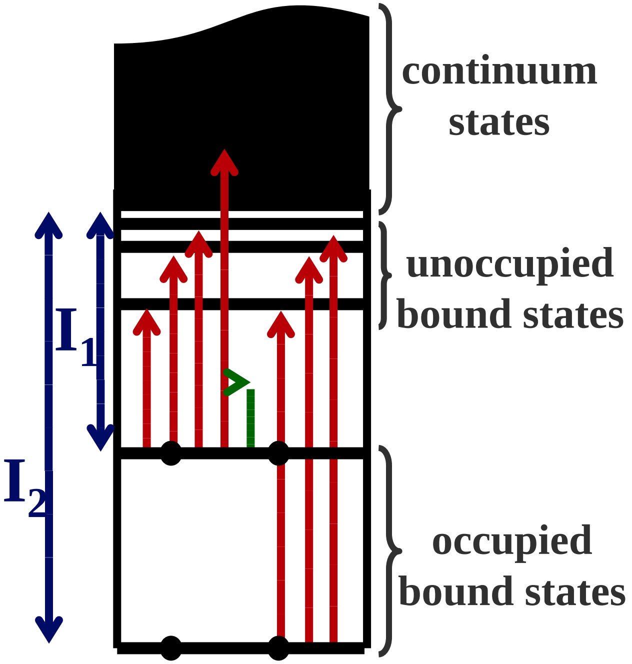
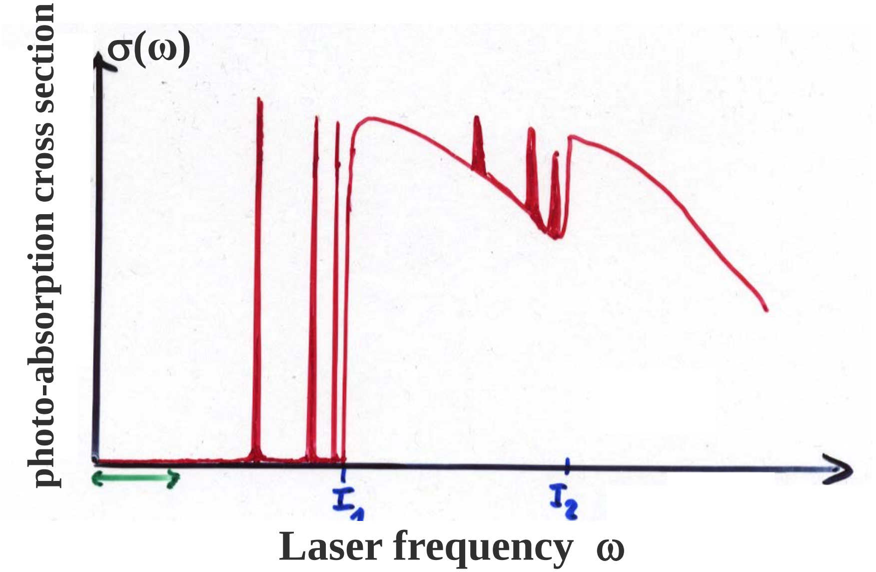
Reminder: Photo-absorption in weak lasers





No absorption if ω < lowest excitation energy

LINEAR RESPONSE THEORY

$t = t_0$: Interacting system in ground state of potential $v_0(r)$ with density $\rho_0(r)$

$t > t_0$: Switch on perturbation $v_1(r\,t)$ (with $v_1(r\,t_0)=0$).

Density: $\rho(r\,t) = \rho_0(r) + \delta\rho(r\,t)$

Consider functional $\rho[v](r\,t)$ defined by solution of interacting TDSE

Functional Taylor expansion of $\rho[v]$ around v_o:

$$
\begin{aligned}
\rho[v](rt) &= \rho[v_0 + v_1](rt) \\
&= \rho[v_0](rt) && \longrightarrow \rho_o(r) \\
&\quad + \int \left.\frac{\delta\rho[v](rt)}{\delta v(r't')}\right|_{v_0} v_1(r't')\, d^3r' dt' && \longrightarrow \rho_1(rt) \\
&\quad + \frac{1}{2}\int\!\!\int \left.\frac{\delta^2\rho[v](rt)}{\delta v(r't')\,\delta v(r''t'')}\right|_{v_0} v_1(r',t')\, v_1(r'',t'')\, d^3r' d^3r'' dt' dt'' && \longrightarrow \rho_2(rt) \\
&\quad \vdots
\end{aligned}
$$

$\rho_1(r,t)$ = linear density response of interacting system

$$\chi(rt,r't') := \left.\frac{\delta\rho[v](rt)}{\delta v(r't')}\right|_{v_0}$$ = **density-density response function of interacting system**

Analogous function $\rho_s[v_s](r\,t)$ for non-interacting system

$$\rho_S[v_S](rt) = \rho_S[v_{S,0} + v_{S,1}](rt) = \rho_S[v_{S,0}](rt) + \int \left.\frac{\delta\rho_S[v_S](rt)}{\delta v_S(r't')}\right|_{v_{S,0}} v_{S,1}(r't')\, d^3r'dt' + \cdots$$

$$\chi_S(rt,r't') := \left.\frac{\delta\rho_S[v_S](rt)}{\delta v_S(r't')}\right|_{v_{S,0}}$$ = **density-density response function of non-interacting system**

GOAL: Find a way to calculate $\rho_1(r\,t)$ without explicitly evaluating $\chi(r\,t,r't')$ of the interacting system

starting point: Definition of xc potential

$$v_{xc}[\rho](rt) := v_S[\rho](rt) - v_{ext}[\rho](rt) - v_H[\rho](rt)$$

Notes:

- v_{xc} is well-defined through non-interacting / interacting 1-1 mapping.
- $v_S[\rho]$ depends on initial determinant Φ_0.
- $v_{ext}[\rho]$ depends on initial many-body state Ψ_0.

$\Rightarrow$ In general, $v_{xc} = v_{xc}[\rho, \Phi_0, \Psi_0]$

only if system is initially in ground-state then, via HK, Φ_0 and Ψ_0 are determined by ρ_0 and v_{xc} depends on ρ alone.

$$\left.\frac{\delta v_{xc}[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} = \left.\frac{\delta v_S[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} - \left.\frac{\delta v_{ext}[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} - \frac{\delta(t-t')}{|r-r'|}$$

$$\begin{tikzcd}
\left.\frac{\delta v_{xc}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & = & \left.\frac{\delta v_S[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \left.\frac{\delta v_{ext}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \frac{\delta(t-t')}{|r-r'|} \\
f_{xc}(rt,r't') \arrow[u] & & \chi_S^{-1}(rt,r't') \arrow[u] & & \chi^{-1}(rt,r't') \arrow[u] & & W_C(rt,r't') \arrow[u]
\end{tikzcd}$$

$$\left.\frac{\delta v_{xc}[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} = \left.\frac{\delta v_S[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} - \left.\frac{\delta v_{ext}[\rho](rt)}{\delta\rho(r't')}\right|_{\boldsymbol{\rho_0}} - \frac{\delta(t-t')}{|r-r'|}$$

$$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ f_{xc}(rt,r't') & \chi_S^{-1}(rt,r't') & \chi^{-1}(rt,r't') & W_C(rt,r't') \end{array}$$

$$f_{xc} + W_C = \chi_S^{-1} - \chi^{-1}$$

$$\begin{array}{ccccccc}
\left.\dfrac{\delta v_{xc}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & = & \left.\dfrac{\delta v_S[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \left.\dfrac{\delta v_{ext}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \dfrac{\delta(t-t')}{|r-r'|} \\
\uparrow & & \uparrow & & \uparrow & & \uparrow \\
f_{xc}(rt,r't') & & \chi_S^{-1}(rt,r't') & & \chi^{-1}(rt,r't') & & W_C(rt,r't')
\end{array}$$

$$\chi_S \bullet \left| f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \right| \bullet \chi$$

$$\begin{tikzcd}
\left.\frac{\delta v_{xc}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & = & \left.\frac{\delta v_S[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \left.\frac{\delta v_{ext}[\rho](rt)}{\delta\rho(r't')}\right|_{\rho_0} & - & \frac{\delta(t-t')}{|r-r'|} \\
f_{xc}(rt,r't') \arrow[u] & & \chi_S^{-1}(rt,r't') \arrow[u] & & \chi^{-1}(rt,r't') \arrow[u] & & W_C(rt,r't') \arrow[u]
\end{tikzcd}$$

$$\chi_S \bullet \left| f_{xc} + W_C = \chi_S^{-1} - \chi^{-1} \right| \bullet \chi$$

$$\chi_S \left(f_{xc} + W_C \right) \chi = \chi - \chi_S$$

$$\boxed{\chi = \chi_S + \chi_S \left(W_C + f_{xc} \right) \chi}$$

Act with this operator equation on arbitrary $v_1(r\ t)$ and use $\chi\ v_1 = \rho_1$:

$$\boxed{\rho_1\left(rt\right) = \int d^3r'dt'\chi_S\left(rt, r't'\right)\left[v_1\left(rt\right) + \int d^3r''dt''\left\{ W_C\left(r't', r''t''\right) + f_{xc}\left(r't', r''t''\right) \right\} \rho_1\left(r''t''\right) \right]}$$

- Exact integral equation for $\rho_1(r\ t)$, to be solved iteratively
- Need approximation for $f_{xc}\left(r't', r''t''\right) = \left. \frac{\delta v_{xc}\left[\rho\right]\left(r't'\right)}{\delta\rho\left(r''t''\right)} \right|_{\rho_0}$

  (either for f_{xc} directly or for v_{xc})

Adiabatic approximation

$$\boxed{v_{xc}^{\text{adiab}}[\rho](rt) := v_{xc}^{\text{static DFT}}[\rho(t)](rt)}$$

