Toward a NEGF description of photoexcited organic molecules

Gianluca Stefanucci

(1) Universita' di Roma Tor Vergata, Italy
(2) INFN, Sezione Tor Vergata Roma, Italy

Kiel 10-12 March 2019

Outline

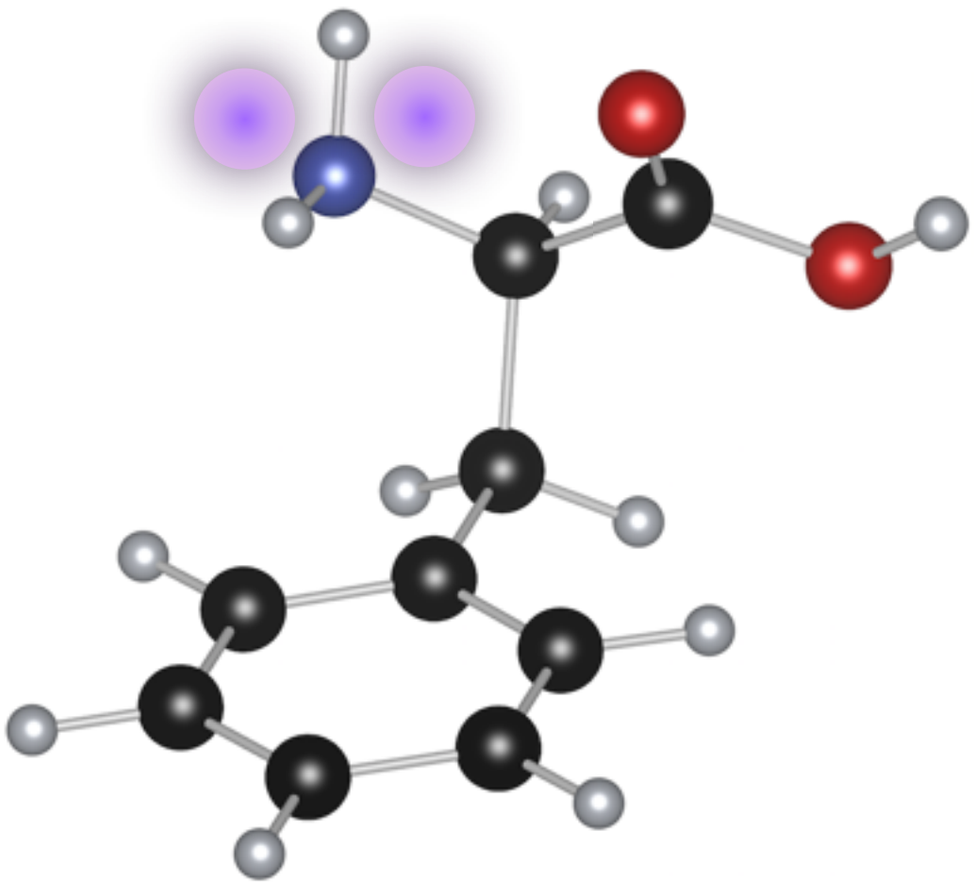
Setting the physical problem and fundamental equations

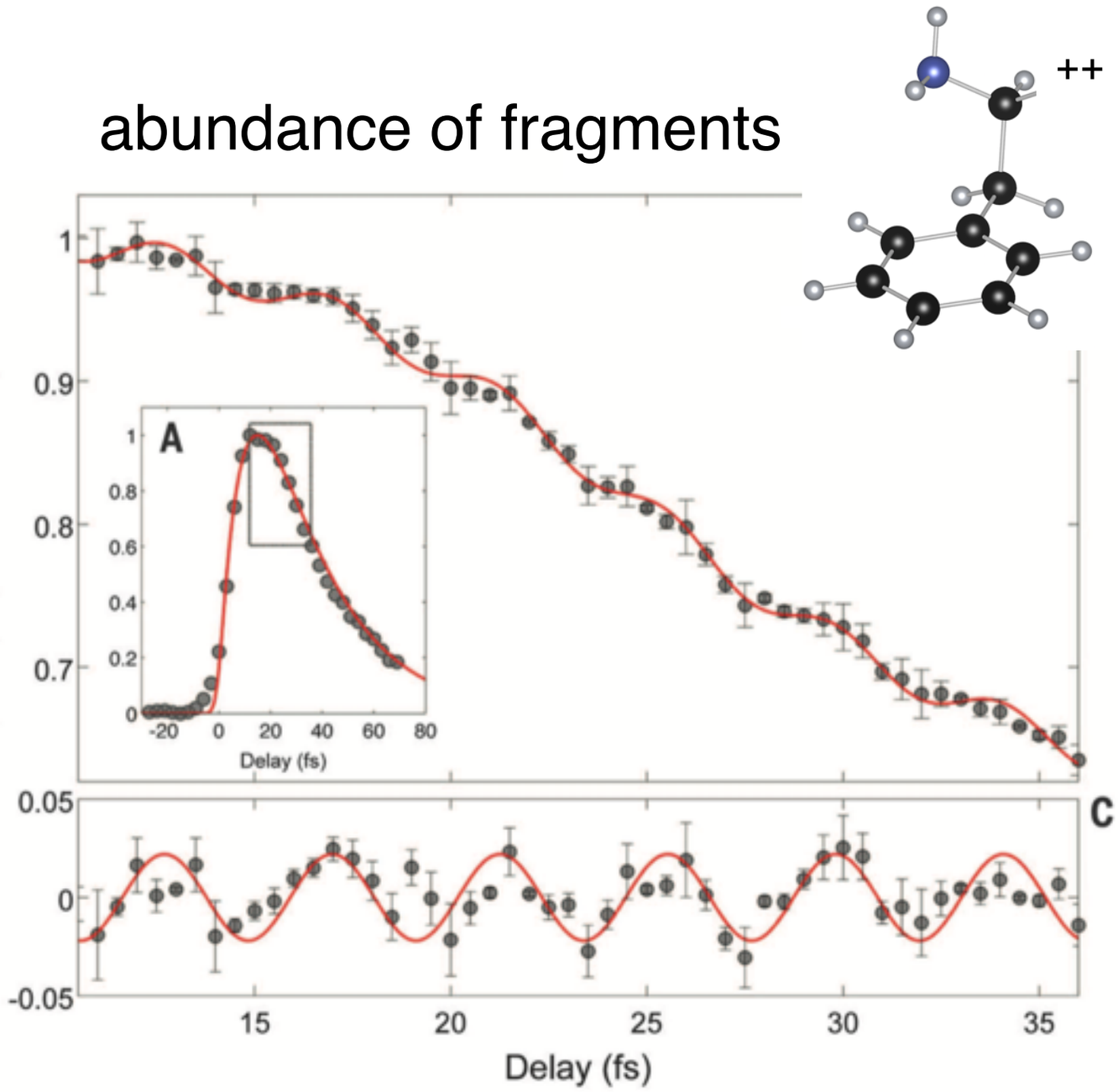
Problems and current solutions

1. initial state
2. mixture consistency
3. ionization
4. correlation in excited states
5. Auger decays

