Resonance Energy Transfer, Interatomic Coulombic and Auger Decay: A Macroscopic-QED Approach

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Abstract

Efficient processes for migration of excitation include resonance energy transfer (RET), in which a single virtual photon is exchanged between an excited donor and an unexcited acceptor, and interatomic Coulombic decay (ICD), in which an initially excited or inner-shell ionised donor relaxes, and an acceptor subsequently absorbs the energy resulting in the emission of a slow electron into the continuum. This slow electron can be damaging to biological tissue. The related, and in some cases competing Auger decay, describes a similar process but within a single atom or molecule which simultaneously acts as donor and acceptor. In this case the exchanged photon energy has to be in the X-ray region.

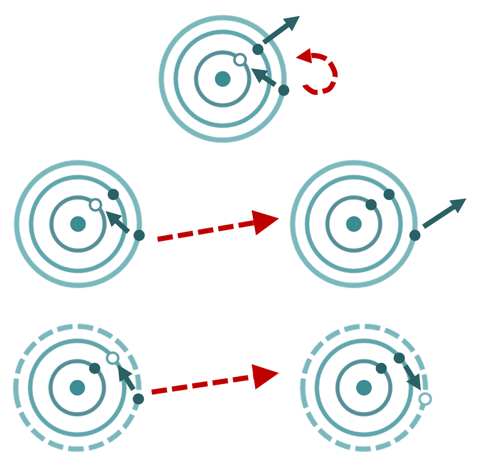
All of these processes may be influenced in an environment by surface or medium polaritons. We study them in the framework of macroscopic QED, where the polaritonic field-matter excitations are encoded in the Green's tensor for the electric and magnetic fields. We present an analytical expression for the Auger decay rate in vacuum as well as its enhancement and suppression by a nearby dielectric surface. We compare ICD rates to Auger rates in different environments. We also study discriminatory RET between chiral molecules and the modification of the free space rate by a solvent medium.

Introduction

Auger decay $\qquad A^{+*} \longrightarrow A^{++} + e^-$

Interatomic Coulombic decay (ICD): $\qquad A^{+*} + B \longrightarrow A^{+} + B^{+} + e^-$

Resonant energy transfer (RET): $\qquad A^{*} + B \longrightarrow A + B^{*}$



Theoretical framework

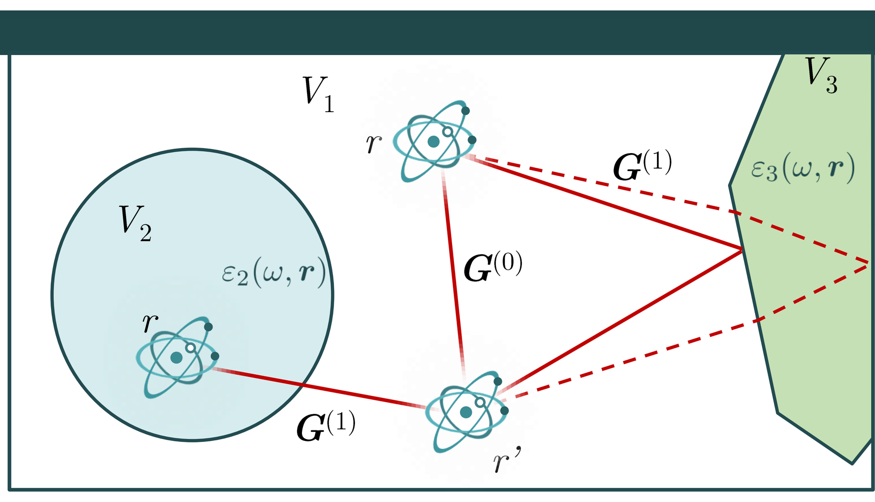
Macroscopic quantum electrodynamics:

→Classical Green's tensor [3]

≙ propagator for excitations of body-field system

$$\hat{\boldsymbol{E}}(\boldsymbol{r}) = \int_0^\infty \mathrm{d}\omega\, \underline{\hat{\boldsymbol{E}}}(\boldsymbol{r},\omega) + \text{H.c.}$$

$$= \int_0^\infty \mathrm{d}\omega \int \mathrm{d}^3r' \mathrm{i}\frac{\omega^2}{c^2}\sqrt{\frac{\hbar}{\pi\varepsilon_0}\mathrm{Im}\,\varepsilon(\boldsymbol{r}',\omega)}\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot\hat{\boldsymbol{f}}(\boldsymbol{r}',\omega) + \text{H.c.}$$



Schematic propagation of field excitation

Bulk and scattering part: $\boldsymbol{G} = \boldsymbol{G}^{(0)} + \boldsymbol{G}^{(1)}$

