THE FRITZ HABER RESEARCH CENTER
FOR MOLECULAR DYNAMICS

Towards time-dependent density functional theory for near-field - electron dynamics

Roi Baer

Institute of Chemistry and the Fritz Haber Center for Molecular Dynamics,
The Hebrew University of Jerusalem,
Jerusalem, Israel

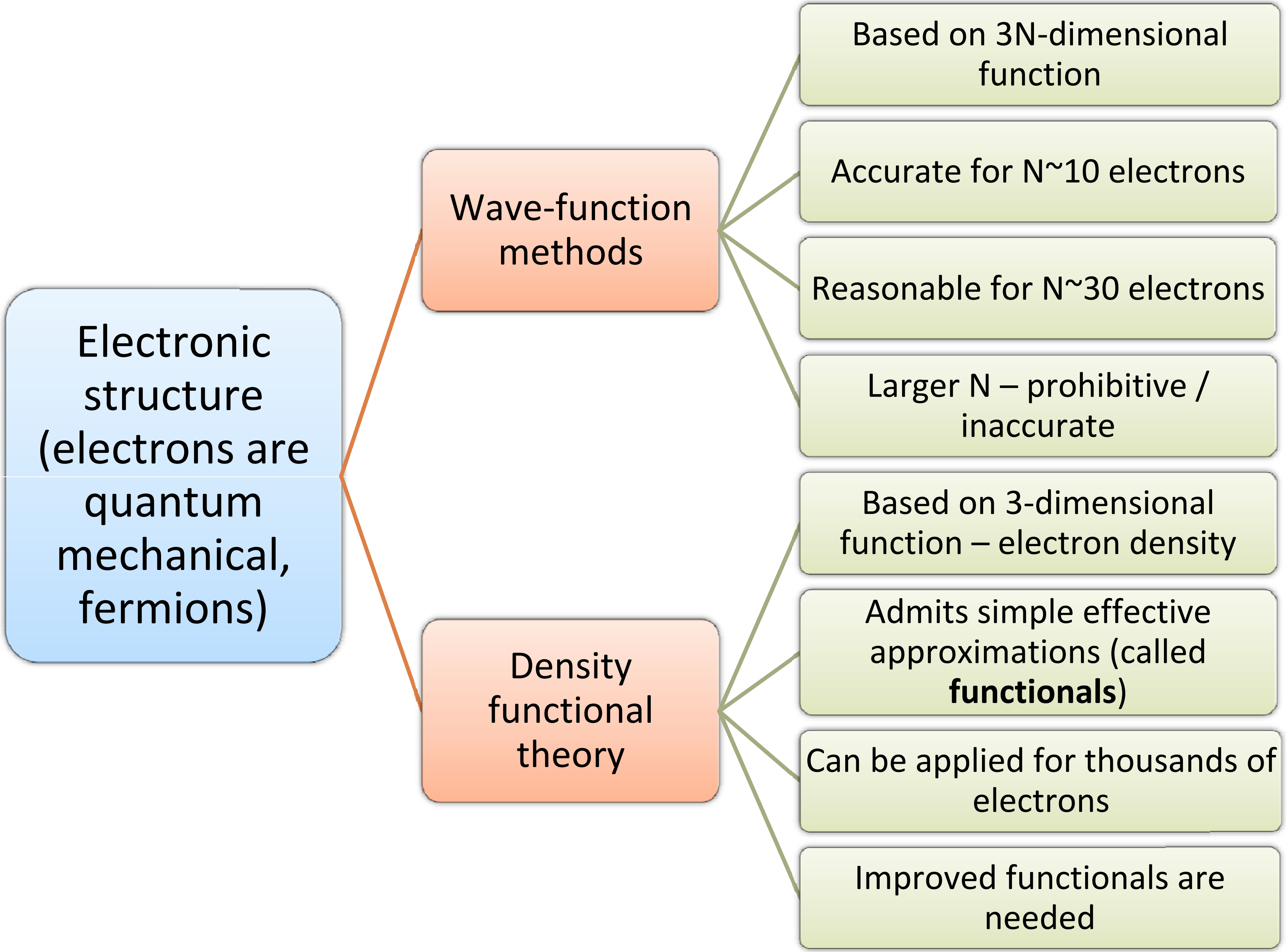
Regensburg, October 2006

Acknowledgments & Thanks

- Thanks to Profs. Dr. Dick and Dr. Baeurle and the entire Dick group for inviting me and hosting me
- Collaborators:
  - Prof. Daniel Neuhauser (UCLA)
  - Dr. Yair Kurzweil (Postdoc, Jerusalem)
  - Ms. Ester Livshits (PhD student, Jerusalem)
- Special thanks: Dr. Yihan Shao from QCHEM Inc.
- Funding:
  - Israel Science Foundation
  - German-Israel Foundation
  - USA-Israel Binational Science Foundation
  - FAME Network of excellence

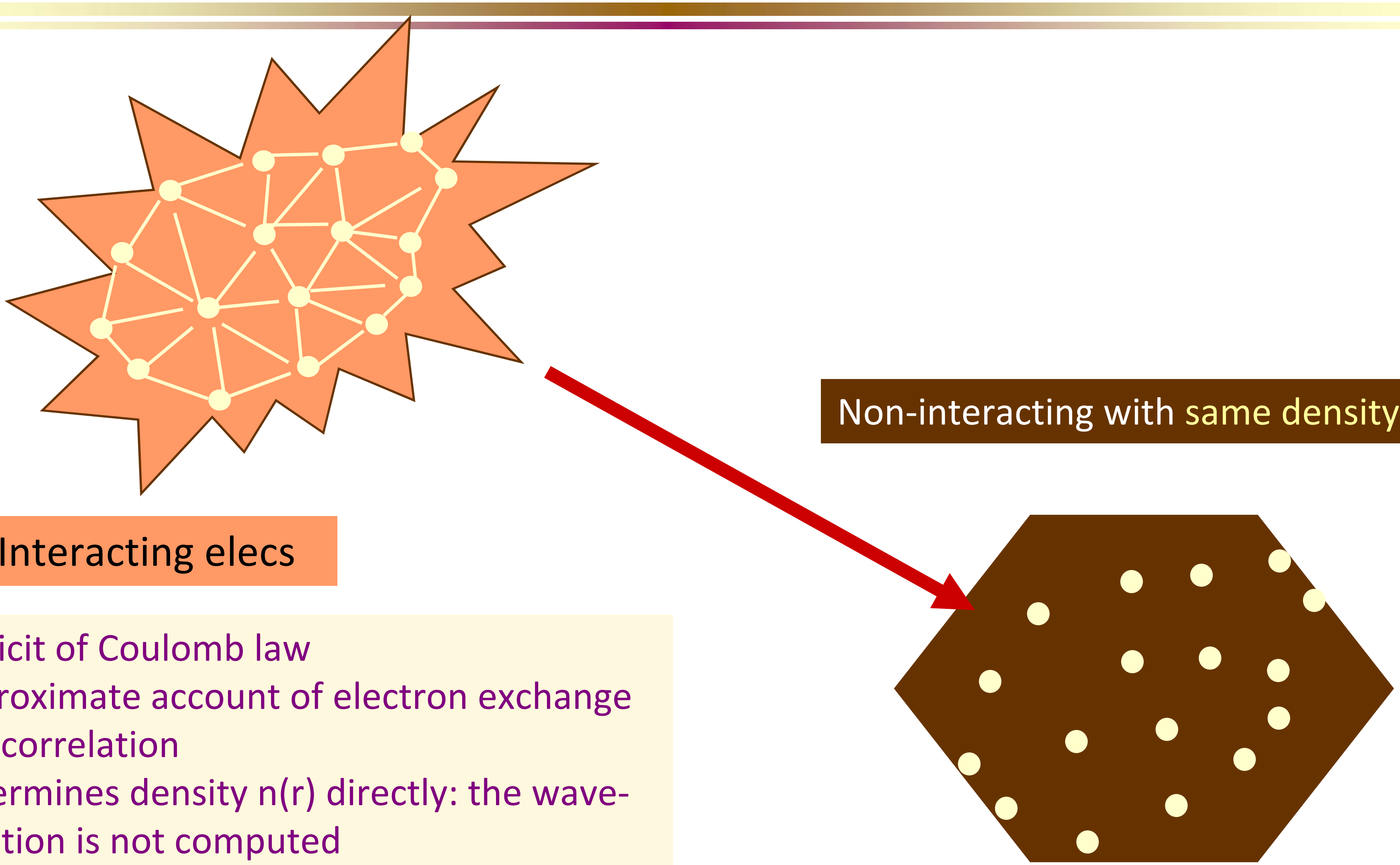
Outline

- Short introduction to DFT, TDDFT and near-field
- Combining DFT with near-field setup: problems
- Relation to self repulsion
- Removing long range self repulsion
- Construction of a “well-tempered” functional, based on 2 parameters
- Studies of near field-electron dynamics and local surface plasmons (LSPs) in metal nanoparticles
- Games: nano-optics based on LSPs



- Electronic structure (electrons are quantum mechanical, fermions)
  - Wave-function methods
    - Based on 3N-dimensional function
    - Accurate for N~10 electrons
    - Reasonable for N~30 electrons
    - Larger N – prohibitive / inaccurate
  - Density functional theory
    - Based on 3-dimensional function – electron density
    - Admits simple effective approximations (called **functionals**)
    - Can be applied for thousands of electrons
    - Improved functionals are needed

DFT in a nutshell



Non-interacting with same density

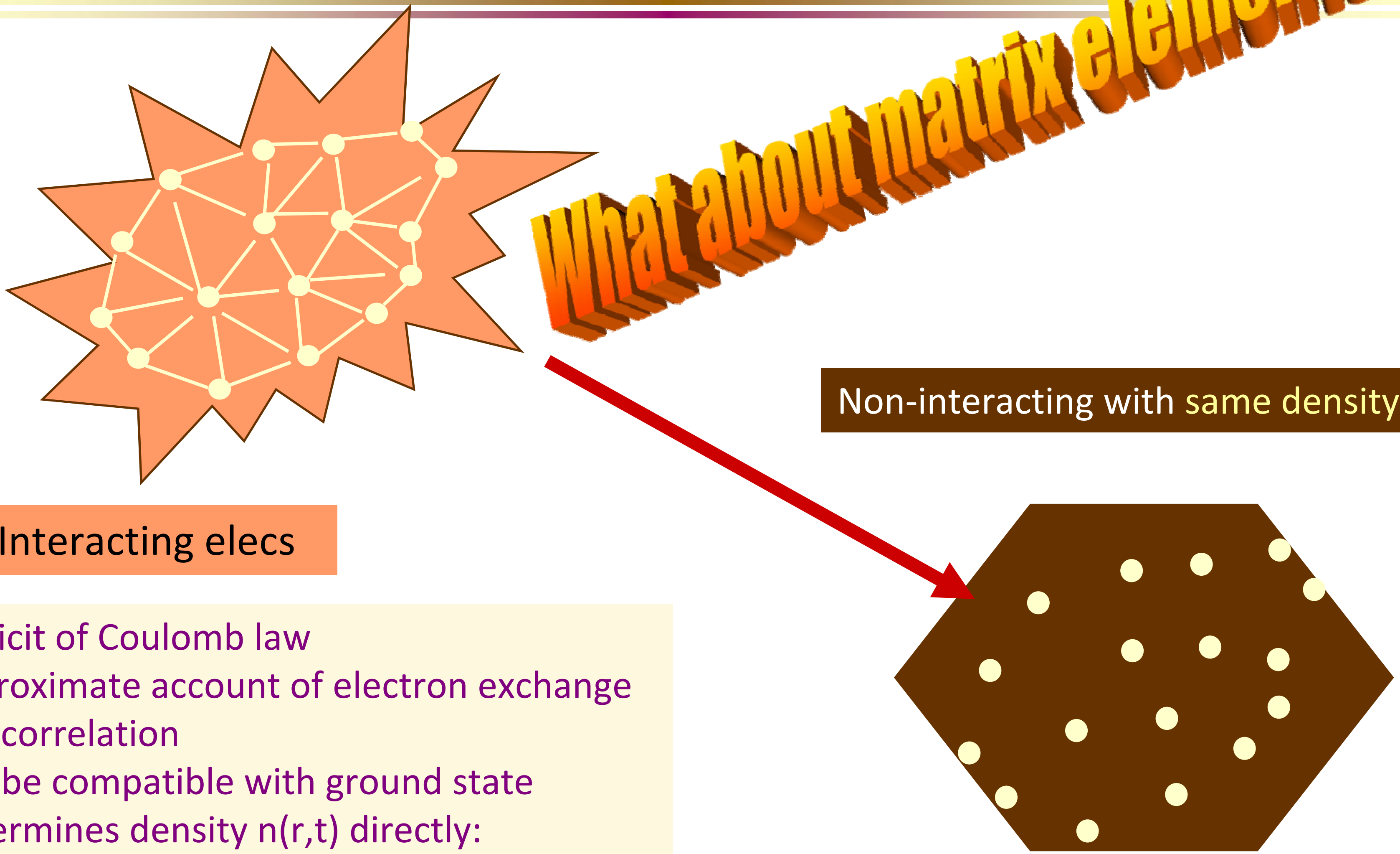
Interacting elecs

- Explicit of Coulomb law
- Approximate account of electron exchange and correlation
- Determines density n(r) directly: the wave-function is not computed
- Determines the electronic energy directly

W. Kohn and L. J. Sham, Phys. Rev 140, A1133 (1965).

Time-dependent DFT

What about matrix elements?



