Diagrammatics with excited atoms

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Topics:

Diagrammatic techniques in molecular QED

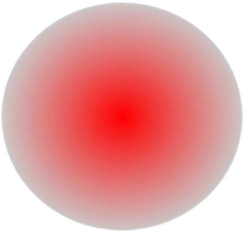
- review: excited atom vs ground state atom - oscillating potentials?
- diagrammatic approach: standard and non-equilibrium
- dispersion forces and FRET

Insight

- essence of the problem in a diagrammatic form
- subtle question: what is an excited atom?

Implications in quantum optics and molecular biophysics

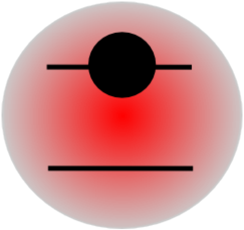
Intramolecular interactions: minimal molecule model

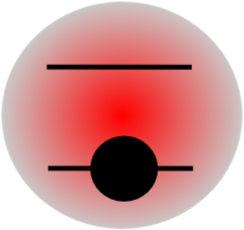


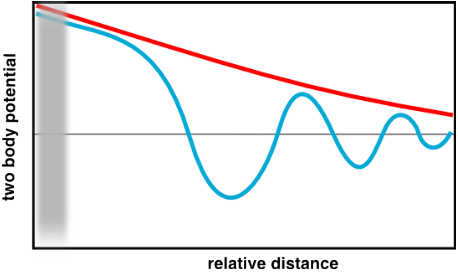
Molecules / atoms

- electrically neutral, no permanent dipole.
- polarizable $\leftrightarrow$ dipole coupling
- single electric dipole transition

Potential between a ground state atom and an excited one?







Well, there's a resonant term and ...

- ... it oscillates!

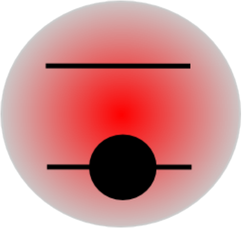
  [Philpott (1966), Gomberoff et al. (1966), Kweon and Lawandy (1993), Power and Thirunamachandran (1993)]

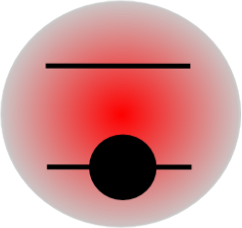
- ... no, it doesn't!

  [Power and Thirunamachandran (1995), Cohen and Mukamel (2003), Sherkunov (2007-2009)]

What exactly is an *excited* atom?

No doubt about two ground state atoms - no resonant term





Dispersion forces

- Thermal and quantum fluctuations
- mutual induction
- potential energy
  - van der Waals (non-retarded)
  - Casimir-Polder (retarded)

But this is not yet the whole story!

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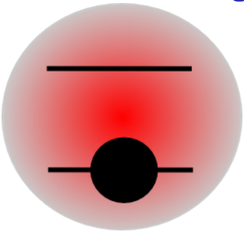

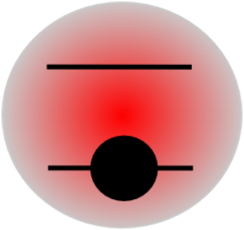

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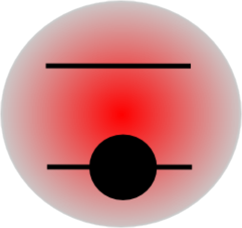
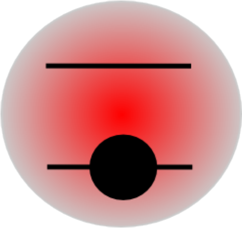
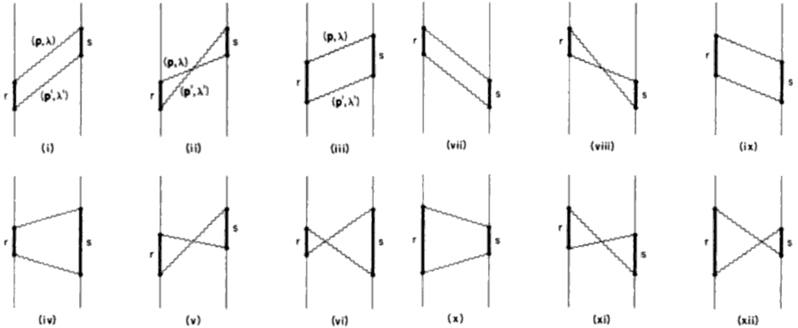




Standard perturbation theory [Craig and Thirunamachandran (1984)]



