Approaching the Quantum Limit for Metal Nanoparticle Plasmonics

Emily Townsend, Alex Debrecht and
Garnett W. Bryant

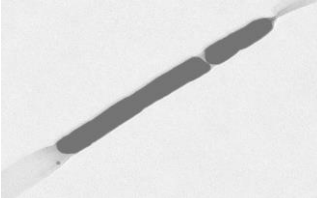
Quantum Measurement Division and the Joint Quantum Institute

National Institute of Standards and Technology, Gaithersburg, MD
University of Maryland, College Park, MD

Quantum plasmonics

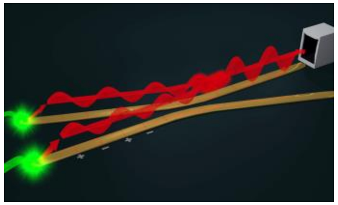
- Understanding metal nanoparticles and nanoantennas: small sizes and small gaps

  … Tunneling, charge spillout and nonlocal response



- Quantum nanoscale communication and single plasmons

  … coherent excitation transport, quantum optics



- Hybrid structures

  … classical or quantized plasmons

Nanohybrids: Classical or Quantum

Different models for nanohybrids

- Quantum dots (QD) as classical dipoles with classical metallic nanoparticles (MNP) …enhancement and quenching
- QD as a two-level quantum emitter with classical MNPs
  - … Nonlinear Fano effect, induced transparency, bistability
  - … Govorov et al, Sadeghi et al, Artuso, Bryant, et al, …
- QD as a two-level quantum emitter and MNPs with quantized plasmons
  - … No bistability, noise effects, correct inclusion of Purcell effect
  - … Near-field quantization: mode quantization as in a cavity
  - … Near-field quantization: spectrum of local oscillators

Matter point of view: approaching the quantum limit for MNPs

Size quantization, quantized matter modes and quantized fields

Matter point of view

Finding the plasmons

- Challenging many "few-body" problem with confinement effects, quantization
- Single-particle vs collective (plasmons) or mixed?
- Size dependence of excitation energies and response
- Spatial character of resonance charge densities

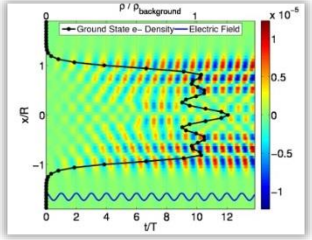
How?

- Density functional theory
  - … MNPs and dimers: Nordlander et al., Aizpurua, Borisov, et al., ET and GWB , …
  - … 1D surface atom chains: Gao et al., Ruud et al., …
  - … Linear molecules, CNT, etc., …: Jacob et al., Aiken, Schatz, et al, Garcia de Abajo et al., …
- Exact approaches: Luttinger theory
- Exact approaches: finite 1D chains
  - … Short chains (<15 atoms): full spectrum
  - … Long chains: selected energy ranges

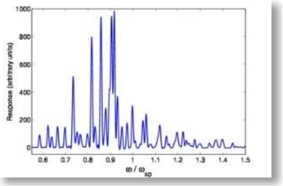
What can be learned about plasmons in small systems?

- Time-dependent density functional theory (TDDFT)

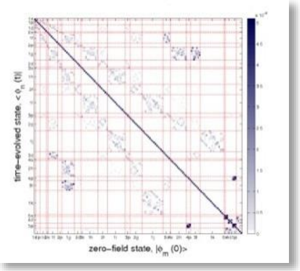
  … Time dependent response or response function



- Size quantization … 100-600 electron MNPs

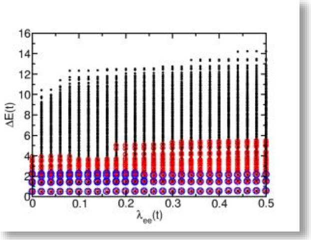


- Collective or single-particle response



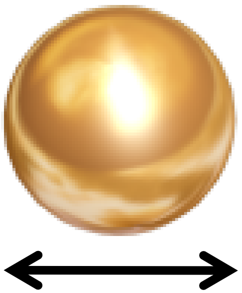
- Characterizing modes: “sloshing” and “inversion”

- Exact approaches: short 1D chains, full spectrum



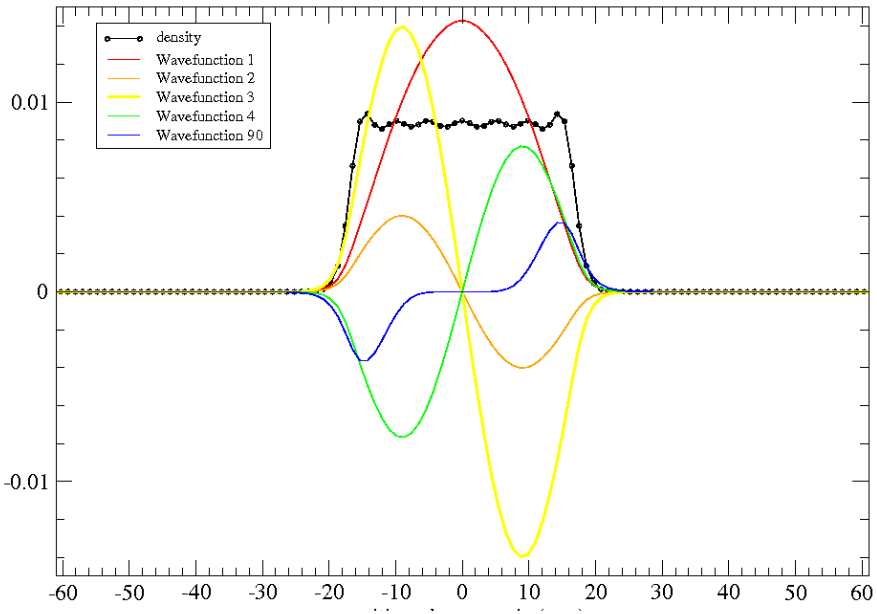
Size quantization: density functional theory

- Spherical Au nanoparticles
- Jellium model
- 100-600 valence electrons



1.47 nm = 27.8 a_0

DFT ground state



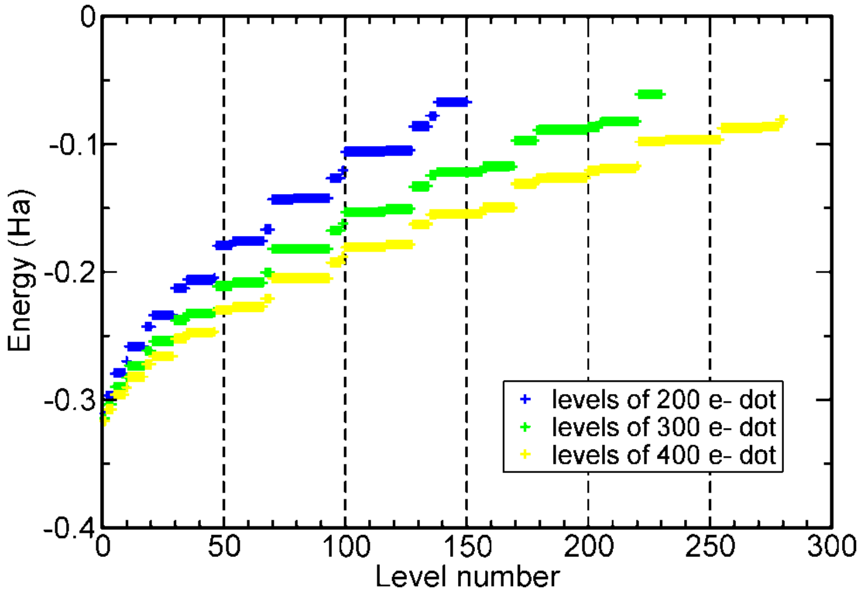
x (a.u.)

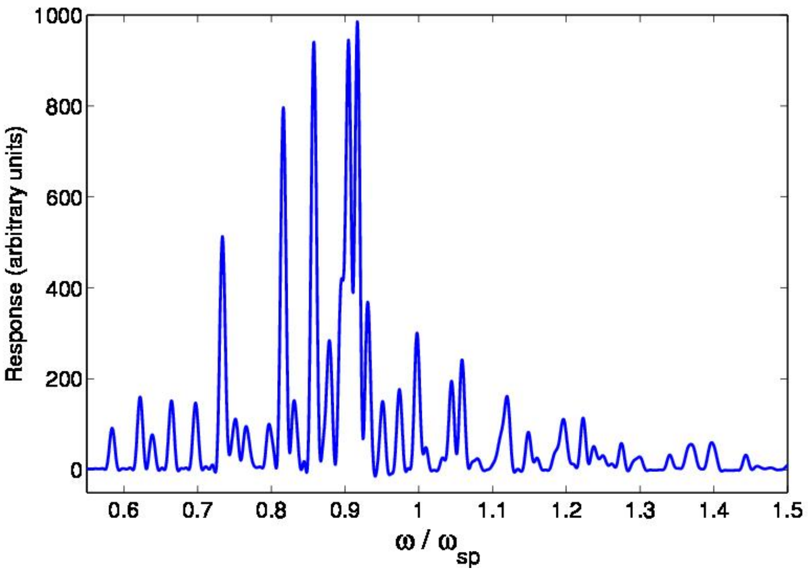
Time Dependent Density Functional Theory

Ground State DFT… find occupied Kohn-Sham orbitals

Time Dependent DFT

- Frequency response from instantaneous impulse
- Simulation time defines peak widths
- Drive on-resonance to characterize resonances





Size quantization: 100-600 electron MNPs

Townsend and Bryant, Nano Lett. **12**, 429 (2012)

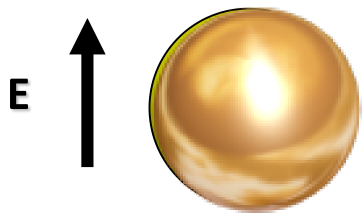
Classical surface plasmons and quantum core plasmons

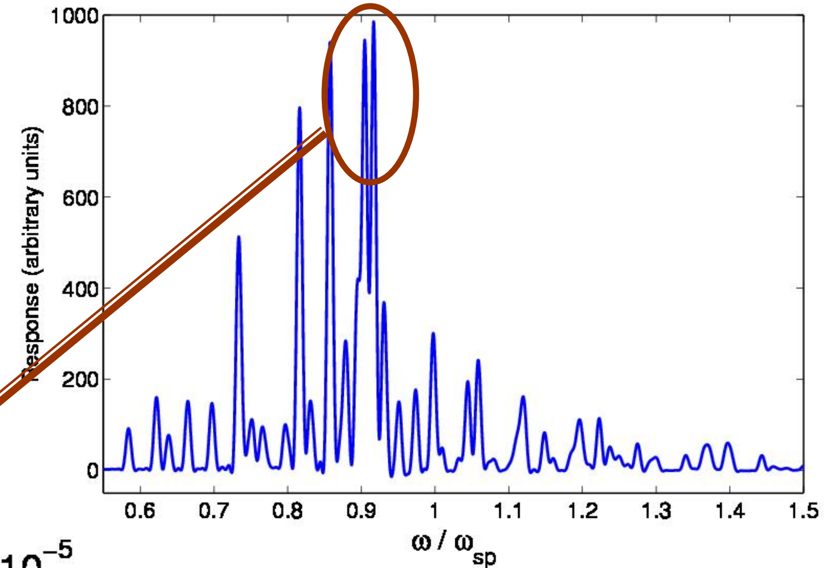
Small spherical MNPs (~ 100 electrons)