Non-interacting with same density

Interacting elecs

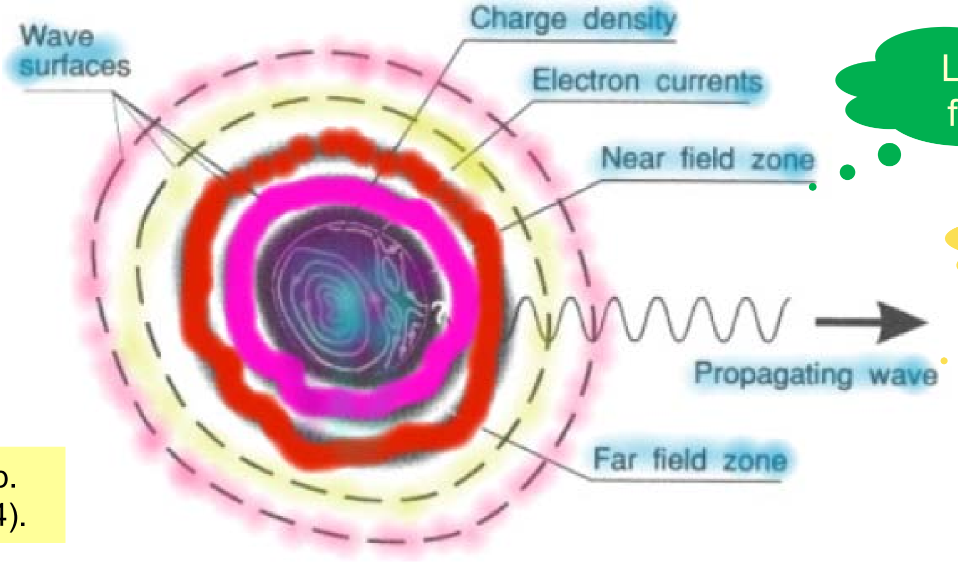
- Explicit of Coulomb law
- Approximate account of electron exchange and correlation
- Can be compatible with ground state
- Determines density n(r,t) directly:
- The wave-function is not computed

E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

Impact of DFT methods

- DFT was embraced by the Chemistry community in mid 90's.
- It has since revolutionized all fields of chemistry
- Tremendously useful in biochemistry and materials science
- TDDFT is newer but is growing fast
- Leads to results comparable and often more reliable than wave-function methods
- Still, as I show both theories still need improvement
  - Dispersion interactions (van der Waals)
  - Polarizability and other static response properties
  - Incorrect charge distribution in weakly interacting systems,
  - Anions and their stability
  - Rydberg excitations

Near-field on the nanoscale



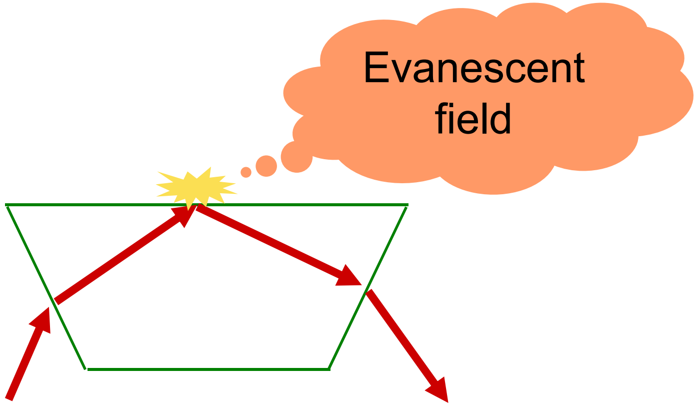
Longitudinal fields v<<c

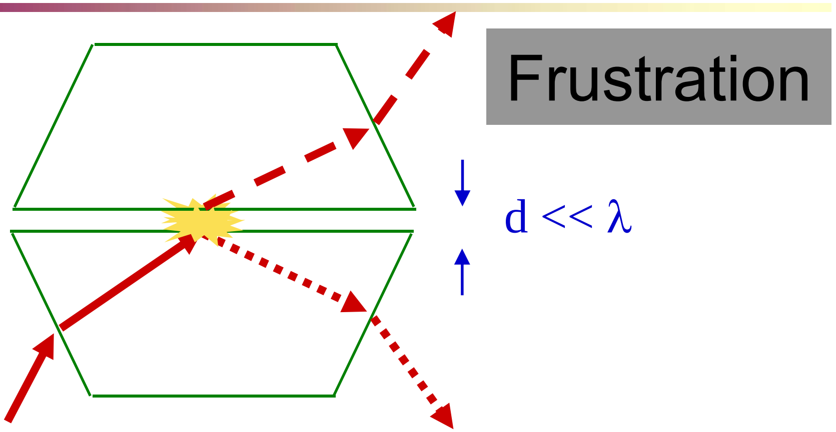
Transverse fields v=c

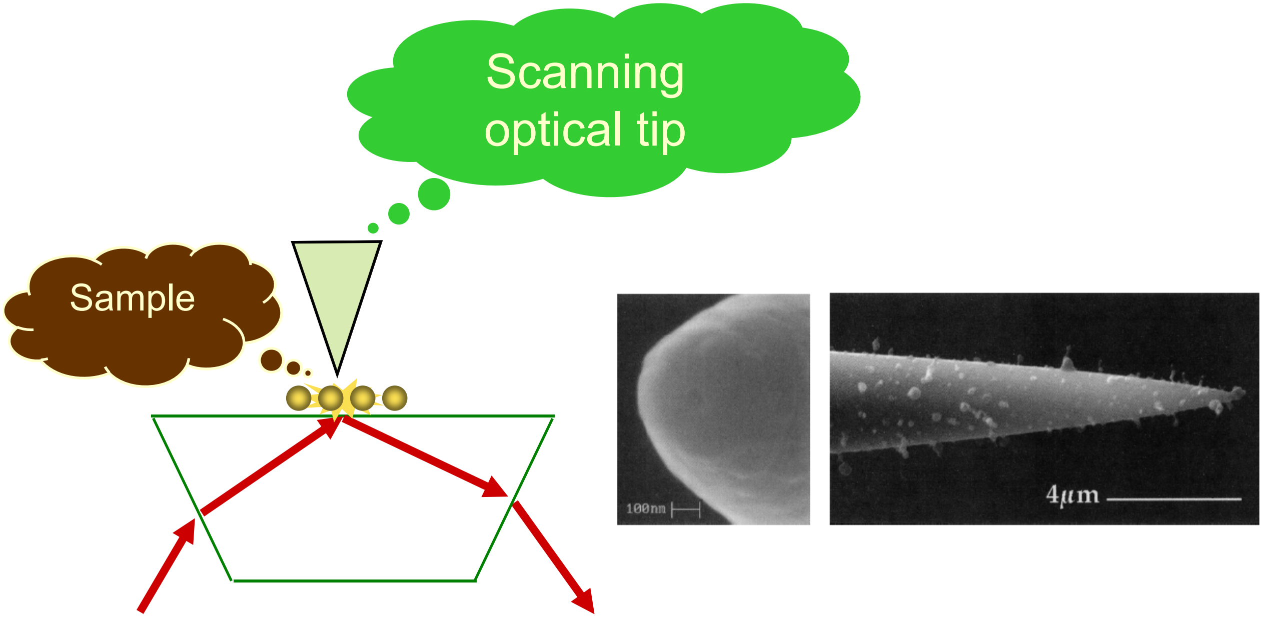
D. Courjon and C. Bainier, Rep. Prog. Phys. **57** (10), 989 (1994).

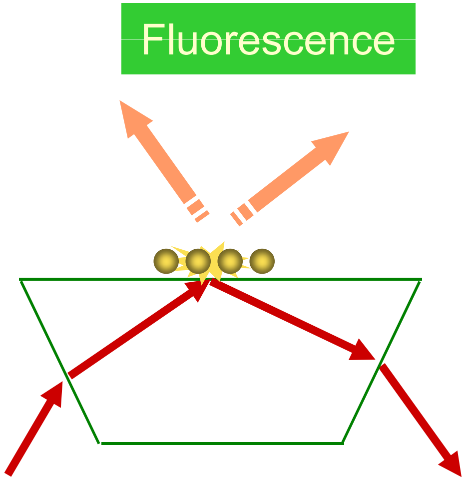
- EM fields with optical frequencies yet change on a 10 nm length scale
  - Spectroscopy, including nonlinear
  - Microscopy
- Plasmonics:
  - Waveguides: Transport of EM energy on nm scale

Near-field scanning optical microscopy





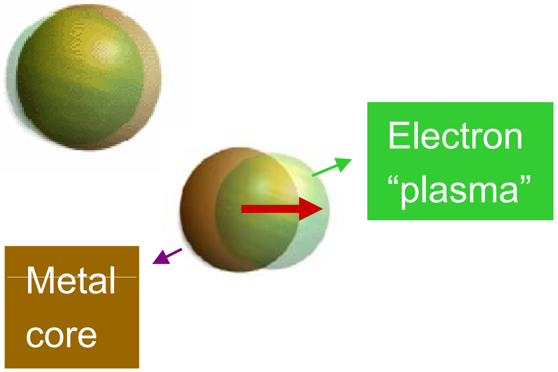




E. Betzig, M. Issacson, and A. Lewis, Appl. Phys. Lett. **51**, 2088 (1987).

EM energy transport on nm scale

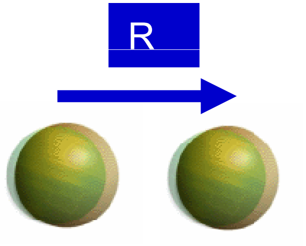
- Local surface plasmon: collective excitation



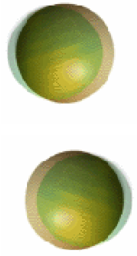
Electron “plasma”

Metal core

- Dipole coupling of two dots

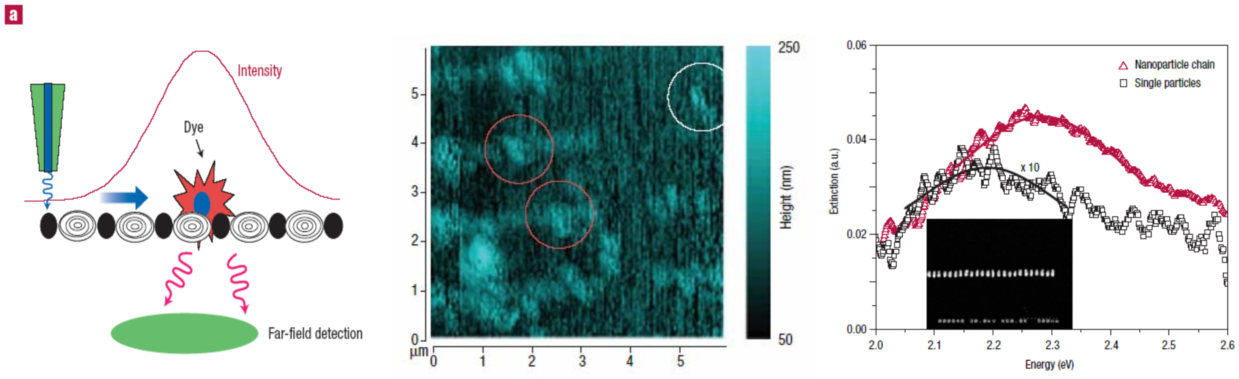


Longitudinal coupling $\alpha = 0$



Transverse coupling $\alpha = 90^o$

$$C = \frac{d_1 d_2 \left(1 - 3\cos^2\alpha\right)}{R^3}$$



S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, and A. A. G. Requicha, Nature Mat. **2**, 229 (2003).

Why TDDFT is a natural choice

- Maxwell's + Schrödinger equations

$$\varepsilon_0\nabla\cdot\mathbf{E}=\rho \qquad \nabla\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t}$$

$$\nabla\cdot\mathbf{B}=0 \qquad \mu_0^{-1}\nabla\times\mathbf{B}=\mathbf{j}+\frac{\partial\mathbf{E}}{\partial t}$$

- Using potentials to describe the fields (Coulomb gauge):

$$\mathbf{E}=-\dot{\mathbf{A}}-\nabla\phi \qquad \mathbf{B}=\nabla\times\mathbf{A} \qquad \nabla\cdot\mathbf{A}=0$$

- We have equations of motion:

$$-\nabla^2\phi(\mathbf{r},t)=\varepsilon_0^{-1}\rho(\mathbf{r},t) \qquad -\nabla^2\mathbf{A}+\frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2}=\mu_0\mathbf{j}_\perp$$

$$\mathbf{j}_\perp=\mathbf{j}-\varepsilon_0^{-1}\nabla\dot{\phi}$$

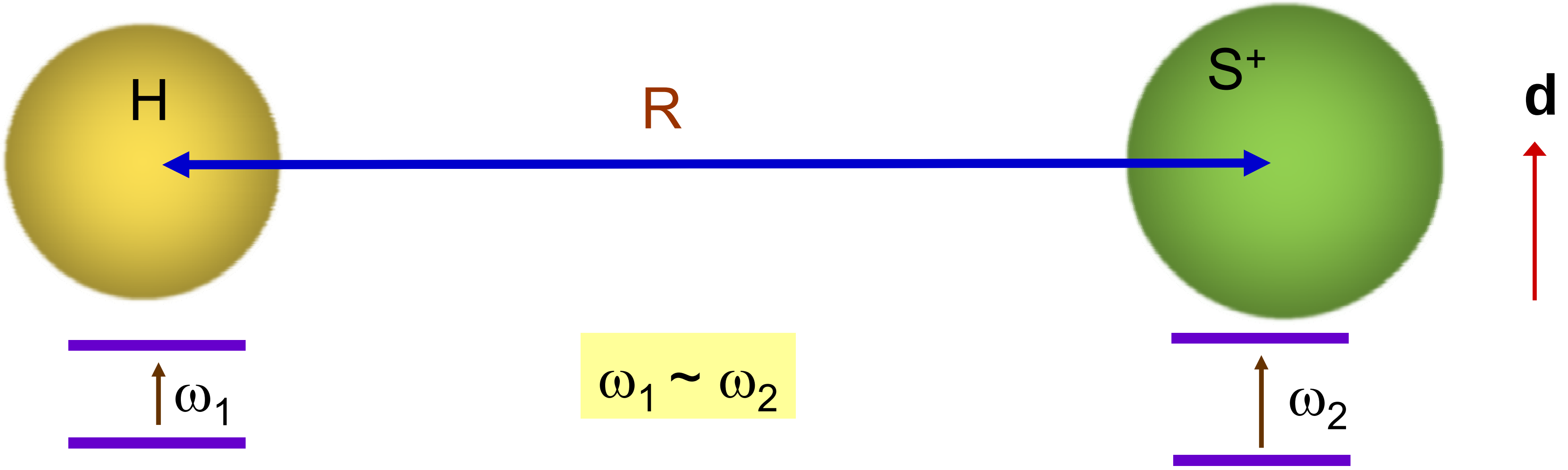
$$i\dot{\Psi}=\left\{\sum_{i=1}^{N}\left(\hat{\mathbf{p}}_i-\frac{q_i}{c}\mathbf{A}(\hat{\mathbf{r}}_i,t)\right)^2+q_i\phi(\hat{\mathbf{r}}_i,t)\right\}\Psi$$

Instantaneous
TD Poisson:
TDDFT/TDCDFT

Retardation.
Wave
propagation
$R\omega \gg c$

Usually can replace A by A_{ext} ($\mu_0 \ll 1$)