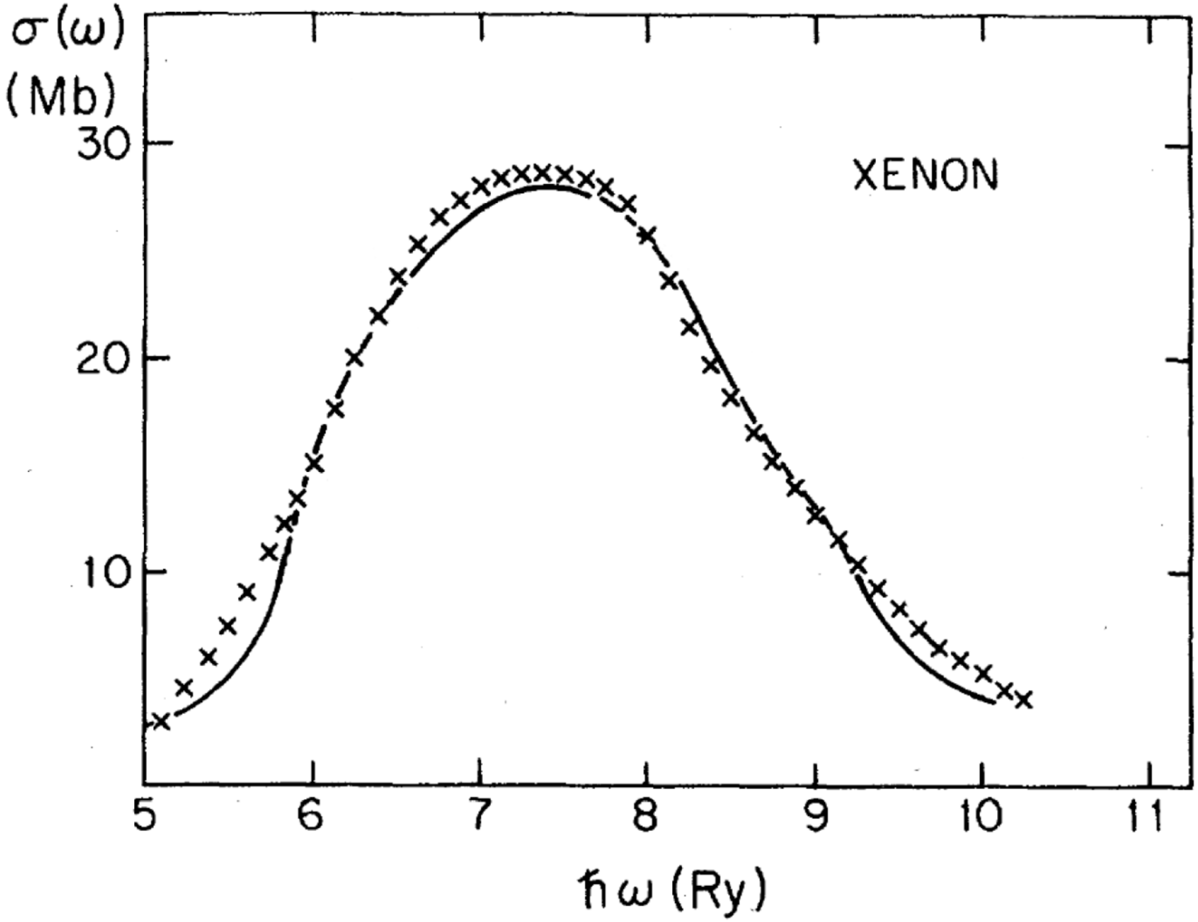
In the adiabatic approximation, the xc potential $v_{xc}(t)$ at time t only depends on the density $\rho(t)$ at the very same point in time.

e.g. adiabatic LDA: $v_{xc}^{\text{ALDA}}(rt) := v_{xc}^{\text{LDA}}(\rho(rt)) = -\alpha\,\rho(rt)^{1/3} + \cdots$

$$\Rightarrow\ f_{xc}^{\text{ALDA}}(rt, r't') = \left.\frac{\delta v_{xc}^{\text{ALDA}}(rt)}{\delta\rho(r't')}\right|_{\rho_0} = \delta(r-r')\,\delta(t-t')\left.\frac{\partial v_{xc}^{\text{ALDA}}}{\partial\rho(r)}\right|_{\rho_0(r)}$$

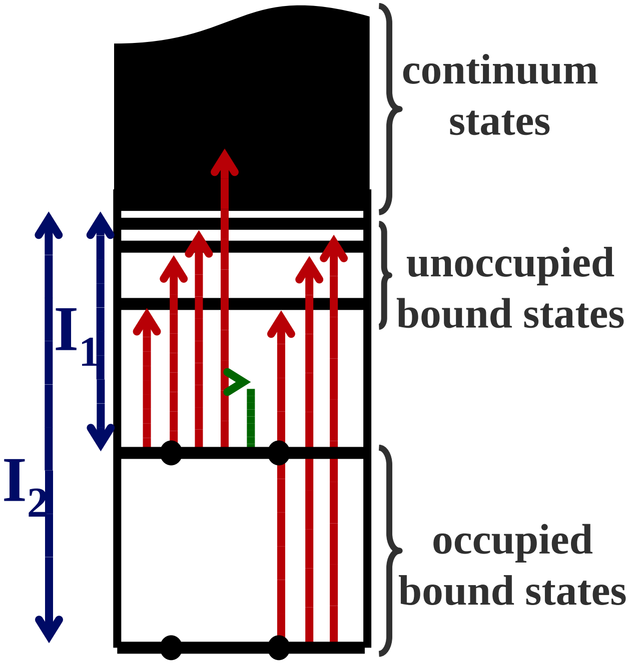
$$= \delta(r-r')\,\delta(t-t')\left.\frac{\partial^2 e_{xc}^{\text{hom}}}{\partial n^2}\right|_{\rho_0(r)}$$

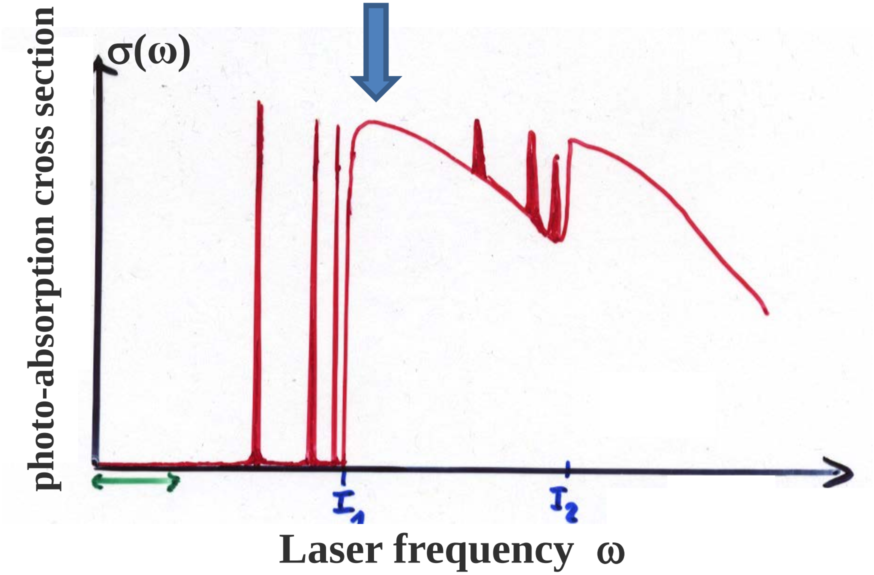
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.



Solid line: self-consistent time-dependent KS calculation [A. Zangwill and P. Soven, PRA <u>21</u>, 1561 (1980)]; crosses: experimental data [R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. <u>188</u>, 1375 (1969)].

Photo-absorption in weak lasers





No absorption if ω < lowest excitation energy

Discrete excitation energies from TDDFT

Standard linear response formalism

$H(t_0)$ = full static Hamiltonian at t_0

$$H(t_0)|m\rangle = E_m|m\rangle$$ ← **exact many-body eigenfunctions and energies of system**

full response function

$$\chi(r,r';\omega) = \lim_{\eta\to 0^+}\sum_m \left(\frac{\langle 0|\hat{\rho}(r)|m\rangle\langle m|\hat{\rho}(r)|0\rangle}{\omega-(E_m-E_0)+i\eta} - \frac{\langle 0|\hat{\rho}(r')|m\rangle\ \langle m|\hat{\rho}(r')|0\rangle}{\omega+(E_m-E_0)+i\eta} \right)$$

⇒ The exact linear density response

$$\rho_1(\omega) = \hat{\chi}(\omega)\,v_1(\omega)$$

has poles at the exact excitation energies $\Omega = E_m - E_0$

Discrete excitation energies from TDDFT

exact representation of linear density response:

$$\rho_1(\omega) = \hat{\chi}_S(\omega)\left(v_1(\omega) + \hat{W}_C\rho_1(\omega) + \hat{f}_{xc}(\omega)\rho_1(\omega)\right)$$

"^" denotes integral operators, i.e. $\hat{f}_{xc}\rho_1 \equiv \int f_{xc}(\vec{r},\vec{r}\,')\rho_1(\vec{r}\,')d^3r'$

where $\hat{\chi}_S(\vec{r},\vec{r}\,';\omega) = \sum_{j,k} \frac{M_{jk}(\vec{r},\vec{r}\,')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta}$

with $M_{jk}(\vec{r},\vec{r}\,') = (f_k - f_j)\varphi_j(\vec{r})\varphi_j^*(\vec{r}\,')\varphi_k(\vec{r}\,')\varphi_k^*(\vec{r})$

$$f_m = \begin{cases} 1 \text{ if } & \varphi_m \text{ is occupied in KS ground state} \\ 0 \text{ if } & \varphi_m \text{ is unoccupied in KS ground state} \end{cases}$$

$\varepsilon_j - \varepsilon_k$ KS excitation energy

$$\left(\hat{1}-\hat{\chi}_S(\omega)\left[\hat{W}_C+\hat{f}_{xc}(\omega)\right]\right)\rho_1(\omega)=\hat{\chi}_S(\omega)v_1(\omega)$$

$\rho_1(\omega) \to \infty$ for $\omega \to \Omega$ (exact excitation energy) but right-hand side remains finite for $\omega \to \Omega$

hence $\left(\hat{1}-\hat{\chi}_S(\omega)\left[\hat{W}_C+\hat{f}_{xc}(\omega)\right]\right)\xi(\omega)=\lambda(\omega)\xi(\omega)$