Charge Migration in Phenylalanine

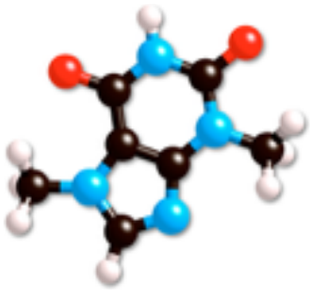
— J. Phys. Chem. Lett. **9**, 1353 (2018) —



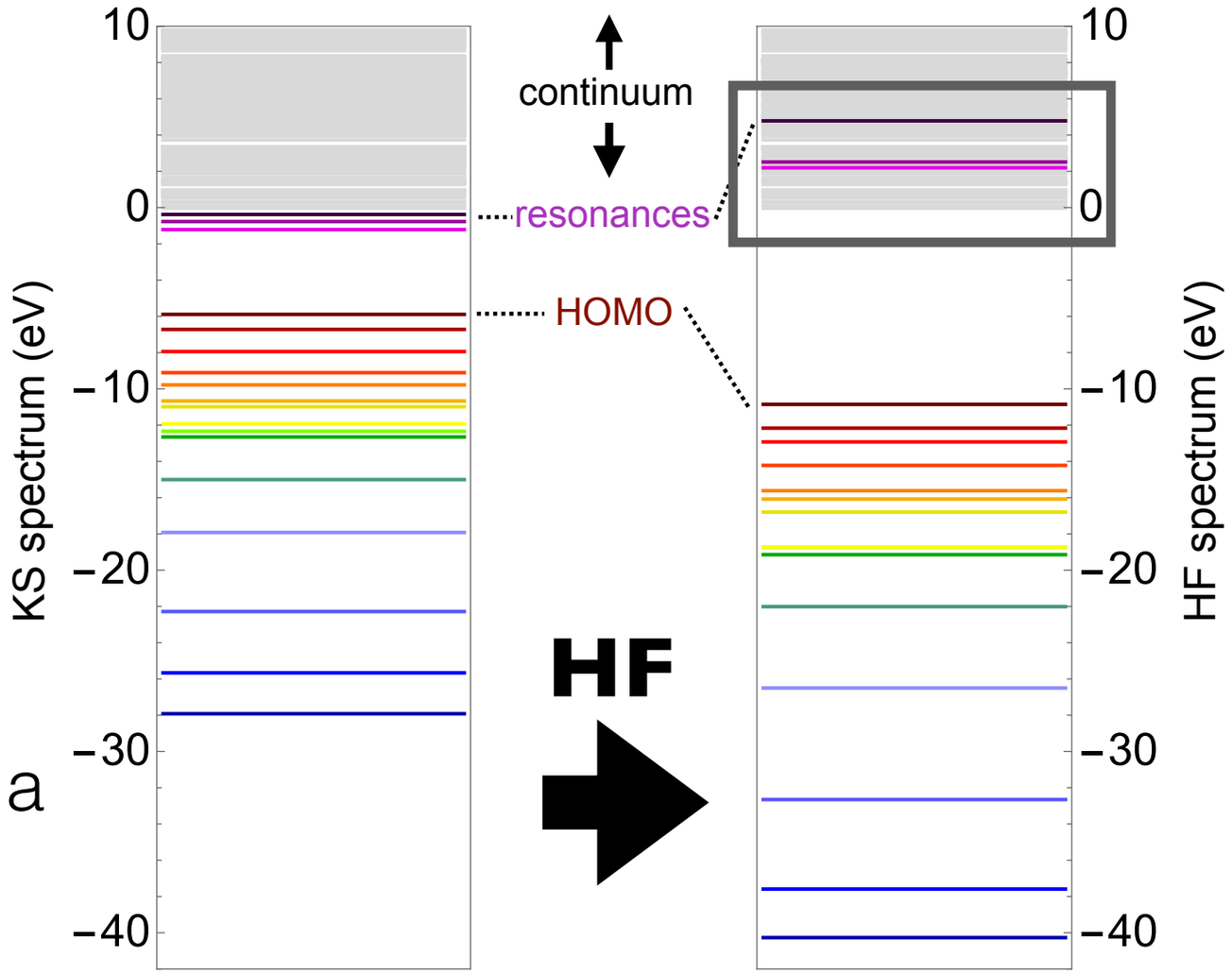


Experiment Calegari et al. Science 2014

Choose a convenient basis



DFT



How good this Hamiltonian is depends on the physics we are interested in. Here we assume it is a **good Hamiltonian**

Many-body Hamiltonian

$$\hat{H} = \sum_{ij} h_{ij} \hat{d}_i^\dagger \hat{d}_j + \frac{1}{2} \sum_{ijmn} v_{ijmn} \hat{d}_i^\dagger \hat{d}_j^\dagger \hat{d}_m \hat{d}_n + \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k$$

$$h = h^{\mathrm{KS}} - V_{\mathrm{Hxc}}$$

Wavefunction description

After the pulse

$$|\Psi^N(t)\rangle = \alpha_0^N e^{-iE_0^N t}|\Psi_0^N\rangle + \sum_{Ik} \alpha_{Ik}^{N-1} e^{-i(E_I^{N-1}+\epsilon_k)t}\hat{c}_k|\Psi_I^{N-1}\rangle$$

neutral state

cationic states

Single-particle density matrix

$$\rho_{ij}(t) = \langle\Psi(t)|\hat{d}_j^\dagger \hat{d}_i|\Psi(t)\rangle = \rho_{ij}^N + \rho_{ij}^{N-1}(t)$$