Dipole coupling theory



$\omega_1 \sim \omega_2$

$$C = \frac{d_H^{01} d_{S^+}^{01}}{R^3}$$

Basically: two QM states: $\left| H_{exc} {S^+}_{gs} \right\rangle, \left| H_{gs} {S^+}_{exc} \right\rangle$

$$H = \begin{pmatrix} \omega_1 & C \\ C & \omega_2 \end{pmatrix} = \bar{E} + \begin{pmatrix} \Delta & C \\ C & -\Delta \end{pmatrix}$$

$$\bar{E} = \underbrace{\frac{\omega_1 + \omega_2}{2}}_{Average} \qquad \underbrace{2\Delta = \omega_1 - \omega_2}_{mismatch}$$

$$E_{\pm} = \bar{E} \pm \Omega \qquad \Omega = \sqrt{\Delta^2 + C^2}$$

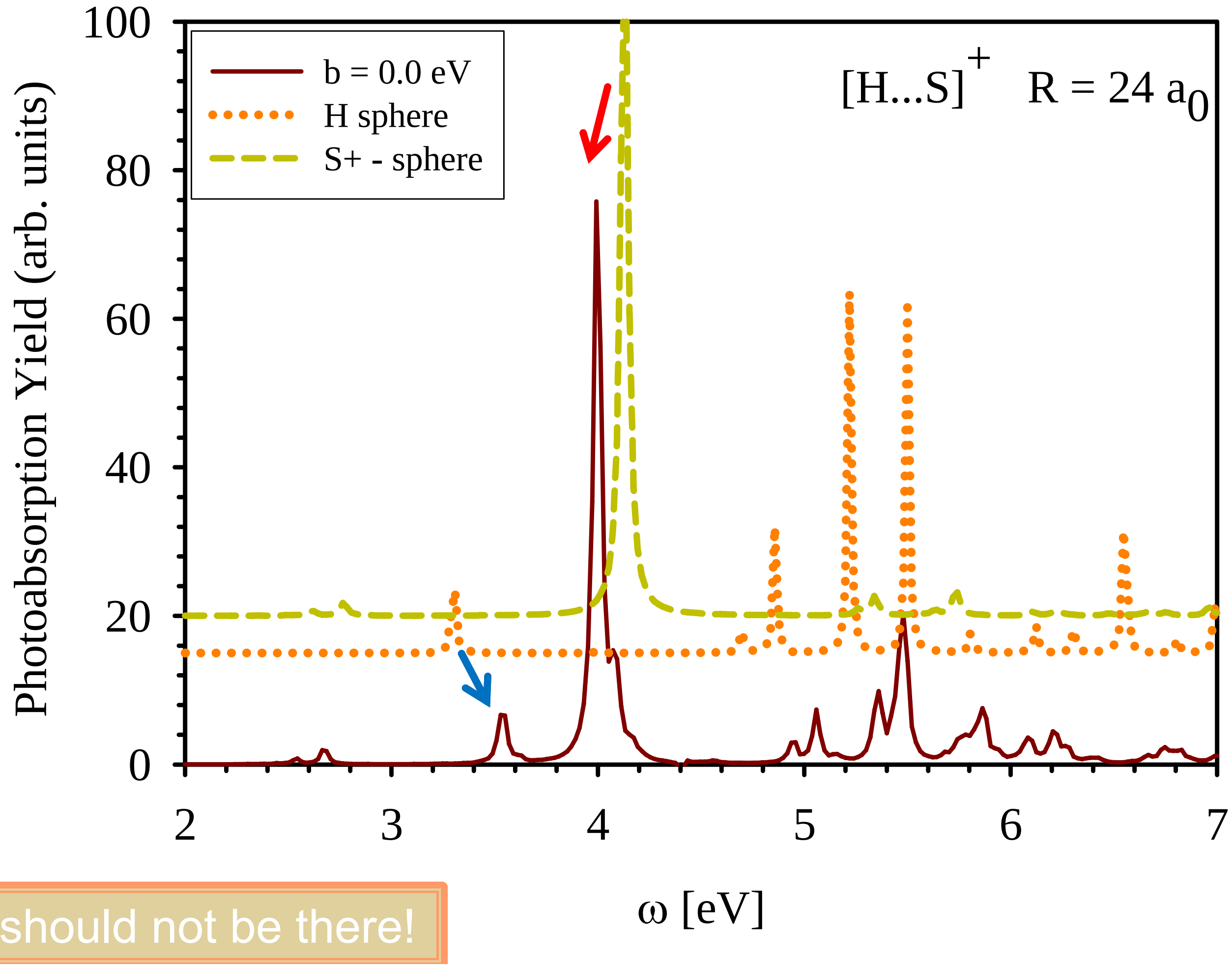
$$C \ll \Delta \quad \rightarrow \quad \Omega = \Delta + \frac{C^2}{2\Delta}$$

$$C \gg \Delta \quad \rightarrow \quad \Omega = C$$

$$\begin{pmatrix} D_+ \\ D_- \end{pmatrix} = \begin{pmatrix} \cos\theta/2 & \sin\theta/2 \\ -\sin\theta/2 & \cos\theta/2 \end{pmatrix} \begin{pmatrix} d_H \\ d_{S^+} \end{pmatrix}$$

$$\tan\theta = \frac{C}{\Delta}$$

Spurious splitting



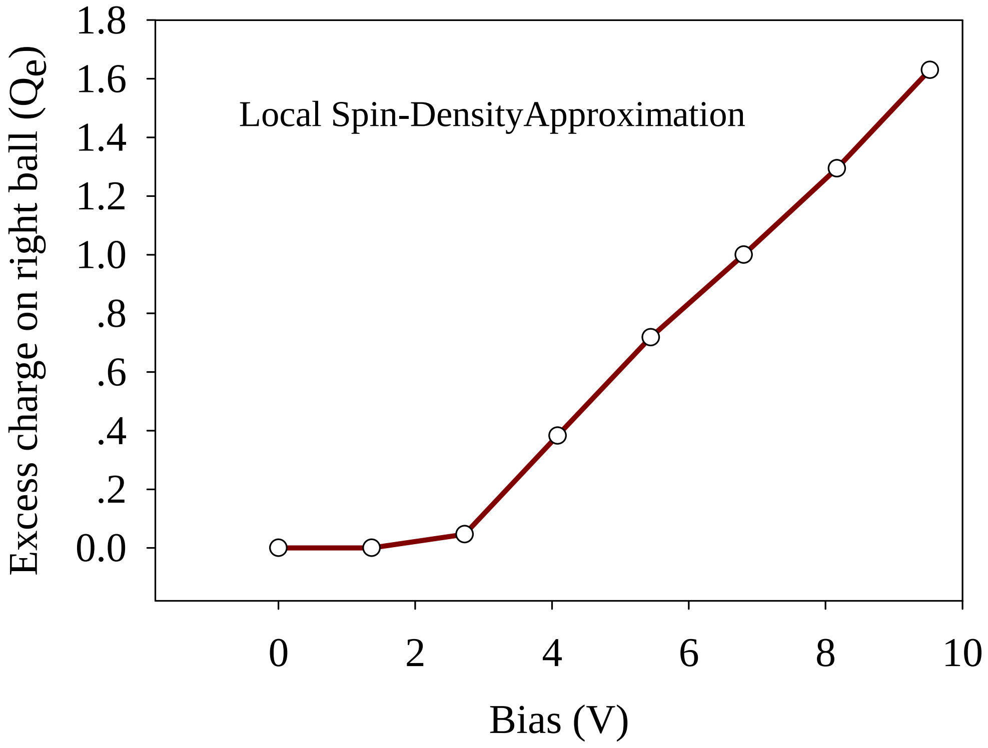
These shifts should not be there!

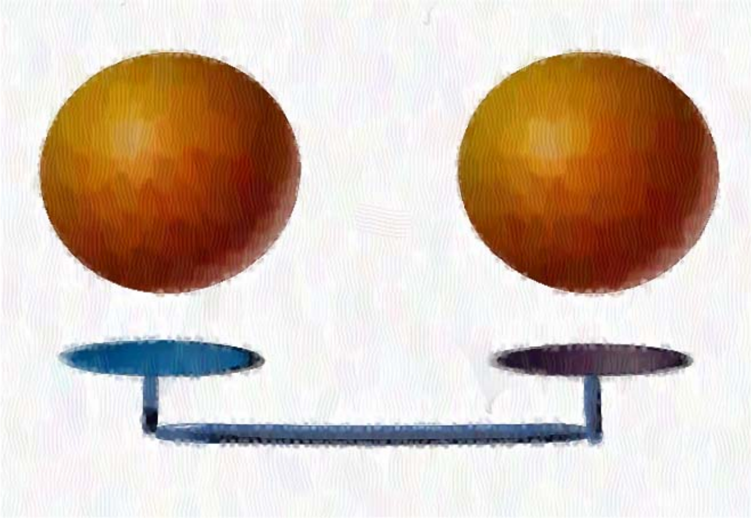
Source of problem: DFT

- Incorrect charge distribution
- The spheres share partial charges
- This makes the HOMO of the system highly nonlocal
- In TDDFT: too much sensitivity in one sphere concerning the other.

Weakly coupled systems have integer number of electrons

LDA/GGA violate charge quantization





2 jellium balls

r_s=2.2

20 elecs each

In the case of the H and S+ spheres, the charge

On each sphere was non-integer, although they were distant

Self repulsion

- An electron is repelled by itself
- The most severe is the self-interaction in the Hartree energy

DFT: the non-physical behavior impairs

- e-Density in weakly-coupled systems (charge quantization)
- Static response (polarizability, etc.)
- Prediction of stability of anions (especially atoms)

Will of course affect TDDFT!

- Charge transfer excitations (Dreuw + Head-Gordon)
- Rydberg states
- Spurious shifts resulting from unphysical ultra-nonlocality

A DFT with correct long-range behavior

- The XC Energy is defined as:

$$E_{XC}[n] = T[n] - T_s[n] + U[n] - E_H[n]$$

- Can write it, using adiabatic connection, as:

$$E_{XC}[n] = \int_0^\infty \left\langle \Psi_{\gamma'} \middle| \hat{W}_{\gamma'} \middle| \Psi_{\gamma'} \right\rangle d\gamma' - E_H[n]$$

$$\hat{W}_\gamma = \frac{1}{2}\sum_{i\neq j} w_\gamma\left(\hat{r}_{ij}\right); \qquad w_\gamma(r) = e^{-\gamma r}$$

- Where:

$$\Psi_\gamma = \text{gs with } n(\mathbf{r}) \text{ under } u_\gamma(r) = \frac{1 - e^{-\gamma r}}{r}$$

J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974).
D. C. Langreth and J. P. Perdew, Sol. Stat. Comm. 17, 1425 (1975).
O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
W. Yang, J. Chem. Phys. 109, 10107 (1998).

Evaluating the integral

- An approximation:

$$\begin{aligned}\int_0^\infty \left\langle \Psi_{\gamma'} \middle| \hat{W}_{\gamma'} \middle| \Psi_{\gamma'} \right\rangle d\gamma' &= \int_0^\gamma \left\langle \Psi_{\gamma'} \middle| \hat{W}_{\gamma'} \middle| \Psi_{\gamma'} \right\rangle d\gamma' + \int_\gamma^\infty \left\langle \Psi_{\gamma'} \middle| \hat{W}_{\gamma'} \middle| \Psi_{\gamma'} \right\rangle d\gamma' \\ &\approx \int_0^\gamma \left\langle \Psi_0 \middle| \hat{W}_{\gamma'} \middle| \Psi_0 \right\rangle d\gamma' + \int_\gamma^\infty \left\langle \Psi_\infty \middle| \hat{W}_{\gamma'} \middle| \Psi_\infty \right\rangle d\gamma'\end{aligned}$$

- Leading to:

$$\int_0^\infty \left\langle \Psi_{\gamma'} \middle| \hat{W}_{\gamma'} \middle| \Psi_{\gamma'} \right\rangle d\gamma' \approx \left\langle \Psi_0 \middle| \hat{U}_\gamma \middle| \Psi_0 \right\rangle + \left\langle \Psi_\infty \middle| \hat{Y}_\gamma \middle| \Psi_\infty \right\rangle$$

$$\hat{U}_\gamma = \frac{1}{2} \sum_{i \neq j} u_\gamma \left(\hat{r}_{ij} \right) \qquad \hat{Y}_\gamma = \frac{1}{2} \sum_{i \neq j} y_\gamma \left(\hat{r}_{ij} \right)$$

$$u_\gamma(r) = \left(1 - e^{-\gamma r} \right) \big/ r \qquad y_\gamma(r) = e^{-\gamma r} \big/ r$$

The approximation is exact ?!

$$E_{XC}[n] \approx \langle \Psi_0 | \hat{U}_\gamma | \Psi_0 \rangle + \langle \Psi_\infty | \hat{Y}_\gamma | \Psi_\infty \rangle - E_H[n]$$

$$y_\gamma(r) = e^{-\gamma r}/r \qquad u_\gamma(r) = \left(1 - e^{-\gamma r}\right)/r$$

The error in the approximation is:

$$\Delta E_{XC}^{\gamma} = \left[T[n] + \langle \Psi_\infty | \hat{U}_\gamma | \Psi_\infty \rangle\right] - \left[T_s[n] + \langle \Psi_0 | \hat{U}_\gamma | \Psi_0 \rangle\right]$$

when $\gamma = 0$ $\quad \Delta E_{XC}^{\gamma=0} = T[n] - T_s[n] \geq 0$

when $\gamma = \infty$ $\quad \Delta E_{XC}^{\gamma=\infty} = E_c[n] \leq 0$

Conclusion: There exists $0 \leq \gamma \leq \infty$ for which the approximation is `Exact`

Summary of theory

- Turn off the Coulomb interaction from the inside out
- The following is the *exact* Kohn-Sham energy functional

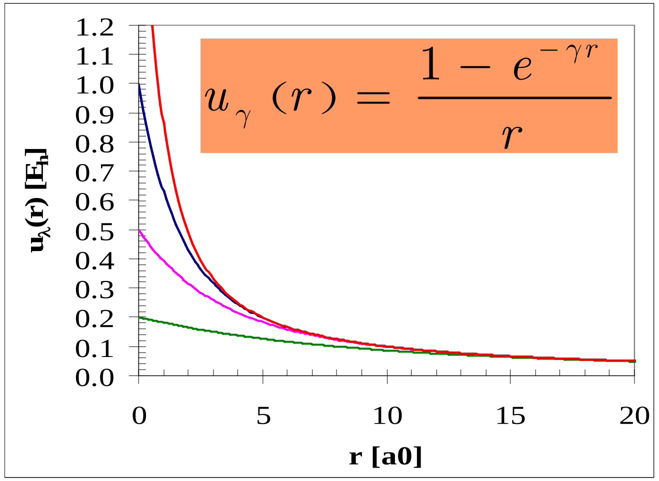
$$E_{v,N}[n] = T_s[n] + E_{ext}[n] + E_H[n] + K_X^{\gamma}[n] + E_{XC}^{\gamma}[n]$$

$$K_X^{\gamma}[n] = \frac{1}{2}\int \left|P[n](\mathbf{r},\mathbf{r}')\right|^2 u_{\gamma}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3r d^3r'$$

$$\begin{aligned} E_{XC}^{\gamma}[n] &= \left\langle \Psi_{\infty}\left|\hat{Y}_{\gamma}\right|\Psi_{\infty}\right\rangle - \frac{1}{2}\int n(\mathbf{r}) n(\mathbf{r}') y_{\gamma}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3r d^3r' \\ &= \frac{1}{2}\int \left[g(\mathbf{r},\mathbf{r}') - 1\right] n(\mathbf{r}) n(\mathbf{r}') y_{\gamma}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3r d^3r' \end{aligned}$$

$$y_{\gamma}(r) = \frac{e^{-\gamma r}}{r} \qquad \Psi_{\infty} = \text{exact wf}$$

- Need approximations for γ[*n*], $E^{\gamma}_{XC}[n]$



R. Baer and D. Neuhauser, Phys. Rev. Lett. 94, 043002 (2005).

Related prior work:

- Savin in *Recent Advances in Density Functional Methods Part I*, edited by D. P. Chong (World Scientific, Singapore, 1995), p. 129.
- Hirao et al J. Chem. Phys. 115 (8), 3540 (2001).