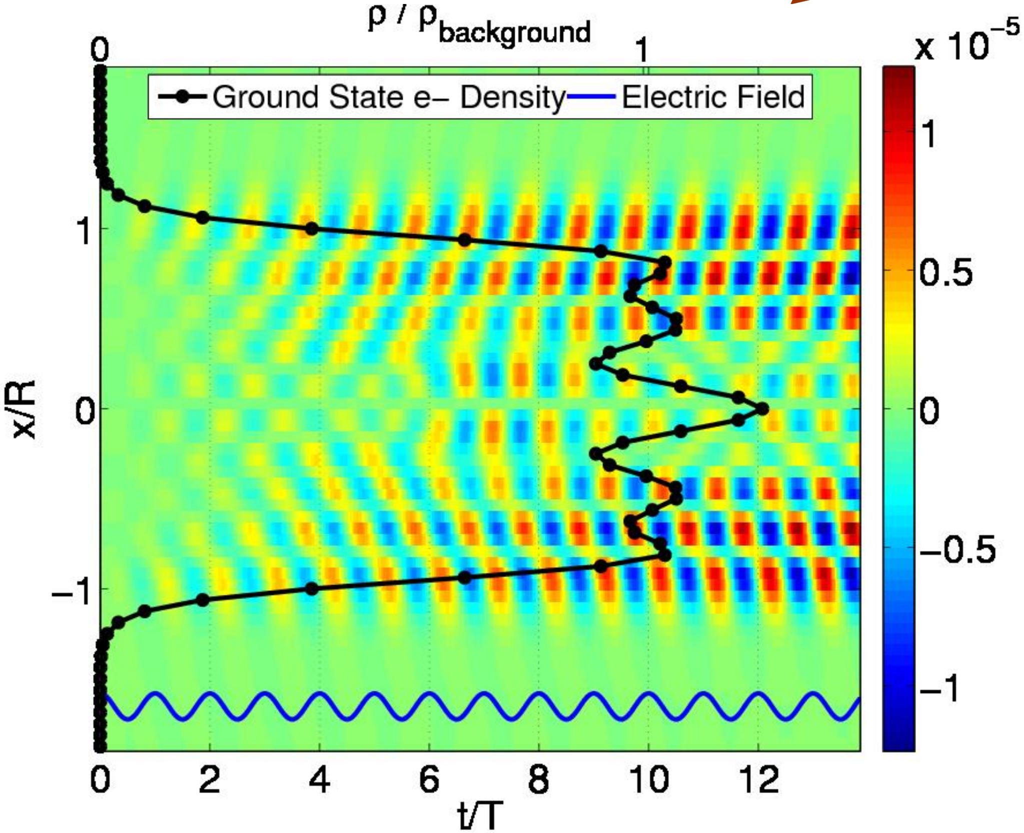
- Discrete modes
- Excitations: $\Delta L = \pm 1$
- Many-electron collective response or single-particle response
- Charge oscillations: surface, core or both?

Transition to classical surface plasmons (300-600 electrons)

Classical Surface Plasmon

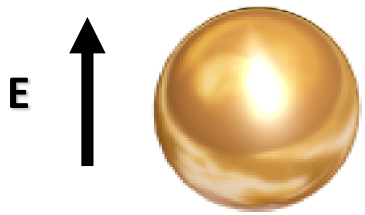


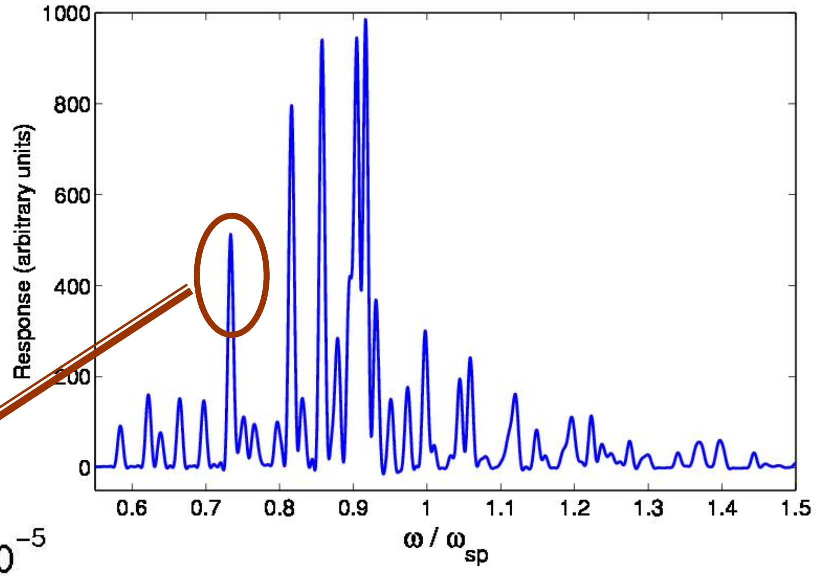


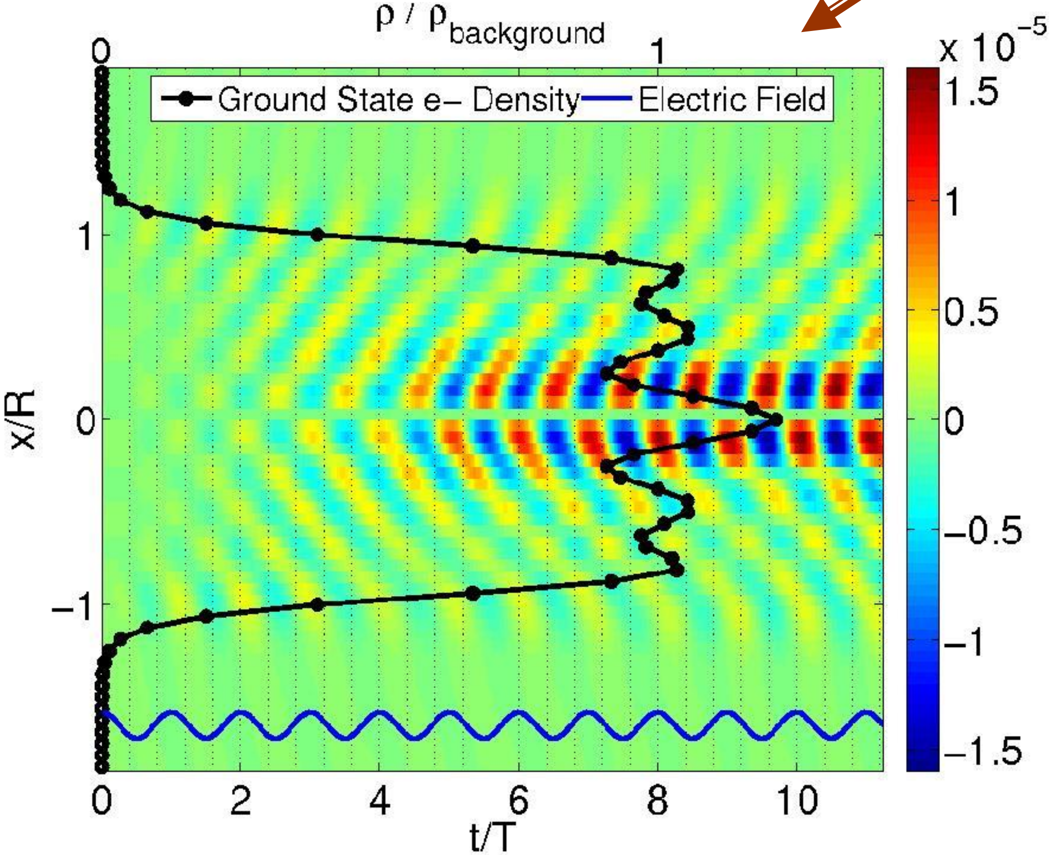


Surface charge oscillations

Quantum Core Plasmon



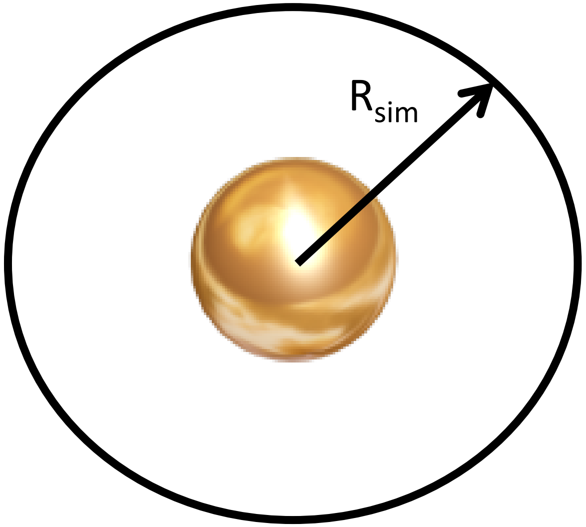


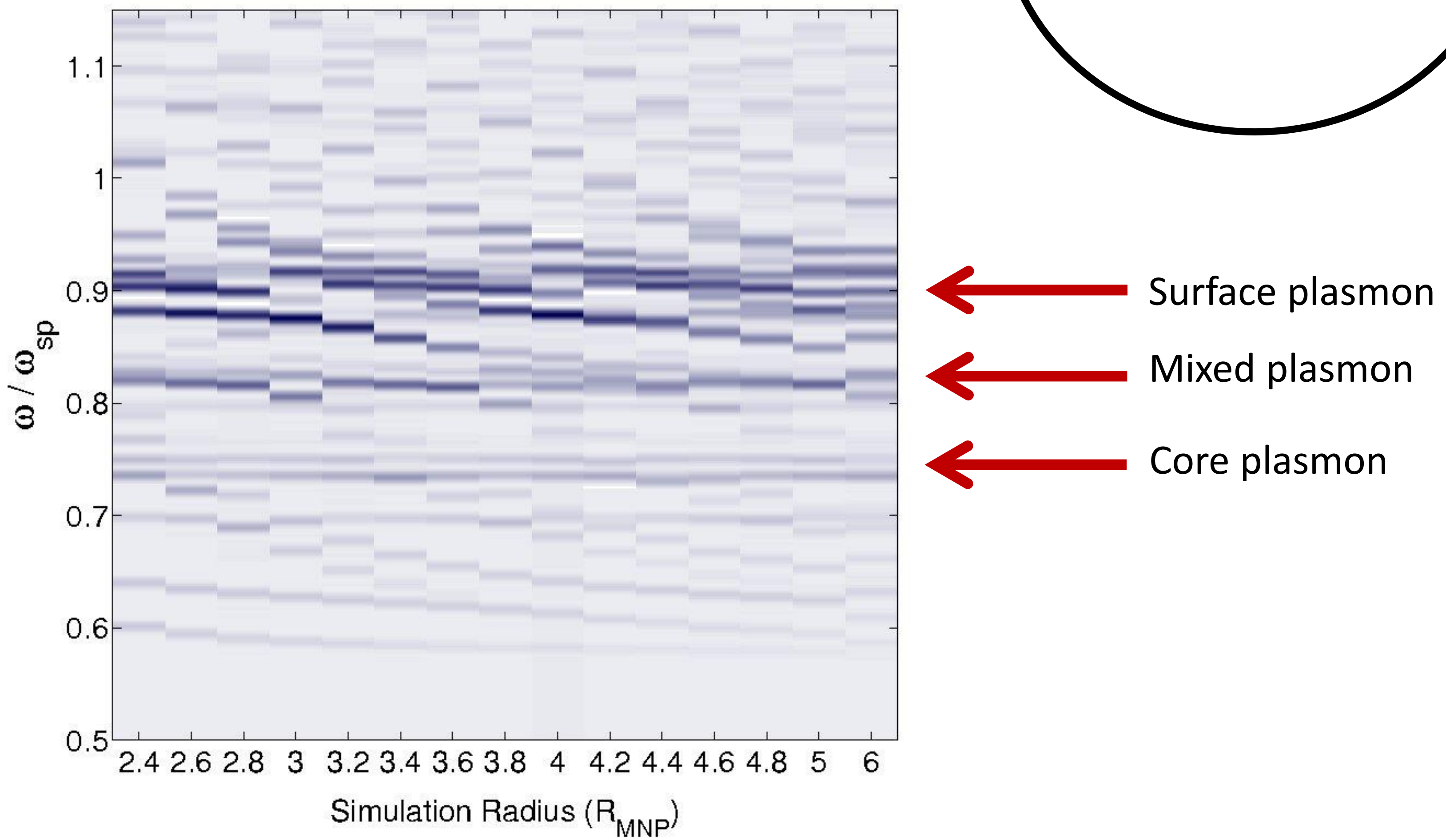


Quantum core plasmon

Core charge oscillation with weak surface oscillation

Robust solutions…dependence on simulation size





Dependence on MNP size

•Surface plasmon (the collective response?) becomes dominant for 600 e MNPs

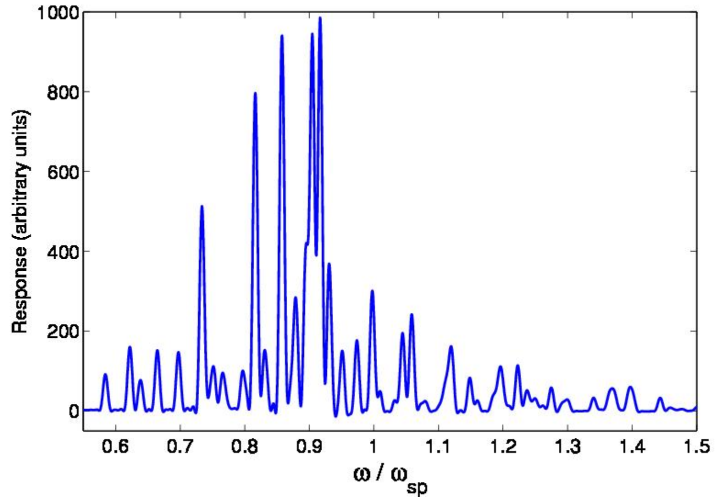
•Core plasmon and mixed plasmons much weaker

