Collective dipole oscillations in nuclei, metal clusters and C_{60} molecules

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(xivnpw, Kazimierz, 28. Sept. 2007)

1. Nuclei and metal clusters
   - classical models for GDR in nuclei
   - variational principle and RPA, sum rules etc.
   - local current approximation (LCA), fluid dynamics
   - applications to metal clusters

2. C_{60} molecules*)
   - recent experiments
   - jellium model; TDLDA and LCA
   - comparison of theory and experiment

*) in collaboration with:

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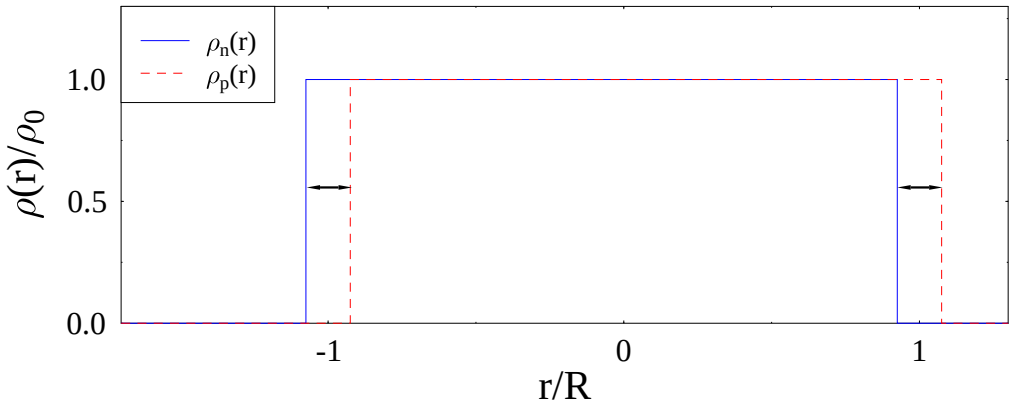
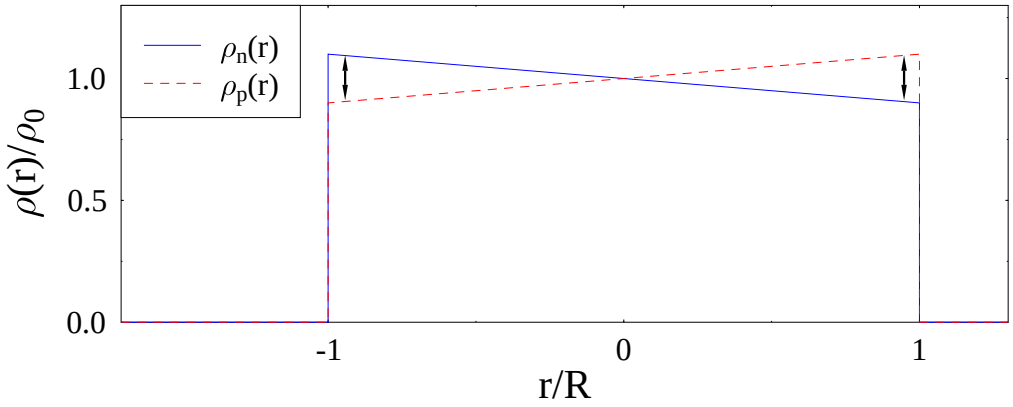
Classical models for GDR in nuclei

Goldhaber-Teller (Tassie) mode: pure translation:



Steinwedel-Jensen (Migdal) mode: compressional dipole mode:



Best fit to experiment: requires combination of both modes!

Microscopic approaches: mean field: RPA, TDHF, ...

Semi-microscopic approaches: Scaling model, fluid dynamics, ...

General variational principle

Schrödinger equation with full many-body Hamiltonian:

$$\hat{H} = \hat{T}+\hat{V}: \quad \hat{H}|\nu\rangle = E_\nu|\nu\rangle = (E_0+\hbar\omega_\nu)|\nu\rangle \quad \nu = 1, 2, \ldots$$

Rewrite as equations of motion: (cf. Rowe)

$$\begin{aligned} \langle 0|\mathcal{O}_\nu[\hat{H}, \mathcal{O}_\nu^\dagger]|0\rangle &= \hbar\omega_\nu \langle 0|\mathcal{O}_\nu\mathcal{O}_\nu^\dagger|0\rangle \\ \langle 0|\mathcal{O}_\nu[\hat{H}, \mathcal{O}_\nu]|0\rangle &= \hbar\omega_\nu \langle 0|\mathcal{O}_\nu\mathcal{O}_\nu|0\rangle = 0 \end{aligned}$$

with

$$\mathcal{O}_\nu^\dagger|0\rangle = |\nu\rangle, \quad \mathcal{O}_\nu|\nu\rangle = |0\rangle, \quad \text{and} \quad \mathcal{O}_\nu|0\rangle = 0$$

