Reminder: Photo-absorption in weak lasers

No absorption if $\omega < \text{lowest excitation energy}$
t = t_0 : Interacting system in ground state of potential v_0(r) with density ρ_0(r)

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

Density: \( ρ(r, t) = ρ_0(r) + δρ(r, t) \)

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

**Functional Taylor expansion of \( ρ[v] \) around \( v_0 \):**

\[
ρ[v](r, t) = ρ[v_0 + v_1](r, t) \\
= ρ[v_0](r, t) \\
+ \int \frac{δρ[v](r, t)}{δv(r', t')} v_1(r', t') d^3r' dt' \\
+ \frac{1}{2} \int \int \frac{δ^2ρ[v](r, t)}{δv(r', t')δv(r'', t'')} v_1(r', t') v_1(r'', t'') d^3r' d^3r'' dt' dt'' \\
\vdots
\]

\( → ρ_o(r) \)  \hspace{1cm} \( → ρ_1(r, t) \)  \hspace{1cm} \( → ρ_2(r, t) \)
$$\rho_1(r,t) = \text{linear density response of interacting system}$$

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

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

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

$$\chi_s(rt, r't') := \left. \frac{\delta \rho_s[v_s](rt)}{\delta v_s(r't')} \right|_{v_{s,0}} = \text{density-density response function of non-interacting system}$$
**GOAL:** Find a way to calculate $\rho_1(\mathbf{r}, t)$ without explicitly evaluating $\chi(\mathbf{r}, r', \mathbf{t}', t')$ of the interacting system.

**starting point:** Definition of xc potential

$$v_{xc}[\rho](\mathbf{r}, t) := v_S[\rho](\mathbf{r}, t) - v_{ext}[\rho](\mathbf{r}, t) - v_H[\rho](\mathbf{r}, t)$$

**Notes:**
- $v_{xc}$ is well-defined through non-interacting/interacting 1-1 mapping.
- $v_S[\rho]$ depends on initial determinant $\Phi_0$.
- $v_{ext}[\rho]$ depends on initial many-body state $\Psi_0$.

$\Rightarrow$ In general, $v_{xc} = v_{xc}[\rho, \Phi_0, \Psi_0]$ only if system is initially in ground-state then, via HK, $\Phi_0$ and $\Psi_0$ are determined by $\rho_0$ and $v_{xc}$ depends on $\rho$ alone.
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_s[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{|r-r'|}
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}
\]

\[f_{xc}(rt, r't') \uparrow \]

\[\chi^{-1}_S(rt, r't') \uparrow \]

\[\chi^{-1}(rt, r't') \uparrow \]

\[W_C(rt, r't') \uparrow \]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{ext}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta(t-t')}{|r-r'|}
\]

\[
f_{xc}(rt, r't') \quad \chi_S^{-1}(rt, r't') \quad \chi^{-1}(rt, r't') \quad W_C(rt, r't')
\]

\[
f_{xc} + W_C = \chi_S^{-1} - \chi^{-1}
\]
\[
\left. \frac{\delta v_{xc} [\rho](rt)}{\delta \rho (r't')} \right|_{\rho_0} = \left. \frac{\delta v_S [\rho](rt)}{\delta \rho (r't')} \right|_{\rho_0} - \left. \frac{\delta v_{\text{ext}} [\rho](rt)}{\delta \rho (r't')} \right|_{\rho_0} - \frac{\delta (t - t')}{|r - r'|}
\]

\[
\chi_S \cdot f_{xc} (rt, r't') + W_C (rt, r't') = \chi_S^{-1} - \chi^{-1} \cdot \chi
\]
\[
\frac{\delta v_{xc}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} = \frac{\delta v_S[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta v_{\text{ext}}[\rho](rt)}{\delta \rho(r't')} \bigg|_{\rho_0} - \frac{\delta (t-t')}{|r-r'|}
\]

\[
f_{xc}(rt, r't') \quad \chi_s^{-1}(rt, r't') \quad \chi^{-1}(rt, r't') \quad W_C(rt, r't')
\]

\[
\chi_s \cdot f_{xc} + W_C = \chi_s^{-1} - \chi^{-1} \cdot \chi
\]

\[
\chi_s \left(f_{xc} + W_C\right) \chi = \chi - \chi_s
\]
\[ \chi = \chi_S + \chi_S \left( W_C + f_{xc} \right) \chi \]

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

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

- Exact integral equation for \( \rho_1(r,t) \), to be solved iteratively
- Need approximation for \( f_{xc} (r't',r''t'') \)
  (either for \( f_{xc} \) directly or for \( v_{xc} \))

\[
f_{xc} (r't',r''t'') = \frac{\delta v_{xc} [\rho](r't')}{\delta \rho (r''t'')} \bigg|_{\rho_0}
\]
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.

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

\[ f_{xc}^{\text{ALDA}} (rt, r\prime t\prime) = \left. \delta v_{xc}^{\text{ALDA}} (rt) \right|_{\rho_0} = \delta (r - r\prime) \delta (t - t\prime) \left. \frac{\partial v_{xc}^{\text{ALDA}}}{\partial \rho(r)} \right|_{\rho_0(r)} \]

\[ = \delta (r - r\prime) \delta (t - t\prime) \left. \frac{\partial^2 e_{xc}^{\text{hom}}}{\partial n^2} \right|_{\rho_0(r)} \]
Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold.