Time-dependence of observables contained in $\rho^{N-1}(t)$, a quantity **independent** of ρ^N

NEGF description

$$\left[i\frac{d}{dz} - h_{\mathrm{HF}}(z)\right] G(z,z') = \delta(z,z') + \mathcal{I}_{\mathrm{ion}}(z,z') + \mathcal{I}_{\mathrm{c}}(z,z')$$

$$\mathcal{I}_{\dots}(z,z') \equiv \int d\bar{z}\, \Sigma_{\dots}(z,\bar{z}) G(\bar{z},z')$$

$\Sigma_{\mathrm{c},ij}(z,\bar{z})$: correlation self-energy

$\Sigma_{\mathrm{ion},ij}(z,\bar{z}) = \sum_k \left(\mathbf{E}(z)\cdot\mathbf{D}_{ik}\right) g_k(z,\bar{z}) \left(\mathbf{E}(\bar{z})\cdot\mathbf{D}_{kj}\right)$: ionization self-energy

GKBA

$$\dot{\rho}(t) + i\left[h_{\mathrm{HF}}(t), \rho(t)\right] = -\mathcal{I}_{\mathrm{c}}(t) - \mathcal{I}_{\mathrm{ion}}(t) - \mathrm{h.c.}$$

$$\mathcal{I}_{\dots}(t) = \mathcal{I}^{<}_{\dots}(t,t)$$

PROBLEMS and CURRENT SOLUTIONS

1 Initial state

$$\dot{\rho}(t) + i\left[h_{\mathrm{HF}}(t), \rho(t)\right] = -\mathcal{I}_{\mathrm{c}}(t) - \mathrm{h.c.}$$

computed with an adiabatic switched-on interaction

$$\rho_0 = \lim_{t\to\infty} \rho(t),$$

initial-correlation integral (PRB 2018)

$$\dot{\rho}(t) + i\left[h_{\mathrm{HF}}(t), \rho(t)\right] = -\mathcal{I}_{\mathrm{c}}(t) - \mathcal{I}_{\mathrm{ion}}(t) - \mathcal{I}_{\mathrm{ic}}(t) - \mathrm{h.c.},$$

low-intensity fields imply **highly accurate thermalizations** for the pump-induced variations to overcome remnant fluctuations; **out of reach**

thermalization is not always guaranteed: **GKBA stability is system dependent**

Huge effort to correct only slightly the HF ground state

1

Initial state
Current solution in 2nd Born

In the absence of external field

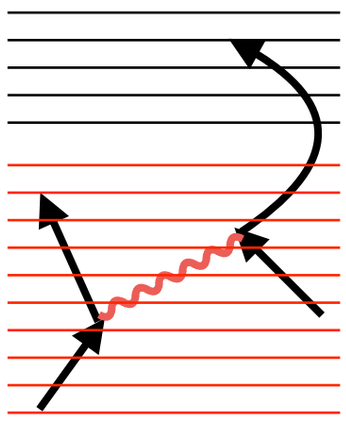
$$\dot{\rho}(t) + i\left[h_{\rm HF}(t), \rho(t)\right] = -\mathcal{I}_{\rm c}(t) - {\rm h.c.}$$

Explicitely $\mathcal{I}_{\rm c} = \mathcal{I}_{\rm c}^{<}(t) - \mathcal{I}_{\rm c}^{>}(t)$

$$w_{mqsj} = v_{mqsj} - v_{mqjs}$$

$$\mathcal{I}_{\rm c}^{\lessgtr}(t) = \sum_{mnpqrsk} v_{irpn} w_{mqsj} \int_0^t dt'\; G^{\lessgtr}_{nm}(t,t') G^{\lessgtr}_{pq}(t,t') G^{\gtrless}_{sr}(t',t) G^{\gtrless}_{kj}(t',t).$$

We split the set of interacting HF levels in **occupied** and **unoccupied**.
We **set to zero** all Coulomb integrals with **more than two** indices in the unoccupied sector