These can also be obtained by a general **variational principle**:
[S. Kümmel and M. Brack, Phys. Rev. A **64**, 022506 (2001)]

$$\frac{\delta E_3[\hat{Q}]}{\delta \hat{Q}} = 0\,, \qquad E_3[\hat{Q}] := \sqrt{\frac{m_3[\hat{Q}]}{m_1[\hat{Q}]}}$$

with

$$m_1[\hat{Q}] := \frac{1}{2}\,\langle 0|\left[\hat{Q}, \left[\hat{H}, \hat{Q}\right]\right]|0\rangle$$

$$m_3[\hat{Q}] := \frac{1}{2}\,\langle 0|\left[\left[\hat{H}, \hat{Q}\right], \left[\left[\hat{H}, \hat{Q}\right], \hat{H}\right]\right]|0\rangle$$

$\hat{Q}$ is a most general, nonlocal hermitean operator!
Successive orthogonalization of $\hat{Q}_1$, $\hat{Q}_2$,... yields exact spectrum:

$$E_3(\hat{Q}_\nu) = \hbar\omega_\nu\,, \quad \nu = 1, 2, \ldots \qquad [\hat{Q}_\nu \propto \mathcal{O}_\nu^\dagger + \mathcal{O}_\nu]$$

Random phase approximation (RPA)

Choose ground state as $|HF\rangle$ plus $2p-2h$ excitations:

$$|0\rangle \rightarrow |\mathrm{RPA}\rangle := \left(1 + \sum_{pp'hh'} \gamma^{pp'hh'} a_p^\dagger a_{p'}^\dagger a_h a_{h'}\right) |\mathrm{HF}\rangle$$

Excitation operators (nonlocal!) for $1p$-$1h$ excitations:

$$\hat{Q} \rightarrow Q_\nu^{(ph)\dagger} := \sum_{ph} \left(x_\nu{}^{ph} a_p^\dagger a_h - y_\nu{}^{ph} a_h^\dagger a_p \right)$$

Variational principle $\delta E_3(Q_\nu^{(ph)\dagger}) = 0$ yields standard RPA equations!

HF $\rightarrow$ DFT/Kohn-Sham (+LDA): RPA $\rightarrow$ TD-DFT (TDLDA)

Sum rule approach

$$E_\nu \simeq E_3(Q_\nu) = \sqrt{\frac{m_3[Q_\nu]}{m_1[Q_\nu]}}$$

with suitable (model) local operators $Q_\nu(\mathbf{r})$
Due to theorems by Thouless (and others), we may use $|HF\rangle$ instead of $|\mathrm{RPA}\rangle$ for computing $m_1[Q_\nu]$, $m_3[Q_\nu]$!

[Bohigas, Lane and Martorell, 1979; + many others]

Local current approximation (LCA)

Only assumptions: $\hat{Q} \rightarrow Q(\mathbf{r})$ (**local** function), $|0\rangle \rightarrow |HF\rangle$

Then, $Q(\mathbf{r})$ defines a **local displacement field ($\sim$ current)**:

$$\mathbf{u}(\mathbf{r}) = -\frac{\hbar^2}{m}\boldsymbol{\nabla} Q(\mathbf{r})$$

For $\hat{V}$ = Coulomb interaction, we get:

$$m_1[Q] = m_1[\mathbf{u}] = \frac{m}{2\hbar^2}\int \mathbf{u}(\mathbf{r})\cdot\mathbf{u}(\mathbf{r})\,\rho(\mathbf{r})\,d^3r$$

$m_3[\mathbf{u}]$ is functional of ground-state densities $\rho(\mathbf{r})$, $\tau(\mathbf{r})$ (and current density, see "current-DFT", Vignale and Kohn 1996) in terms of HF (or KS) g.s. wave functions $\phi_i(\mathbf{r})$

Variation $\delta E_3[Q]/\delta Q(\mathbf{r}) = 0$ leads to **fluid dynamical eigenvalue equations**: [S. Kümmel, PhD thesis (Regensburg 2000)]

$$\frac{\delta m_3[\mathbf{u}]}{\delta u_j(\mathbf{r})} = (\hbar\omega_\nu)^2\,\frac{m}{\hbar^2}\,\rho(\mathbf{r})\,u_j(\mathbf{r}) \qquad (j = x, y, z)$$

coupled nonlinear 4. order partial differential equations for $u_j(\mathbf{r})$; extremely hard to solve!

Requires $\rho(\mathbf{r})=\sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2$, $\tau(\mathbf{r})=\sum_{i=1}^{N}|\nabla\phi_i(\mathbf{r})|^2$ using g.s. wave functions $\phi_i(\mathbf{r})$

$\Rightarrow$ **"quantum fluid dynamics"** (includes "zero sound"!)

Finite-basis LCA

Expand $Q(\mathbf{r})$ in a **finite set of basis functions** $\{Q_p(\mathbf{r})\}$:

$$Q(\mathbf{r}) = \sum_{p=1}^{M} c_p Q_p(\mathbf{r})$$

Variational principle then yields a set of M **secular equations**:

$$(*) \quad \det|C_{pp'} - (\hbar\omega_\nu)^2 B_{pp'}| = 0\,, \qquad p, p' = 1, 2, \ldots, M$$

(approximation to RPA equations!), with

$$B_{pp'} = \langle 0|\,[Q_p, [H, Q_{p'}]]\,|0\rangle$$
$$C_{pp'} = \langle 0|\,[[H, Q_p], [[H, Q_{p'}], H]]\,|0\rangle$$

Solution of $(*)$ yields excitation energies $\hbar\omega_\nu$ and operators Q_ν creating the collective states $|\nu\rangle$

Basis set $\{Q_p(\mathbf{r})\}$ must be suitably chosen!