•Width of main peaks defines surface plasmon width?

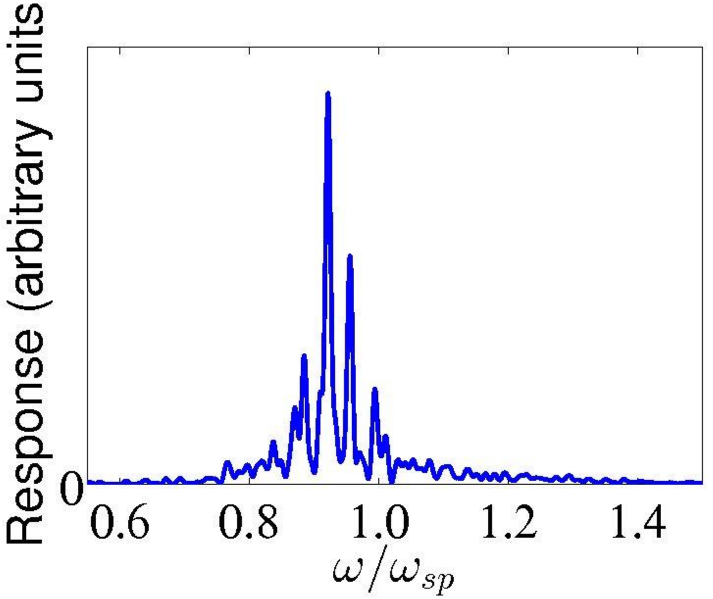
•Implication for quantization model

… Single mode or multimode?

100 electron MNP



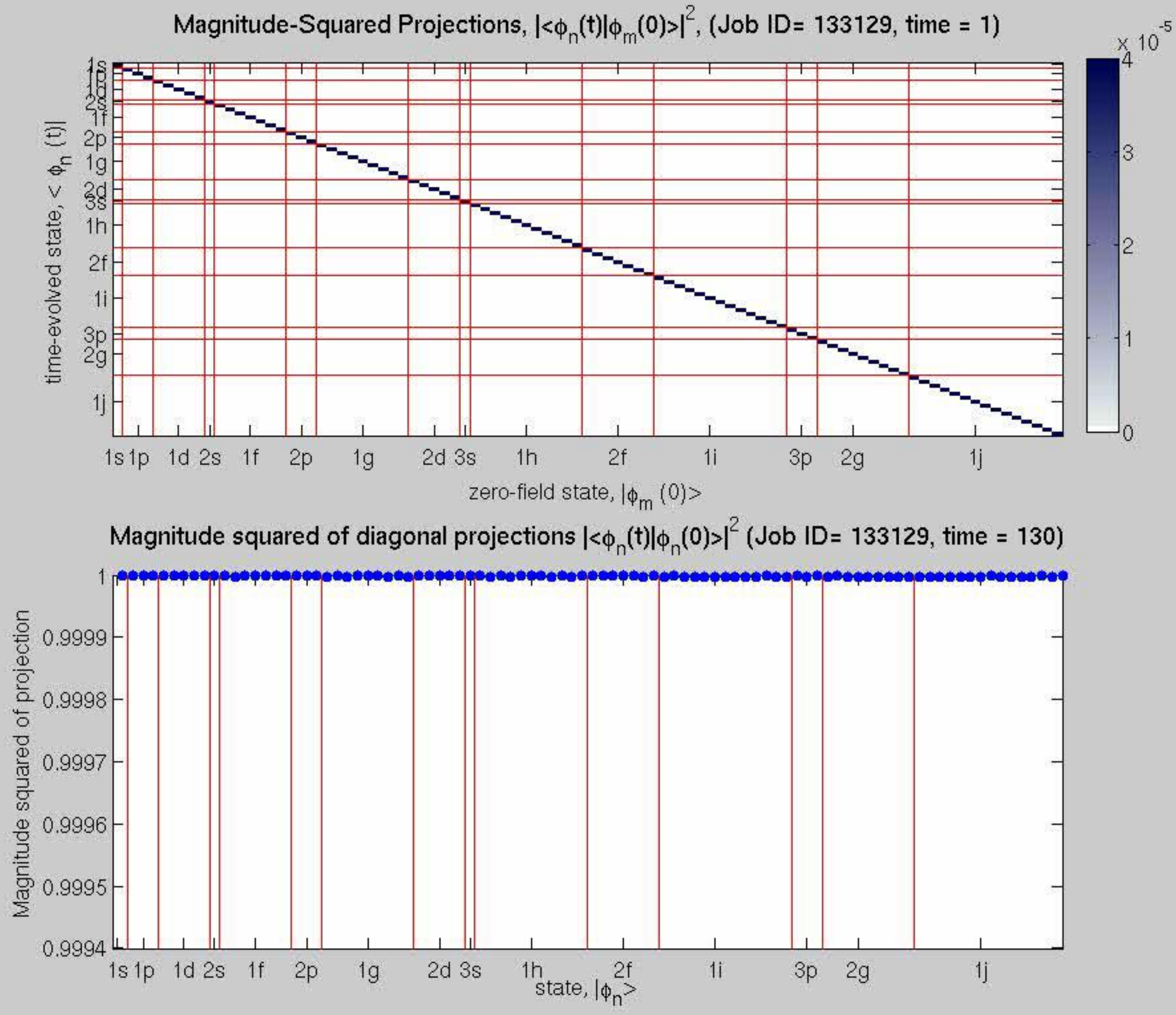
600 electron MNP



Collective or single-particle?

Time dependent overlaps between the evolving Kohn-Sham orbitals and the t=0 (ie ground state) Kohn-Sham orbitals

- Diagonal overlaps … change in level occupation
- Off diagonal overlaps … transitions with $\Delta L = \pm 1$
- Which are single-particle or collective
- Linear or non-linear?
- TDDFT or response function?

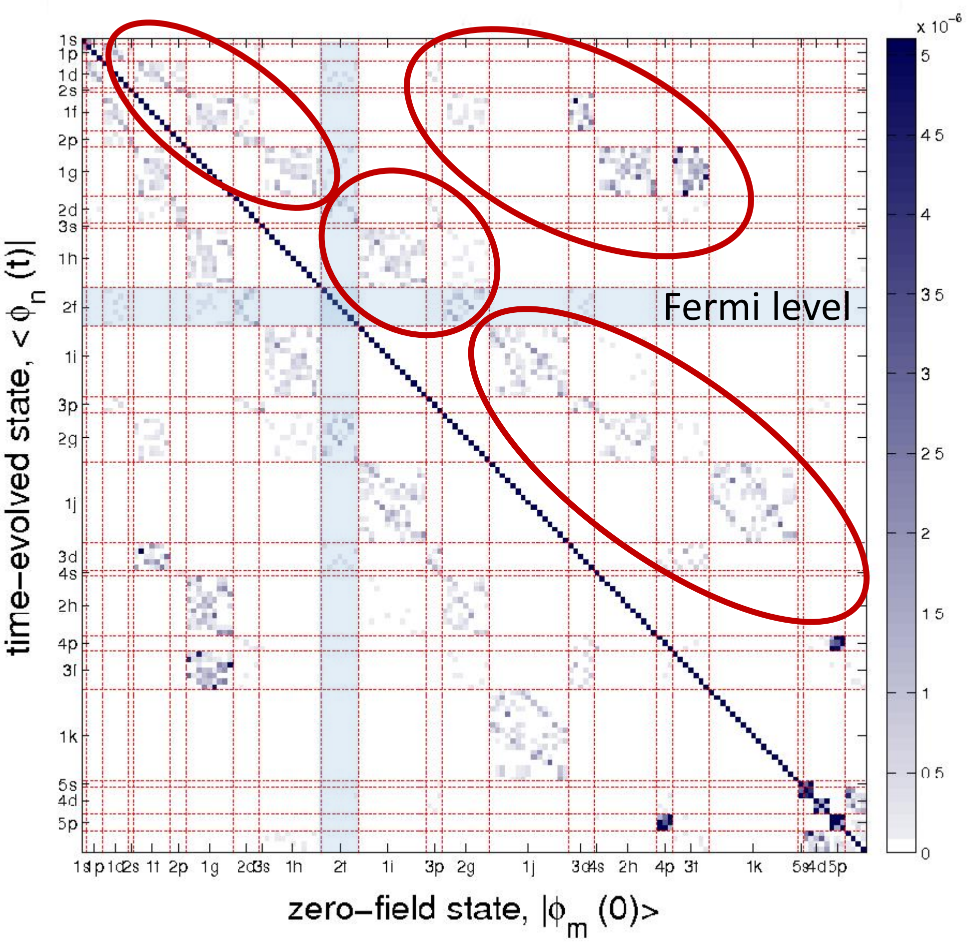


Magnitude-Squared Projections, |<φn(t)|φm(0)>|², (Job ID= 133129, time = 1)
x 10^-5
4
3
2
1
0
1s
1p
1d
2s
1f
2p
1g
2d
3s
1h
2f
1i
3p
2g
1j
time-evolved state, < φn (t)|
zero-field state, |φm (0)>
Magnitude squared of diagonal projections |<φn(t)|φn(0)>|² (Job ID= 133129, time = 130)
1
0.9999
0.9998
0.9997
0.9996
0.9995
0.9994
Magnitude squared of projection
state, |φn>

