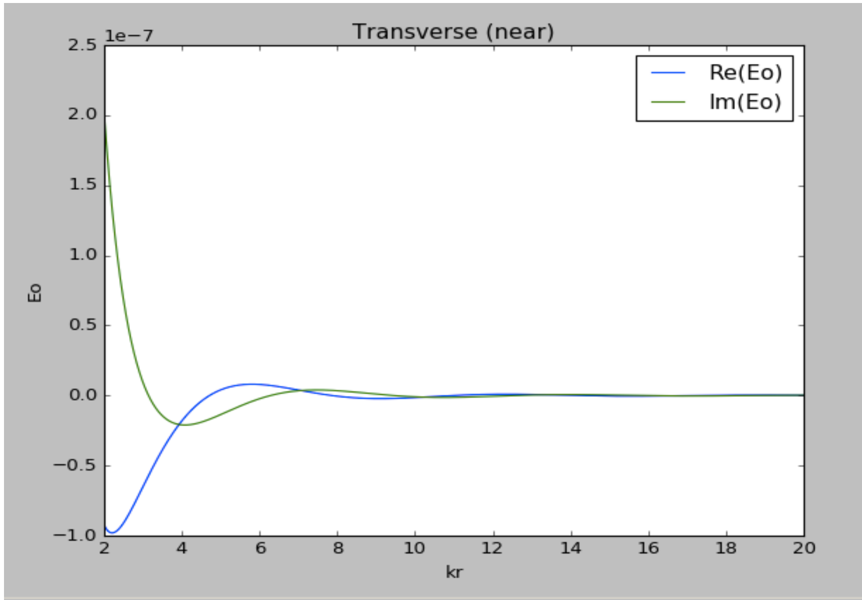


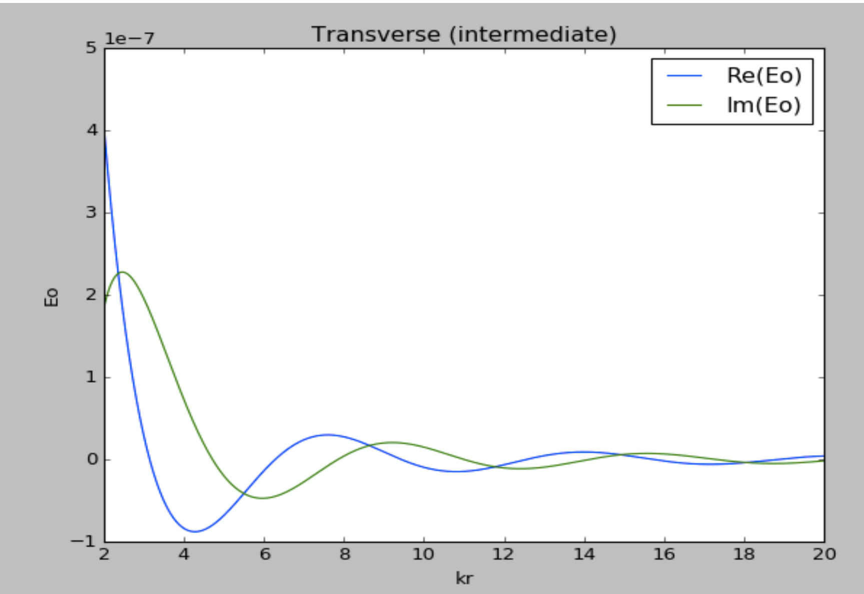


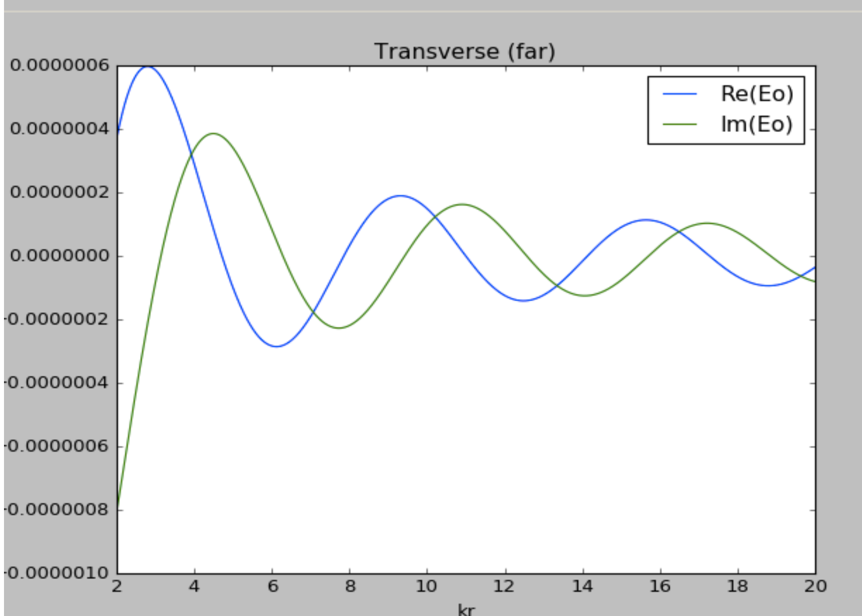
$$E_R \equiv E_{||} = \frac{2\vec{\mu}k^3}{4\pi\varepsilon_0}\exp(ikR)\left[-\frac{i}{(kR)^2}+\frac{1}{(kR)^3}\right]\cos\vartheta \qquad \vartheta = 0$$

Equation 3.4a: R. Grinter and G. A. Jones, *J. Chem. Phys.* 145, 074107, (2016).

Transverse Component







$$\sin\vartheta = 1$$

$$E_\Theta \equiv E_\perp = \frac{\vec{\mu}k^3}{4\pi\varepsilon_0}\exp(ikR)\left[-\frac{1}{kR} - \frac{i}{(kR)^2} + \frac{1}{(kR)^3}\right]\sin\vartheta$$

The electronic coupling: arbitrary orientation

$$\mathrm{Re}(W) = -\frac{k^3}{2\pi\varepsilon_0}\left\{M'_R\right\}\left[\frac{\sin kR}{(kR)^2} + \frac{\cos kR}{(kR)^3}\right] + \frac{k^3}{4\pi\varepsilon_0}\left\{M'_\Theta + M'_\Phi\right\}\left[\frac{\cos kR}{kR} - \frac{\sin kR}{(kR)^2} - \frac{\cos kR}{(kR)^3}\right]$$

$$\mathrm{Im}(W) = -\frac{k^3}{2\pi\varepsilon_0}\left\{M'_R\right\}\left[-\frac{\cos kR}{(kR)^2} + \frac{\sin kR}{(kR)^3}\right] + \frac{k^3}{4\pi\varepsilon_0}\left\{M'_\Theta + M'_\Phi\right\}\left[\frac{\sin kR}{kR} + \frac{\cos kR}{(kR)^2} - \frac{\sin kR}{(kR)^3}\right]$$

$$M'_R = \mu'_R\left[+\mu_x \sin\vartheta\cos\varphi + \mu_y \sin\vartheta\sin\varphi + \mu_z\cos\vartheta\right]$$