Scaling approach (Bohigas *et al.*):

Use only **one** operator $Q(\mathbf{r})$, e.g.:

$Q_d = z \;\Rightarrow$ pure translation, $m_1(Q_d) \propto N$ (TRK sum rule)
$Q_0 = r^2 \;\Rightarrow$ radial compression, "breathing mode"
$Q_2 = r^2 Y_{20} \;\Rightarrow$ quadrupole oscillation (GQR)
etc.
(Note: $\Delta Q = \boldsymbol{\nabla}\cdot\mathbf{u} = 0 \;\Rightarrow$ incompressible flow!)

LCA $\equiv$ generalized scaling approach

LCA with a set of operators $\{Q_p(\mathbf{r})\}$ corresponds to **collective Hamiltonian**:

$$H_{coll} = \frac{1}{2} \sum_{p,p'=1}^{M} (B_{pp'}\, \dot{\alpha}_p \dot{\alpha}_{p'} + C_{pp'}\, \alpha_p \alpha_{p'})$$

describing coupled harmonic oscillations with **velocity fields**:

$$\mathbf{v}_p(\mathbf{r}, t) = \dot{\alpha}_p(t) \mathbf{u}_p(\mathbf{r})$$

obeying the continuity equation

Response to external field $\mathbf{Q}_{ext}$

Strength function:

$$S_{\mathbf{Q}_{ext}}(E) = \sum_{\nu>0} |\langle \nu | \mathbf{Q}_{ext} | 0 \rangle|^2 \delta(E - \hbar\omega_\nu)$$

Energy-weighted moments:

$$m_k(\mathbf{Q}_{ext}) = \int_0^\infty E^k S_{\mathbf{Q}_{ext}}(E)\, dE = \sum_{\nu>0} (\hbar\omega_\nu)^k |\langle \nu | \mathbf{Q}_{ext} | 0 \rangle|^2$$

Photo-absorption cross section $\sigma(\omega)$ in long-wavelength limit:

$$\sigma(\omega) = (4\pi\omega/3c)\, S_{dip}(E = \hbar\omega) \qquad (\text{“optic response”})$$

with $\mathbf{Q}_{ext} = Q_{dip} = ez$, $\omega =$ frequency of external electric field

Static polarizability: $\alpha_{pol}(\mathbf{Q}_{ext}) = 2\, m_{-1}(\mathbf{Q}_{ext})$

Collective electronic excitations in metal clusters

Metal cluster = bound system of N metal atoms
(with w valence electrons each)
$\Rightarrow wN$ electrons oscillate against ionic cores!

First experiments with sodium clusters ($w = 1$):
W. Knight $et\ al.$, Phys. Rev. Lett. **52**, 2141 (1984)

First calculations using spherical jellium model:
W. Ekardt, Phys. Rev. B **29**, 1558 (1984)

For extensive review articles, see:
W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993)
M. Brack, Rev. Mod. Phys. **65**, 677 (1993)

Jellium model:
Replace ionic distribution by continuous spherical charge distribution with radius R:

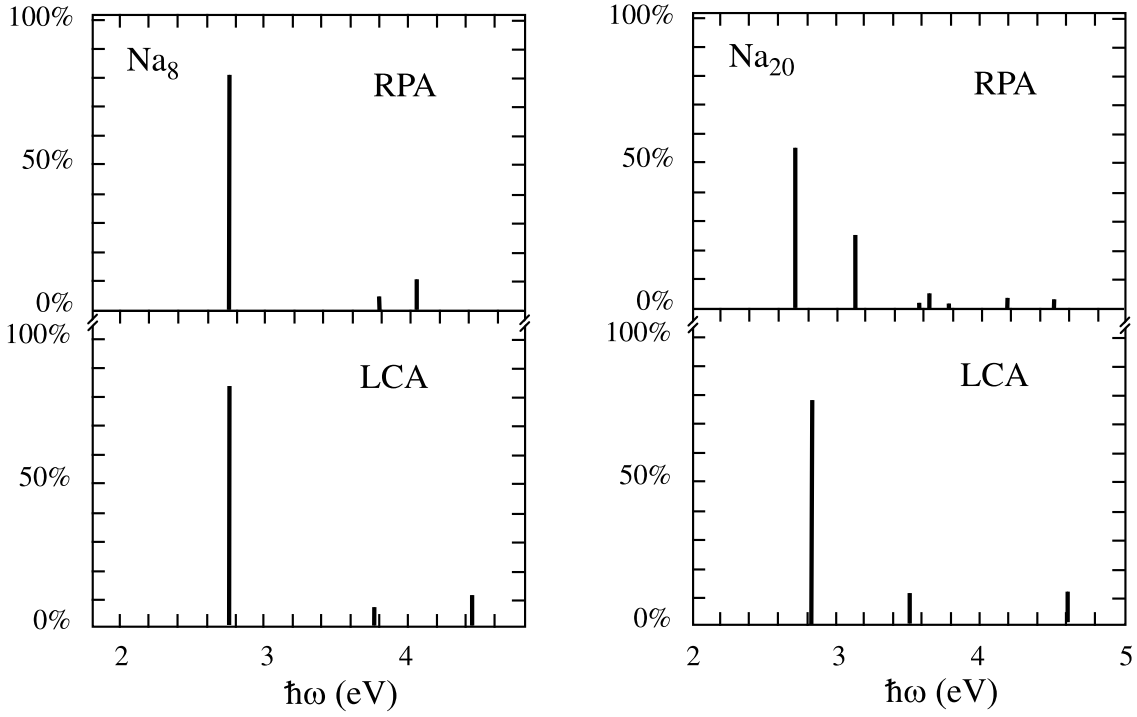
$$\rho_I(r) = \rho_0\,\Theta(r - R)$$

choose ρ_0 such that $\int \rho_I(r)\,d^3r = ewN$

LCA vs RPA for spherical sodium clusters

using spherical jellium model

Sum-rule weighted dipole spectrum:



RPA: C. Yannouleas *et al.*, Phys. Rev. Lett. **63**, 255 (1989)
LCA: P.-G. Reinhard *et al.*, Phys. Rev. A **41**, 5568 (1990)

In LCA: use of following basis of operators:*)

$\{Q_p(\mathbf{r})\} = er^p Y_{10}(\theta)\,, \quad p = 1,4,7(,10) \quad (\Delta Q_p \neq 0 \text{ for } p>1)$

$M = 3$-4 coupled modes are sufficient for convergence!

*)Alternatively: use Bessel functions

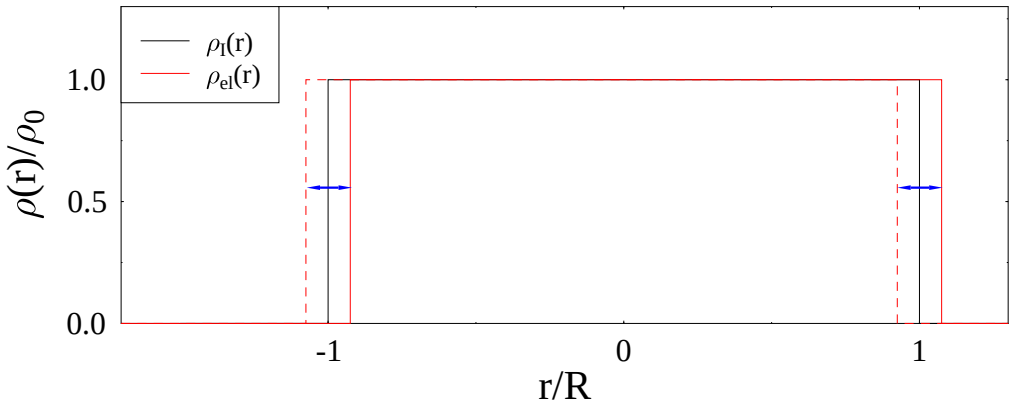
Main peak in fair agreement with experiment (slight blue shift)

Coupling of surface and volume plasmons

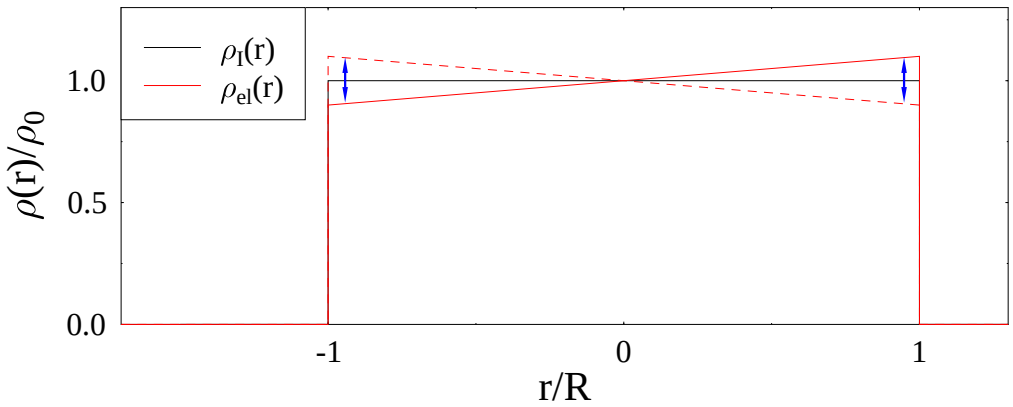
Main peak with most of dipole sum rule: pure translation ($p = 1$, $Q_d = ez$):