γ=1 Approximation

- We do not know the n dependence of γ
- Let’s take a constant $\gamma[n] = \text{const}=1\text{a}_0^{-1}$

$$E_{XC}^{\gamma}[n] = \left\langle \Psi_\infty \middle| \hat{Y}_\gamma \middle| \Psi_\infty \right\rangle - \frac{1}{2}\int n(\mathbf{r})\, n(\mathbf{r}')\, y_\gamma\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3r\, d^3r'$$

$$\approx \int \varepsilon_{XC}^{\gamma}(n(\mathbf{r}))\, n(\mathbf{r})\, d^3r$$

$$\varepsilon_{XC}^{\gamma} = \varepsilon_{X}^{\gamma} + \varepsilon_{C}^{\gamma}$$

$$\varepsilon_{X}^{\gamma} = \quad \text{known analytical Yukawa XE per particle for HEG}$$

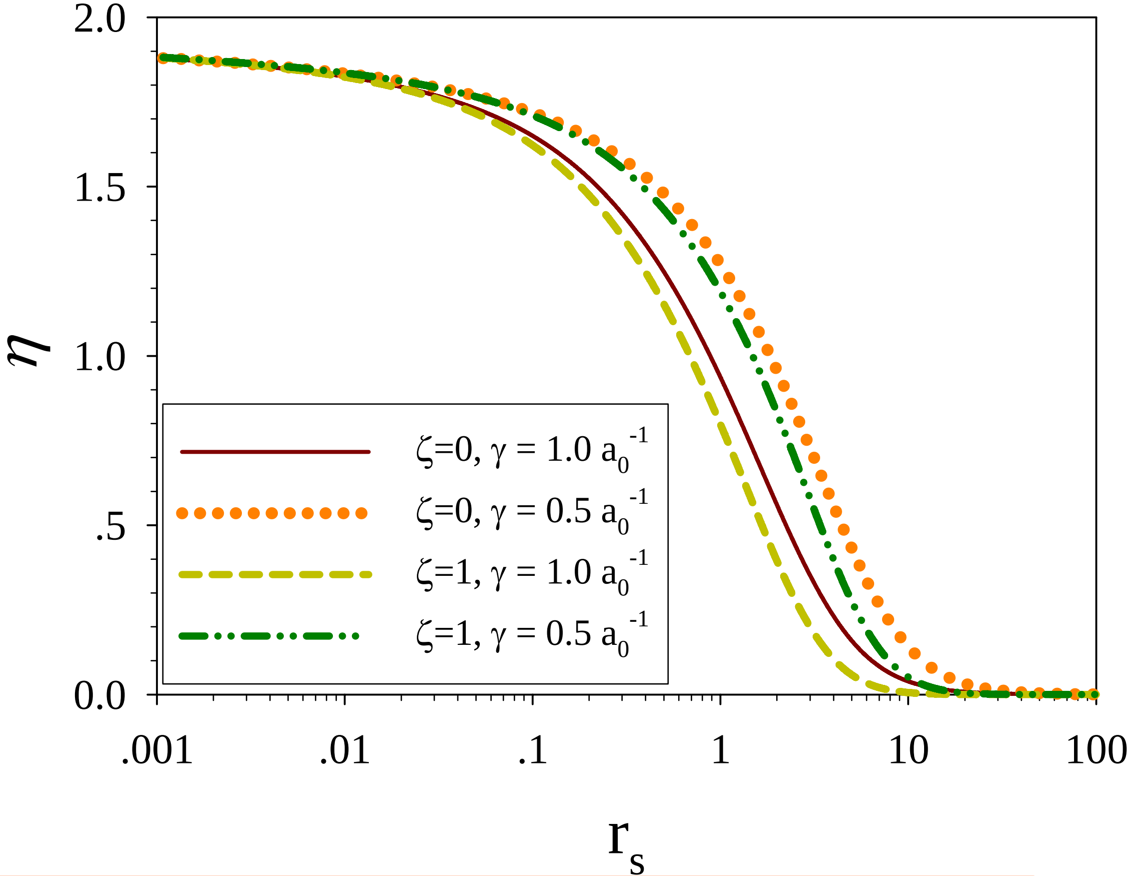
$$\varepsilon_{C}^{\gamma} = \eta\varepsilon_{LDA}^{HEG} = \text{Remaining CE per particle for HEG}$$

$$E_X = \underbrace{K_X^{\gamma}}_{\substack{\text{nonlocal}\\ \text{c-Yukawa X}}} + \underbrace{\int \varepsilon_X^{\gamma}(n)\, n\, d^3r}_{\text{Local Yukawa X}}$$

Caveat: Not exact for HEG!

The value of η for HEG

$$\eta = \frac{1}{2\varepsilon_c^{LDA}} \int \left(1 - g^{HEG}\left(\mathbf{r}-\mathbf{r}'\right)\right) n\left(\mathbf{r}\right) n\left(\mathbf{r}'\right) y_\gamma\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3r d^3r'$$

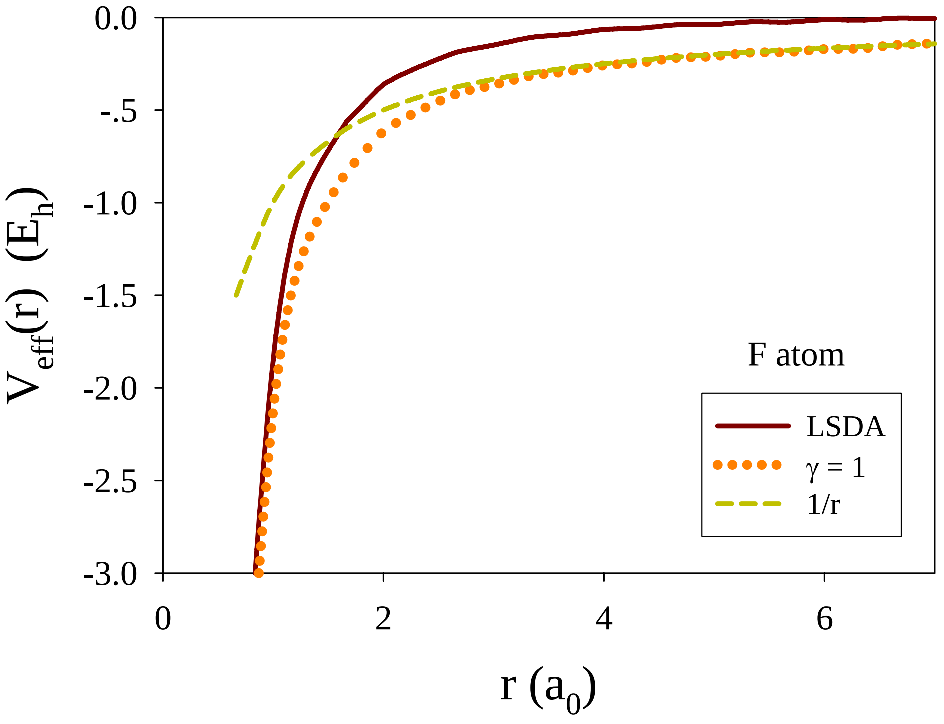


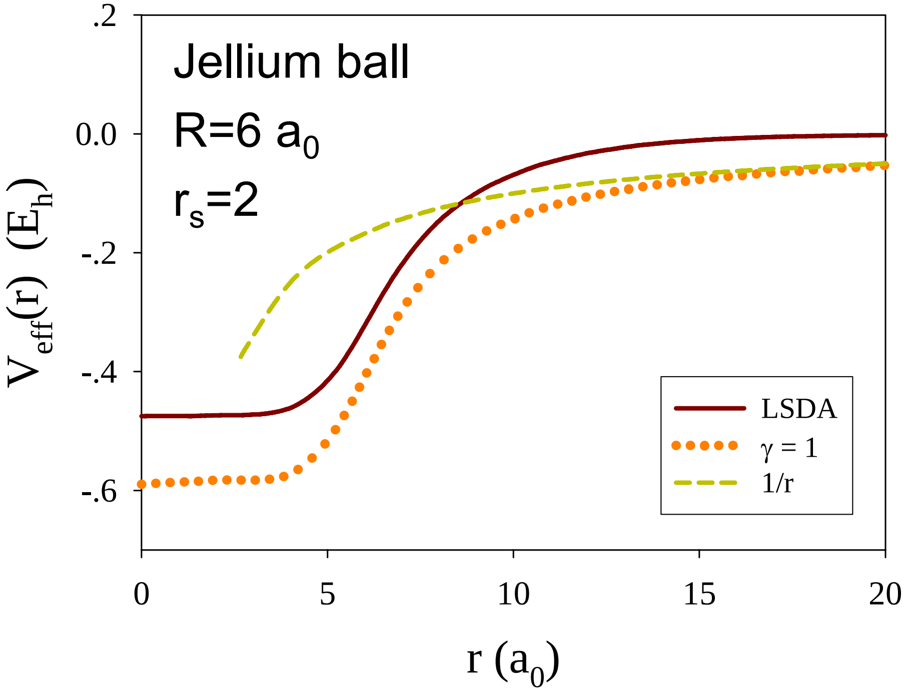
R. Baer E. Livshits and D. Neuhauser, Chem. Phys. **329**, 266 (2006)

Pair correlation function taken from:
P. Gori-Giorgi and J. P. Perdew, Phys. Rev. B 66, 165118 (2002).

Correct asymptotic potential

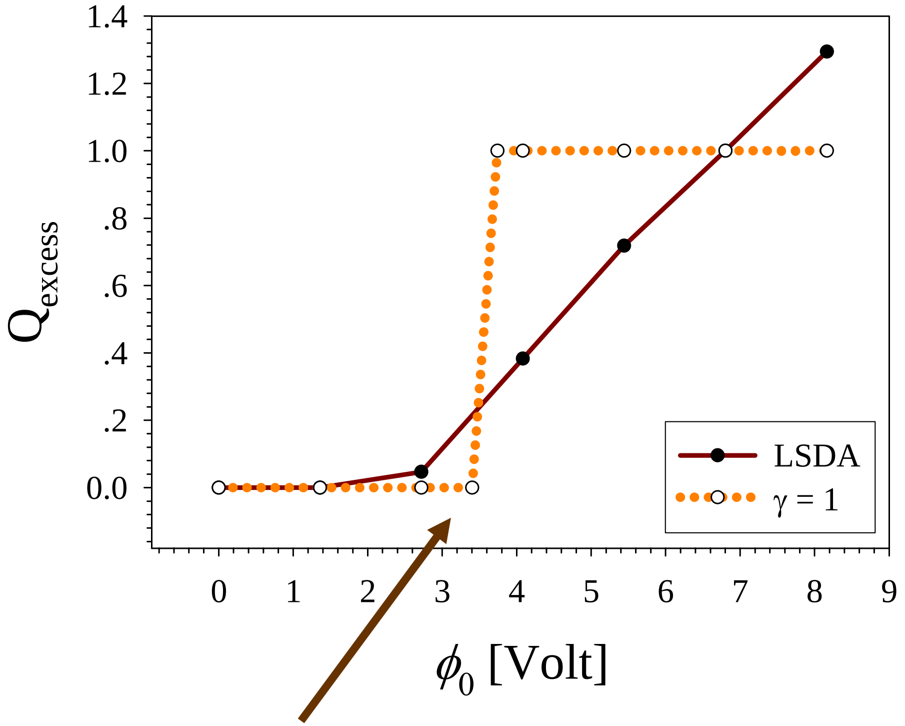
The asymptotic effective potential of neutral system should be → -1/r



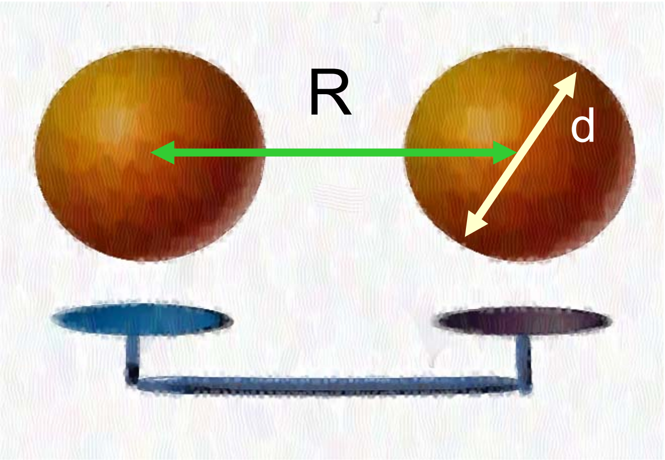


R. Baer E. Livshits and D. Neuhauser, Chem. Phys. **329**, 266 (2006).

Charge transfer under bias: quantization



ϕ_c = 3.7V



$$\phi_c \approx IP - EA - \frac{1}{R-d}$$

$$R = 28a_0 \qquad d = 12a_0$$

ΔSCF (eV)			HOMO (eV)		
IP	EA	Φ_c	IP	EA	Φ_c
5.6	0.5	3.5	6.2	0.8	3.7

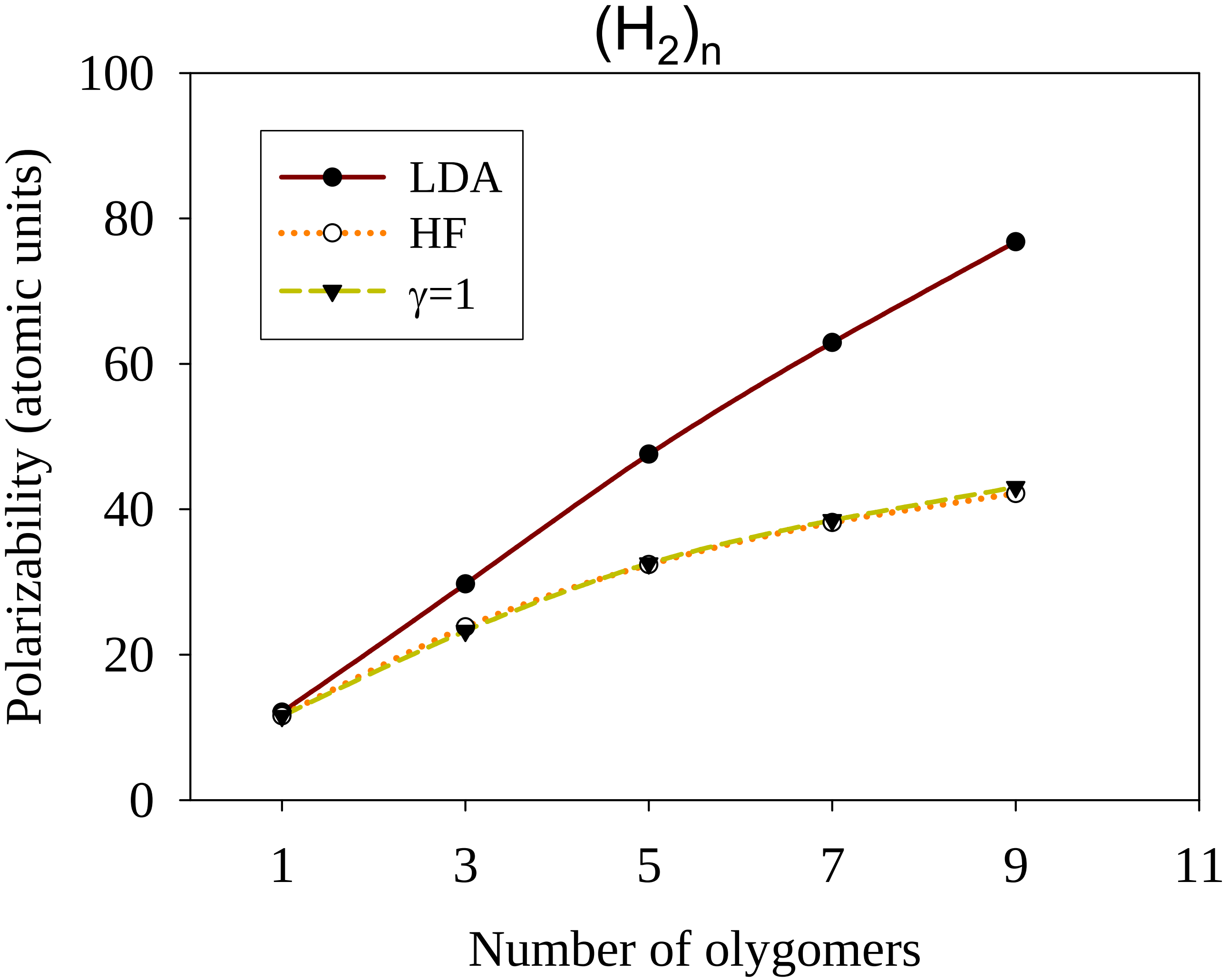
R. Baer E. Livshits and D. Neuhauser, Chem. Phys. **329**, 266 (2006)

Chemical Bond, Atomic EA

Atom (X)	ΔE (X_2) kcal/mol	R_e (X_2) Angstrom	ω_e (X_2) cm^{-1}	EA (X) eV
C	Exp. 145 $\gamma=1$ 132 LSDA 169	1.242 1.27 1.25	1855 1810 1770	1.26 1.33
N	Exp. 225 $\gamma=1$ 223 LSDA 256	1.098 1.06 1.089	2358 2540 2520	Unstable Unstable
O	Exp. 118 $\gamma=1$ 122 LSDA 167	1.208 1.14 1.20	1580 1640 1590	1.46 1.50
F	exp. 37 $\gamma=1$ 35 LSDA 75	1.412 1.330 1.390	916 1200 1000	3.40 3.73