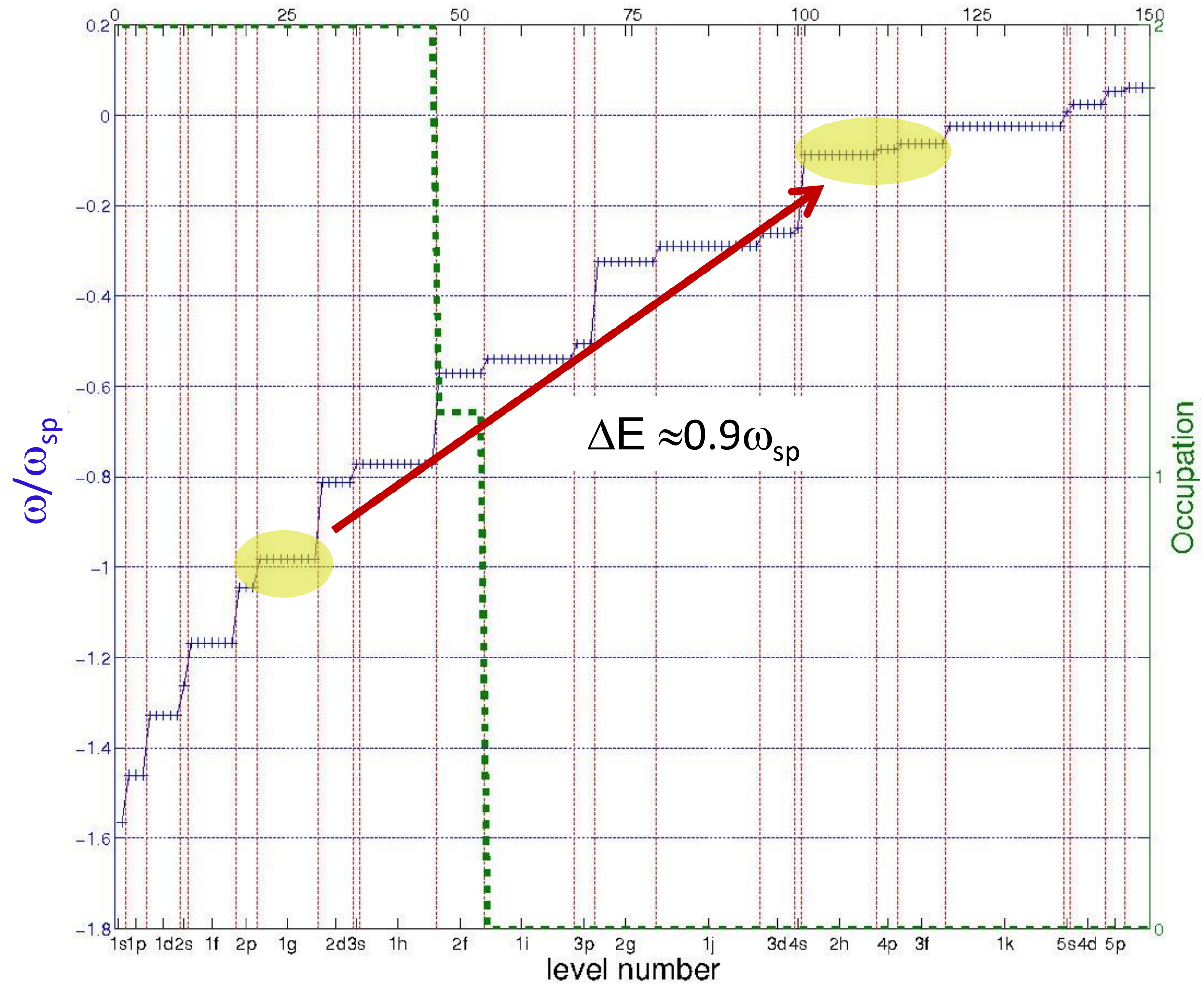
Collective or single-particle?

4 classes of transitions

Surface plasmon: 100e MNP



Collective or single-particle?



Characterizing modes: “sloshing” and “inversion”

- Problem: modes are mixed
- What characterizes plasmonic response: “sloshing”
- What characterizes single-particle component: “inversion”
- Change in shell occupation
- Time-dependence and Fourier (spectral) response

Frequency content of each resonance: sloshing vs inversion

Townsend and Bryant, J. of Optics **16**, 114002 (2014)

Temporal response: shell occupation for 100 electron MNPs

- Fermi level E_f is in the 2f shell
- Emptying shells (blue)
- Filling shells (red)

For core and surface plasmons, temporal response of shell occupations shows

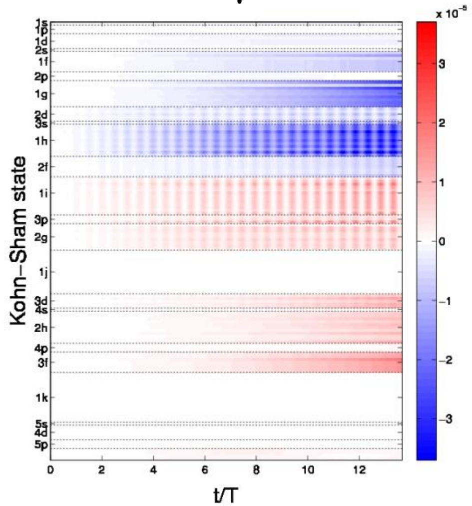
Sloshing

- Charge oscillating between filled shells just below the Fermi level E_f and empty shells just above E_f
- Plasmonic component, stronger for surface plasmons

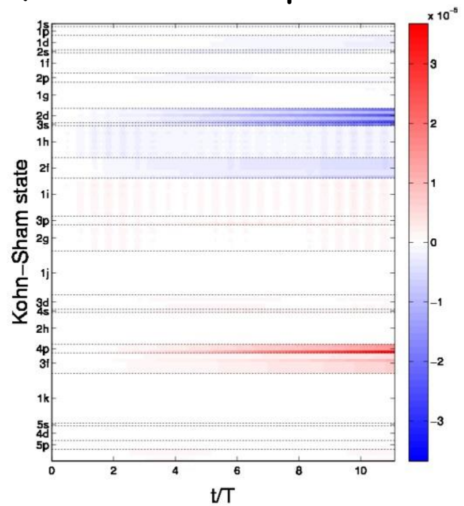
Inversion

- Charge continuously emptying from filled shells far below E_f to empty shells far above E_f
- Single-particle transitions, stronger for core plasmons

Surface plasmon

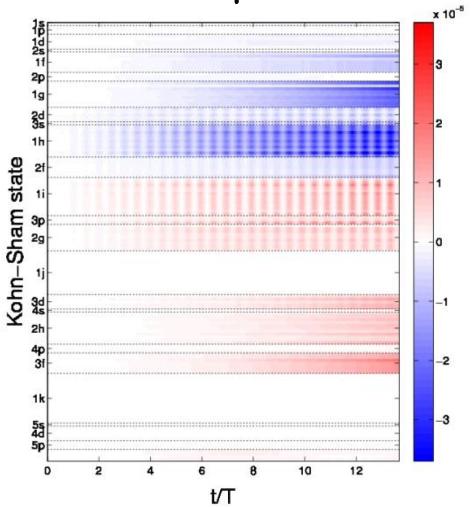


Quantum core plasmon

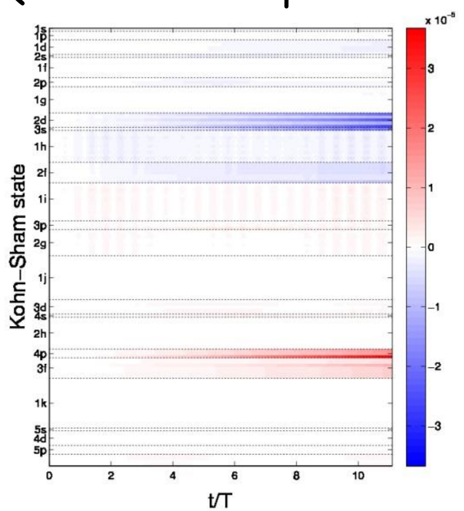


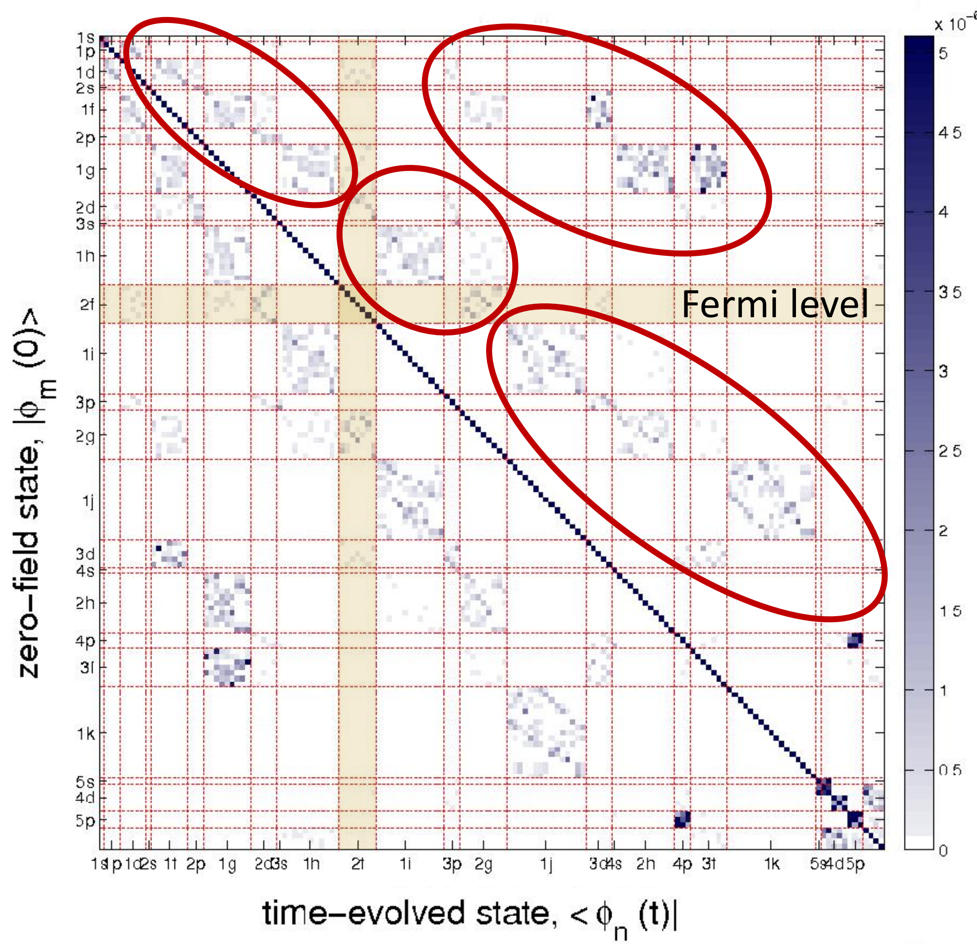
Where in the MNP are these transitions?