$$M'_\Theta = \mu'_\Theta\left[-\mu_x \cos\vartheta\cos\varphi - \mu_y \cos\vartheta\sin\varphi + \mu_z\sin\vartheta\right]$$

$$M'_\Phi = \mu'_\Phi\left[+\mu_x \sin\varphi - \mu_y \cos\varphi\right]$$

R. Grinter and G. A. Jones. *J. Chem. Phys.* 145, 074107, (2016).

Overview of the VSH description

The spherical wave description of photon fields is complementary to the plane wave description, in particular;

- It is very useful in the case of spherically symmetric and isotropic situations
- There is a rigorous definition of different types of transitions (electric dipole, magnetic dipole, electric quadrupole, etc.) and this can in principle be linked directly to electronic states
- The both electric and magnetic fields can be easily extracted and mapped over space (and in principle time).
- The transverse and longitudinal field components fall out naturally

Future Directions

There are several possible directions this work can be taken;

- The development of a graphical interface for visualizing vector fields on the surface of a sphere
- Investigation of higher order effects. e.g. quadrupole emission and higher order couplings in EET
- Application to high a.m. light?

People

- Dr Roger Grinter – Major collaborator on this project
- Dr Colm Gillis - Recently graduated PhD student
- Mr James Frost – PhD student
- Mr Dale Green – PhD student
- Prof Andrews & his group