$\lambda(\omega) \to 0$ for $\omega \to \Omega$

This condition rigorously determines the exact excitation energies, i.e.,

$$\left(\hat{1}-\hat{\chi}_S(\Omega)\left[\hat{W}_C+\hat{f}_{xc}(\Omega)\right]\right)\xi(\Omega)=0$$

This leads to the (non-linear) eigenvalue equation

(See T. Grabo, M. Petersilka, E. K. U. G., J. Mol. Struc. (Theochem) 501, 353 (2000))

$$\boxed{\sum_{q'}\left(A_{qq'}(\Omega)+\omega_q\delta_{qq'}\right)\beta_{q'}=\Omega\beta_q}$$

where

$$A_{qq'}=\alpha_{q'}\int d^3r\int d^3r'\Phi_q(r)\left(\frac{1}{|r-r'|}+f_{xc}(r,r',\Omega)\right)\Phi_{q'}(r')$$

$q=(j,a)$ double index

$$\alpha_q=f_a-f_j$$

$$\Phi_q(r)=\varphi_a^*(r)\varphi_j(r)$$

$$\omega_q=\varepsilon_a-\varepsilon_j$$

Atom	Experimental Excitation Energies $^1S\to{}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	$\Delta\epsilon_{KS} + K$
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

$$\Delta E = \underbrace{\Delta\epsilon_{KS}}_{\epsilon_j - \epsilon_k} + K$$

$$\boxed{K = \int d^3r \int d^3r' \, \varphi_j(r)\,\varphi_j^*(r')\,\varphi_k(r')\,\varphi_k^*(r)\left(\frac{1}{|r-r'|} + f_{xc}(r,r')\right)}$$

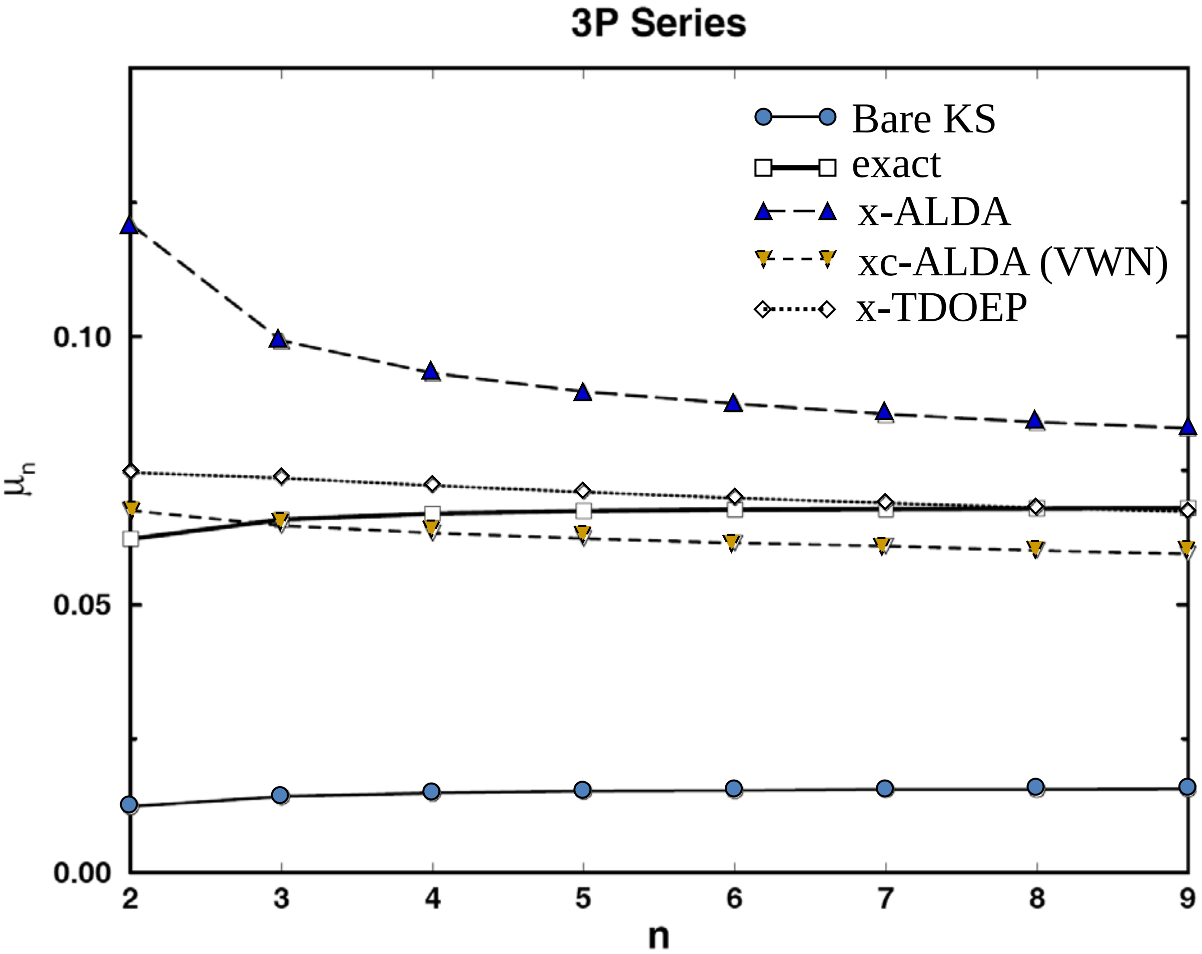
Excitation energies of CO molecule

State		Ω_{expt}	KS-transition	$\Delta\epsilon_{KS}$	$\Delta\epsilon_{KS} + K$
A	$^1\Pi$	0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	$^3\Pi$	0.2323			0.2238
I	$^1\Sigma^-$	0.3631	$1\Pi \rightarrow 2\Pi$	0.3626	0.3626
D	$^1\Delta$	0.3759			0.3812
a'	$^3\Sigma^+$	0.3127			0.3181
e	$^3\Sigma^-$	0.3631			0.3626
d	$^3\Delta$	0.3440			0.3404

T. Grabo, M. Petersilka and E.K.U. Gross, J. Mol. Struct. (Theochem) 501, 353 (2000)

approximations made: v_{xc}^{LDA} and f_{xc}^{ALDA}

Quantum defects in Helium $E_n = -\frac{1}{2\left(n-\mu_n\right)^2}$ [a.u.]



M. Petersilka, U.J. Gossmann and E.K.U.G., in: Electronic Density Functional Theory: Recent Progress and New Directions, J.F. Dobson, G. Vignale, M.P. Das, ed(s), (Plenum, New York, 1998), p 177 - 197.

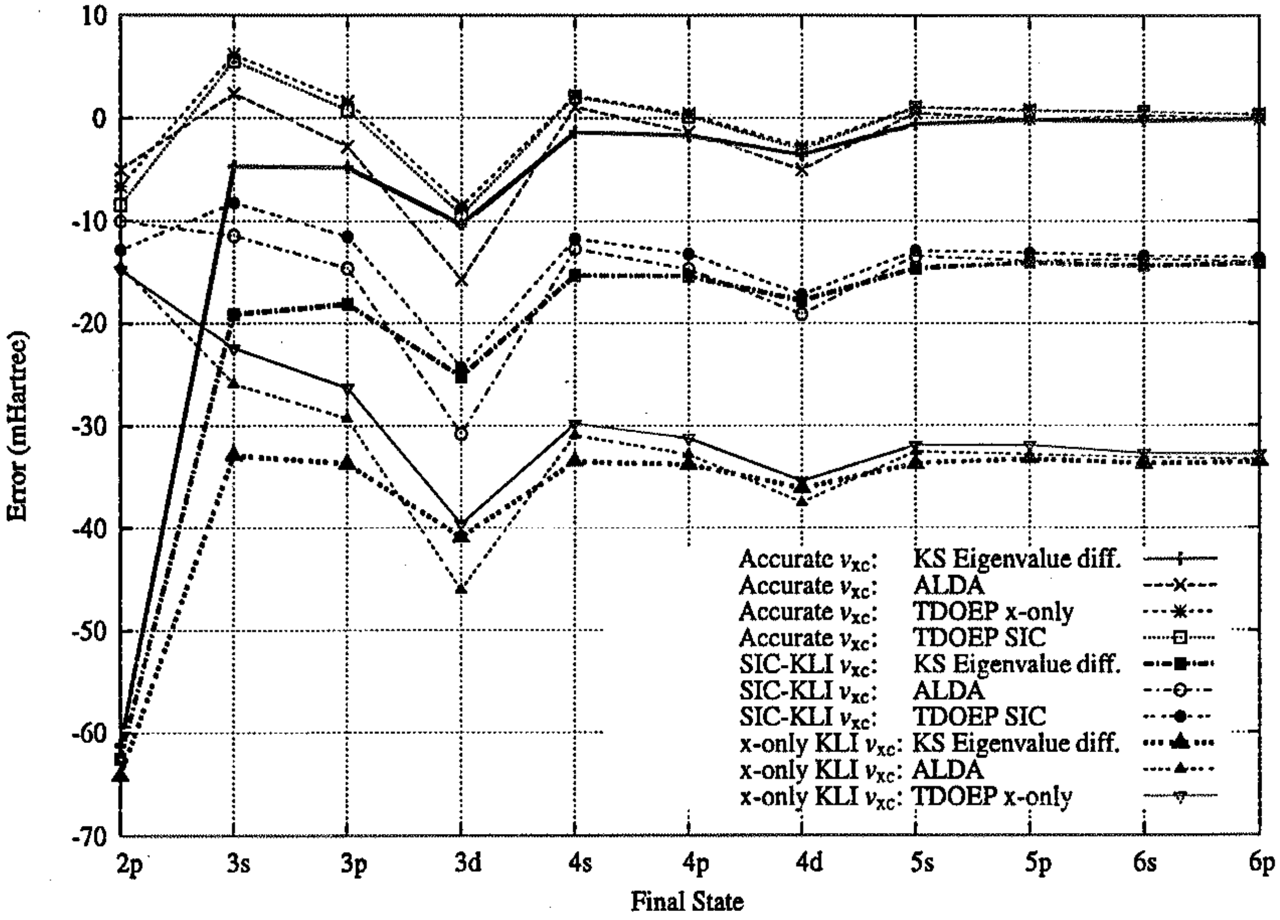


Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye, the errors of the discrete excitation energies were connected with lines.