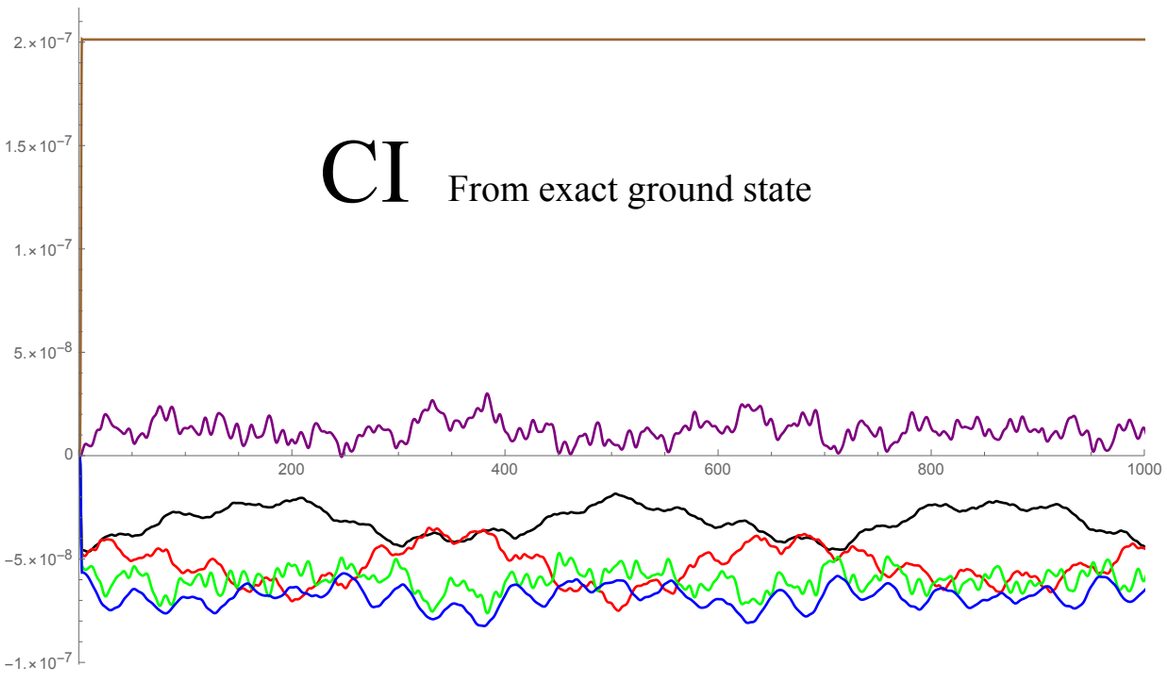


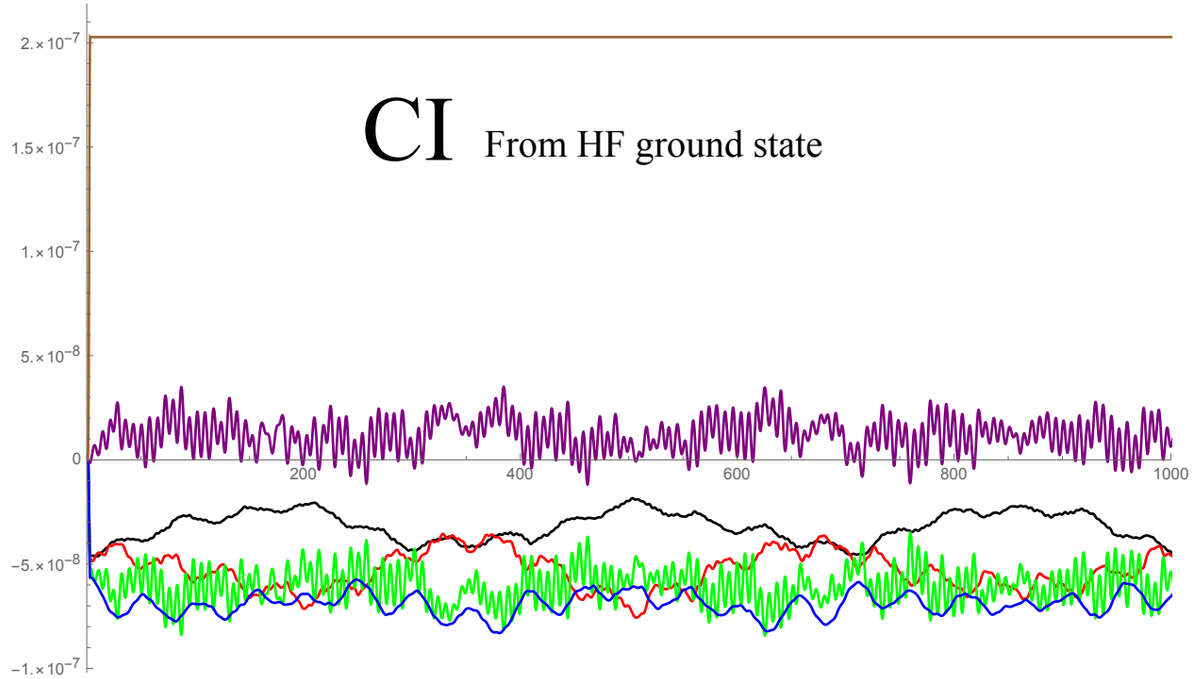
HF density matrix is stationary

1 *Initial state*
Current solution in 2nd Born

In organic molecules the correlated ground state is very close to the HF ground state

Comparison of HF occupations in a model glycine using CI





2 Mixture consistency

After the pump

$$\rho_{ij}(t) = \langle \Psi(t) | \hat{d}_j^\dagger \hat{d}_i | \Psi(t) \rangle = \rho_{ij}^N + \rho_{ij}^{N-1}(t)$$

Since the sectors with N and N-1 particles are **independent**, solving

$$\dot{\rho}^N + i \left[h_{\mathrm{HF}}[\rho^N], \rho^N \right] = -\mathcal{I}_{\mathrm{c}}[\rho^N] - \mathrm{h.c.}$$

$$\dot{\rho}^{N-1} + i \left[h_{\mathrm{HF}}[\rho^{N-1}], \rho^{N-1} \right] = -\mathcal{I}_{\mathrm{c}}[\rho^{N-1}] - \mathrm{h.c.} \qquad (1)$$

and calculating $\rho = \rho^N + \rho^{N-1}$ should be equivalent to solving

$$\dot{\rho} + i \left[h_{\mathrm{HF}}[\rho], \rho \right] = -\mathcal{I}_{\mathrm{c}}[\rho] - \mathrm{h.c.} \qquad (2)$$

However, **this is not even true in HF**. Since all time-dependence comes from ρ^{N-1}, **is it more accurate to solve (1) or (2)??**

2 Mixture consistency
Empirical evidence and more tests

From comparisons with CI we found **more accurate** to work with a **mixed density matrix** as generated by the ionizing pump

Systematic tests are needed

They are centainly possible in HF

Beyond HF the NEGF equations should be solved either using the **correlation blocks** (PRB 2012) or a **clever Hamiltonian on the vertical track**

3 Ionization

The ionization self-energy

$$\Sigma_{\mathrm{ion},ij}(z,\bar{z}) = \sum_k \left(\mathbf{E}(z)\cdot\mathbf{D}_{ik}\right) g_k(z,\bar{z}) \left(\mathbf{E}(\bar{z})\cdot\mathbf{D}_{kj}\right)$$

with

$$\left[i\frac{d}{dz} - \epsilon_k\right] g_k(z,z') = \delta(z,z')$$

is accurate only for **single-photon ionization**

The non-perturbative ionization self-energy is

$$\Sigma_{\mathrm{ion},ij}(z,\bar{z}) = \sum_{kk'} \left(\mathbf{E}(z)\cdot\mathbf{D}_{ik}\right) g_{kk'}(z,\bar{z}) \left(\mathbf{E}(\bar{z})\cdot\mathbf{D}_{k'j}\right)$$

where continuum-continuum coupling

$$\left[i\frac{d}{dz} - \epsilon_k\right] g_{kk'}(z,z') - \sum_{k''} \left(\mathbf{E}(z)\cdot\mathbf{D}_{kk''}\right) g_{k''k'}(z,z') = \delta_{kk'}\delta(z,z')$$