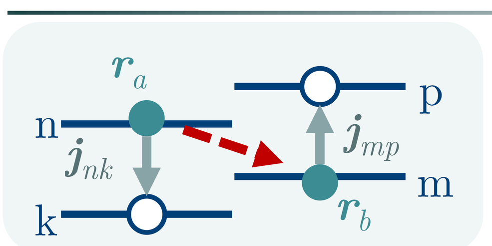
(Second order) Atomic process rate: $\quad \Gamma = \sum_f \frac{\partial}{\partial t}|\langle f|\,\hat{S}^{(2)}(t)\,|i\rangle|^2$

With scattering matrix: $\quad \hat{S}^{(2)}(t) = \frac{1}{\hbar^2}\int_{-\infty}^{t}\mathrm{d}t_a\int_{-\infty}^{t_a}\mathrm{d}t_b\,\hat{V}(t_a)\hat{V}(t_b)$

And minimal coupling: $\quad \hat{V}(t) = \int \mathrm{d}V\,\hat{\rho}(\boldsymbol{r},t)\hat{\phi}(\boldsymbol{r},t) - \hat{\boldsymbol{j}}(\boldsymbol{r},t)\cdot\hat{\boldsymbol{A}}(\boldsymbol{r},t)$

Electron-electron scattering rates in an environment

General:



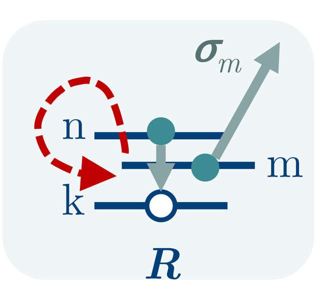
$$\Gamma = \sum_{m,p,n}\delta(\omega_{kn}-\omega_{mp})\frac{2\pi\mu_0^2}{\hbar^2}\left|\iint \mathrm{d}V_a\mathrm{d}V_b\,\boldsymbol{j}^a_{nk}\cdot\mathbf{G}(\boldsymbol{r}_a,\boldsymbol{r}_b,\omega_{kn})\cdot\boldsymbol{j}^b_{mp}\right|^2$$

Integration over electronic structure → High computational effort!

→ Dipole approximation & isotropic averaging:

Auger:

- Source point = absorption point
- Interference with exchange term of indistinguishable electrons



$$\Gamma_{\text{aug}} = \sum_{m,n} 2\pi\sigma(\omega_{kn})\gamma_{nk}\,\mathrm{Tr}\left[\mathbf{G}(\boldsymbol{R},\boldsymbol{R},\omega_{kn})\mathbf{G}^*(\boldsymbol{R},\boldsymbol{R},\omega_{kn})\right] + \Gamma_{\text{intf}}$$

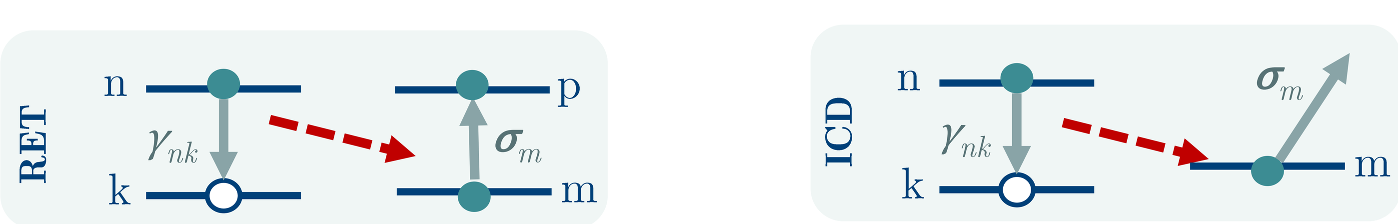
spontaneous decay rate: $\quad \gamma_{nk} = \frac{\omega_{kn}^2|\boldsymbol{d}_{nk}|^2}{3\pi\hbar c^3\varepsilon_0}$

ionisation cross section: $\quad \sigma(\omega_{kn}) = \frac{\pi\omega_{mp}|d_{mp}|^2}{3\varepsilon_0 c\hbar}$

Introducing finite sized atom (Gaussian profile) [4]:

$$\lim_{\delta\boldsymbol{r}\to 0}\mathbf{G}^{(0)}_{\text{gauss}}(\boldsymbol{r},\boldsymbol{r}+\delta\boldsymbol{r},\omega_{kn}) = \int \mathrm{d}V'\frac{e^{-|\boldsymbol{r}'-\boldsymbol{r}|^2/a^2}}{\pi^{3/2}a^3}\mathbf{G}^{(0)}(\boldsymbol{r}',\boldsymbol{r}+\delta\boldsymbol{r},\omega_{kn})$$