(M. Petersilka, E.K.U.G., K. Burke, Int. J. Quantum Chem. 80, 534 (2000))

Failures of ALDA in the linear response regime

- **H_2 dissociation is incorrect:**

$$E\left({}^1\Sigma_u^+\right) - E\left({}^1\Sigma_g^+\right) \xrightarrow[R\to\infty]{} 0$$ **(in ALDA)**

(see: Gritsenko, van Gisbergen, Görling, Baerends, JCP <u>113</u>, 8478 (2000))

- **response of long chains strongly overestimated**

(see: Champagne et al., JCP <u>109</u>, 10489 (1998) and <u>110</u>, 11664 (1999))

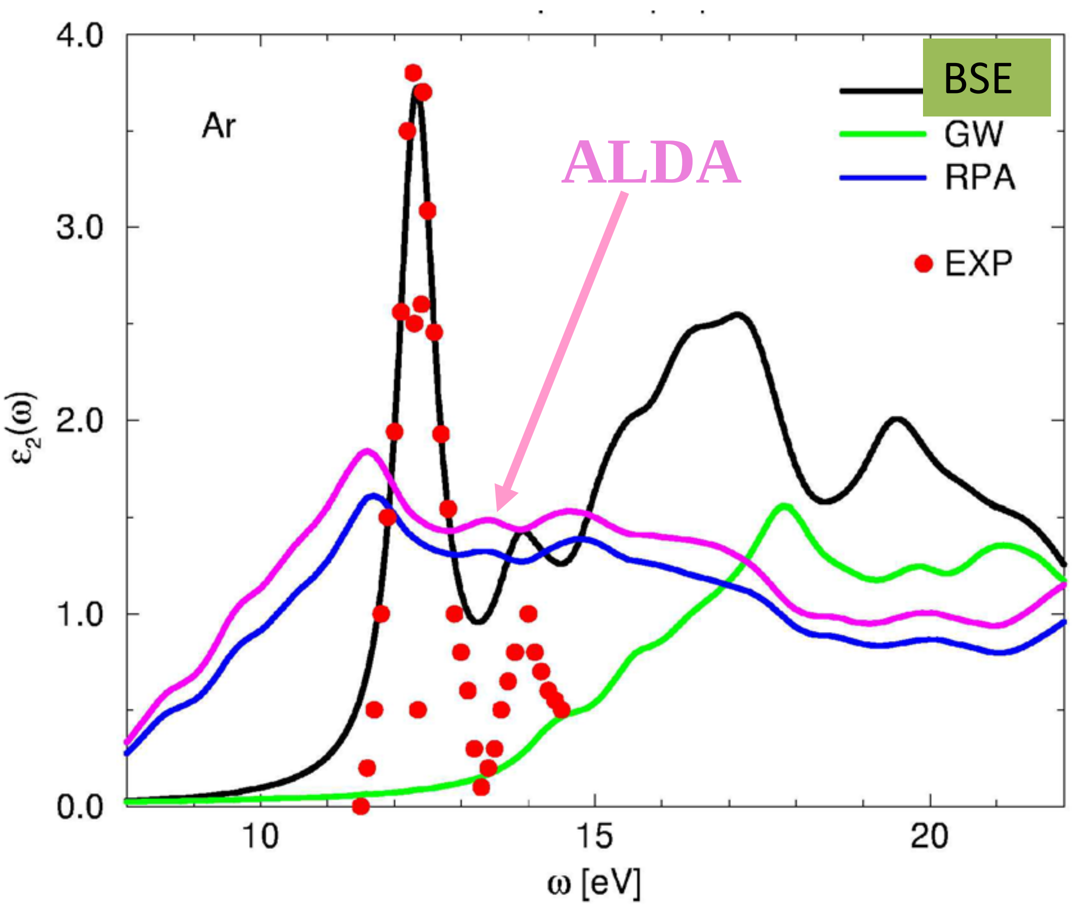
- **in periodic solids,** $f_{\mathbf{xc}}^{\mathbf{ALDA}}\left(q,\omega,\rho\right) = c\left(\rho\right)$ **whereas,**

for insulators, $f_{\mathbf{xc}}^{\mathbf{exact}} \xrightarrow[q\to 0]{} 1/q^2$ **divergent.**

- **charge-transfer excitations not properly described**

(see: Dreuw et al., JCP <u>119</u>, 2943 (2003))

Solid Argon



L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)

Excitons are <u>completely missing</u> for simple xc functionals like ALDA!

EXPLANATION:

TDDFT response equation: bare Coulomb interaction and xc kernel only appear as a sum (v+ f_{xc}).

v(q) diverges like $1/q^2$ for q → 0
f_{xc} → const (in ALDA)

Hence results are close to $f_{xc} = 0$ (RPA) in the q → 0 limit.

CONCLUSION:

Approximations for f_{xc} are needed which, for q → 0, correctly diverge like $1/q^2$. Such approximations can be derived from many-body perturbation theory (see, e.g., L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)).

$$\boxed{\varepsilon^{-1}(\mathbf{q},\omega) = 1 + \chi_S(\mathbf{q},\omega) v(\mathbf{q}) \left[1 - \left(v(\mathbf{q}) + f_{xc}^{\text{approx}}(\mathbf{q},\omega) \right) \chi_S(\mathbf{q},\omega) \right]^{-1}}$$

Two problems of ALDA need to be fixed:

- **Onset of absorption is dictated by χ_0 , i.e. is identical to the LDA gap for ω-independent kernel (such as ALDA)**
- **Description of excitons requires $1/q^2$ behavior**

Bootstrap kernel

(Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011))

$$\boxed{f_{xc}^{\text{boot}}(\mathbf{q},\omega)=\frac{\varepsilon^{-1}(\mathbf{q},\omega=0)}{\tilde{\chi}^{00}(\mathbf{q},\omega=0)}}$$

$$\boxed{f_{xc}^{\text{appr}}(\mathbf{q},\omega)=\frac{1}{\chi_S(\mathbf{q},\omega)}-\frac{1}{\tilde{\chi}(\mathbf{q},\omega)}+f_{xc}^{\text{boot}}(\mathbf{q})}$$

where $\tilde{\chi}$ is a single-particle response function that has the right gap, e.g. from G_0W_0 , or LDA/GGA+Scissors.

$$\varepsilon^{-1}(\mathbf{q},\omega)=1+\chi_0(\mathbf{q},\omega)v(\mathbf{q})\left[1-\left(v(\mathbf{q})+\mathrm{f}_{xc}^{\text{appr}}(\mathbf{q},\omega)\right)\chi_0(\mathbf{q},\omega)\right]^{-1}$$

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(Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011))

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$$\varepsilon^{-1}(\mathbf{q},\omega)=1+\chi_0(\mathbf{q},\omega)v(\mathbf{q})\left[1-\left(v(\mathbf{q})+f_{xc}^{\mathrm{appr}}(\mathbf{q},\omega)\right)\chi_0(\mathbf{q},\omega)\right]^{-1}$$

$$\boxed{\varepsilon^{-1}(\mathbf{q},\omega)=1+\tilde{\chi}(\mathbf{q},\omega)v(\mathbf{q})\left[1-\left(v(\mathbf{q})+f_{xc}^{\mathrm{boot}}(\mathbf{q},\omega)\right)\tilde{\chi}(\mathbf{q},\omega)\right]^{-1}}$$