Ionization

The ionization self-energy

$$\Sigma_{\mathrm{ion},ij}(z,\bar{z}) = \sum_k \left(\mathbf{E}(z)\cdot\mathbf{D}_{ik}\right) g_k(z,\bar{z}) \left(\mathbf{E}(\bar{z})\cdot\mathbf{D}_{kj}\right)$$

with

$$\left[i\frac{d}{dz} - \epsilon_k\right] g_k(z,z') = \delta(z,z')$$

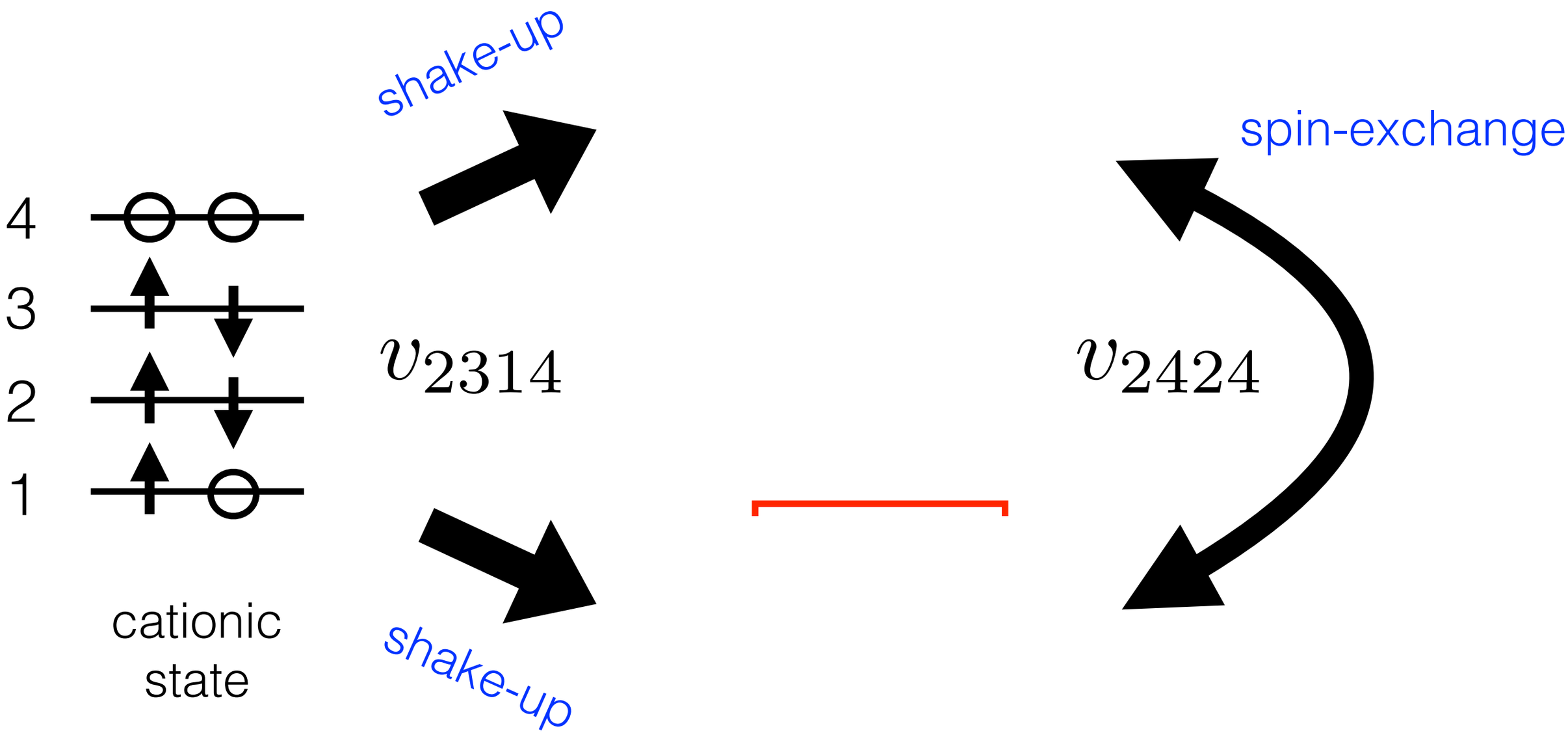
is accurate only for **single-photon ionization**

Currently, **continuum states** for dipole couplings are the **unoccupied KS states**

Improvements are possible, see e.g. Ruberti et al *J. Chem Phys.* **141**, 164126 (2104), but they need to be checked