$$E_3(Q_d) = \hbar\omega_{Mie} = \sqrt{\frac{\hbar^2}{m}\frac{e^2N}{R^3}}$$

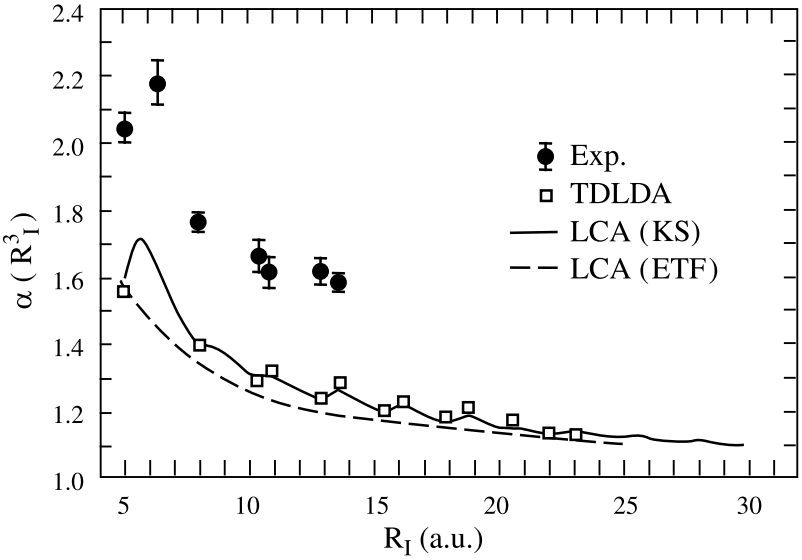
"Mie surface plasmon":



Remaining dipole strength at higher energies: coupled compressional modes with $p>1$, "volume plasmons":



Static electric dipole polarizabilities



Exp: W. Knight *et al.*, Phys. Rev. B **31**, 2539 (1985)
LCA: M. Brack, Phys. Rev. B **39**, 3533 (1989)
TDLDA: W. Ekardt, Phys. Rev. B **29**, 1558 (1984)
(theory: both with spherical jellium model)

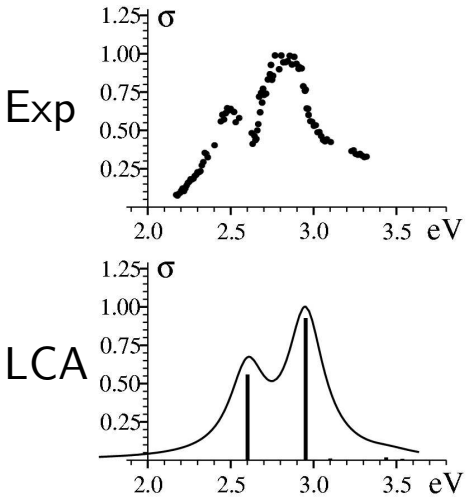
Missing polarizability: due to missing ionic structure in the theoretical calclulations (same reason for blue-shift of Mie plasmon)

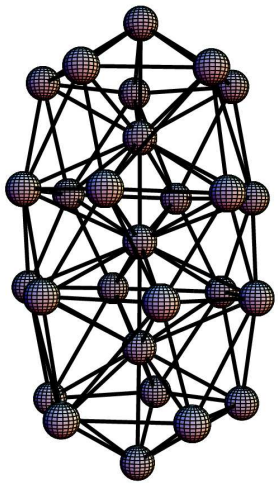
Ionic structure:
can be obtained in molecluar dynamics calculation, but microsopic RPA response becomes prohibitive for large clusters ($N \gtrsim 20$). But LCA is still possible!

Optic response of larger Na clusters

Na 27+

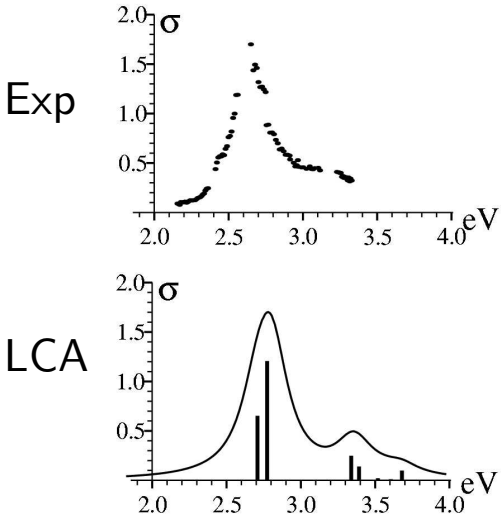
CAPS

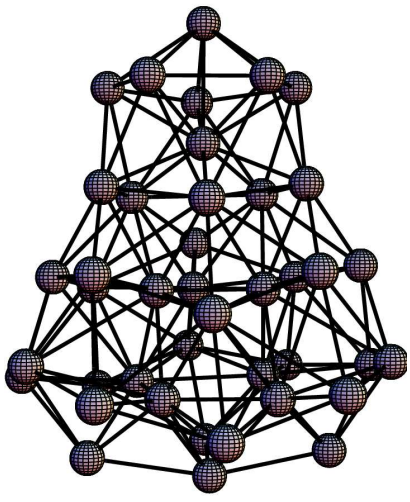




Na41+

CAPS



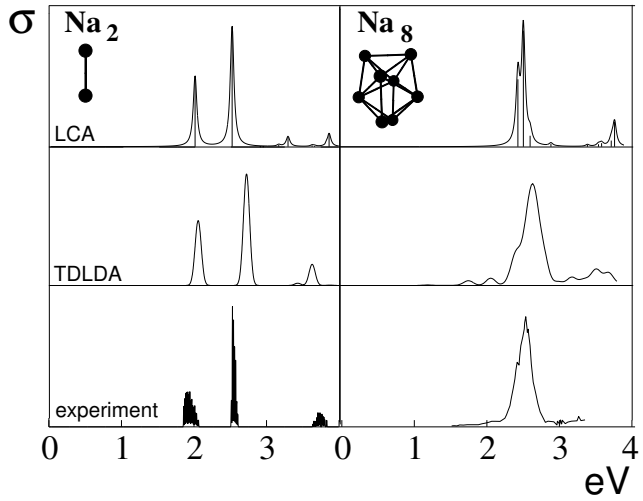


Exp: M. Schmidt, H. Haberland, Eur. Phys. J. D **6**, 109 (1999)