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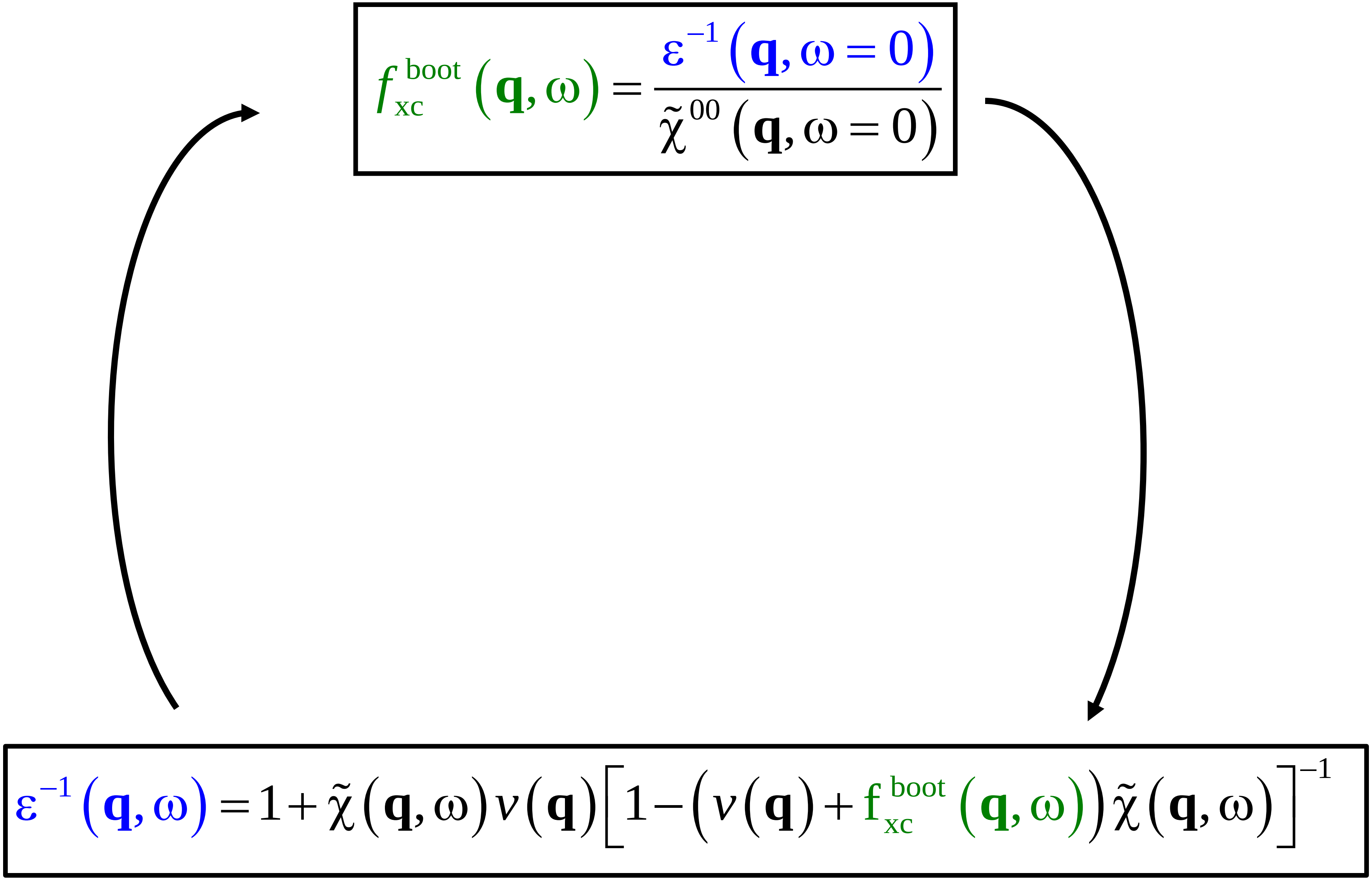
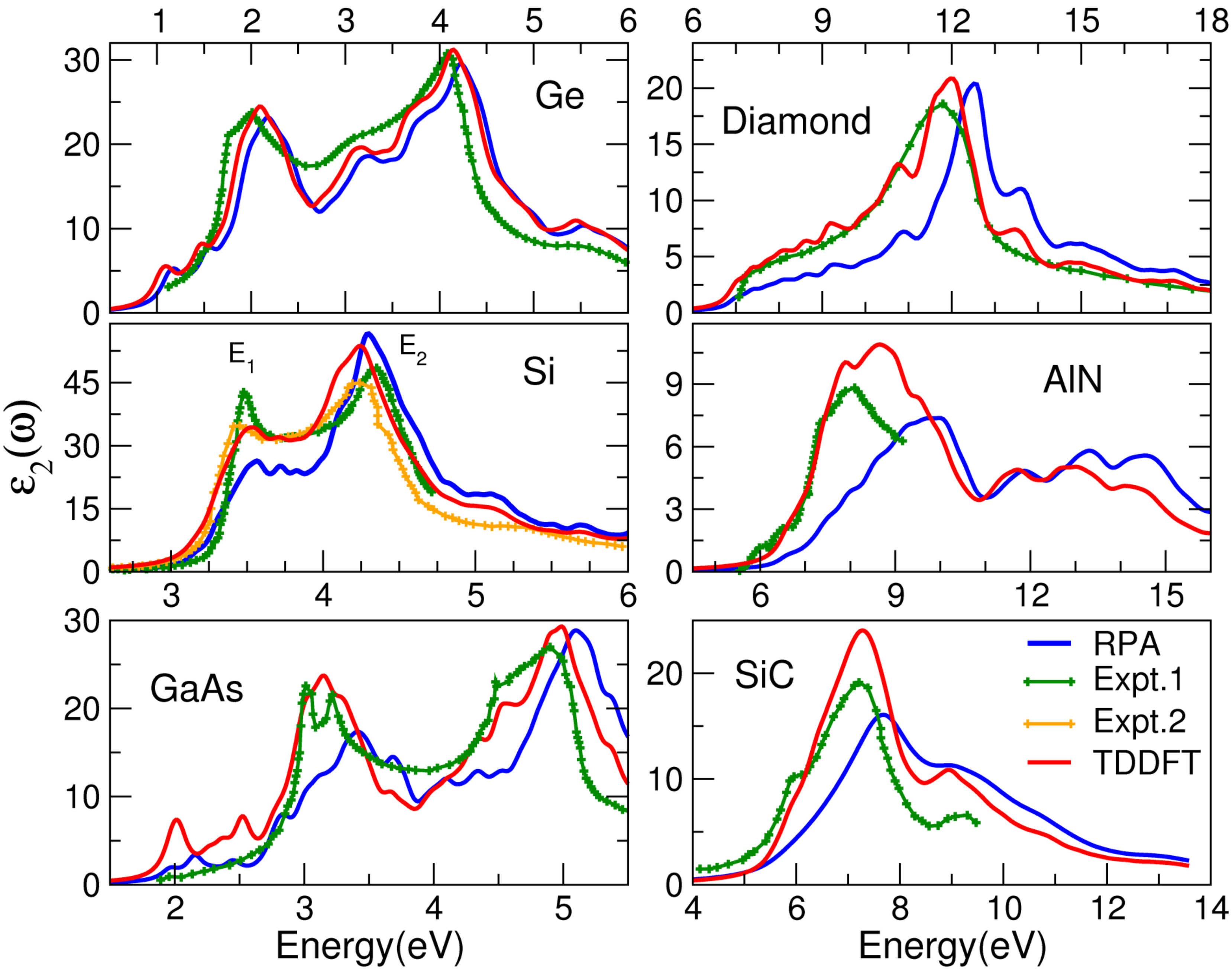
(Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011))



$$\boxed{f_{\mathrm{xc}}^{\mathrm{boot}}(\mathbf{q},\omega)=\frac{\varepsilon^{-1}(\mathbf{q},\omega=0)}{\tilde{\chi}^{00}(\mathbf{q},\omega=0)}}$$

$$\boxed{\varepsilon^{-1}(\mathbf{q},\omega)=1+\tilde{\chi}(\mathbf{q},\omega)v(\mathbf{q})\left[1-\left(v(\mathbf{q})+f_{\mathrm{xc}}^{\mathrm{boot}}(\mathbf{q},\omega)\right)\tilde{\chi}(\mathbf{q},\omega)\right]^{-1}}$$