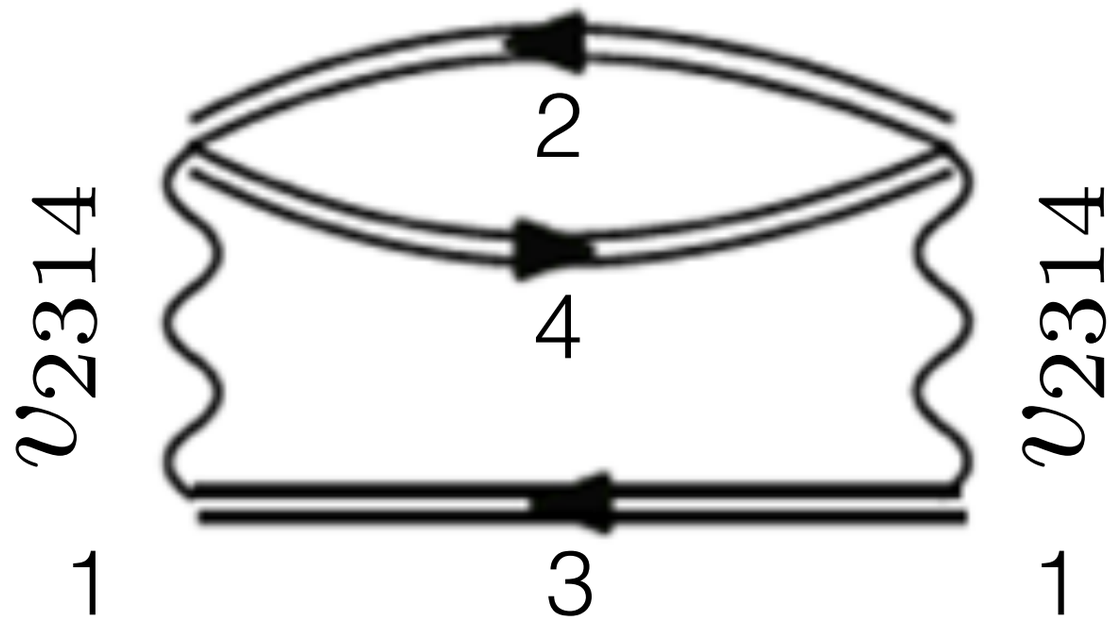
Correlation in excited states

The ubiquitous spin-exchange scattering



Correlation in excited states

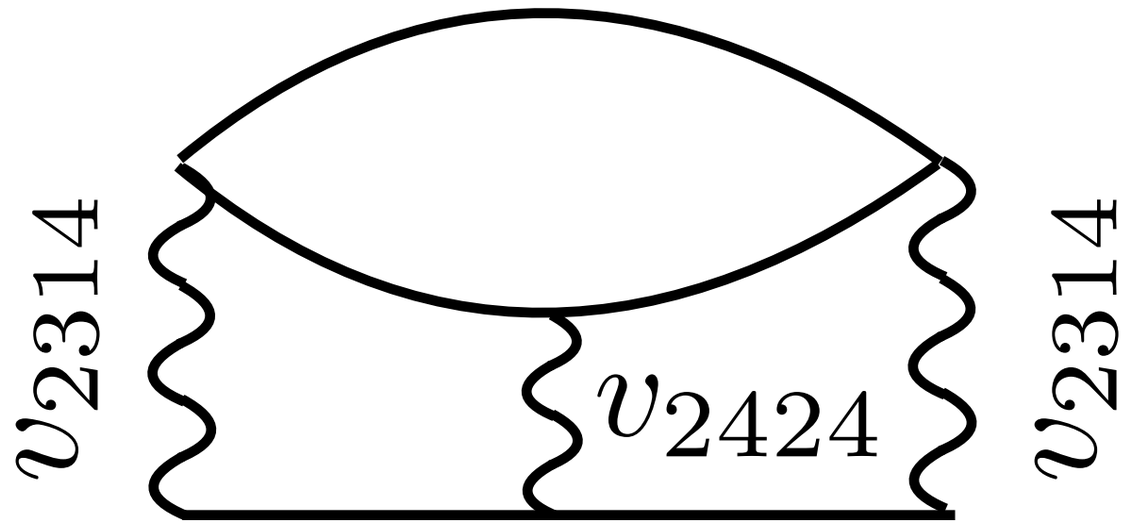
Shake-up processes are described by the second-order self-energy



Spin-exchange requires diagrams beyond 2B

Correlation in excited states

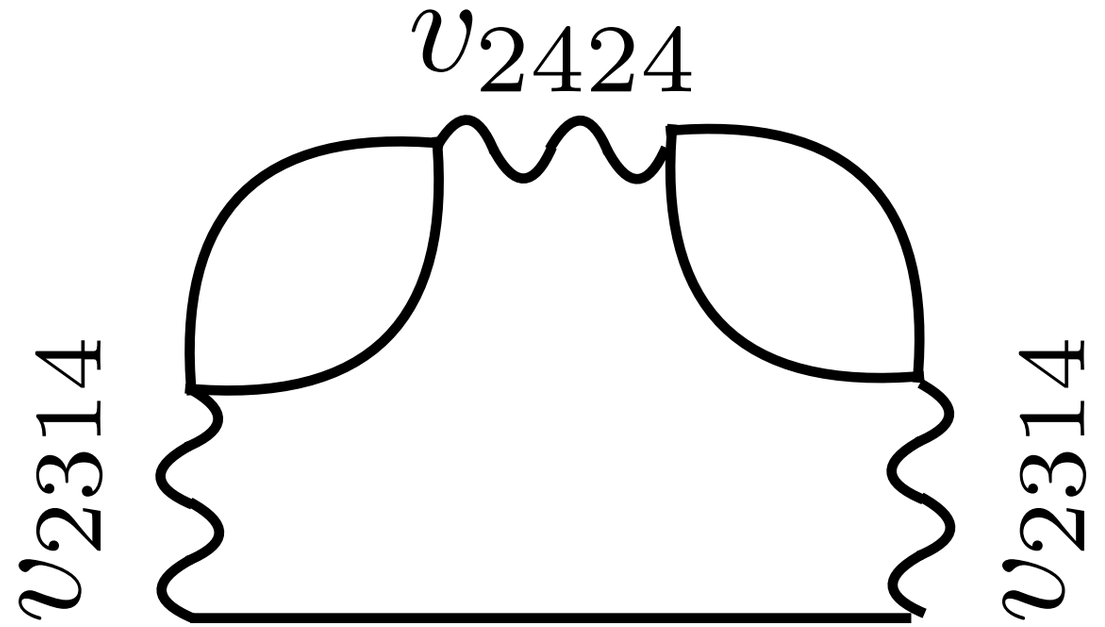
Shake-up processes are described by the second-order self-energy