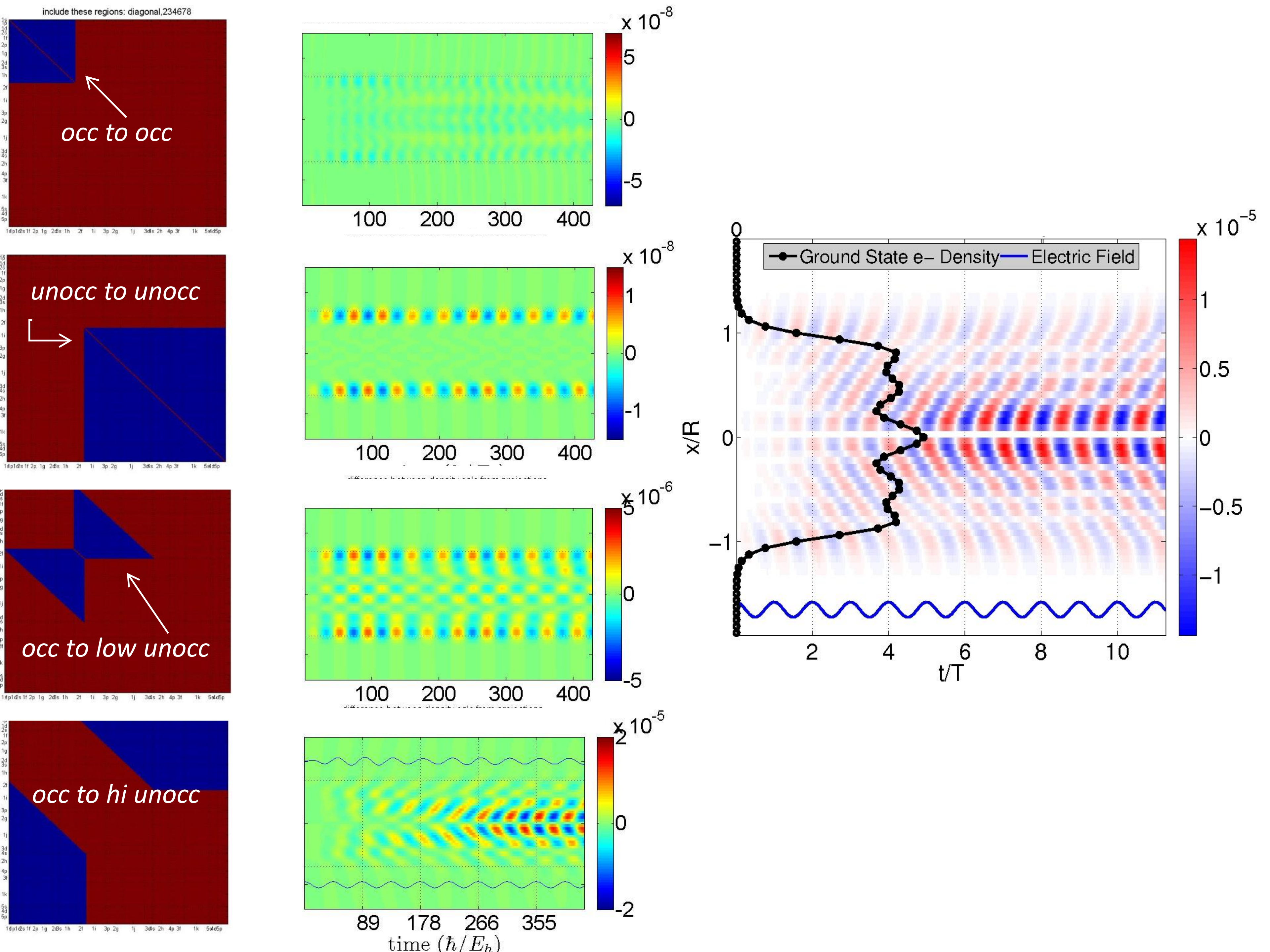
Surface plasmon

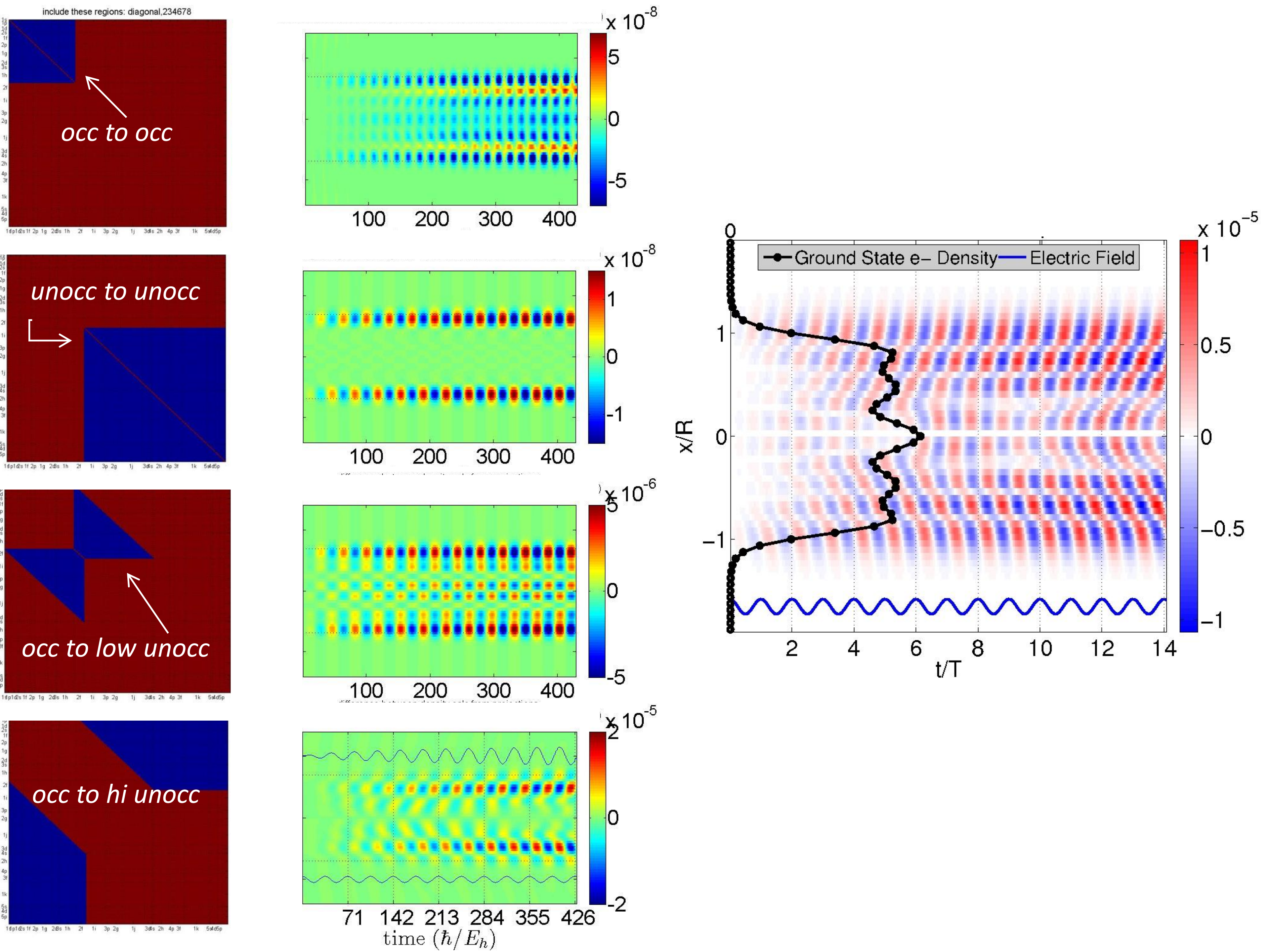


Quantum core plasmon






include these regions: diagonal,234678
occc to occ
x 10^-8
5
0
-5
100
200
300
400
unocc to unocc
x 10^-8
1
0
-1
occ to low unocc
x 10^-6
5
0
-5
occ to hi unocc
x 10^-5
2
0
-2
89
178
266
355
time (ħ/E_h)
Ground State e− Density
Electric Field
x/R
t/T
x 10^-5
1
0.5
0
−0.5
−1
2
4
6
8
10



include these regions: diagonal,234678
occ to occ
unocc to unocc
occ to low unocc
occ to hi unocc
x 10^-8
5
0
-5
100
200
300
400
x 10^-8
1
0
-1
x 10^-6
5
0
-5
x 10^-5
2
0
-2
71
142
213
284
355
426
time (ħ/E_h)
Ground State e− Density
Electric Field
x/R
t/T
x 10^-5
1
0.5
0
−0.5
−1

Density functional theory: what is missing?

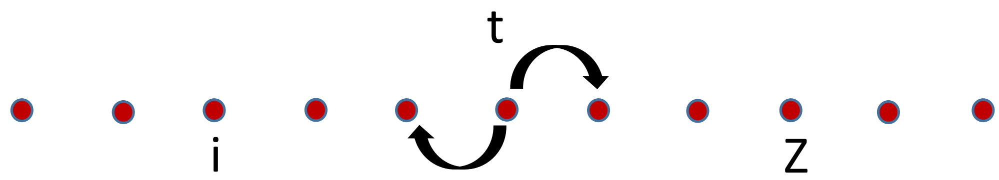
- Optically driven states…no dark resonances
- No correlation effects in charge densities
- Quantized excitations ?
- Fermions or bosons?

Use exact approach for simple 1D chain models
to investigate these effects

Finite 1D chain: simple toy model

1D plasmons: linear molecules, atomic chains on surfaces, P dopants in Si

- Coulomb-coupled, half-filled band of electrons: 1 spinless electron per 2 sites
- Kinetic energy: nearest-neighbor hopping



- Atom-electron coupling: $Z = n_e/n_{site}$

$$V_{nuc}(i) = -\sum_j \lambda_{nuc} Z/(|i-j| + \xi_{nuc})$$

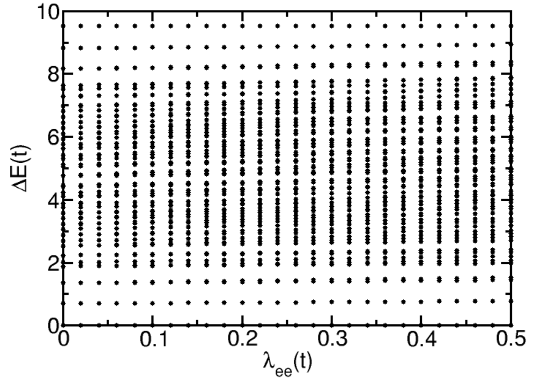
- Electron-electron interaction:

$$V_{ee}(i,j) = \lambda_{ee}/(|i-j| + \xi_{ee})$$

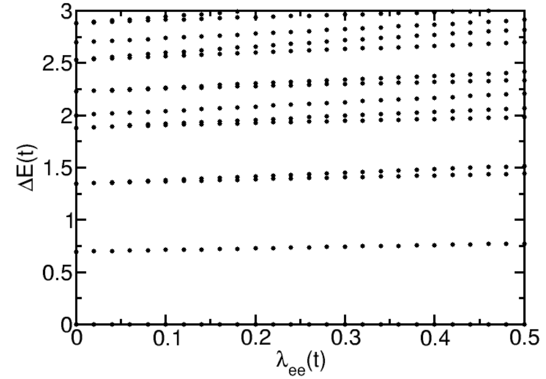
- Charge neutrality: $\lambda_{nuc} = \lambda_{ee}$
- Applied field along the chain axis: $E(i - i_{mid})$