LCA: S. Kümmel, M. Brack, P.G. Reinhard, Phys. Rev. B **58**, R1774 (1998), using CAPS (= cylindrically averaged pseudo-potential) model and Car-Parrinello molecular dynamics

Optic response in small sodium clusters

Photo-absorption cross section (dipole spectrum):



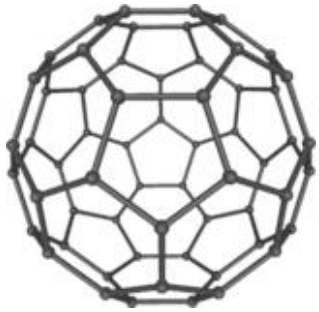
LCA (CAPS): S. Kümmel *et al.*, Eur. J. Phys. D **11**, 239 (2000)
TDLDA: L. Vasiliev *et al.*, Phys. Rev. Lett. **82**, 1919 (1999)
Exp: W. Frederickson, W. Watson, Phys. Rev. **30**, 429 (1997);
C. Wang *et al.*, Chem. Phys. Lett. **166**, 26 (1990)

Note the good agreement of LCA with experiment! (including presence of "volume plasmon")

Finite width of theoretical curves: by Lorentzian folding with experimental width!

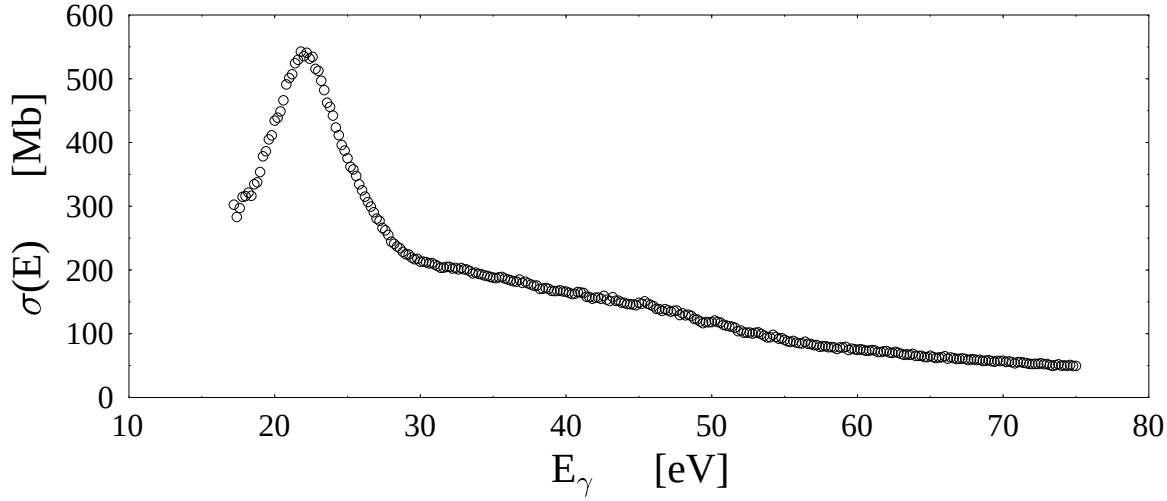
Collective electronic excitations in C_{60} molecules

The Buckminster fullerene ("buckey ball") C_{60}:



has 60 C atoms with
4 valence electrons each
$\Rightarrow N = 240$ electrons
oscillate against ionic cores

Experimental photoabsorption cross section [1]:



Fit by two Lorentzians:
$E_1 = 22$ eV, $\Gamma = 7.6$ eV ("surface plasmon")
$E_2 = 38$ eV, $\Gamma = 29$ eV ("volume plasmon")

[1] S. W. J. Scully *et al.*, Phys. Rev. Lett. **94**, 065503 (2005)

Jellium model for C_{60} molecules

Replace ionic density by jellium density:
$spherical\ shell$ with radius R and thickness Δ:

$$\rho_I(r) = \rho_0[\Theta\,(R_2 - r) - \Theta\,(r - R_1)]$$

with $R_1 = R - \Delta/2$, $R_2 = R + \Delta/2$;
ρ_0 chosen such that

$$\int \rho_I(r)\, d^3r = -\int \rho_{el}(r)\, d^3r = Ne = 240\, e$$

$\Rightarrow$ yields external potential $V_I(r)$ for 240 electrons with two-body Coulomb interaction

TDLDA:

a) get ground state electron density $\rho_{el}(r)$ solving self-consistent Kohn-Sham equations with LDA functional for exchange and correlation (xc) energy
b) do continuum RPA to get dipole excitation spectrum