RET / ICD:



$$\Gamma_{ab} = \sum_{m,n} 2\pi\sigma(\omega_{kn})\gamma_{nk}\,\mathrm{Tr}\left[\mathbf{G}(\boldsymbol{R}_a,\boldsymbol{R}_b,\omega_{kn})\mathbf{G}^*(\boldsymbol{R}_b,\boldsymbol{R}_a,\omega_{kn})\right]$$

with $\sigma(\omega_{kn})$ = ionisation /absorption cross section for ICD /RET

Auger decay

Free space: Comparison to numerical values in F-like ions:

$$\Gamma^{(0)} = \frac{4c^4}{3\pi^2a^6\omega_{kn}^4}\sigma_{\text{tot}}(\omega_{kn})\gamma_{nk}$$

with $a = \frac{2a_0}{Z-0.3}$ (Slater radius of 1s orbital [5])

a_0 : Bohr radius ; Z : number of protons

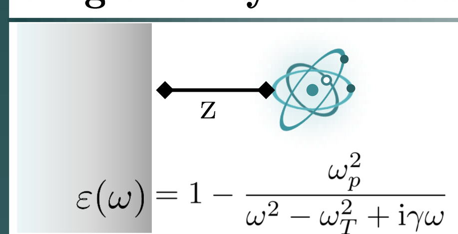
Ion	Z	Analytical $\Gamma^{(0)}/\gamma_{nk}$	Numerical $\Gamma_{\text{num}}/\gamma_{nk}$	relative
Ne^{+}	10	571.5	53.18	10.8
Mg^{3+}	12	285.0	29.08	9.8
Si^{5+}	14	162.6	16.75	9.8
S^{7+}	16	96.2	10.17	9.4
Ar^{9+}	18	59.7	6.46	9.2
Ca^{11+}	20	39.4	4.36	9.0

Γ_{num} : numerical rates given by [6]

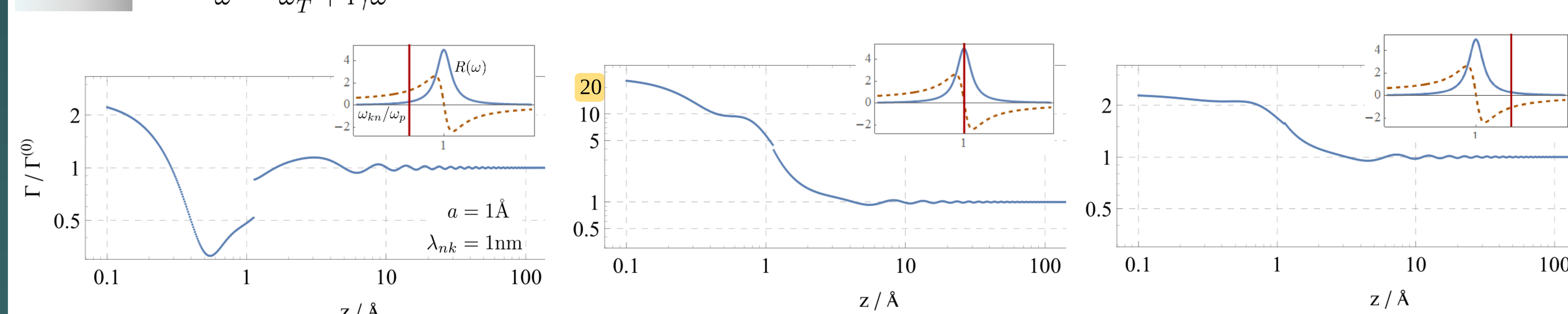
$\sigma_m(\omega_{kn})$: photoionization cross section given by [7].

Next • *Different ion families* • *Find factor* • *Test different atomic size profiles*

Auger decay near dielectric plate:



Next • *Auger in medium* • *Atom assisted Auger decay*



Chiral RET in media

$$\Gamma_{\text{RET}} = \sum_{\lambda_i\in\{e,m\}}\Gamma_{\lambda_1\lambda_2\lambda_3\lambda_4} = 2\pi\frac{c^4}{\omega_{kn}^4}\sum_{\lambda_i}\sigma_{\lambda_1\lambda_3}\gamma_{\lambda_2\lambda_4}\mathrm{Tr}\Big[\mathbf{G}_{\lambda_1\lambda_2}(\boldsymbol{r}_b,\boldsymbol{r}_a)\mathbf{G}^{*T}_{\lambda_3\lambda_4}(\boldsymbol{r}_b,\boldsymbol{r}_a)\Big]$$