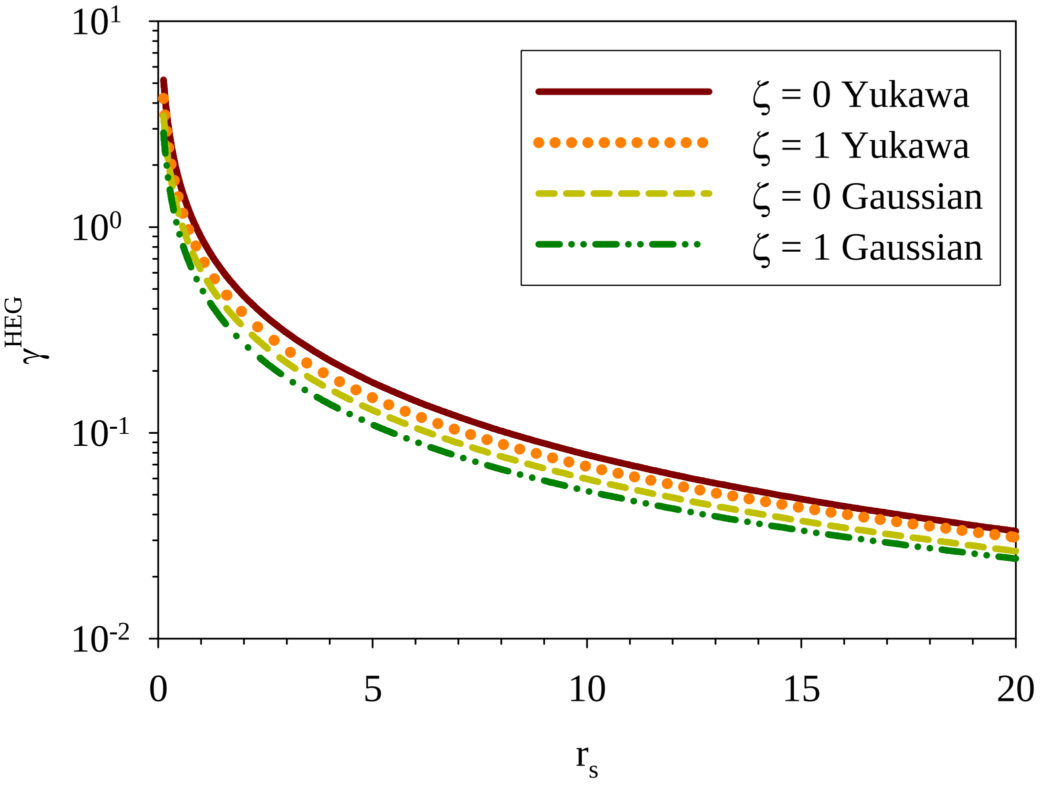
R. Baer and D. Neuhauser, Phys. Rev. Lett. 94, 043002 (2005).

Polarizability



Enforce compatibility with HEG

- The exact HEG parameter: $\gamma_{HEG}(r_s)$
  $\eta(\gamma_{HEG}(r_s), r_s)=1$
- Can use for molecule
- Get a theory which
  - has correct long range
  - Compatible with HEG
- Caveats:
  - Can be absurd
  - Or: has small effect



R. Baer E. Livshits and D. Neuhauser, Chem. Phys. **329**, 266 (2006).

2 parameter Semiempirical functional

$$E_{XC}[n] = w\varepsilon_X^{\gamma}(n) + K^{\gamma}[n] + E_c^{LYP}$$

Fit to atomization energy and bond lengths [G2(1) database of 55 molecules, using QCHEM®. cc-pVTZ basis.] Obtaining: γ=0.5 and w=0.9

Atomization energy	BNL-LYP	B3LYP
Average Error (kcal)	(-16) +2.1 (+15)	(-9) +2.7 (16)
RMS Error (kcal)	5.8	4.6
Average Relative Error	-1.2%	-1.5%
RMS Average Relative Error	6.8%	4.9%

Bond lengths	BNL-LYP	B3LYP
Average Error (A)	(-0.07) +0.01 (+0.07)	(-0.02) +0.01 (0.05)
RMS Error (A)	+0.02	+0.01
Average Relative Error	+1.1%	0.7%
RMS Average Relative Error	1.7%	0.9%

E. Livshits and R. Baer, work in progress

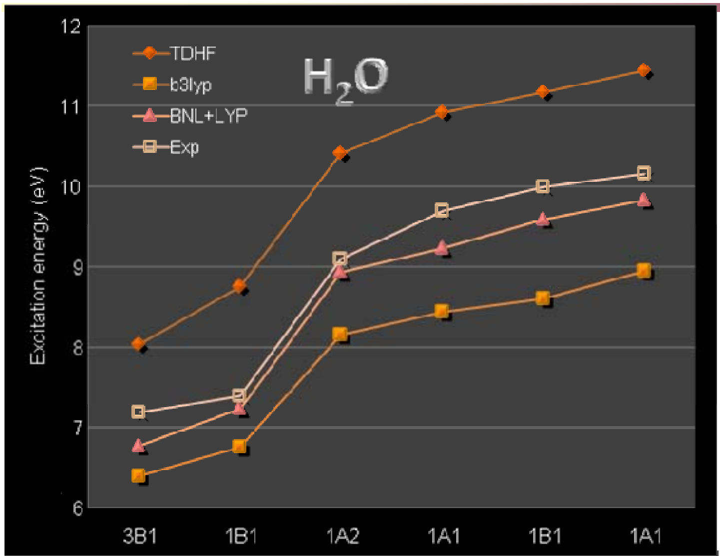
IP's and EA's

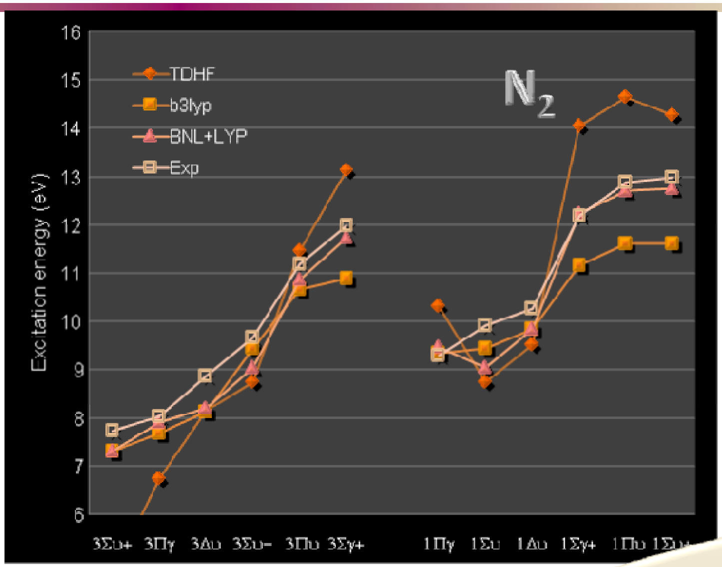
IP	Experiment	BNL-LYP		B3LYP	
		by ΔSCF	by HOMO	by ΔSCF	by HOMO
BeH	8.2	8.3	8.2	8.4	16.8
CH	10.6	10.8	10.8	10.9	6.9
NH	13.5	13.4	13.2	13.5	9.0
OH	13.0	16.0	12.8	16.0	8.5
CN	13.6	15.6	14.3	15.0	10.4

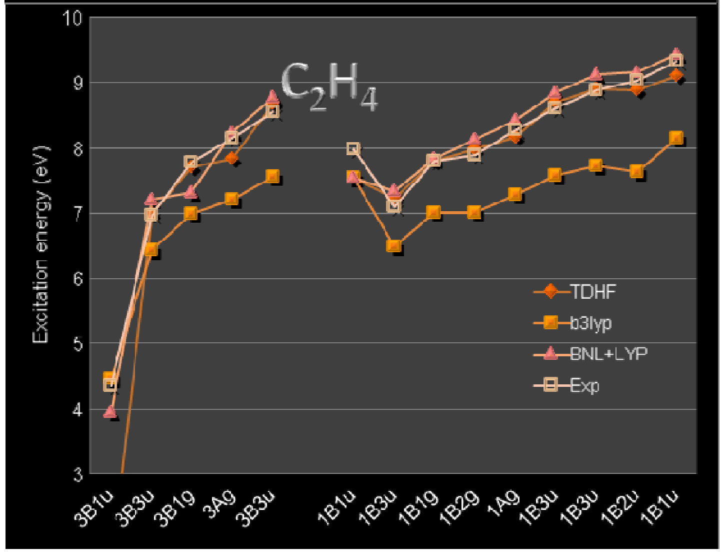
EA	Experiment	BNL-LYP		B3LYP	
		by ΔSCF	by HOMO	by ΔSCF	by HOMO
BeH	0.7	0.1	0.4	0.2	unbound
CH	1.2	0.7	1.1	0.7	unbound
NH	0.4	-0.6	0.4	-0.6	unbound
OH	1.8	0.6	0.9	0.6	unbound
CN	3.9	3.9	4.4	3.6	0.4

E. Livshits and R. Baer, work in progress

Vertical excitations with new functional







For each
func

Oscillator strengths

C_2H_4	TDHF	B3LYP	BNL-LYP	Exp
$^1B_{1u}$	39.9	26.14	36.71	29
$^1B_{3u}$	8.56	5.75	7.61	4

N_2	TDHF	B3LYP	BNL-LYP	Exp
$^1\Pi_u$	0.0121	0.0729	0.1409	0.243
$^1\Sigma_u$	0.6283	0.031	0.2865	0.279

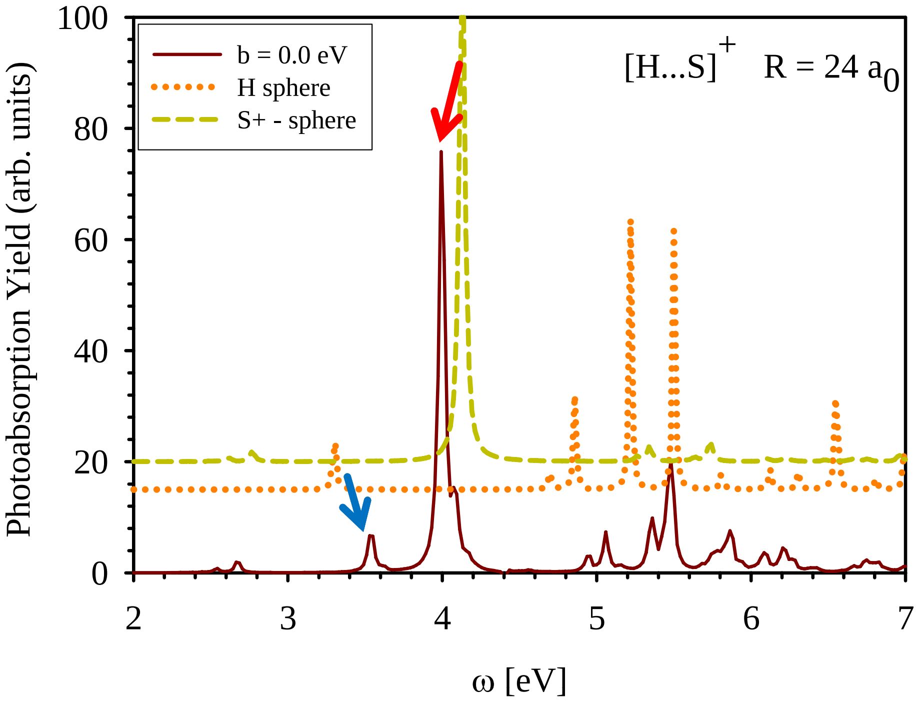
S. Hirata and M. Head-Gordon, Chem. Phys. Lett. 314, 291 (1999).

Balanced functional

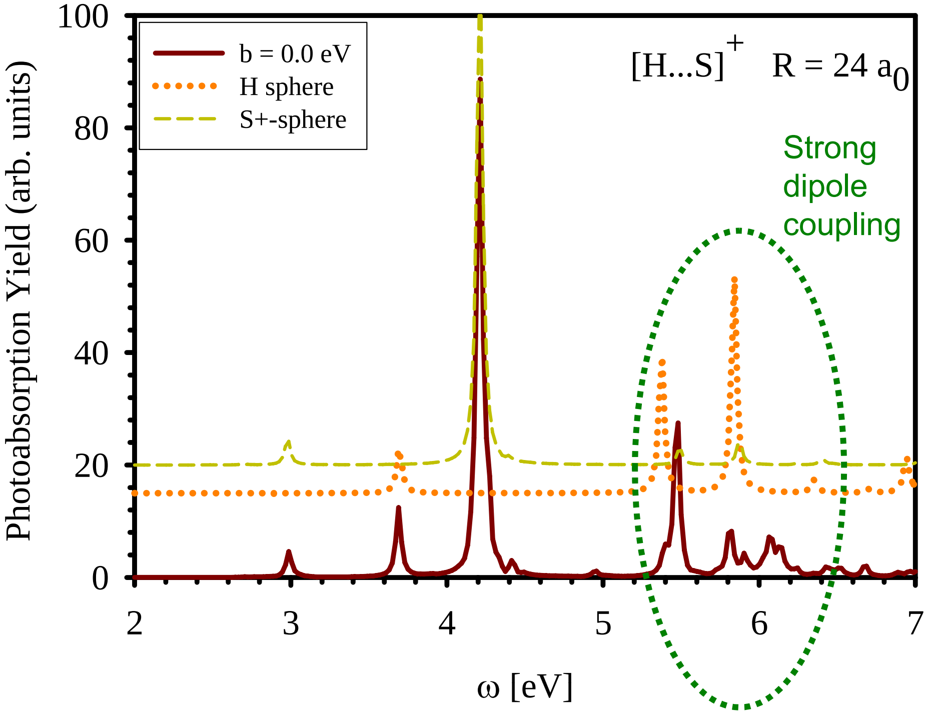
- New functional is balanced
- Can do atomization energies and structures very similar to B3LYP (somewhat less well)
- Better than B3LYP in:
  - Charge quantization
  - Consistency of IP's
  - EA for small systems
  - Static Polarizability
  - Vertical excitations
  - Rydberg excitations