Ge
Diamond
Si
E1
E2
AlN
GaAs
SiC
RPA
Expt.1
Expt.2
TDDFT
$\varepsilon_2(\omega)$
Energy(eV)
Energy(eV)
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3
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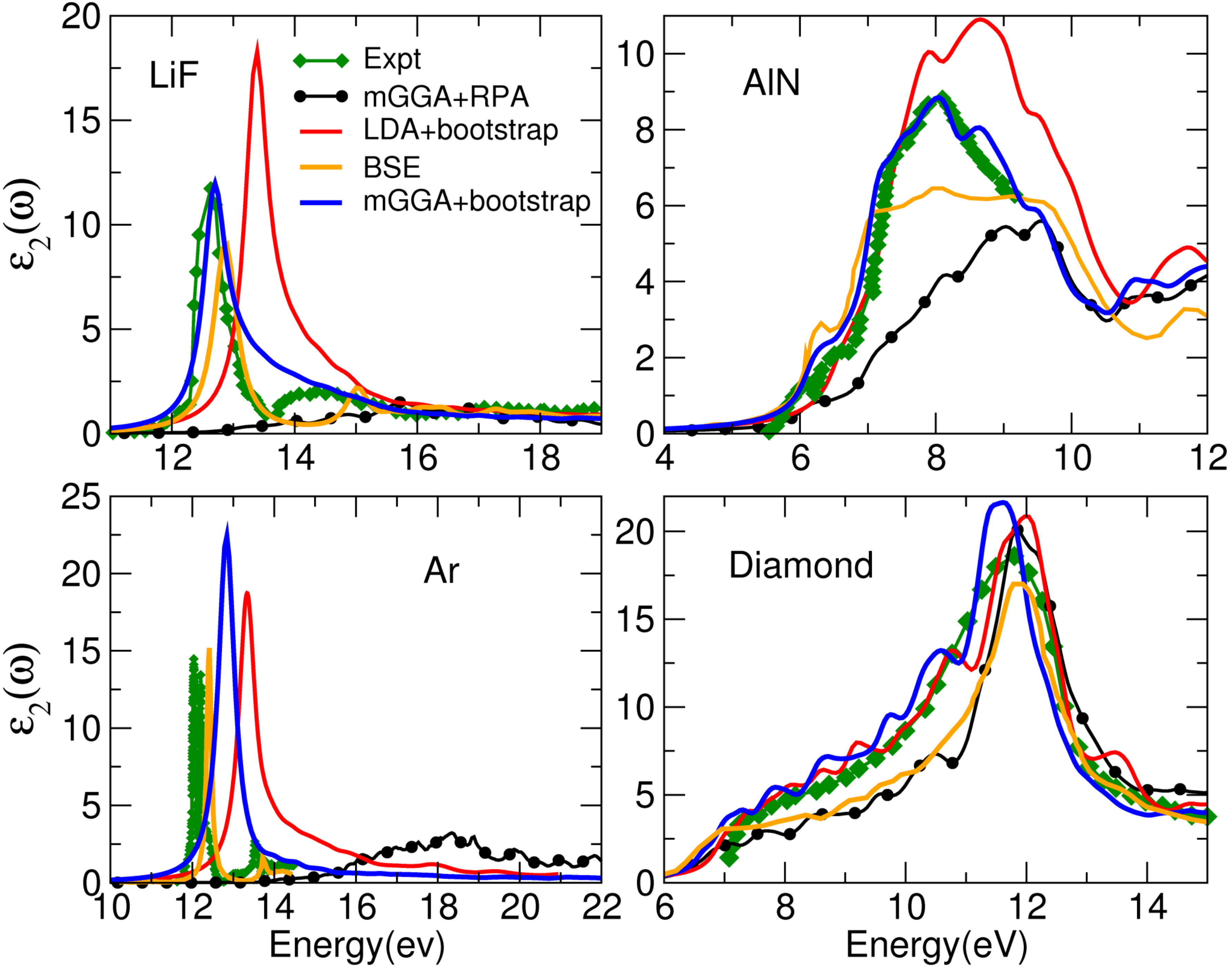
LiF
AlN
Ar
Diamond
Expt
mGGA+RPA
LDA+bootstrap
BSE
mGGA+bootstrap
$\varepsilon_2(\omega)$
$\varepsilon_2(\omega)$
Energy(ev)
Energy(eV)
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5
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15
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16
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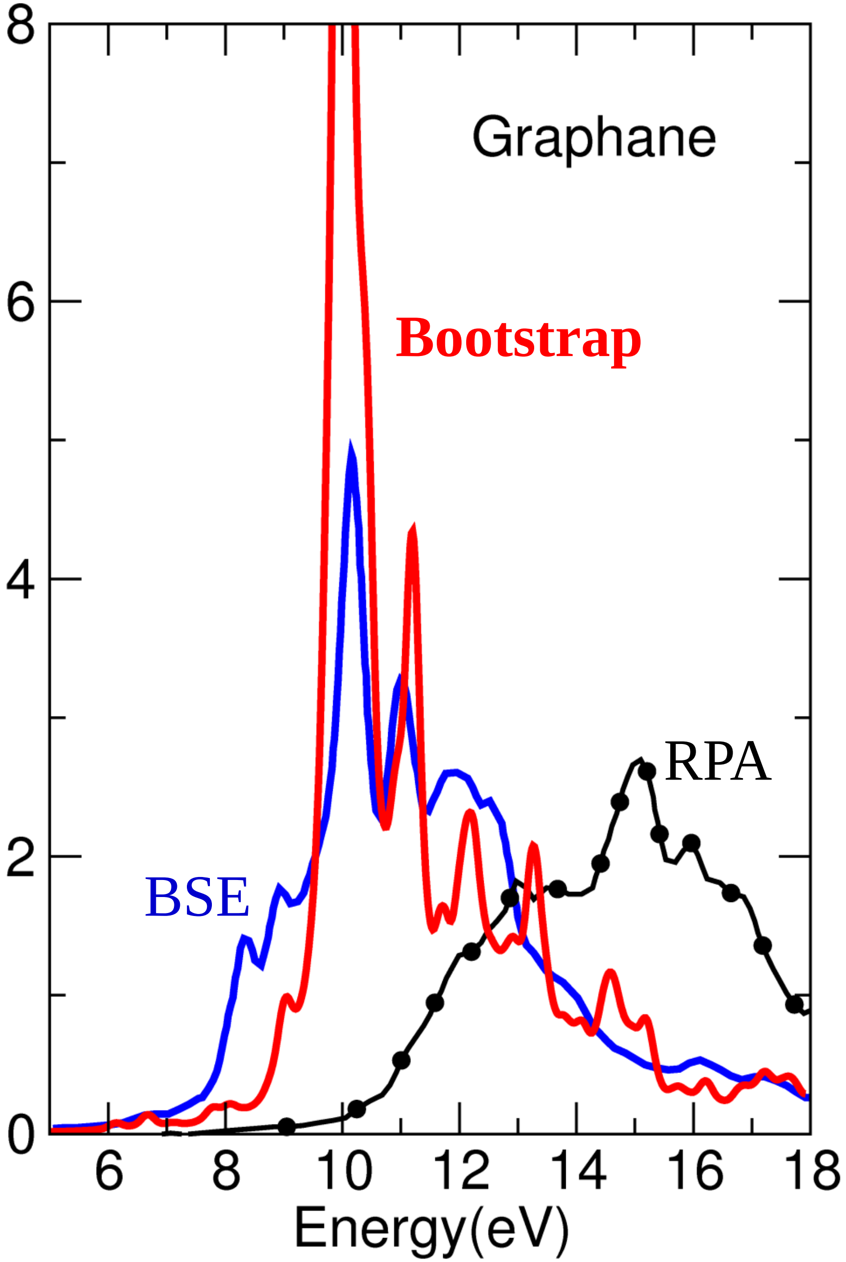
8
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16
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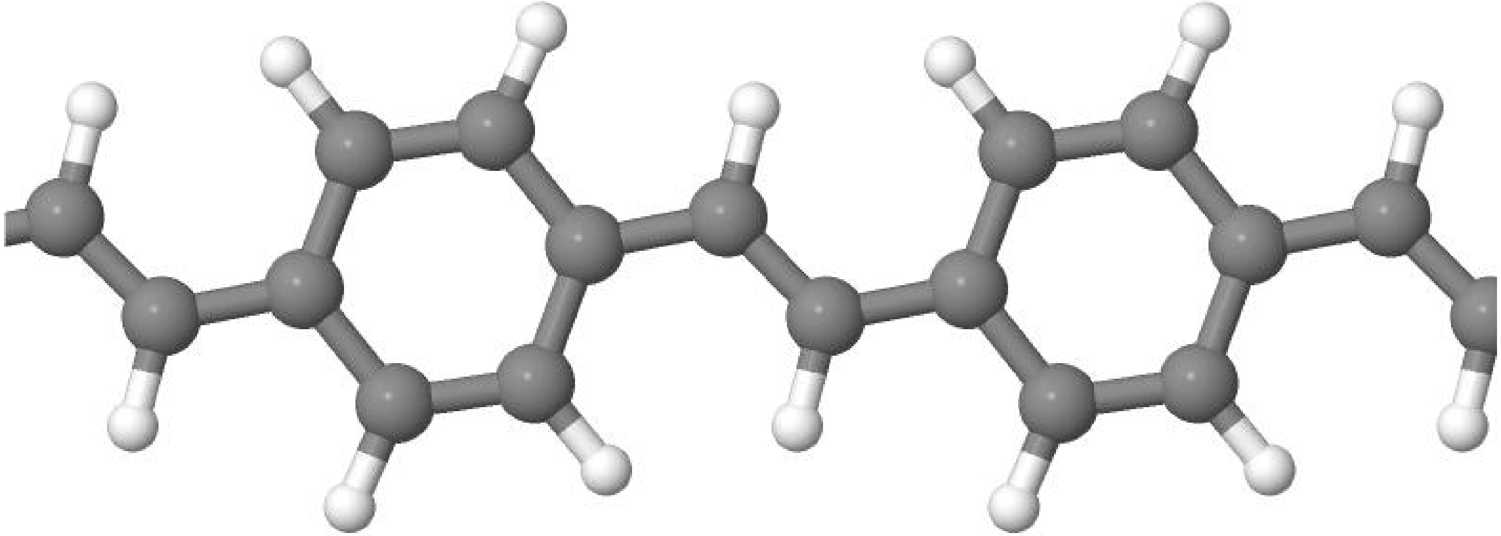
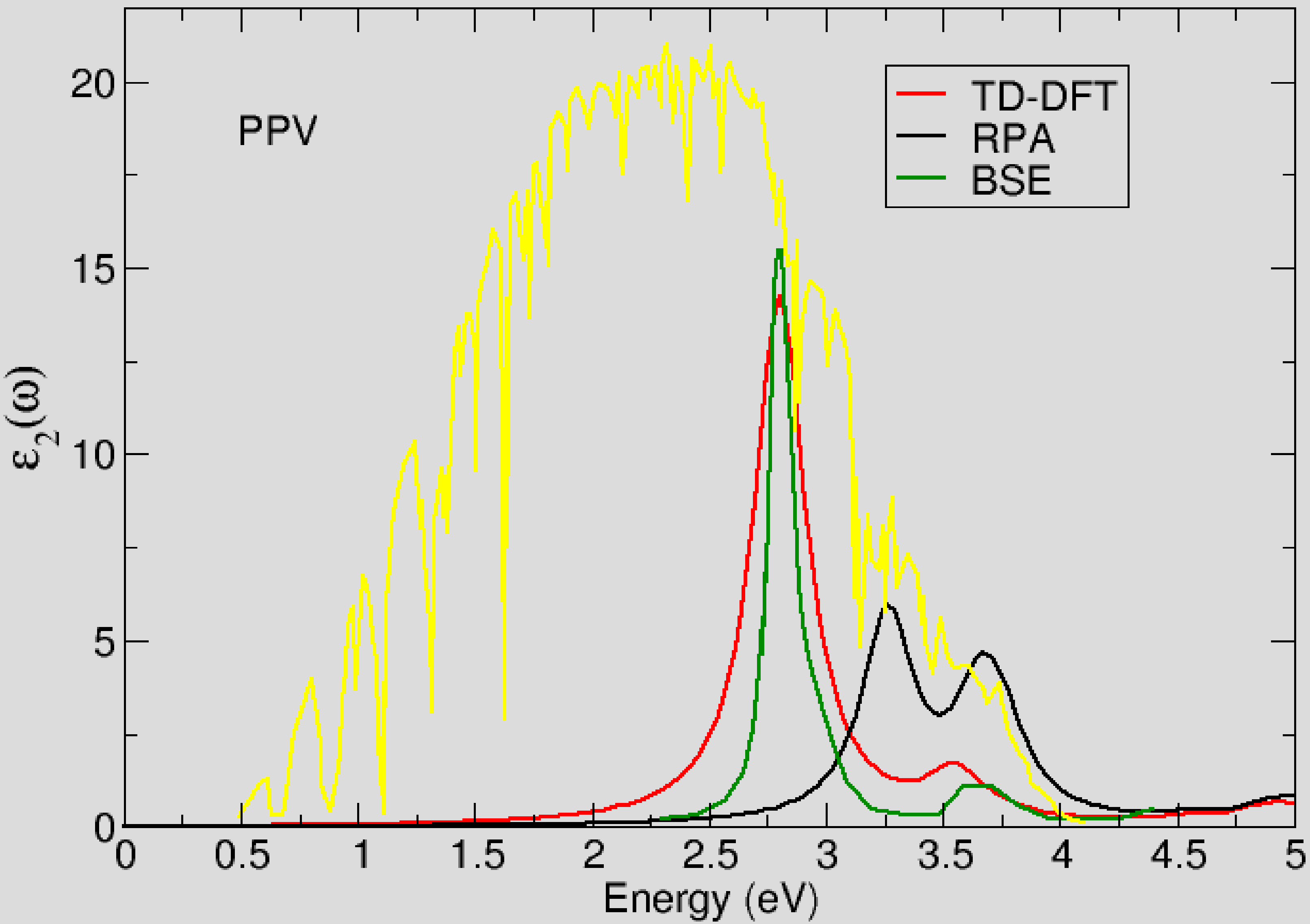
Energy(eV)
Graphane
Bootstrap
RPA
BSE