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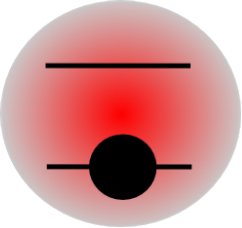
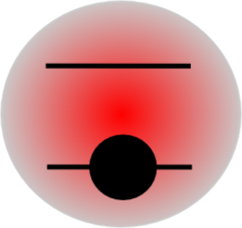
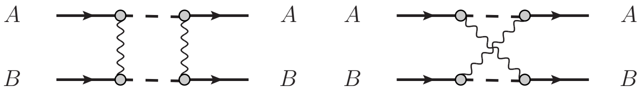




Feynman diagram technique [Schiefele and Henkel (2010)]

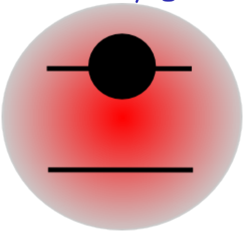


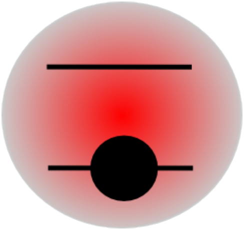
T-matrix approach $\underbrace{\Delta E}_{\textit{energyshift}} + \frac{i}{2}\underbrace{\Gamma}_{\textit{width}} = \langle f|\mathbf{T}|i\rangle$

time-ordered products, Wick's theorem → Feynman diagrams

- very efficient formalism
- universal contribution (no resonances)

Excited state / ground state: FRET





Förster resonant energy transfer (FRET)

- one atom excited distinguishable, no entanglement, ...
- resonant energy transfer [Förster (1948)]
- *"A Mechanical Force Accompanies Fluorescence Resonance Energy Transfer (FRET) "*[Cohen and Mukamel (2003)]
  $\longrightarrow$ Förster force

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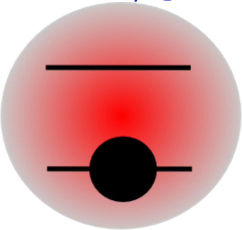

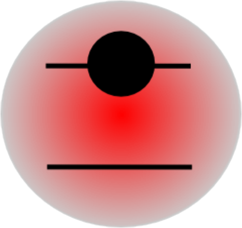

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Limits of Feynman formalism and non-equilibrium QFT

Implications

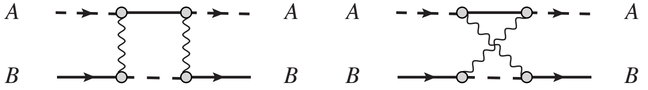
- Feynman technique: $|i\rangle$ *and* $|f\rangle$ known $\longrightarrow$ breaks down
- decay processes contribute
- system can equilibrate

Recipe of non-equilibrium QFT: [Keldysh (1964)]

- define $|i\rangle$ (preparation)
- *free* evolution: $\langle f|\mathbf{T}|i\rangle \mapsto \langle i|S(-\infty,\infty)\mathbf{T}|i\rangle$ $\longrightarrow$ time arrow
- need some more diagrams

Excited state / ground state: diagrammatics

Feynman formalism

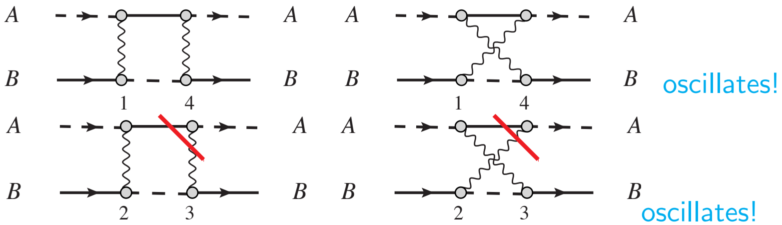


oscillates!

Excited state / ground state: diagrammatics

Keldysh / closed time-path contour formalism

[Sherkunov (2005), Schiefele and Henkel (2010)]



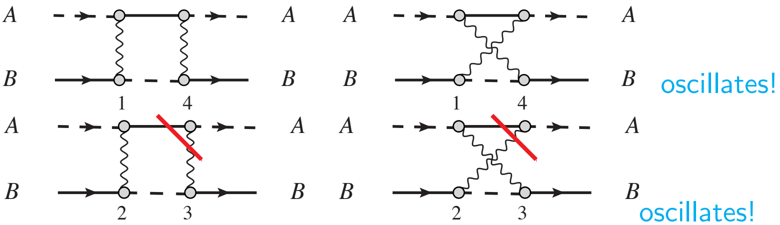
Additional processes

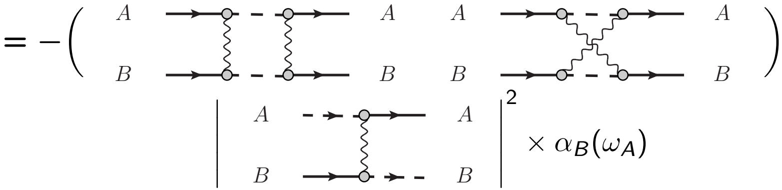
- other final states *constructed* behind the red line
  $\Leftrightarrow$ *free* evolution: $|f\rangle = S(\infty, -\infty)|i\rangle$
- time arrow