LCA:

a) use exact ground-state density $\rho_{el}(r)$ to calculate inertia and restoring force tensors $B_{pp'}$, $C_{pp'}$ for M coupled modes
b) solve secular equation

Classical limits for dipole modes

– ignore kinetic and xc-correlation energies
– use $\rho_{el}(r) = -\rho_I(r) =$ jellium density
– expand to first order in Δ/R

a) pure *translational* dipole mode ($Q = ez$):

$$E_3(Q_1^1) = \sqrt{\frac{\hbar^2}{m}\frac{Ne^2}{3R^2\Delta}} = \hbar\omega_{Mie} \qquad \text{(surface plasmon)}$$

b) pure *compressional breathing* mode ($Q = er^2$):

$$E_3(Q_0^2) = \sqrt{\frac{\hbar^2}{m}\frac{Ne^2}{R^2\Delta}} = \hbar\omega_{vol} \qquad \text{(volume plasmon)}$$

c) coupling of one translational ($Q = ez$) with $M-1$ compressional dipole modes ($Q = er^pY_{10}$, $p > 1$):
secular equation can be solved analytically. Result:

– one surface plasmon: $\hbar\omega_1 \simeq \hbar\omega_{Mie}$
– $M-1$ volume plasmons: $\hbar\omega_\nu \simeq \hbar\omega_{vol}$ (ν=2,...,M)
(both slightly blue shifted; $\hbar\omega_{vol}$ more than $\hbar\omega_{Mie}$)

$\Rightarrow$ coupling causes attraction of the two pure modes and a slight overall blue shift!

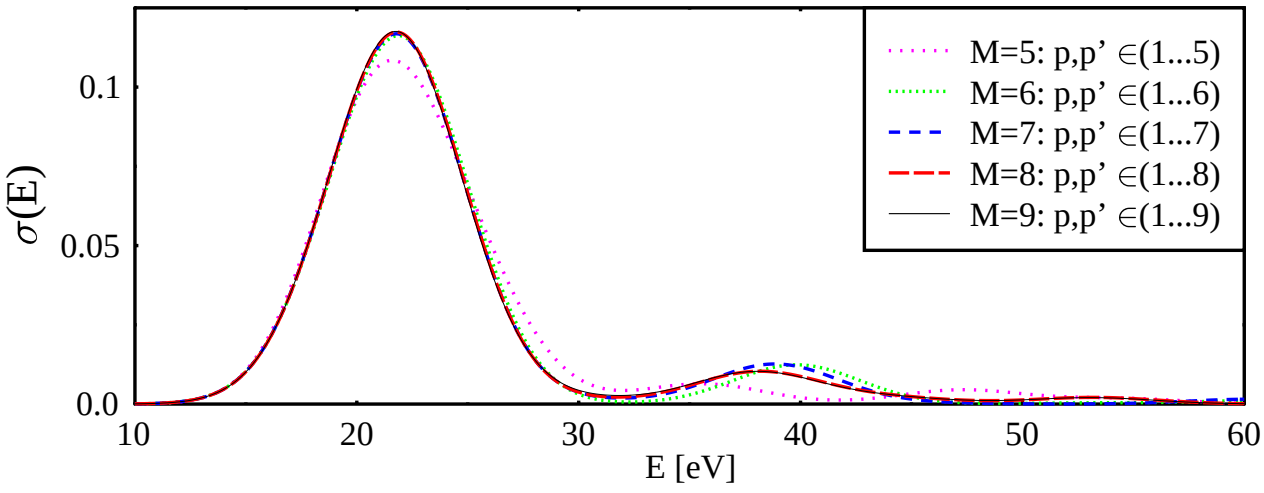
Details of full LCA calculation

– Basis for local operators $Q(\mathbf{r})$ (dipole, $L = 1$):

$$Q_p(\mathbf{r}) = e\, r^p\, Y_{10}(\theta)\,, \qquad p = 1, 2, \ldots, M$$

– $B_{pp'}$ and $C_{pp'}$ calculated with the quantum-mechanical density $\rho(r)$ obtained in TDLDA and the semi-classical kinetic energy functional $\tau_{ETF}[\rho(r)]$
– Spectrum $\hbar\omega_\nu$ is convoluted with a Lorentzian of width $\Gamma = 5$ eV to simulate continuum effects