Spin-exchange requires diagrams beyond 2B

Correlation in excited states

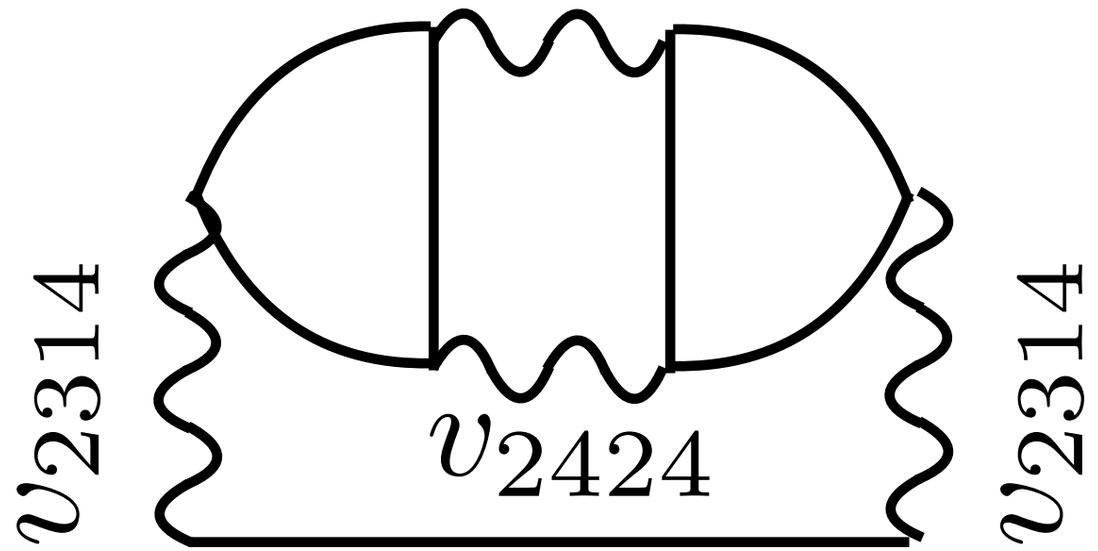
Shake-up processes are described by the second-order self-energy



Spin-exchange requires diagrams beyond 2B

Correlation in excited states

Shake-up processes are described by the second-order self-energy



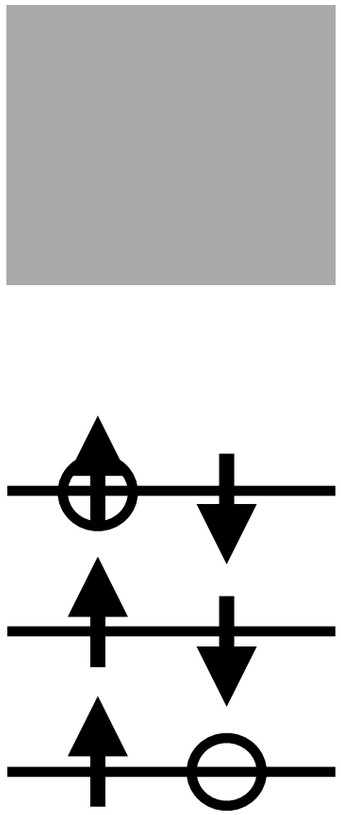
Spin-exchange requires diagrams beyond 2B

Which are the relevant diagrams? Certainly infinitely many

Can they be included without spoiling the computational gain of GKBA?

Is the self-energy or the collision integral the most convenient quantity for approximations?

5 Auger decays



Interaction with continuum states has to be included

Unfeasible size of the density matrix for NEGF

5 Auger decays
A possible solution — PRA 2018

$$\dot{\rho}(t) + i\,[h_{\rm HF}(t), \rho(t)] = -\mathcal{I}_{\rm c}(t) - \mathcal{I}_{\rm ion}(t) - I_{\rm ic}(t) - I_{\rm Auger}(t) - \text{h.c.}$$

$$\Sigma^{\lessgtr}_{{\rm Auger},ij}(t,\bar{t}) = \sum_{mn\,pq}\sum_{\mu} G^{\lessgtr}_{mn}(t,\bar{t})$$

continuum index

$$\times\Big[G^{\lessgtr}_{\mu}(t,\bar{t})G^{\gtrless}_{pq}(\bar{t},t)\big(v^{A}_{iqm\mu}w^{A}_{\mu npj} + v^{A}_{iq\mu m}w^{A}_{n\mu pj}\big) + G^{\lessgtr}_{pq}(t,\bar{t})G^{\gtrless}_{\mu}(\bar{t},t)v^{A}_{i\mu pm}w^{A}_{nq\mu j}\Big],$$

$$\dot{f}_{\mu} = -\mathcal{J}_{\mu}[\rho,f] - \mathcal{J}^{*}_{\mu}[\rho,f]$$

$$\mathcal{J}_{\mu}(t) = \int_{0}^{t} d\bar{t}\,[K^{>}_{\mu\mu}(t,\bar{t})f^{<}_{\mu}(\bar{t}) + K^{<}_{\mu\mu}(t,\bar{t})f^{>}_{\mu}(\bar{t})]$$

$$K^{\lessgtr}_{\mu\nu}(t,\bar{t}) = i\sum_{mn\,pq\,sr} v^{A}_{\mu rpm}w^{A}_{nqsv} \times G^{\lessgtr}_{mn}(t,\bar{t})G^{\lessgtr}_{pq}(t,\bar{t})G^{\gtrless}_{sr}(\bar{t},t)e^{-i\epsilon_{\nu}(\bar{t}-t)}$$

5

Auger decays
Open problems

Focussing on the μ - dependence

$$\dot{\rho} = A[\rho] + \sum_{IJ\mu} B_{\mu}^{IJ}[\rho] v_{\mu I} w_{\mu J} f_{\mu}$$

$$\dot{f}_{\mu} = \sum C_{\mu}^{IJ}[\rho] v_{\mu I} w_{\mu J} f_{\mu}$$

The continuum occupations are, in general, anisotropic
due to anisotropy of Coulomb integrals