PPV




PPV
TD-DFT
RPA
BSE
$\varepsilon_2(\omega)$
0
5
10
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20
0
0.5
1
1.5
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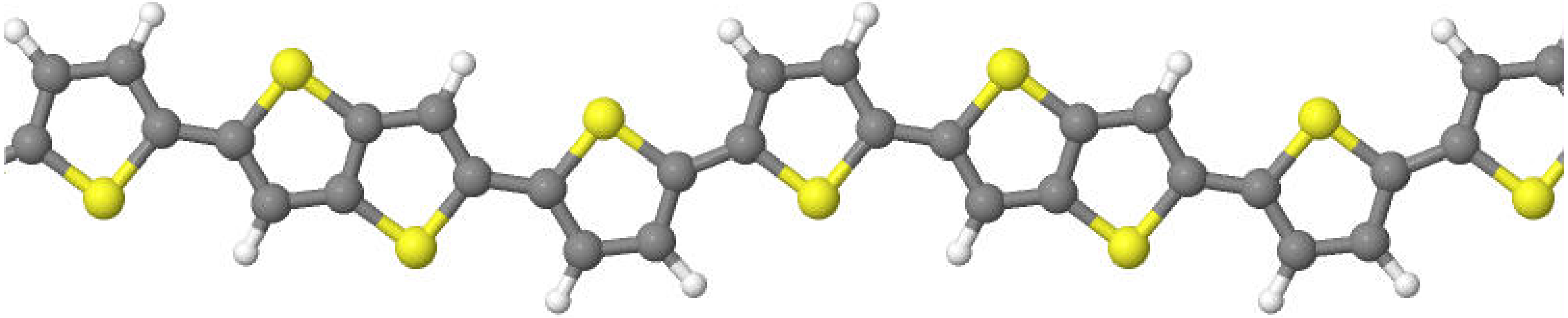
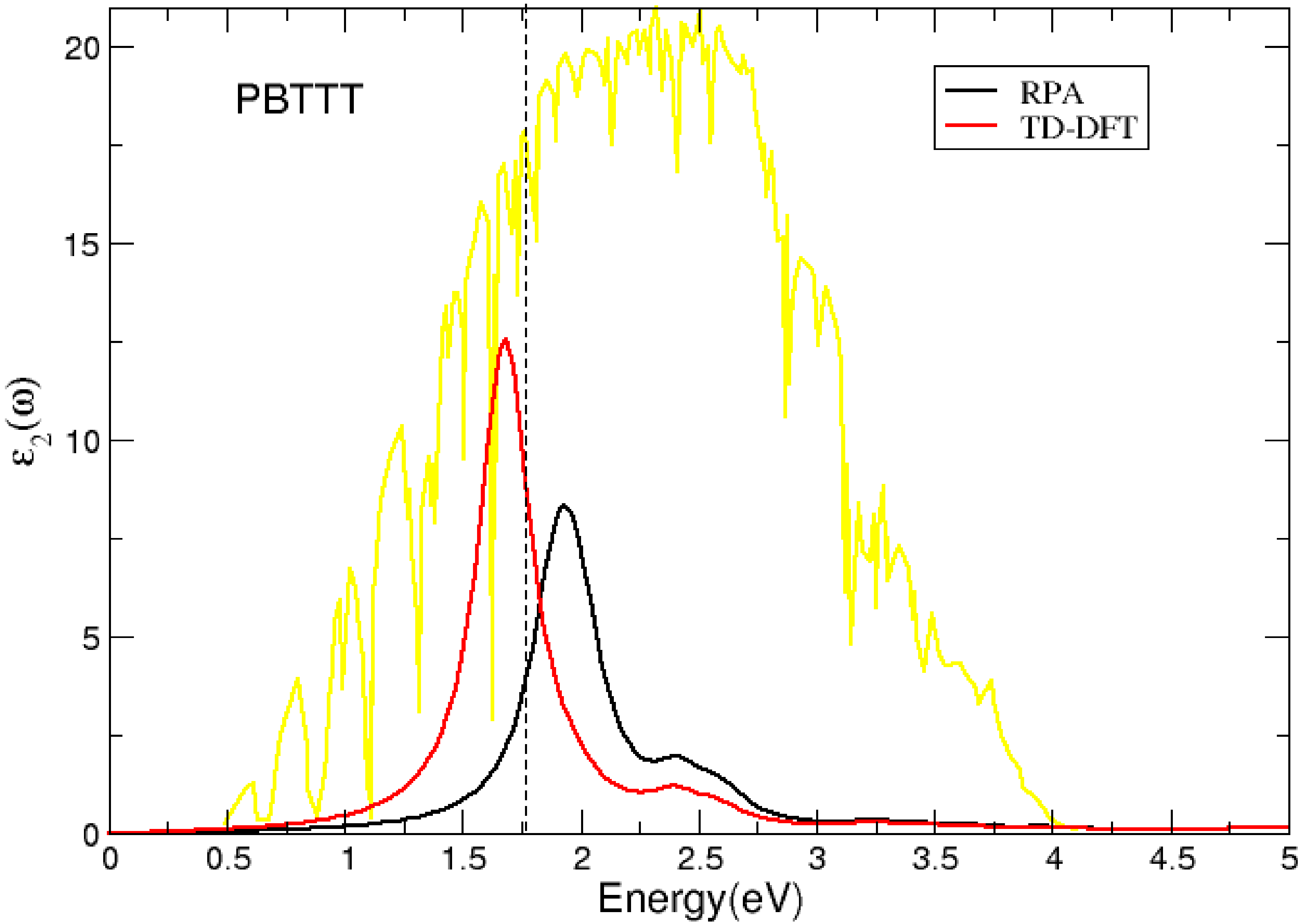
2.5
3
3.5
4
4.5
5
Energy (eV)

PBTTT




PBTTT
RPA
TD-DFT
ε₂(ω)
0
5
10
15
20
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Energy(eV)

Exchange-Correlation kernel

derivative discontinuity

PARSEC

Ultrafast Phenomena

Hyperpolarizabilities

Demagnetization by Light

Jaguar

Bond-Breaking

initial-state dependence

Stochastic Fields

Fragment-Based TDDFT

Q-Chem

Open Quantum Systems

Optical excitations

Molecular Electronics

excited states

Strong Fields

GAMESS

Radiationless decay

Excitons

quantum transport

Time Propagation

ADF

Functional Development

memory

NWChem

van der Waals coefients

Dissipation

EELS

Spartan

Decoherence

Electric Fields

TDDFT

Thermoelectrics

YAMBO

Nanostructures

minerals

ARPES

Octopus

TURBOMOLE

GPAW

Nonadiabatic Dynamics

Polyradical

TeraChem

CP2K

Spin-Flip

Q-bits

Friction

Biomolecules

Gaussian

ORCA

Non-Linear Phenomena

Non-Equilibrium

color of dyes

Correlation Energies

Weak Interactions

Optimal Control

Exchange-Hole Dipole Moment

Above-threshold ionisation

Dalton

Firefly

ab-initio-molecular-dynamics

exact-exchange kernel

pump-probe

Harmonic Generation

Conical Intersections

Time-Dependent Electron Localization Function (TD-ELF)

GOAL

Time-resolved visualization of the breaking and formation of chemical bonds.

How can one give a rigorous mathematical meaning to chemical concepts such as

- **Single, double, triple bonds**
- **Lone pairs**

Note:

- Density $\rho_\sigma(\mathbf{r})$ is not useful!
- Orbitals are ambiguous (w.r.t. unitary transformations)

$$D_{\sigma}\left(\vec{r},\vec{r}'\right)=\sum_{\sigma_3\sigma_4\ldots\sigma_N}\int d^3r_3\ldots\int d^3r_N\left|\Psi\left(\vec{r}\sigma,\vec{r}'\sigma,\vec{r}_3\sigma_3\ldots,\vec{r}_N\sigma_N\right)\right|^2$$

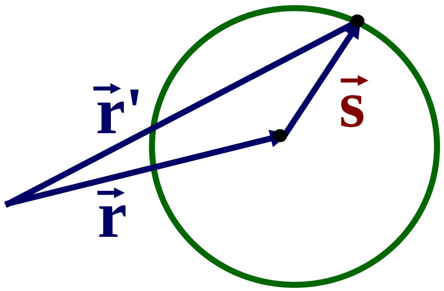
= diagonal of two-body density matrix

= probability of finding an electron with spin σ at $\vec{r}$ and another electron with the same spin at $\vec{r}'$.

$$P_{\sigma}\left(\vec{r},\vec{r}'\right):=\frac{D_{\sigma\sigma}\left(\vec{r},\vec{r}'\right)}{\rho_{\sigma}\left(\vec{r}\right)}$$

= conditional probability of finding an electron with spin σ at $\vec{r}'$ if we know with certainty that there is an electron with the <u>same</u> spin at $\vec{r}$.

Coordinate transformation



If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $P_\sigma(\vec{\mathbf{r}}, \vec{\mathbf{r}} + \vec{\mathbf{s}})$ is the (conditional) probability of finding another electron at $\vec{\mathbf{s}}$, where $\vec{\mathbf{s}}$ is measured from the reference point $\vec{\mathbf{r}}$.

Spherical average $$p_\sigma(\vec{r}, |\vec{s}|) = \frac{1}{4\pi}\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi P_\sigma(\vec{r}, |\vec{s}|, \theta, \varphi)$$

If we know there is an electron with spin σ at $\vec{\mathbf{r}}$, then $p_\sigma(\vec{\mathbf{r}}, \mathbf{s})$ is the conditional probability of finding another electron <u>at the distance</u> **s** from $\vec{\mathbf{r}}$.

Expand in a Taylor series:

$$p_\sigma(\vec{r}, s) = \underbrace{p_\sigma(\vec{r}, 0)}_{0} + \underbrace{\left.\frac{dp_\sigma(\vec{r}, s)}{ds}\right|_{s=0}}_{0} \cdot s + \frac{1}{3}C_\sigma(\vec{r})s^2$$

The first two terms vanish.