Excited state / ground state: diagrammatics

Keldysh / closed time-path contour formalism

[Sherkunov (2005), Schiefele and Henkel (2010)]





- negative ground-state dispersion interaction + FRET
- oscillations cancel: two-body potential does not oscillate!

Assumptions and consequences

Preparation and free evolution (non-entangled, distinguishable)
⇒ non-oscillating resonant contribution

- is due to the Förster transfer process

  [Cohen and Mukamel (2003)]

- decay rates better known than Förster force
- well-tunable through resonance

  [Cohen and Mukamel (2003), Sherkunov (2009)]

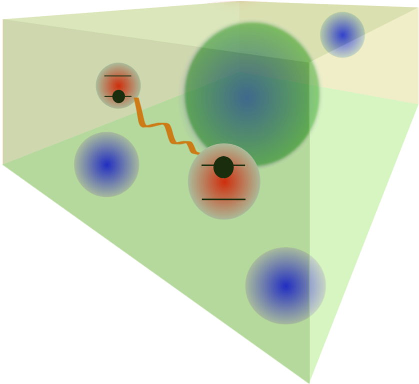
Steady (pumped) state

- could bring back the oscillations!
- analogy to excited atom-wall potential (supposedly oscillating)
- time-scales

Implications in molecular biophysics

Biochemical reactions in a cell: $A + B^* \rightarrow AB$

- diffusion limits kinetics
- pure diffusion gives too low rates [Berg *et al* (1981), Fröhlich (1973)]
- non-oscillating long range Förster force $\rightarrow$ state-selective drift [M. Pettini's group]



temperature, medium, general spectra, pumping?

Take home messages

Diagram technique

- very efficient and intuitive
- non-equilibrium situations are subtle

Ground state atom vs. excited atom

- ancient but obscure problem
- review the conditions of the formalisms used
- free evolution after preparation
  $\longrightarrow$ no oscillation, life-time consistent with Förster transfer

Highly relevant implications from quantum optics to biophysics

Know what you mean when you say excited atom!

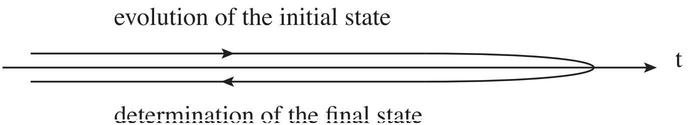
Details: Closed time contour formalism

Green's function, e.g. atom,

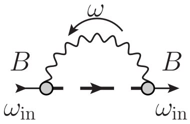
$$g(r', r) = \langle f|\, \overbrace{TS(\infty, -\infty)\Psi(r')\Psi^\dagger(r)}^{\text{time ordering}}\, |i\rangle$$

$$\langle f| = \langle i|\, S(-\infty, \infty)$$

$$\begin{aligned} g(r', r) &= \langle i|S(-\infty, \infty)TS(\infty, -\infty)\Psi(r')\Psi^\dagger(r)|i\rangle \\ &=: \langle i|\, \underbrace{T_c S_c(-\infty, -\infty)\Psi(r')\Psi^\dagger(r)}_{\text{contour ordering}}\, |i\rangle \end{aligned}$$



Details: Formulae



$$= -i \int \frac{d\omega}{2\pi} \, \frac{D_{11}(\omega, r_B, r_B)}{\omega - \omega^B + i\epsilon}$$

Now dress the photon propagator D_{11} by the second (excited atom)

$$\begin{aligned} D_{11}^{g,e}(x', x) = & - i \int dx_1 \int dx_2 \, \{ \\ & \quad D_{11}(x', x_1)\Pi_R^e(x_1, x_2)D_{11}(x_2, x) - \\ & - D_{11}(x', x_1)\Pi_{12}^e(x_1, x_2)D_{11}(x_2, x) + \\ & + D_{11}(x', x_1)\Pi_{12}^e(x_1, x_2)D_{11}(x_2, x) - \\ & - D_{11}(x', x_1)\Pi_{12}(x_1, x_2)D_A(x_2, x) + \\ & + \mathcal{O}(D_{12}, \Pi_{22})\} \ . \end{aligned}$$