Small, linear 1D chains: dependence on Coulomb coupling λ_{ee}

Full spectrum

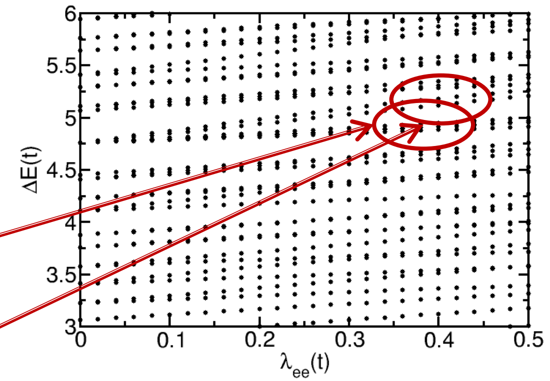


Low energy



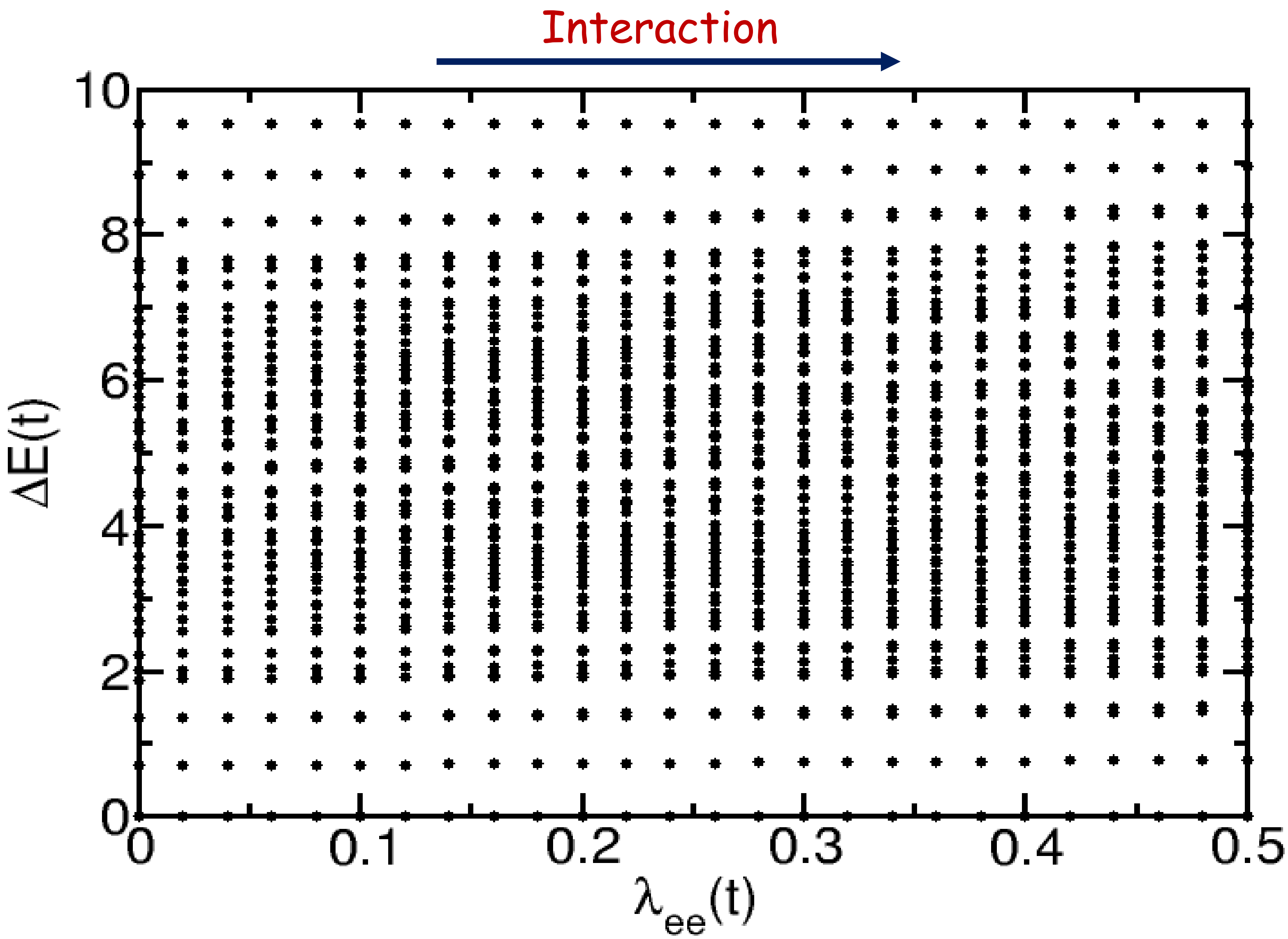
... 8 sites, 70 states
... charge neutral
... bounded spectrum

Higher energy

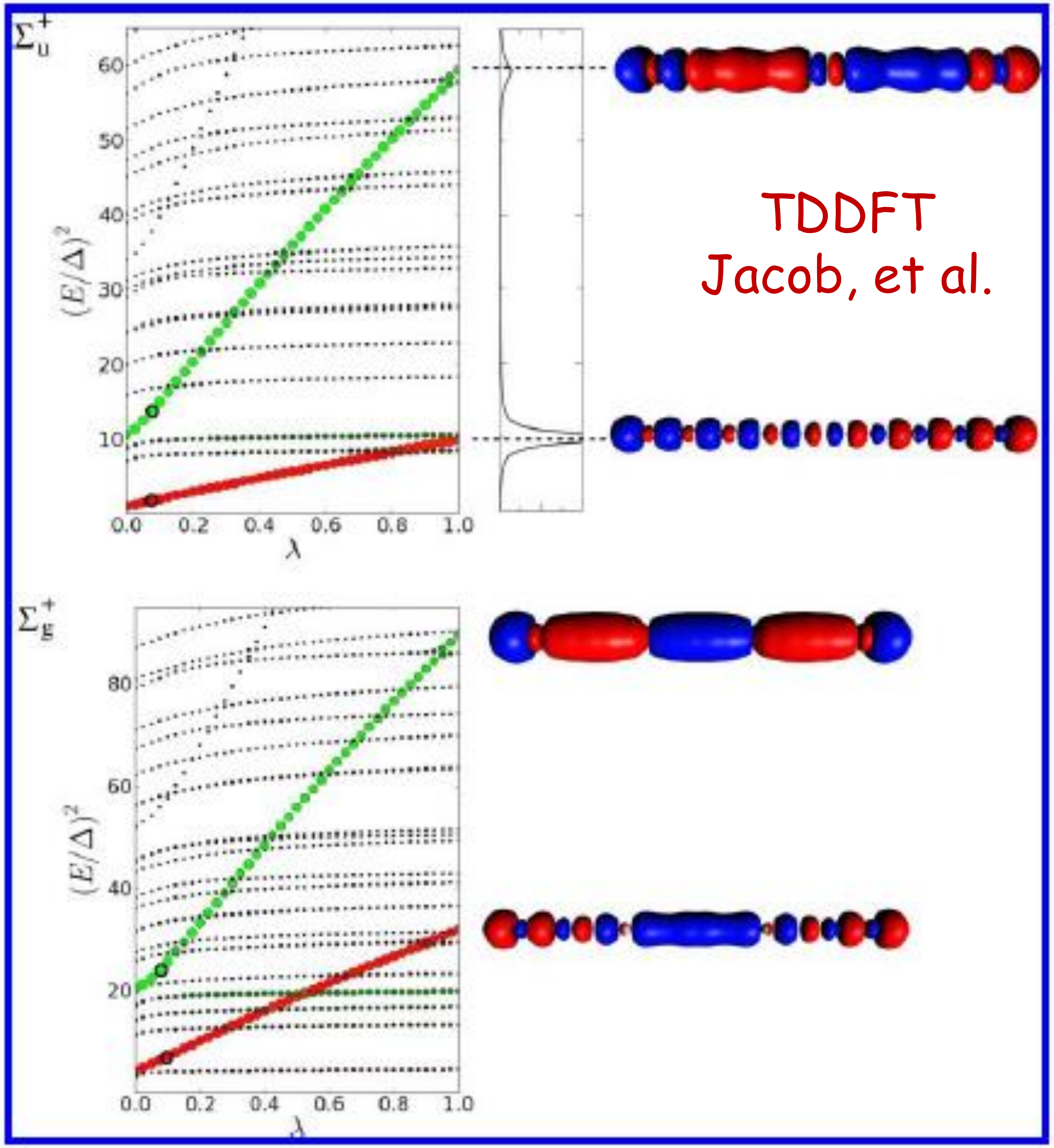


Two types(?) of states
... weak dependence on strength (single particle excitations ?)
... stronger increase in excitation energy (plasmonic ?)

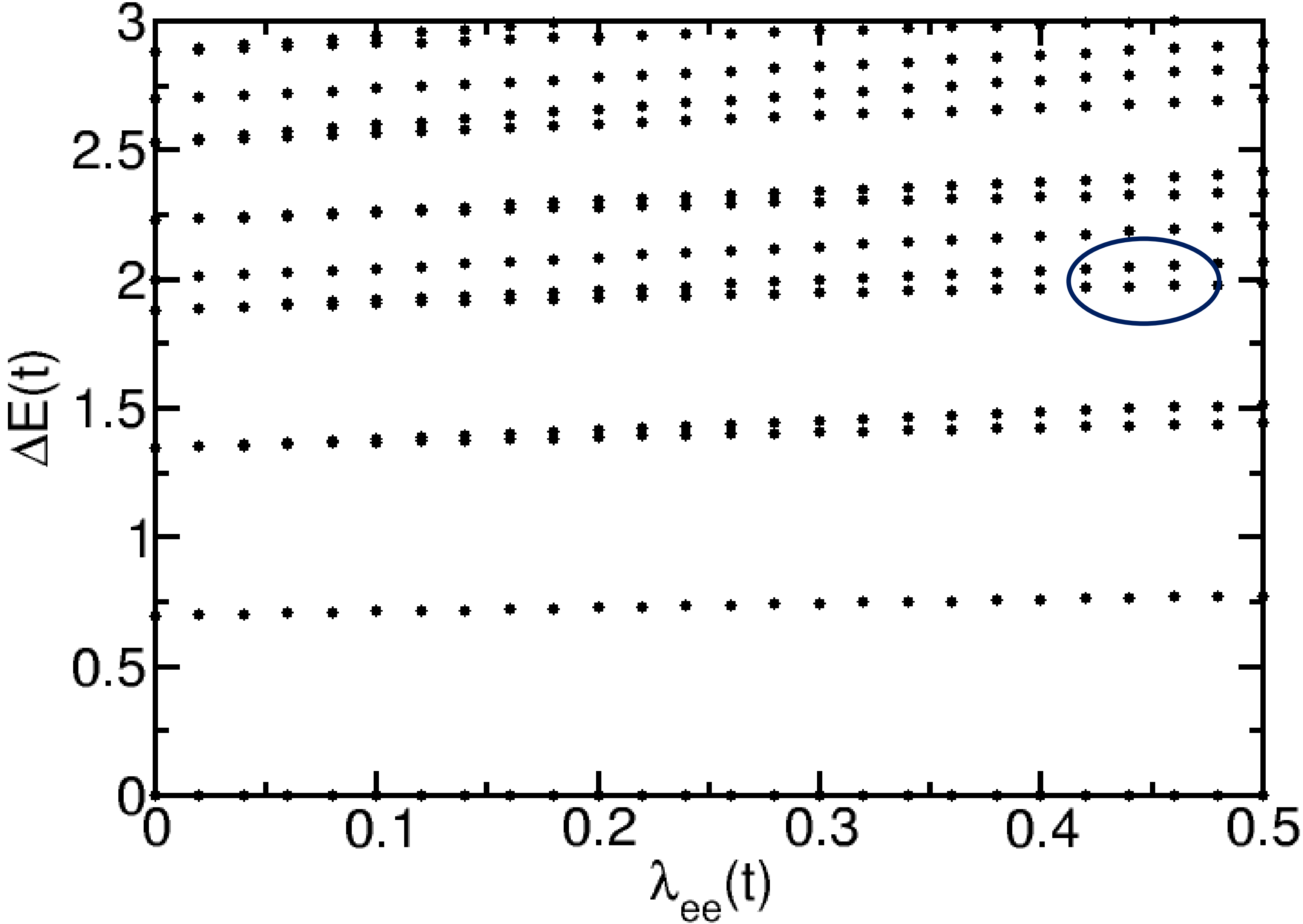
Small, linear 1D chains: dependence on Coulomb coupling λ_{ee}