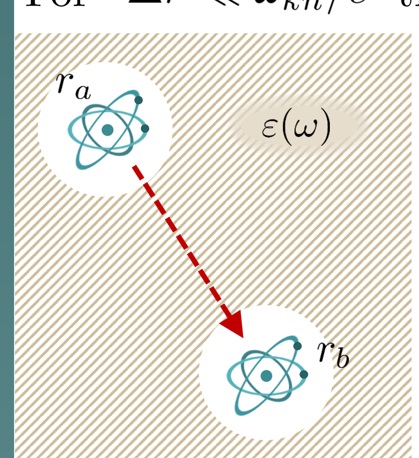
$\mathbf{G}_{ee} = \frac{\omega_{kn}}{\mathrm{i}c}\mathbf{G}\frac{\omega_{kn}}{\mathrm{i}c}$ $\quad$ $\mathbf{G}_{em} = \frac{\omega_{kn}}{\mathrm{i}c}\mathbf{G}\times\nabla_a$	$\sigma_{ee} = \sigma_{\text{abs}}(\omega_{kn})$	$\gamma_{ee} = \gamma_{nk}(\omega_{kn})$
	$\sigma_{mm} \propto \lvert\boldsymbol{m}^{mp}\rvert^2$	$\gamma_{mm} \propto \lvert\boldsymbol{m}^{nk}\rvert^2$
$\mathbf{G}_{mm} = \nabla_b\times\mathbf{G}\times\nabla_a$ $\quad$ $\mathbf{G}_{em} = \nabla_b\times\mathbf{G}\frac{\omega_{kn}}{\mathrm{i}c}$	$\sigma_{em} = -\sigma_{me} \propto \boldsymbol{d}_{mp}\cdot\boldsymbol{m}_{pm}$	$\gamma_{em} = -\gamma_{me} \propto \boldsymbol{d}_{kn}\cdot\boldsymbol{m}_{nk}$

σ_{em} and γ_{me} change sign for different handedness [8]

→ rate discriminates between enantiomers

Example: Chiral RET rate in dielectric medium

For $\Delta r \ll \omega_{kn}/c$ the discriminating part Γ_{discr} of the rate is given by:



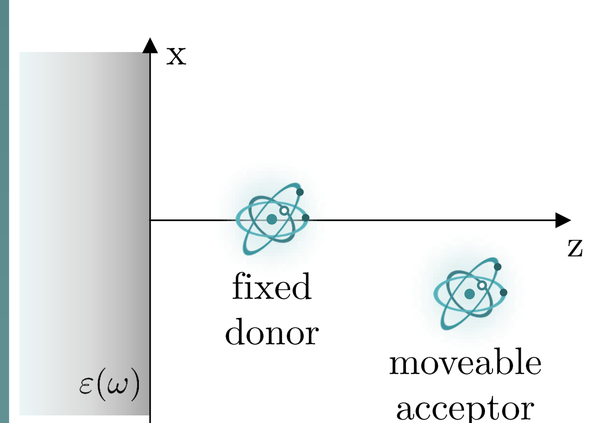
$$\Gamma_{\text{discr}} \approx \Gamma_{eemm} + \Gamma_{mmee}$$

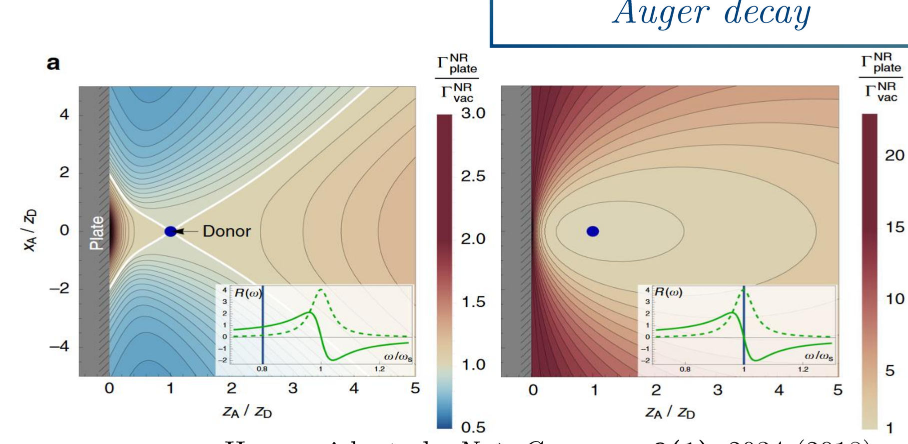
$$= \underbrace{\frac{1}{|\varepsilon(\omega_{kn})|^2}}_{\text{screening}}\underbrace{\left|\frac{3\varepsilon(\omega_{kn})}{2\varepsilon(\omega_{kn})+1}\right|^2}_{\text{LFE}} \times \underbrace{\frac{1}{18\pi c^2\varepsilon_0\hbar}\frac{1}{\Delta r^6}(\boldsymbol{d}_{kn}\cdot\boldsymbol{m}_{nk})(\boldsymbol{d}_{mp}\cdot\boldsymbol{m}_{pm})}_{\text{free space rate}}$$

Next • *Rate in chiral medium*

ICD near dielectric half space

Next • *Relative to Auger decay*





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