$C_\sigma(\vec{r})$ is a measure of electron localization.

Why? $C_\sigma(\vec{r})$, being the s^2-coefficient, gives the probability of finding a second like-spin electron very near the reference electron. If this probability very near the reference electron is low then this reference electron must be very localized.

$C_\sigma(\vec{r})$ small means strong localization at $\vec{r}$

$\mathbf{C}_\sigma$ is always ≥ 0 (because $\mathbf{p}_\sigma$ is a probability) and $\mathbf{C}_\sigma(\vec{\mathbf{r}})$ is not bounded from above.

Define as a useful visualization of localization
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

$$\boxed{\mathrm{ELF} = \frac{1}{1+\left(\frac{C_\sigma(\vec{r})}{C_\sigma^{\mathrm{uni}}(\vec{r})}\right)^2}}$$

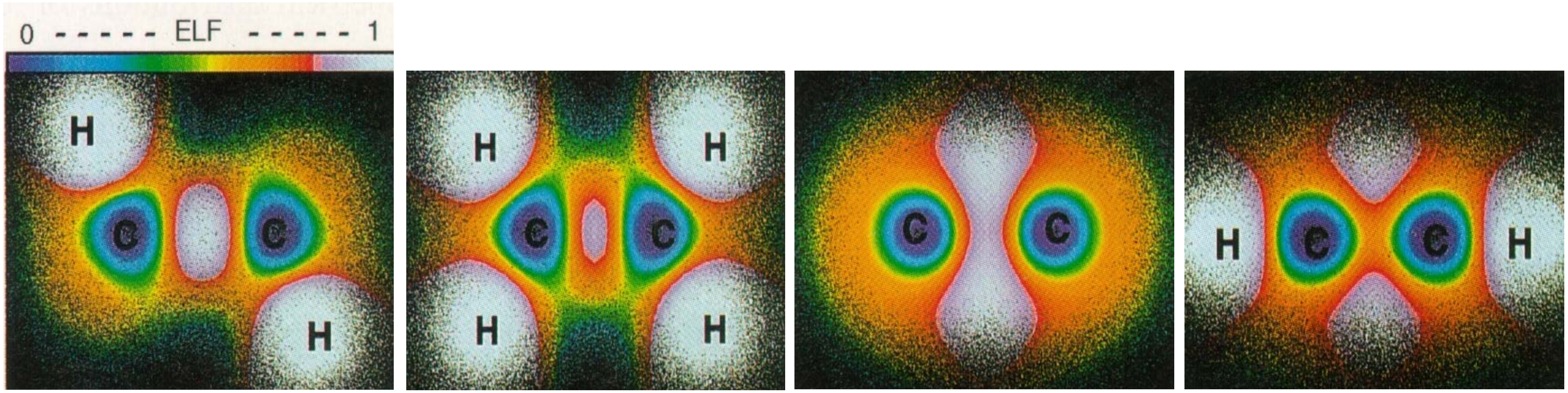
where

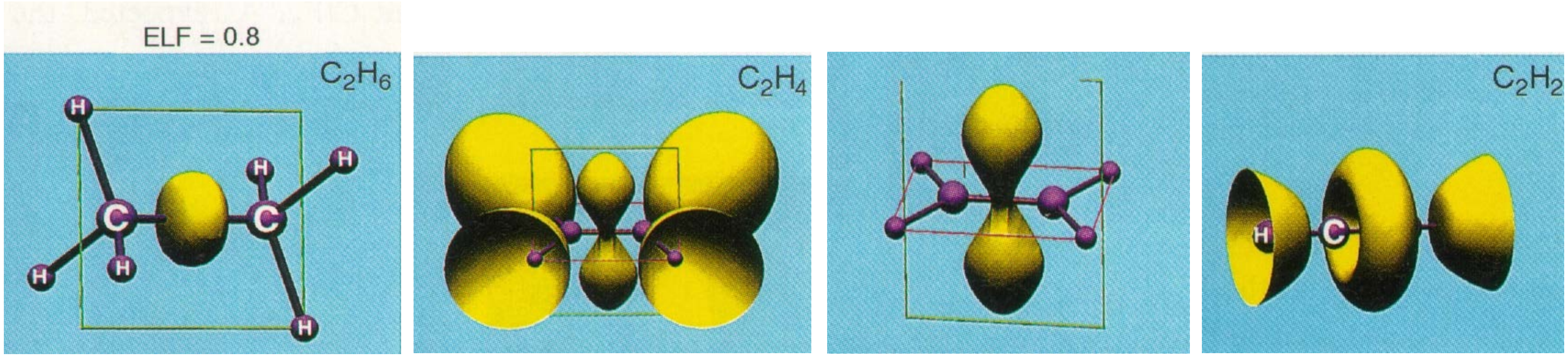
$$C_\sigma^{\mathrm{uni}}(\vec{r}) = \frac{3}{5}\left(6\pi^2\right)^{2/3}\rho_\sigma^{5/3}(\vec{r}) = \tau_\sigma^{\mathrm{uni}}(\vec{r})$$

is the kinetic energy density of the uniform gas.

Advantage: ELF is dimensionless and $0 \leq \mathrm{ELF} \leq 1$

ELF

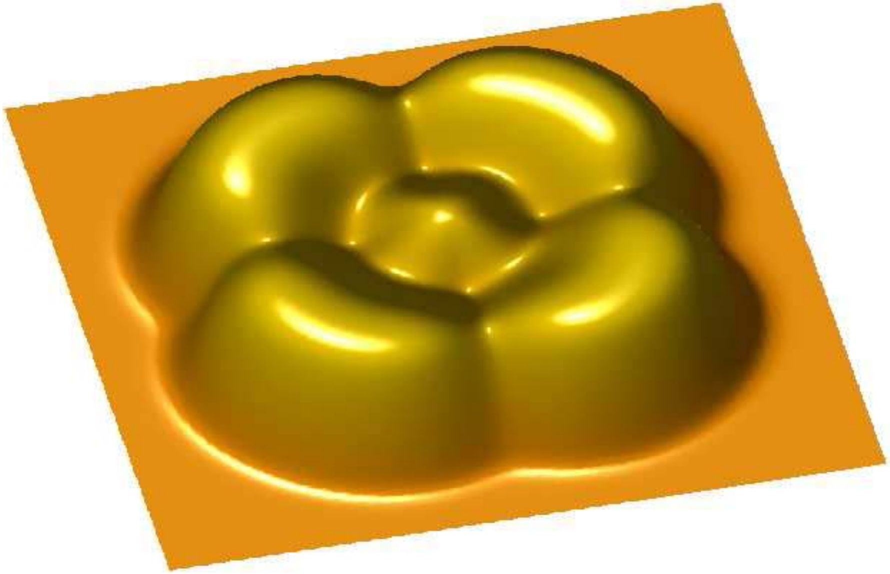




A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, Angew. Chem. Int. Ed. <u>36</u>, 1808 (1997)

12-electron 2D quantum dot with four minima

Density



ELF

E. Räsänen, A. Castro and E.K.U. Gross, Phys. Rev. B 77, 115108 (2008).

For a determinantal wave function one obtains

in the static case:

$$C_\sigma^{\mathrm{det}}\left(\vec{r}\right)=\sum_{i=1}^{N_\sigma}\left|\nabla\varphi_{i\sigma}\left(\vec{r}\right)\right|^2-\frac{1}{4}\frac{\left(\nabla\rho_\sigma\left(\vec{r}\right)\right)^2}{\rho_\sigma\left(\vec{r}\right)}$$

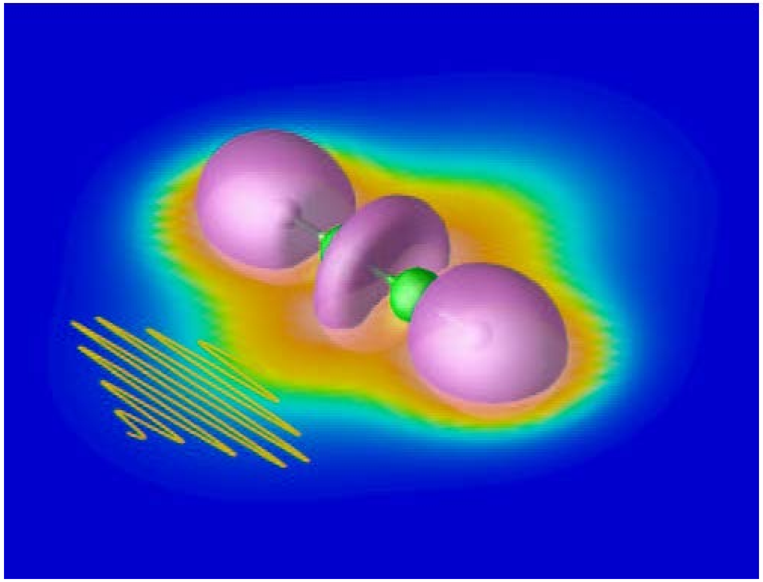
(A.D. Becke, K.E. Edgecombe, JCP 92, 5397 (1990))

in the time-dependent case:

$$\boxed{C_\sigma^{\mathrm{det}}\left(\vec{r},t\right)=\sum_{i=1}^{N_\sigma}\left|\nabla\varphi_{i\sigma}\left(\vec{r},t\right)\right|^2-\frac{1}{4}\frac{\left(\nabla\rho_\sigma\left(\vec{r},t\right)\right)^2}{\rho_\sigma\left(\vec{r},t\right)}-j_\sigma\left(\vec{r},t\right)^2\Big/\rho_\sigma\left(\vec{r},t\right)}$$

(T. Burnus, M. Marques, E.K.U.G., PRA (Rapid Comm) 71, 010501 (2005))

Acetylene in laser field
($\hbar\omega$ = 17.15 eV, I = 1.2×10^{14} W/cm^{2})



TDELF for acetylene in strong laser field

(ħω = 17.15 eV, I = 1.2×10^{14} W/cm^2)