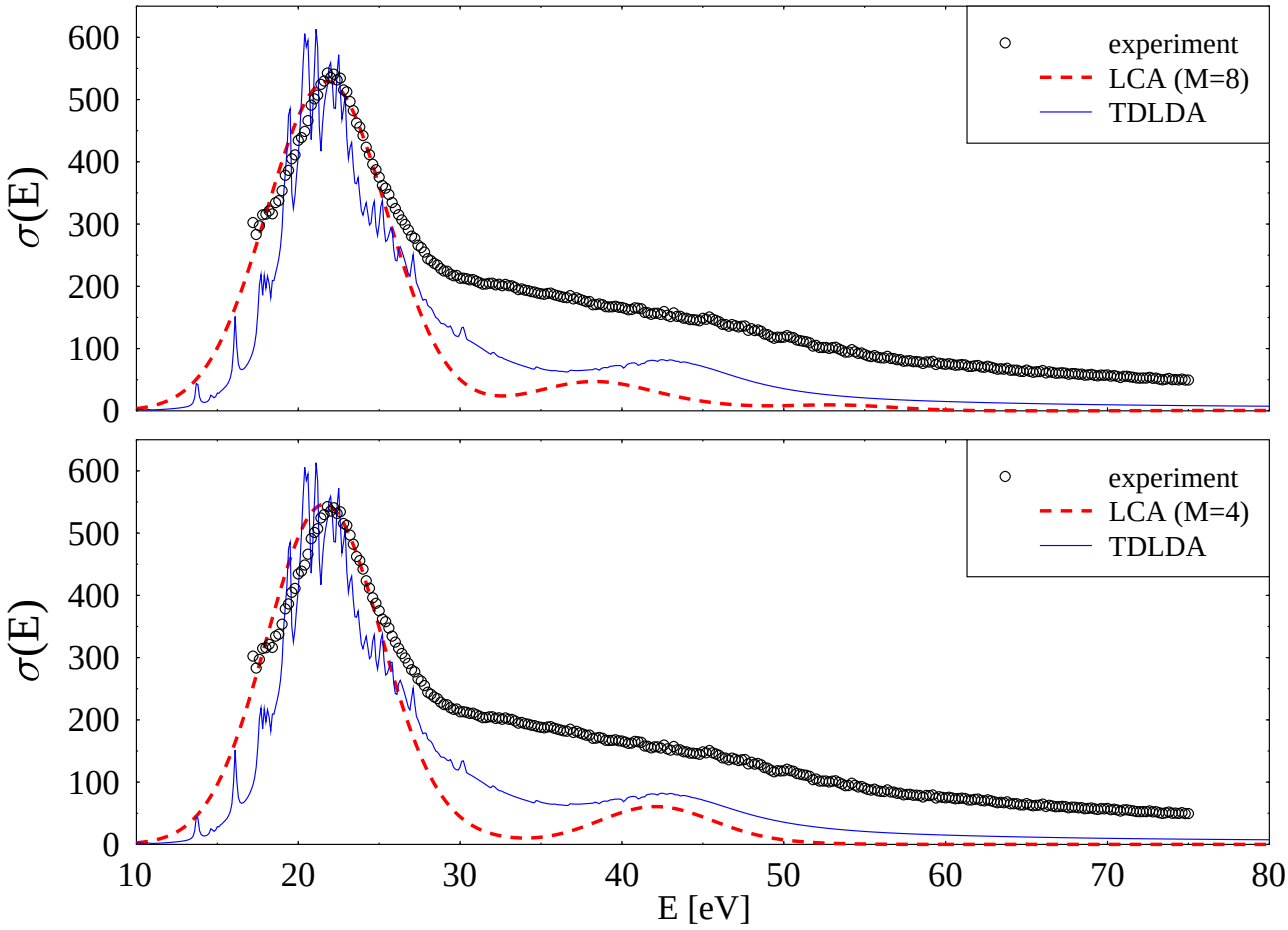
Convergence with respect to basis size M:



Note that convergence is reached for $M = 8$

Comparison of theories with experiment

(○) Experiment versus
— TDLDA ($\simeq$ continuum RPA) [1] and
- - LCA using quantum g.s. density $\rho(r)$ of [1]
(both *red shifted* by 5.5 eV, *heights adjusted !*):



LCA: Upper: with M=8 modes (p, p'=1...8); Lower: with M=4 modes (p, p'=1...4); both Lorentzian-convoluted ($\Gamma = 5$ eV)

[1] A. Rüdel *et al.*, Phys. Rev. Lett. **89**, 125503 (2002)

Summary and conclusions (for C_{60})

- TDLDA with jellium model gives qualitative explanation of experimental cross section
- blue shift ist due to missing ionic structure (like in metal clusters)
- wrong normalization and missing dipole strength in high-energy shoulder are due to missing fragmentation channels
- LCA with exact density $\rho_{el}(r)$ reproduces TDLDA result semi-quantitiatively (with adjusted Lorentzian smoothing) and is far less time consuming than TDLDA
- Small difference LCA/TDLDA may be due to missing π electrons in LCA calculation

Generally (for finite fermion systems):

- LCA is an economic tool for fast and easy semi-quantitative theoretical estimates for collective excitations; applicable also to deformed nuclei or molecules with ionic structure, where full HF-RPA or TDLDA becomes prohibitive!

Thanks

1. To my former students at Regensburg:
   - P. Gleissl (Juniper Networks, Munich, Germany)
   - H. Genzken (Intel, Munich, Germany)
   - S. Kümmel (Univ. Bayreuth, Germany)

2. To my visitors and external collaborators:
   - P. Quentin (Univ. Bordeaux, France)
   - J. Meyer (Univ. Lyon, France)
   - W. Stocker (TU Munich, Germany)
   - P. G. Reinhard (Univ. Erlangen, Germany)

3. To my sponsors:
   - Deutsche Forschungsgemeinschaft

4. To a patient audience!