Back to near-field: Spurious splitting: fixed

LSDA

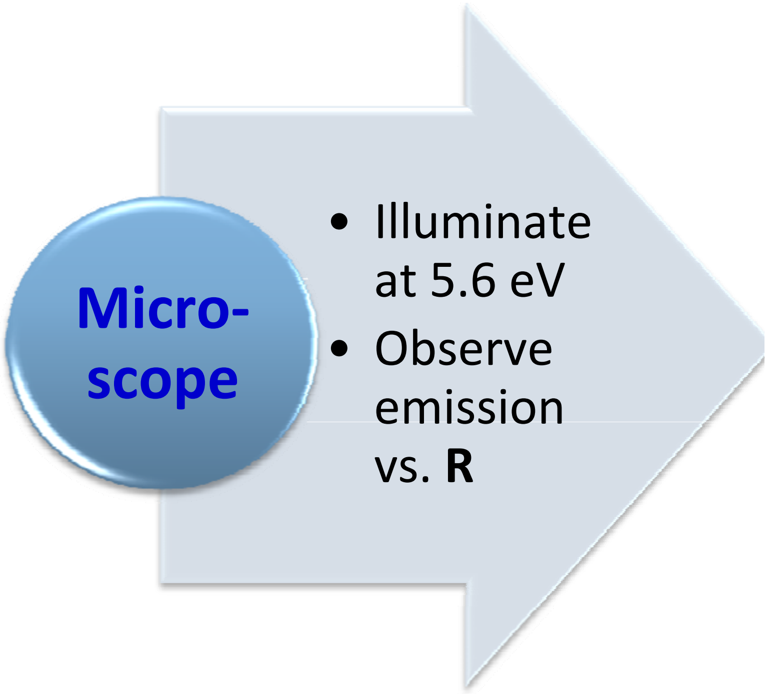


New functional γ = 1



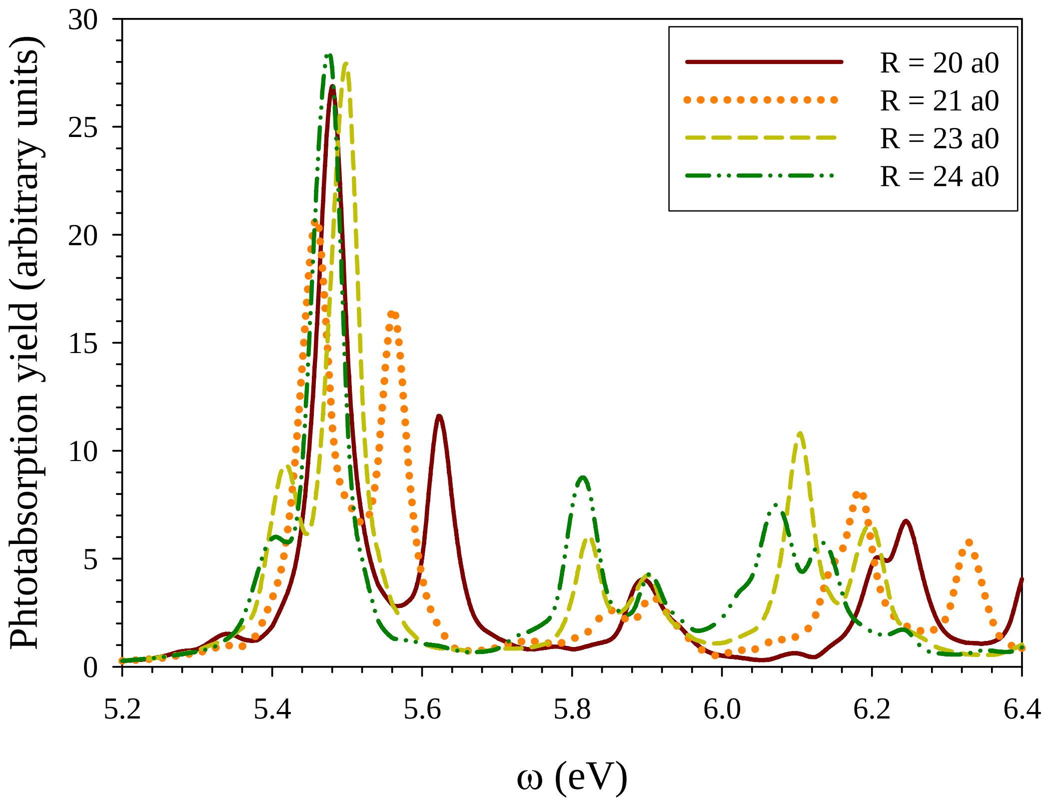
Strong dipole coupling

R. Baer and D. Neuhauser, J. Chem. Phys. 125, 074709 (2006).



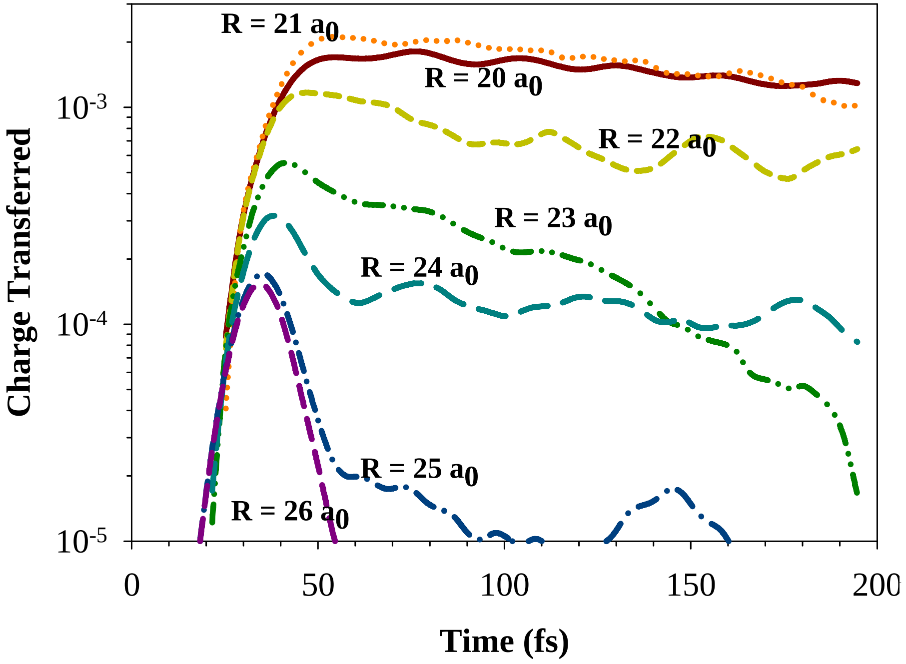
Micro-scope

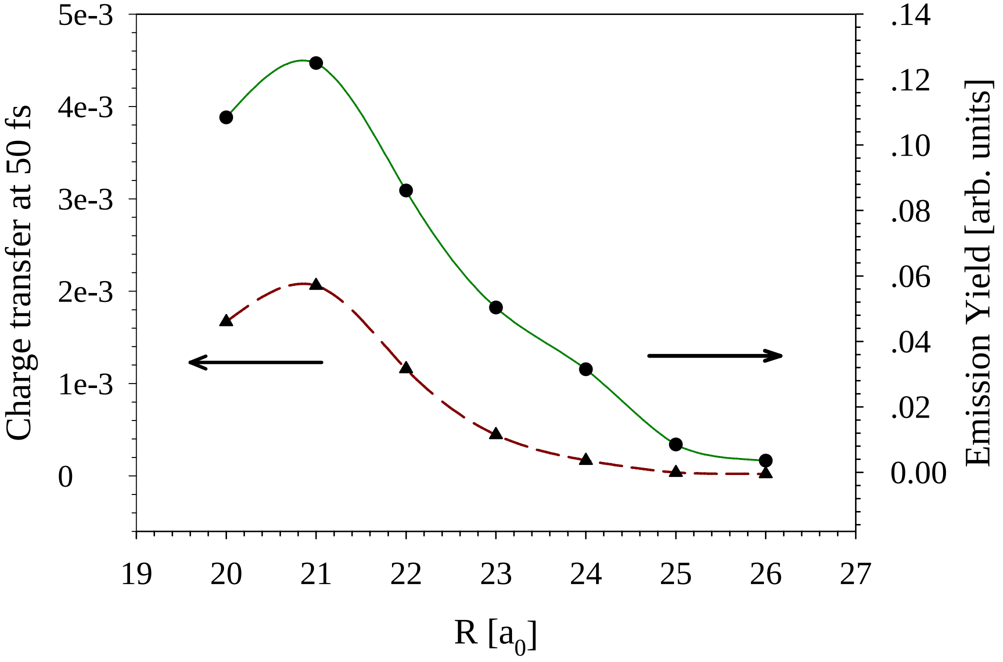
- Illuminate at 5.6 eV
- Observe emission vs. **R**



R. Baer and D. Neuhauser, J. Chem. Phys. 125, 074709 (2006).

Charge transfer dynamics

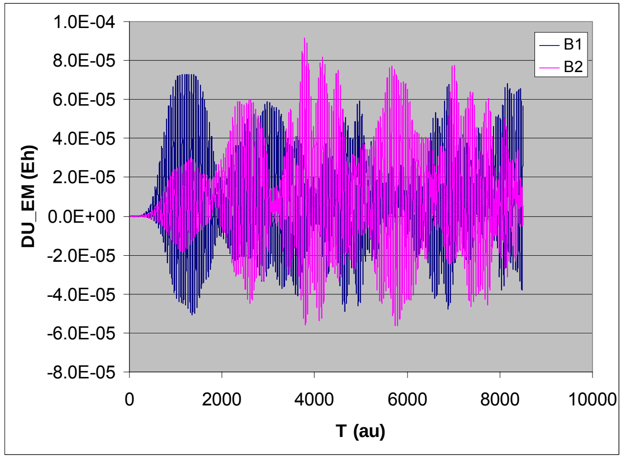


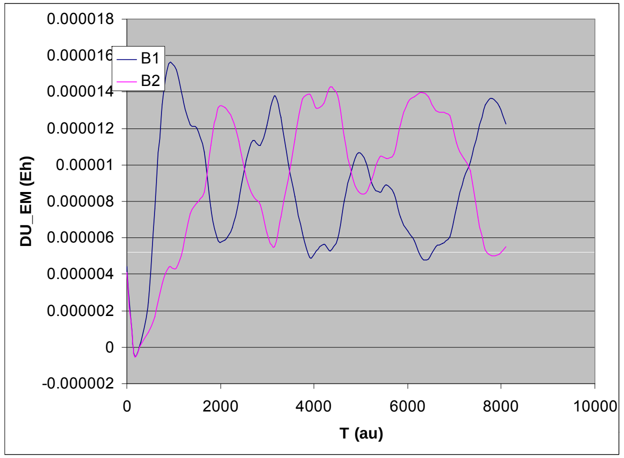


R. Baer and D. Neuhauser, J. Chem. Phys. 125, 074709 (2006).

EM Energy transport

- 2 small silver clusters (diam ~1nm) at small distances (~3 nm)
- We excite left cluster and watch EM energy in left and right clusters
- EM energy oscillates, period equal to coupling. T=50fs
- In this case C=0.1eV
- In experiment large dots and C=0.3eV





M. L. Brongersma, J. W. Hartman, and H. A. Atwater, Phys. Rev. B 62, 16356 (2000).
R. Baer and D. Neuhauser work in progress (2006).

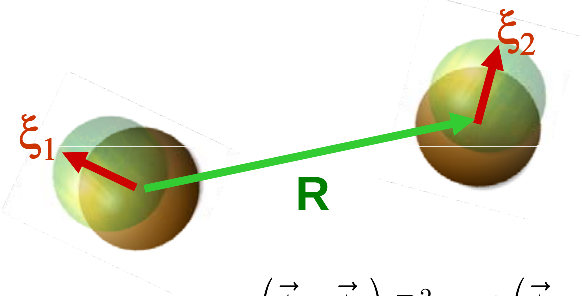
“Optical” devices on molecular scale

- Linear arrays of dipole-coupled centers
- We assume long coherence time
  - Presently not a justified assumption
  - There are encouraging results (Ag)
  - Synthetic challenge: find suitable materials
- Meanwhile, we play with this theoretically: what to expect from such coherent systems?

S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, and A. A. G. Requicha, Nature Mat. **2**, 229 (2003).

Polariton model: Hamiltonian

- Weak excitation
- In noble metal nano-particles, local surface plasmon-polariton
- N-site system, dipole interaction



$$E\left(\vec{\xi}_1,\vec{\xi}_2;\vec{R}\right)=\frac{\left(\vec{\xi}_1\cdot\vec{\xi}_2\right)R^2-3\left(\vec{\xi}_1\cdot\vec{R}\right)\left(\vec{\xi}_2\cdot\vec{R}\right)}{R^5}$$

N sites $\rightarrow 3N$ Hilbert space

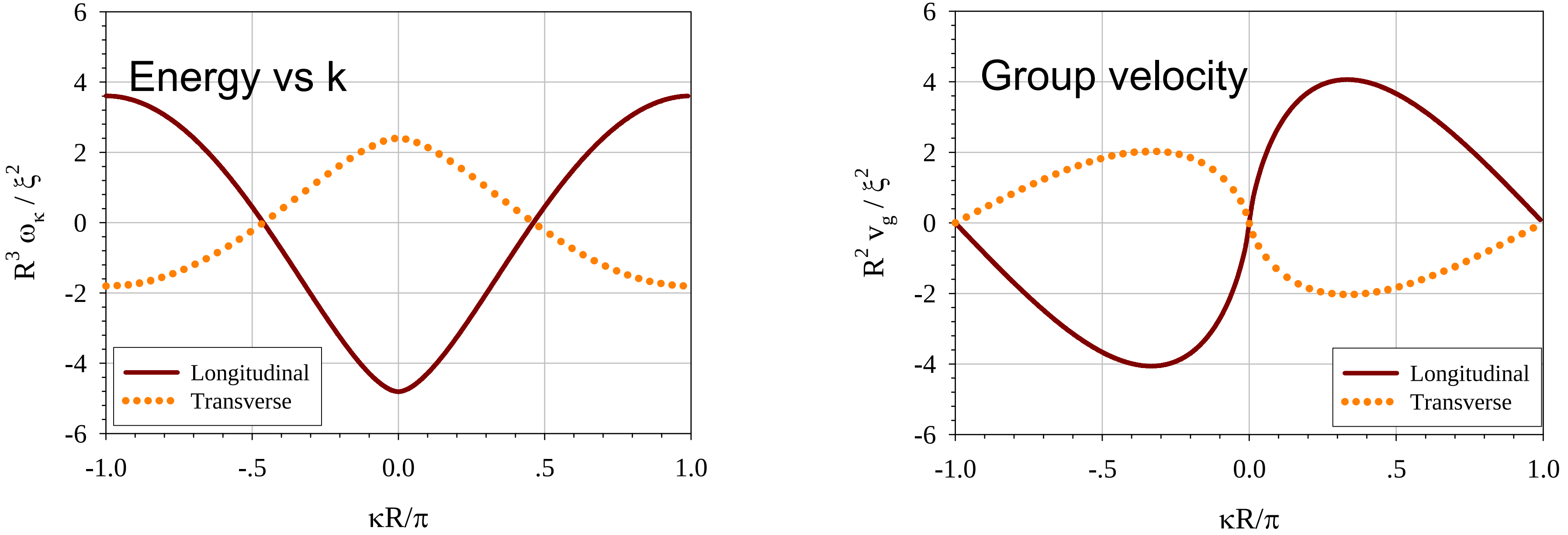
$$\psi_i=\begin{pmatrix}\psi_{i,x}\\ \psi_{i,y}\\ \psi_{i,z}\end{pmatrix}\quad H_{i\alpha,j_\beta}=E\left(\xi_\alpha,\xi_\beta;R_{ij}\right)$$