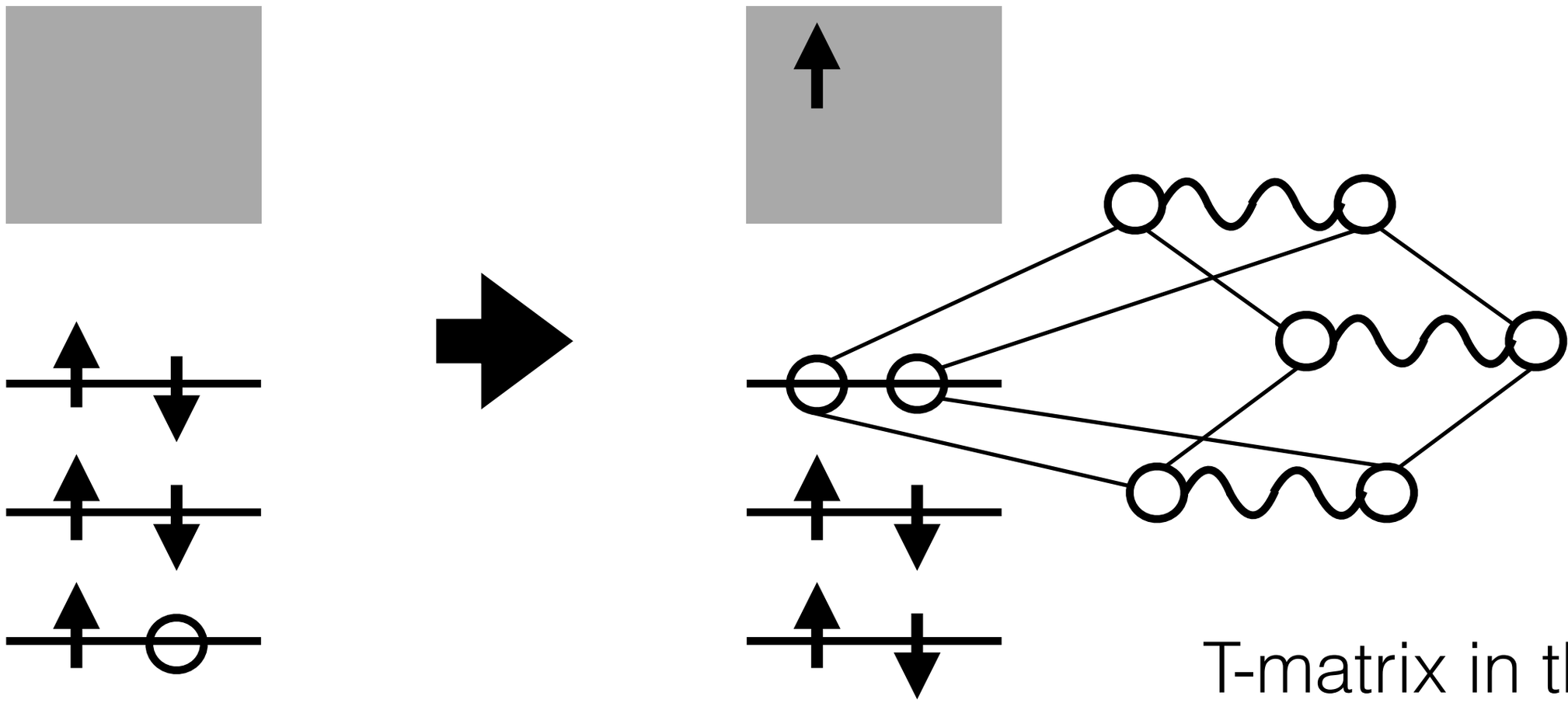
Too many continuum states! 

Is it possible a description in terms of reduced quantities like, e.g.

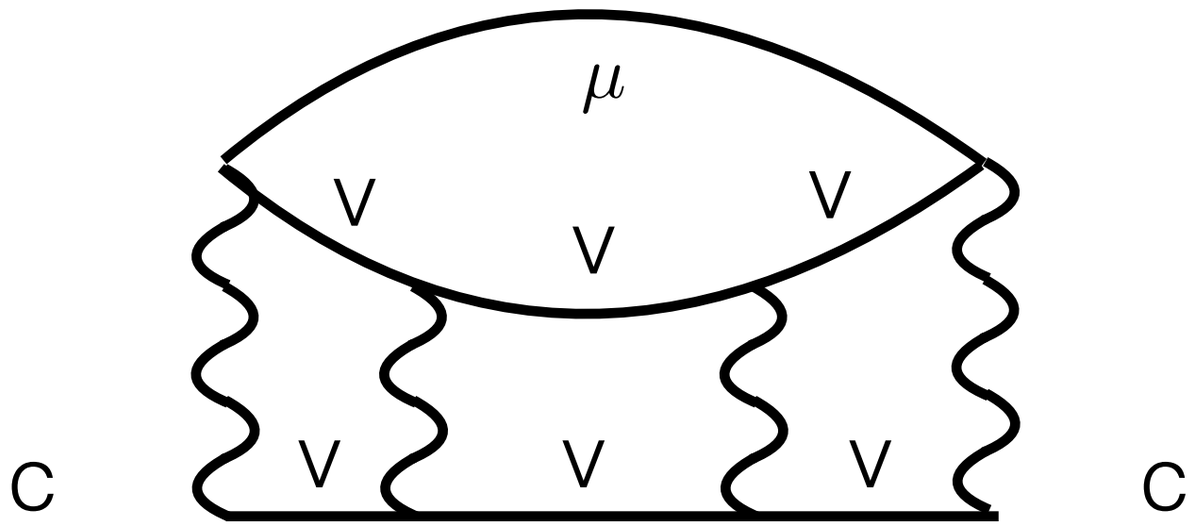
$$f(\epsilon) = \sum_{\mu} g(\epsilon_{\mu}) f_{\mu} \delta(\epsilon - \epsilon_{\mu})$$ **?**

5

Auger decays
Open problems



T-matrix in the
particle-particle channel



How to deal with it?

What is $\Sigma_{vc},\ \Sigma_{vv}$ **?**


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
рахмат
Баярлалаа
спасибо
faafetai lava
mersi
kia ora
barka
welalin
tack
spas
dank je
misaotra
matondo
paldies
grazzi
mahalo
tapadh leat
gracias
vinaka
blagodaram
спасибі
kiitos
dankie
nanni
nandri
dhanyavad
mauruuru
köszönöm
hvala
gràçie
bayarlalaa
bedankt
enkosi
dziękuję
akun dankon aċiū
хвала
asante
manana
obrigada
tenki
murakoze
djiere dieuf
tau
mochchakkeram
дякую
mamnun
chokrane
chnorakaloutioun
gratias ago
gràcies
sulpáy
taiku
go raibh maith agat
sobodi
děkuji
obrigado
sukriya
kop khun krap
sagolun
mèsi
didi madloba
najis tuke
kam sah hamnida
rahmat
terima kasih
ありがとう
tanemirt
rahmet
grazie
arigatô
takk
dakujem
trugarez
dhanyavadagalu
shukriya
mercé
мерси
diolch
xièxie
ευχαριστώ
তোমাকে ধন্যবাদ
감사합니다
merci