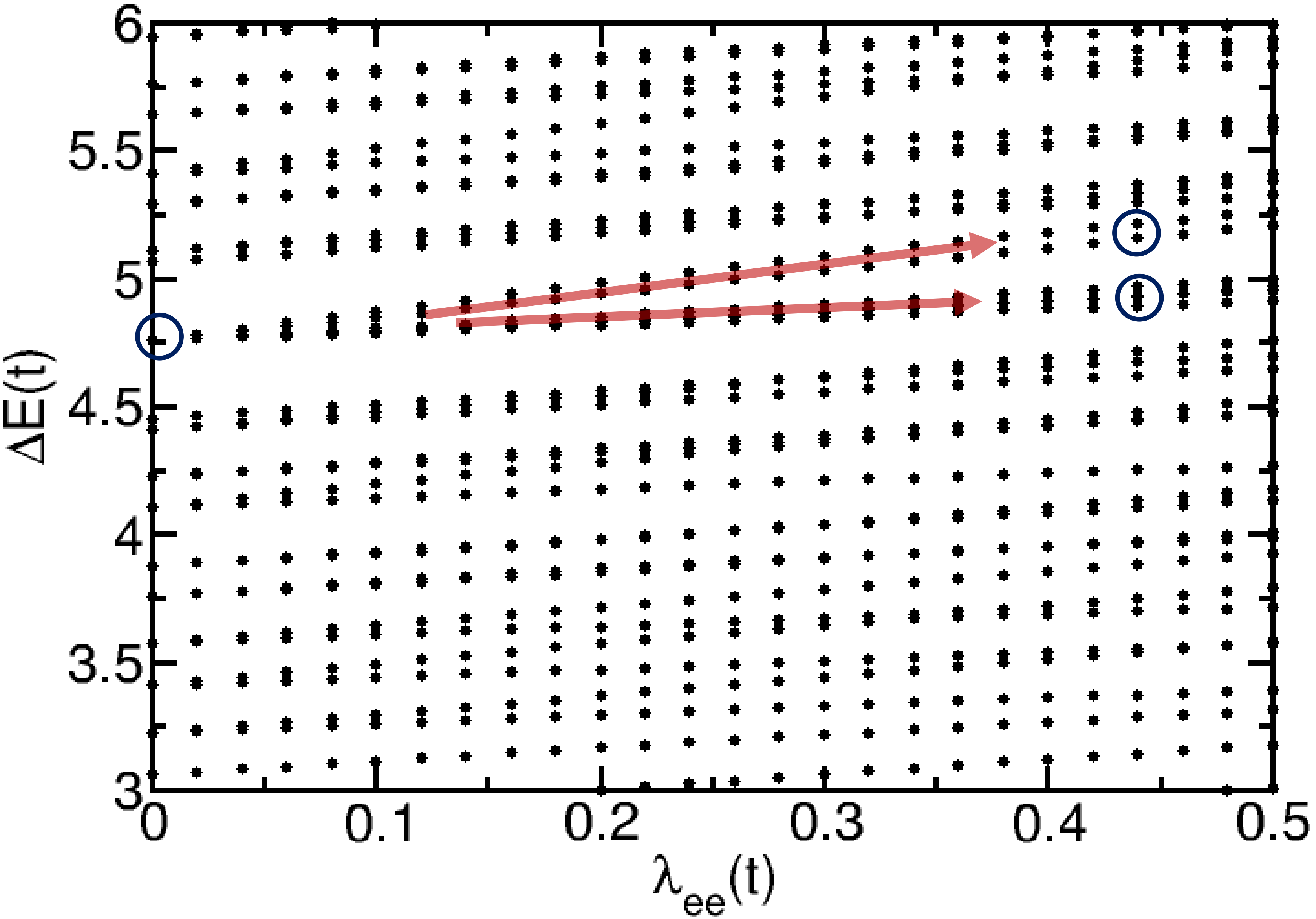
Small, linear 1D chains: dependence on Coulomb coupling λ_{ee}



Small, linear 1D chains: dependence on Coulomb coupling λ_{ee}

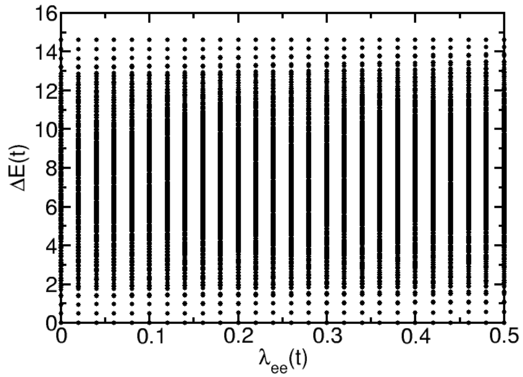


Small, linear 1D chains: dependence on Coulomb coupling λ_{ee}

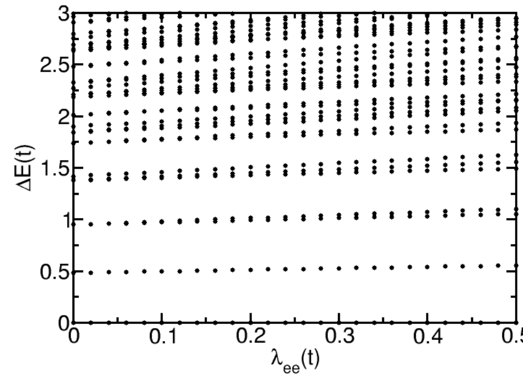


Small, linear 1D chains: length dependence

Full spectrum



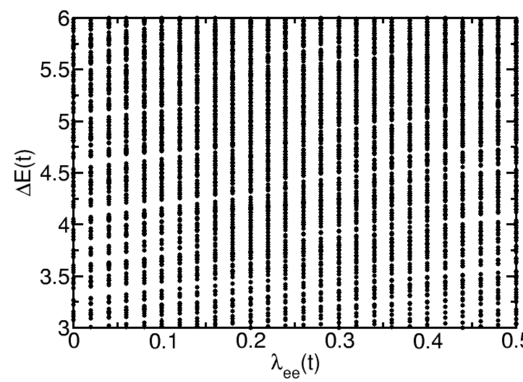
Low energy



... 12 sites, 924 states
... charge neutral

Length dependence
... 10 times denser spectrum
... similar dependence on ee-interaction
... similar length scaling with and without interaction

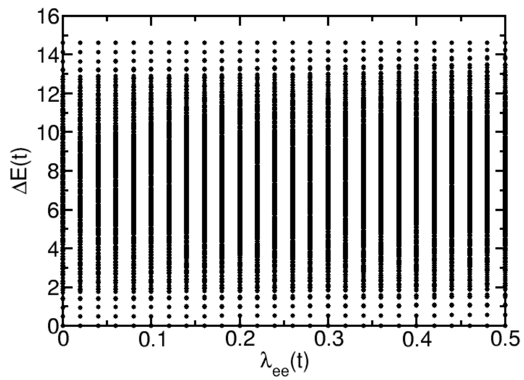
Higher energy

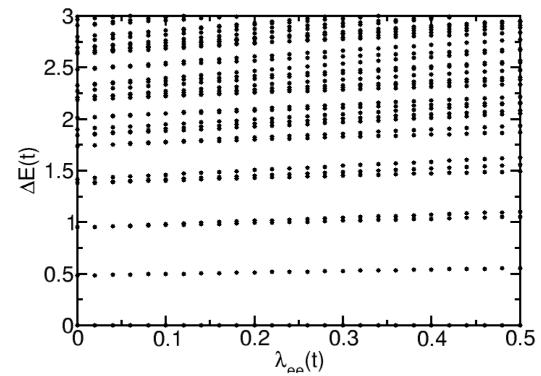


Small, linear 1D chains: bright or dark excitations?

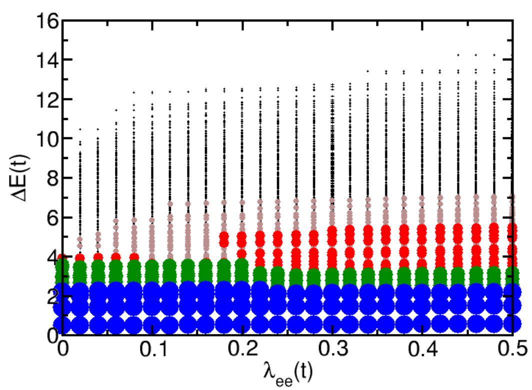
Full spectrum | **Low energy**

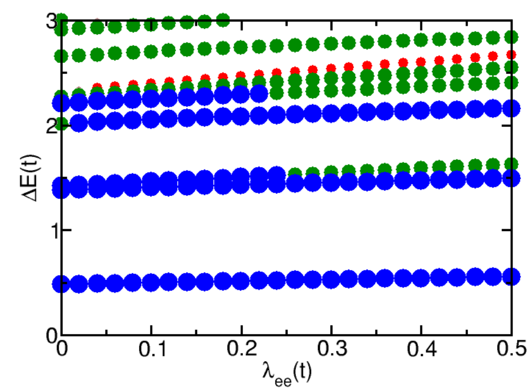
Bright + dark





Bright only

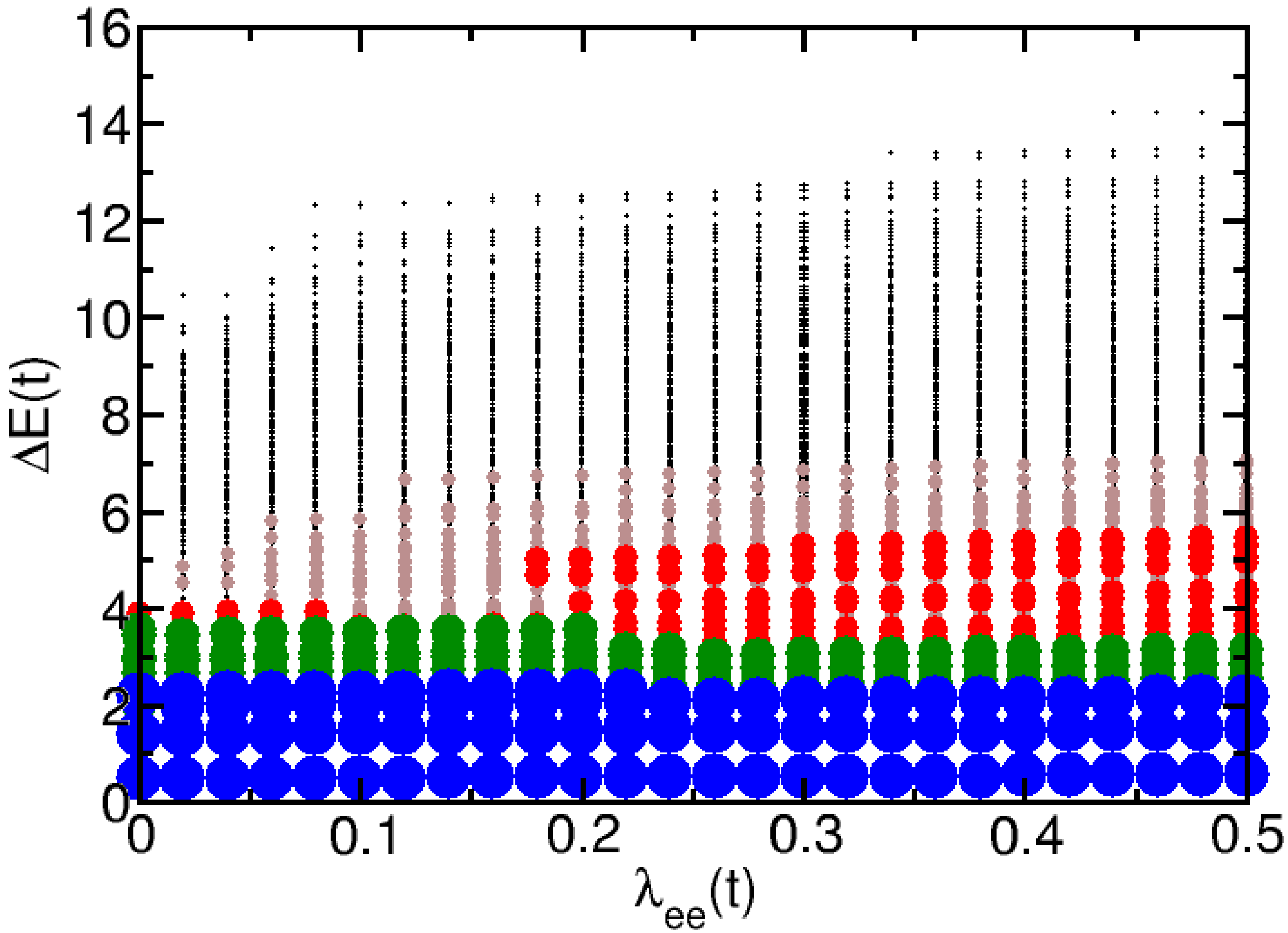




... dark excitations: dipole-forbidden by parity or multi-excitations
... 8 sites: 13% (no interaction), 28% (with interaction) are bright
... 12 sites: <2% (no interaction), 27% (with interaction) are bright