Dynamics - Schrodinger Waves:

$$i\dot{\psi}(t)=H\psi(t)$$

U. Fano, Phys. Rev 103, 1202 (1956).
J. J. Hopfield, Phys. Rev 112, 1555 (1958).

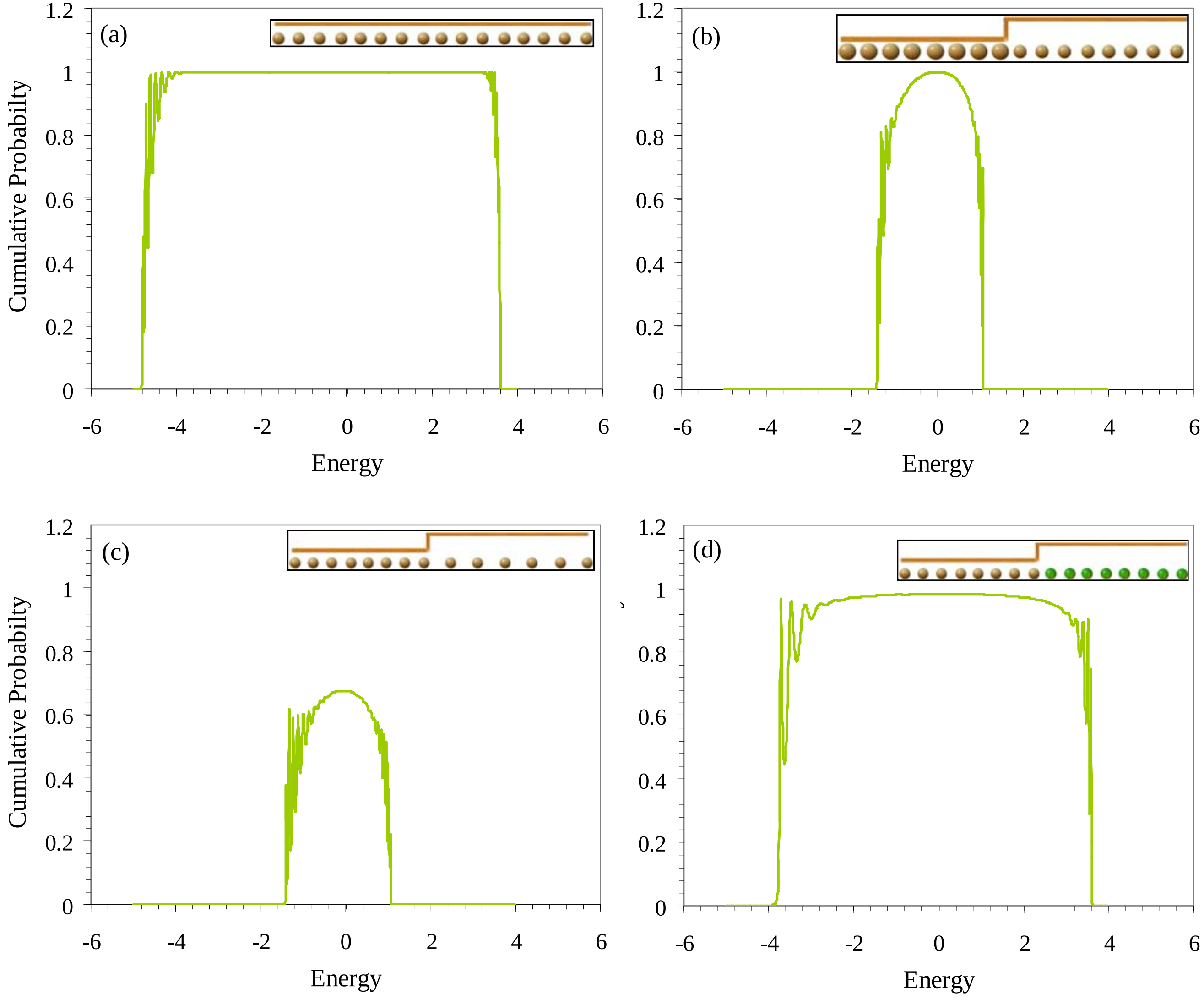
Dispersion relation and group velocity



- Energy bands: L waves [-4.4 → 3.6] T waves [-1.8 → 2.2]
- Longitudinal waves move in direction of k
- Transverse waves move in opposite direction to k "negative refractive index…"
- For low k, the larger k the large velocity. Subsequently – opposite behavior.
- At k=0.46π the two waves have same energy and group velocity light-like (indep. of k)

S. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, A. A. G. Requicha, and B. E. Koel, Proc. SPIE 4810 (2002).
R. Baer and D. Neuhauser, J. Chem Phys,. In press (2006).

Step barriers



ξ–ξ’

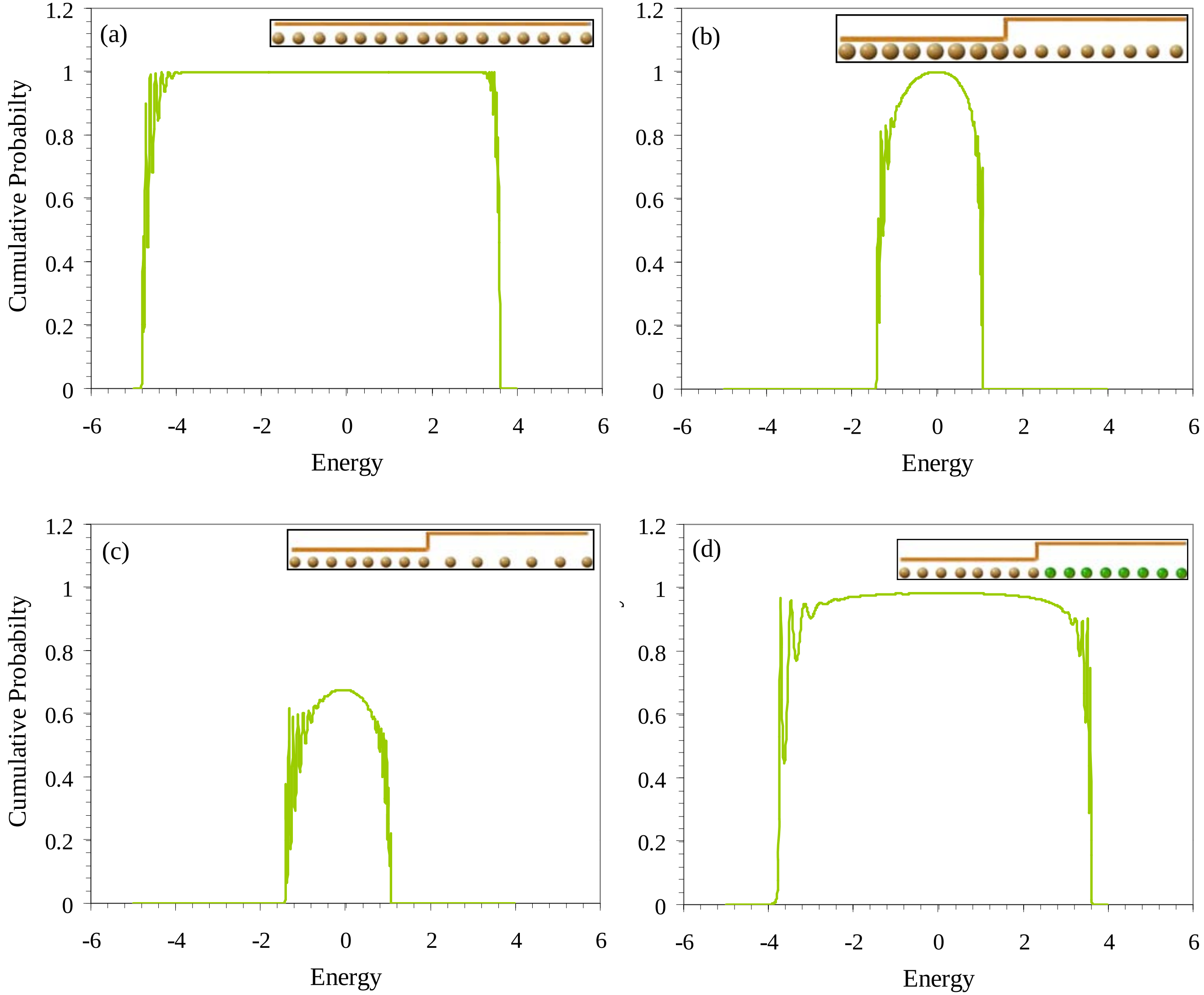
- The bandwidth is smaller
- k doesn’t change

R-R’

- Bandwidth smaller
- Length scale changes
- k change → reduce transmission

ω–ω’

Step barriers



ξ–ξ'

- The bandwidth is smaller
- k doesn't change

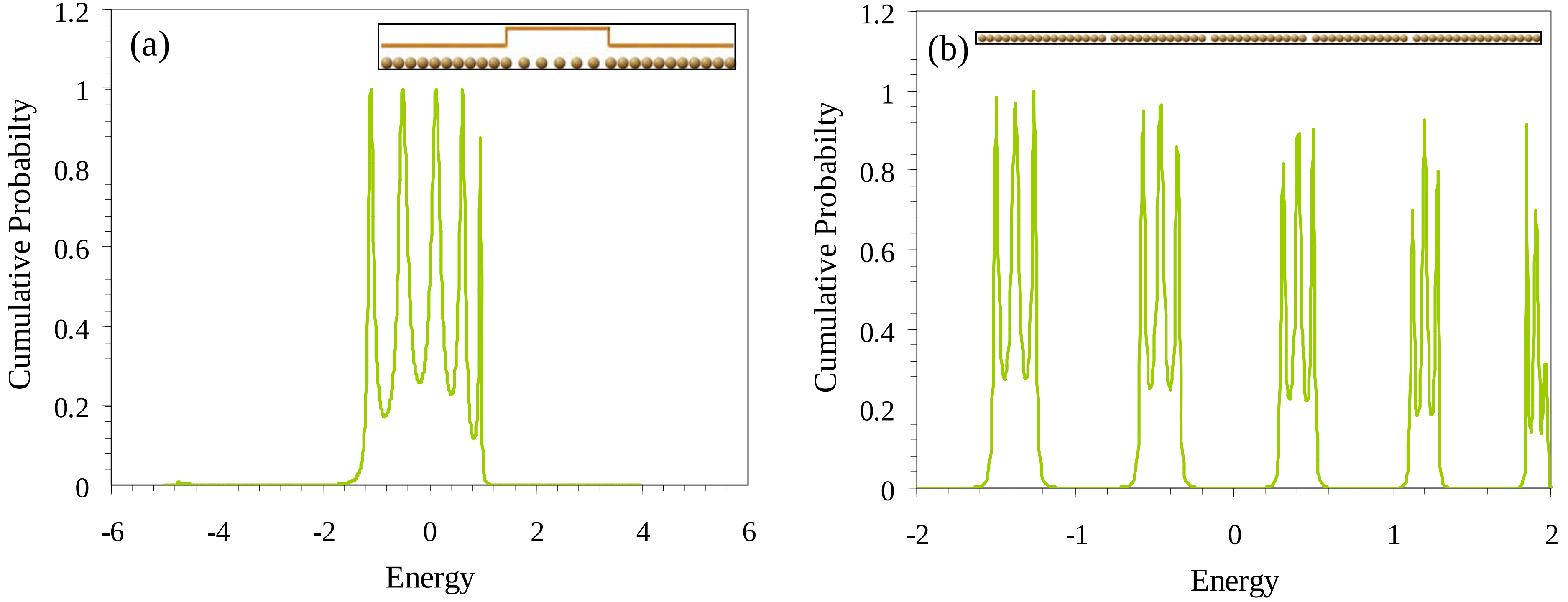
R-R'

- Bandwidth smaller
- Length scale changes
- k change → reduce transmission

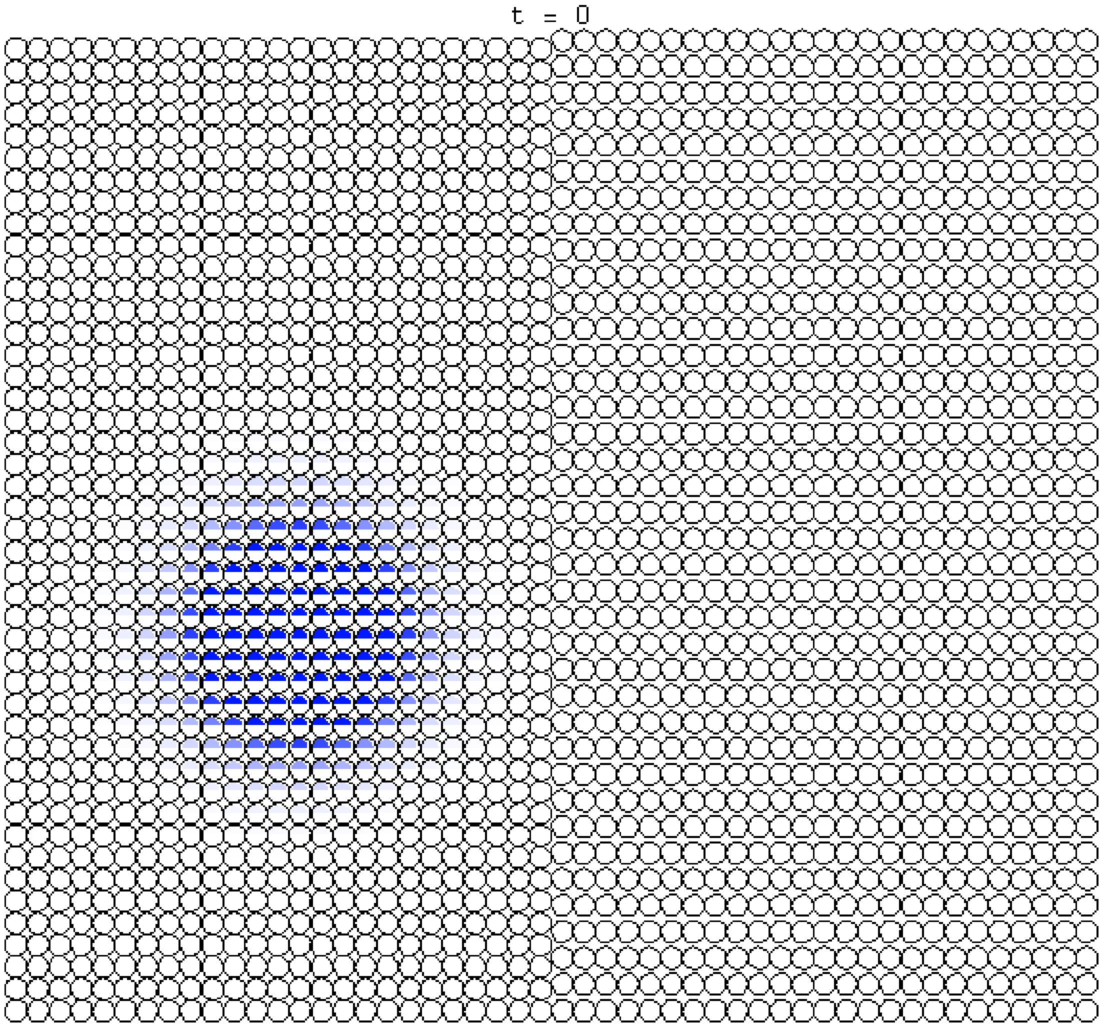
ω−ω'

Interference and total reflection

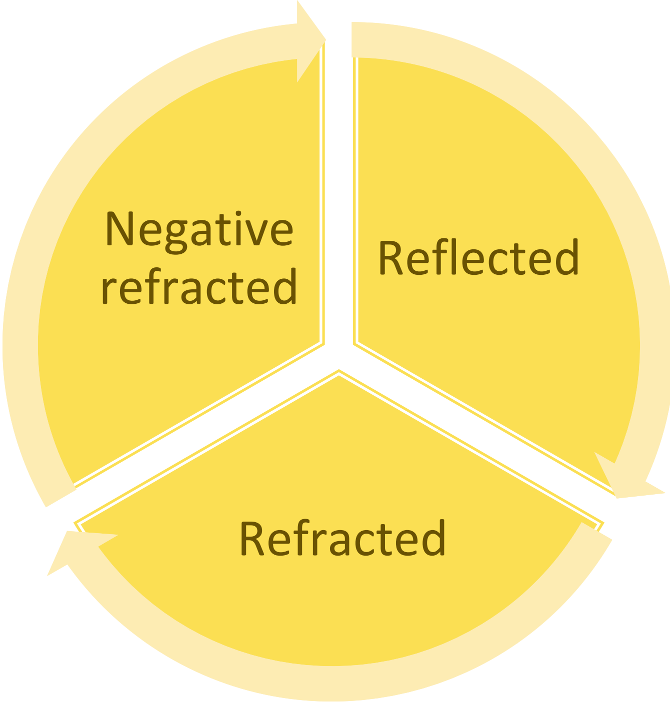
- Using interference one can have total reflection also at E=0



Nano-optics in 2D lattices



Trifurcation:



Negative refracted

Reflected

Refracted

midSummary

- After fixing the self repulsion problem we:
  - Studied the dipole coupled spectrum of a model “tip-system”
  - We saw strong sensitivity to distance when the distance is small – due in part to charge transfer and in part to dipole coupling
- Fantasized about coherent molecular sized optical devices based on dipole coupling

Electron dephasing

- Metals and metallic nanodots are lossy…
- Fast dephasing not well described in usual TDDFT
- Must address "memory effects"
- Must obey known exact constraints
  - Translational invariance (TDDFT)
  - Rotational invariance (TDCDFT)
  - Get for free: also net XC force/Torque is zero
- Based on linear response kernel for the homogeneous electron gas (Gross-Kohn param.)