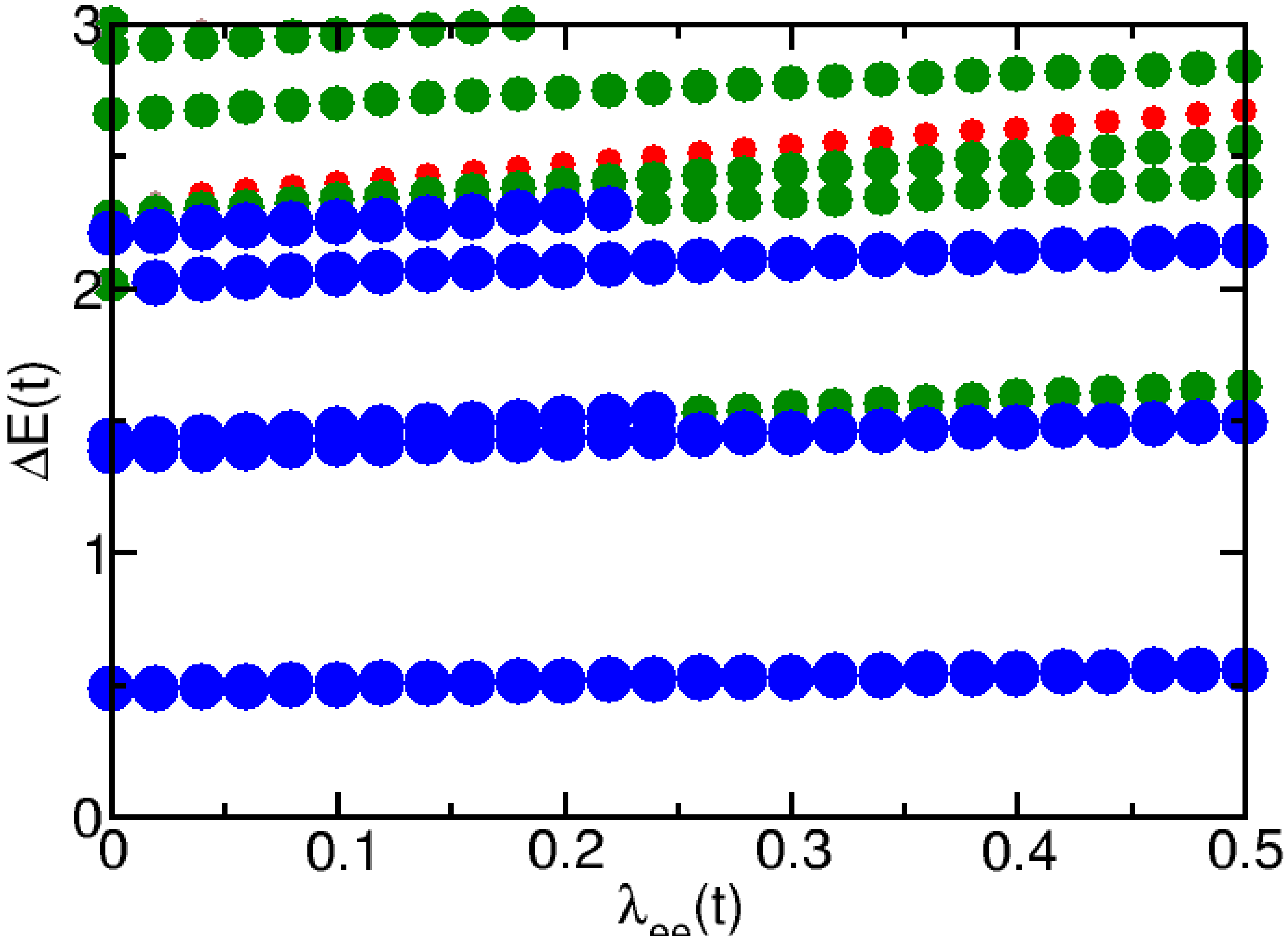
Small, linear 1D chains: where are the plasmons?

what makes a plasmon...smoking gun?



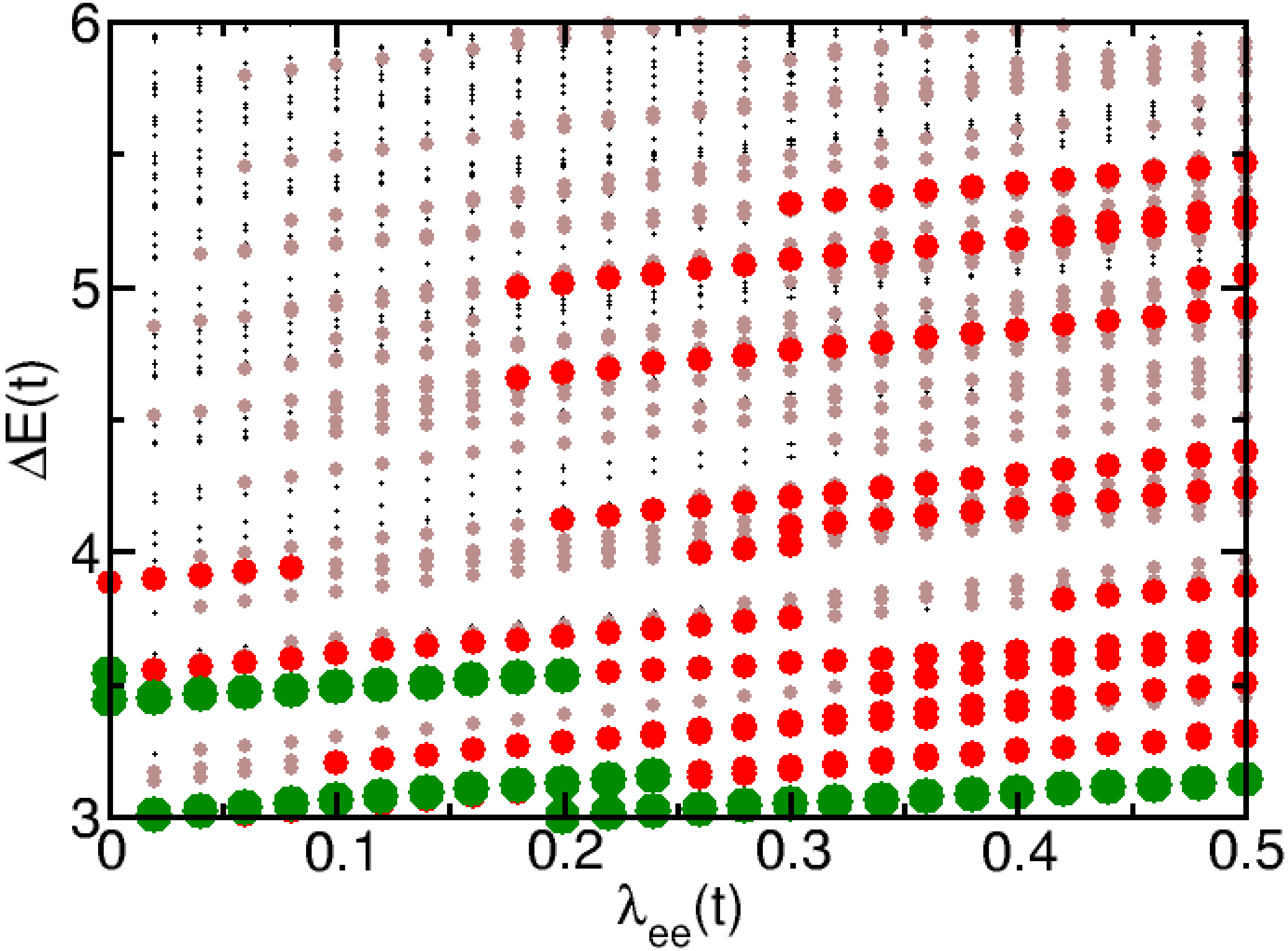
Small, linear 1D chains: where are the plasmons?

what makes a plasmon…smoking gun?



Small, linear 1D chains: where are the plasmons?

what makes a plasmon…smoking gun?



Linear 1D chains: what are the plasmons?

Speculation
… higher energy, multielectron excitations
… Coulomb induced transition dipole moments
… resonant response: no explicit excitation with clear spatial characteristics

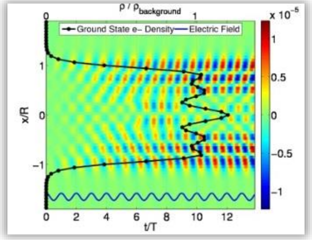
What next?
… driven states
… smoking guns for plasmons
… longer chains: do plasmons clearly appear?

… excitations: bosonic, fermionic or …
… nonlinear effects
… short vs long range

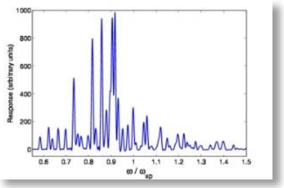
What can be learned about plasmons in small systems?
A matter point of view

- Time-dependent density functional theory (TDDFT)

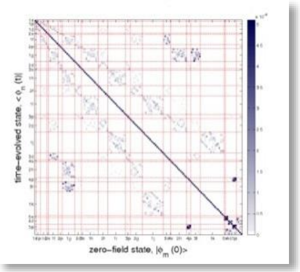
  … Time dependent response or response function



- Size quantization … 100-600 electron MNPs

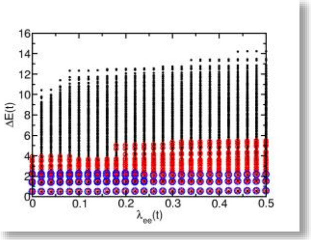


- Collective or single-particle response



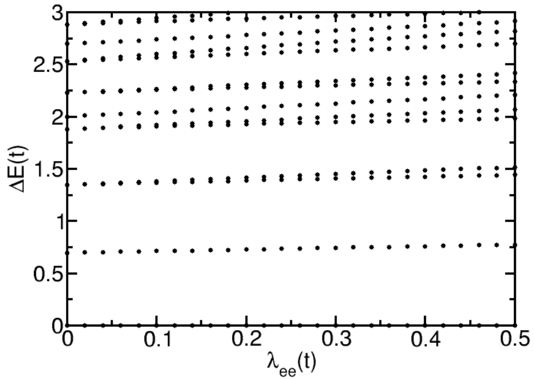
- Characterizing modes: “sloshing” and “inversion”

- Exact approaches: short 1D chains, full spectrum

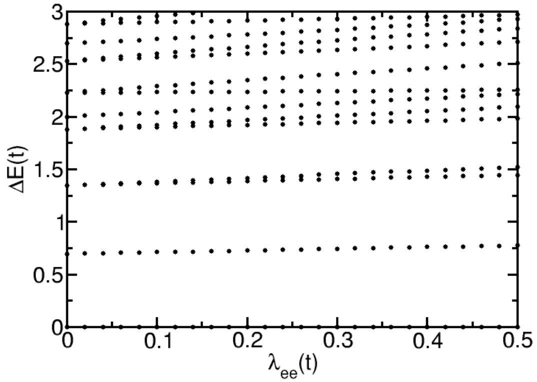


Small, linear 1D chains: dependence on interaction with atoms

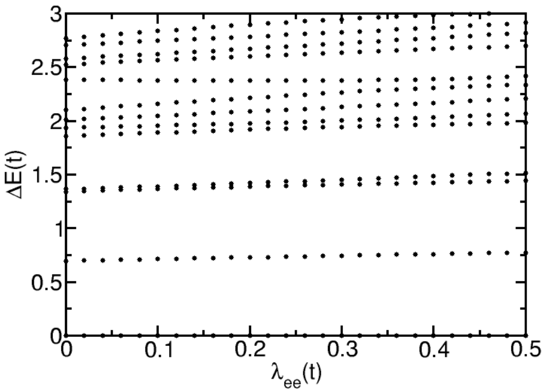
Charge neutral



No atom interaction



Fixed atom interaction



… 8 sites, 70 states

… similar spectra for each type of atom-electron coupling
… similar trends