Vignale, Phys. Rev. Lett. 74, 3233 (1995).
E. K. U. Gross and W. Kohn, Phys. Rev. Lett. 55 (26), 2850 (1985).
Y. Kurzweil and R. Baer, Phys. Rev. B 73 (7), 075413 (2006).

Practical memory

- We follow an idea of Vignale, to obtain TI functional and we add an important ingredient:
- The XC force should be zero (otherwise Ehrenfest's theorem is not obeyed)

$$-\int n(\mathbf{r},t)\nabla v_{XC}(\mathbf{r},t)\,d^3r = 0$$

Memory KS-equation from an action

- The TDDFT dynamical equations are:

$$i\dot{\psi}_n(\mathbf{R},t) = \left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{R},t) + v_H(\mathbf{R},t) + v_{adiab}(\mathbf{R},t) + v_{mem}(\mathbf{R},t)\right]\psi_n(\mathbf{R},t)$$

$$v_{mem}[n](\mathbf{R},t) = V_{mem}[N](\mathbf{R}-\mathbf{D}(t)) + \mathbf{E}_{mem}(t)\cdot(\mathbf{R}-\mathbf{D}(t))M'[n(\mathbf{R},t)]$$

$$V_{mem}[N](\mathbf{r},t) = \int_0^t F'_{mem}\left(N(\mathbf{r},t),t-t'\right)\dot{N}\left(\mathbf{r},t'\right)dt'$$

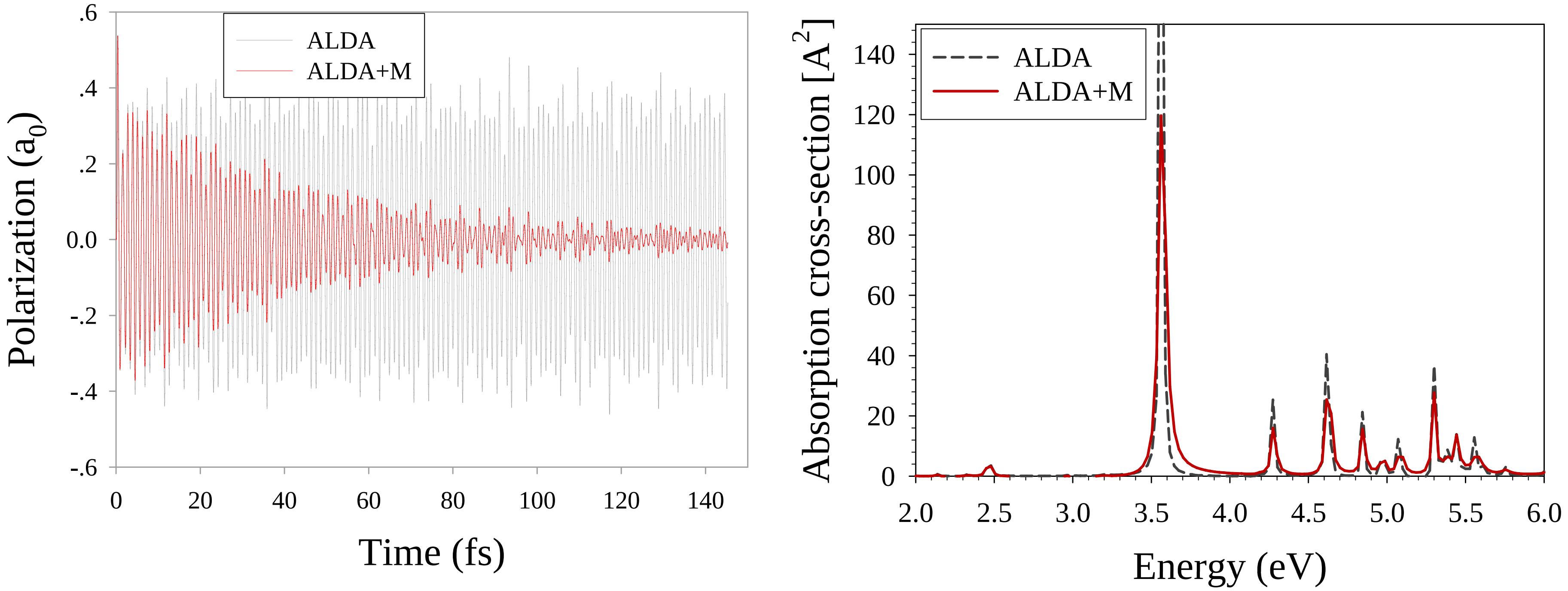
$$N(\mathbf{r},t) = n(\mathbf{r}+\mathbf{D}(t),t) = n(\mathbf{R}(t),t)$$

$$\boxed{\mathbf{E}_{mem}(t) = \frac{1}{Q(t)}\int V_{mem}(\mathbf{r},t)\nabla n(\mathbf{r}+\mathbf{D}(t),t)\,d^3r}$$

Center of mass

$$\mathbf{D}[n](t) = \frac{1}{Q(t)}\int \mathbf{R}M[n(\mathbf{R},t)]\,d^3R \qquad Q(t) = \int M[n(\mathbf{R},t)]\,d^3R$$

Dephasing: dipole oscillations Au_{18} or Ag_{18}

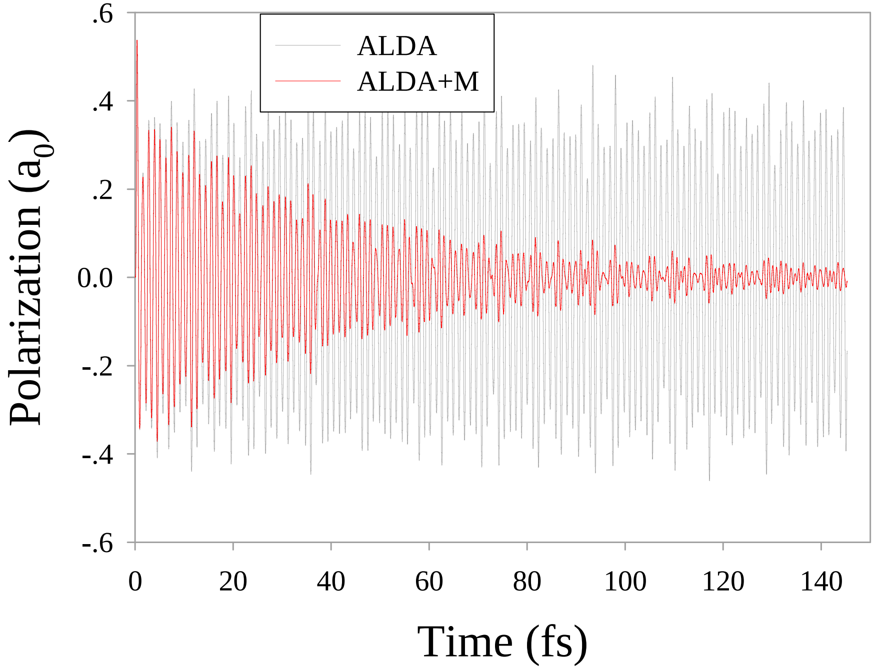


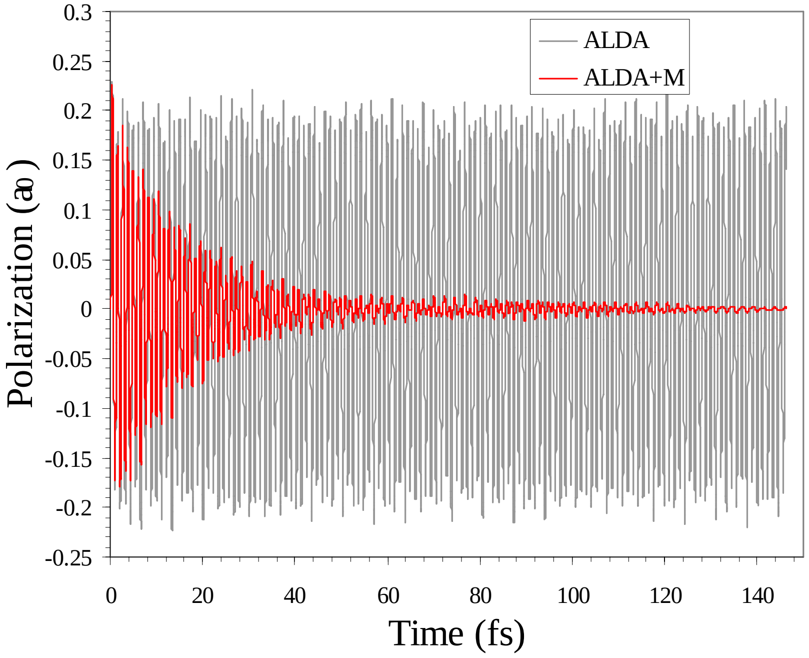
Estimated Decay time: T_2~30 fs.

Too large. Experiments indicate T_2<10 fs

J. Lehmann, M. Merschdorf, W. Pfeiffer, A. Thon, S. Voll, and G. Gerber, Phys. Rev. Lett. 85, 2921 (2000).
Link and El-Sayed, Ann. Rev. Phys. Chem. 54, 331 (2003)..

Atomic core effects on dipole decay





Jellium cluster

T_2 = 30 fs

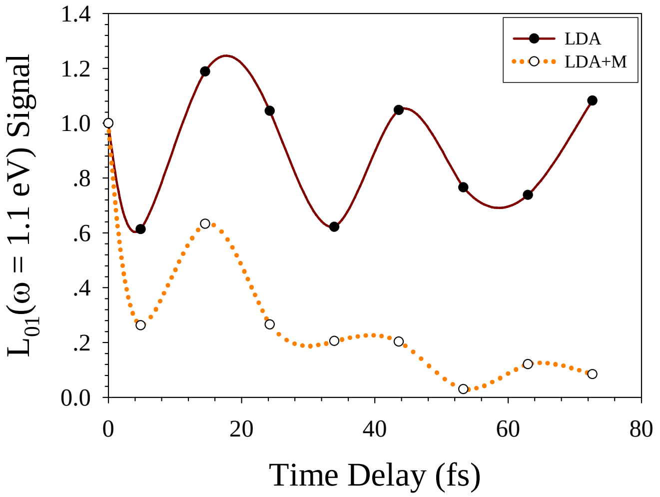
S-electron pp

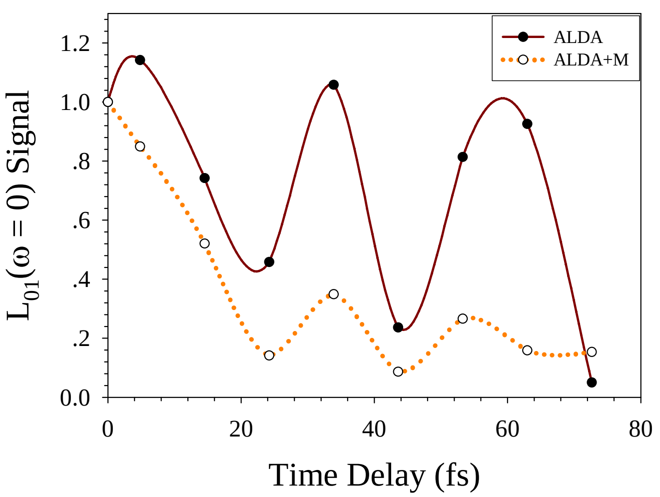
Atomistic cluster

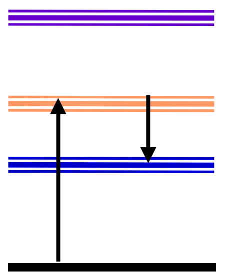
T_2 = 15 fs

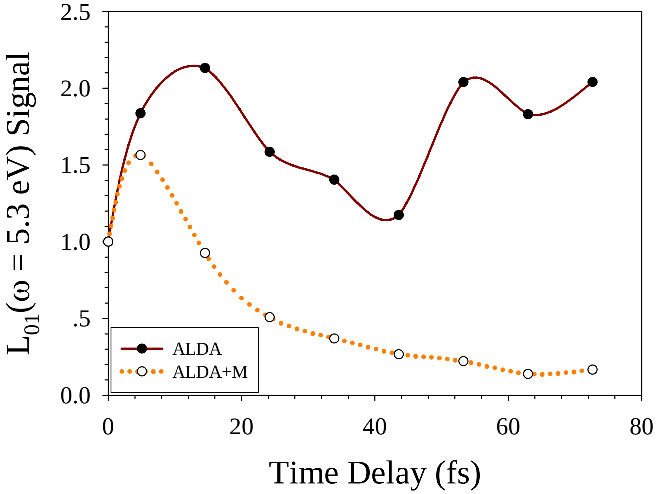
Y. Kurzweil and R. Baer, work in progress (2006).

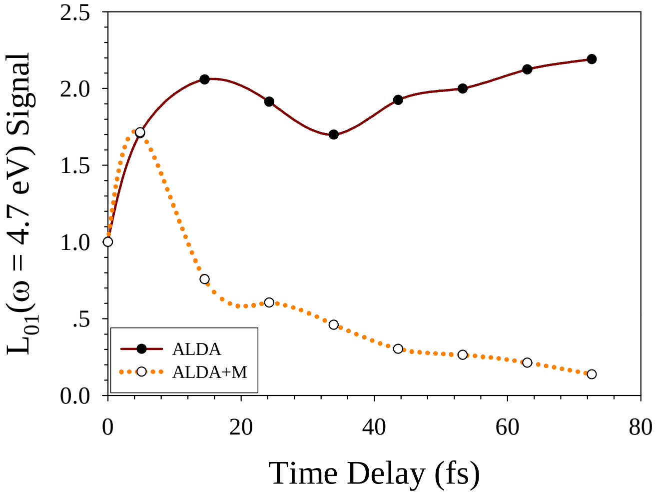
Damping of coherence following plasmon excitation

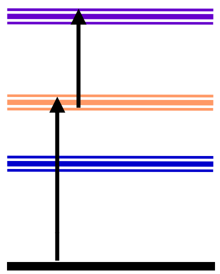












Y. Kurzweil and R. Baer, Phys. Rev. B 73 (7), 075413 (2006).

Summary

- The functional allows incorporation of memory
- Meanwhile, we use HEG memory.
- Could be problematic for finite systems
- We have a method to remove "self memory" (otherwise even the H atom has memory…)
- Found that memory effects can be seen in nonlinear regime, such as pump-probe.
- Found that the atomic potential has a strong effect on the plasmon decay time.