Photo-absorption in weak lasers

No absorption if $\omega < \text{lowest excitation energy}$
Standard linear response formalism

\[ H(t_0) = \text{full static Hamiltonian at } t_0 \]

\[ H\left(t_0\right)|m\rangle = E_m|m\rangle \quad \leftarrow \quad \text{exact many-body eigenfunctions and energies of system} \]

full response function

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

\[ \Rightarrow \text{The exact linear density response} \]

\[ \rho_1(\omega) = \hat{\chi}(\omega) v_1(\omega) \]

has poles at the exact excitation energies \( \Omega = E_m - E_0 \)
Discrete excitation energies from TDDFT

exact representation of linear density response:

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

“\( ^{\wedge} \)” 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

\[ M_{jk}(\vec{r}, \vec{r}') = (f_k - f_j) \phi_j(\vec{r}) \phi_j^*(\vec{r}') \phi_k(\vec{r}') \phi_k^*(\vec{r}) \]

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

\[ \varepsilon_j - \varepsilon_k \quad \text{KS excitation energy} \]
\[
\left( \hat{1} - \hat{\chi}_S (\omega) \left[ \hat{W}_C + \hat{f}_{xc} (\omega) \right] \right) \rho_1 (\omega) = \hat{\chi}_S (\omega) v_1 (\omega)
\]

\[\rho_1(\omega) \to \infty \text{ for } \omega \to \Omega \text{ (exact excitation energy) but right-hand side remains finite for } \omega \to \Omega\]

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

\[\lambda (\omega) \to 0 \text{ for } \omega \to \Omega\]

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

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

where

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

\[ q = (j, a) \text{ double index} \quad \alpha_q = f_a - f_j \]

\[ \Phi_q(r) = \varphi^*_a(r) \varphi_j(r) \quad \omega_q = \varepsilon_a - \varepsilon_j \]

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


\[
\Delta E = \Delta \epsilon_{KS} + K
\]

\[
K = \int d^3r \int d^3r' \varphi_j(r) \varphi_j^*(r') \varphi_k(r') \varphi_k^*(r) \left(\frac{1}{|r-r'|} + f_{xc}(r,r')\right)
\]
# Excitation energies of CO molecule

<table>
<thead>
<tr>
<th>State</th>
<th>$\Omega_{\text{expt}}$</th>
<th>KS-transition</th>
<th>$\Delta\epsilon_{\text{KS}}$</th>
<th>$\Delta\epsilon_{\text{KS} + K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$^1\Pi$</td>
<td>$5\Sigma \rightarrow 2\Pi$</td>
<td>0.2523</td>
<td>0.3267</td>
</tr>
<tr>
<td>a</td>
<td>$^3\Pi$</td>
<td></td>
<td>0.2323</td>
<td>0.2238</td>
</tr>
<tr>
<td>I</td>
<td>$^1\Sigma^-$</td>
<td>$1\Pi \rightarrow 2\Pi$</td>
<td>0.3626</td>
<td>0.3626</td>
</tr>
<tr>
<td>D</td>
<td>$^1\Delta$</td>
<td></td>
<td>0.3759</td>
<td>0.3812</td>
</tr>
<tr>
<td>a'</td>
<td>$^3\Sigma^+$</td>
<td></td>
<td>0.3127</td>
<td>0.3181</td>
</tr>
<tr>
<td>e</td>
<td>$^3\Sigma^-$</td>
<td></td>
<td>0.3631</td>
<td>0.3626</td>
</tr>
<tr>
<td>d</td>
<td>$^3\Delta$</td>
<td></td>
<td>0.3440</td>
<td>0.3404</td>
</tr>
</tbody>
</table>

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

Quantum defects in Helium  

\[ E_n = -\frac{1}{2(n - \mu_n)^2} \]  [a.u.]

**3P Series**

- Bare KS
- exact
- x-ALDA
- xc-ALDA (VWN)
- x-TDOEP

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.

Failures of ALDA in the linear response regime

- H$_2$ dissociation is incorrect:
  \[
  \lim_{R \to \infty} \left( E\left( ^1\Sigma_u^+ \right) - E\left( ^1\Sigma_g^+ \right) \right) = 0 \text{ (in ALDA)}
  \]
  (see: Gritsenko, van Gisbergen, Görling, Baerends, JCP 113, 8478 (2000))

- response of long chains strongly overestimated
  (see: Champagne et al., JCP 109, 10489 (1998) and 110, 11664 (1999))

- in periodic solids, \( f_{xc}^{ALDA}(q, \omega, \rho) = c(\rho) \) whereas, for insulators, \( f_{xc}^{exact}(q \to 0) \to \frac{1}{q^2} \) divergent.

- charge-transfer excitations not properly described
  (see: Dreuw et al., JCP 119, 2943 (2003))
Excitons are completely missing for simple xc functionals like ALDA!
EXPLANATION:
TDDFT response equation: bare Coulomb interaction and xc kernel only appear as a sum \((v + f_{xc})\).

\[
v(q) \text{ diverges like } 1/q^2 \text{ for } q \to 0\\
f_{xc} \to \text{const} \quad (\text{in ALDA})
\]

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

CONCLUSION:
Approximations for \(f_{xc}\) are needed which, for \(q \to 0\), 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)).
Two problems of ALDA need to be fixed:

• Onset of absorption is dictated by $\chi_0$, i.e. is identical to the LDA gap for $\omega$-independent kernel (such as ALDA)

• Description of excitons requires $1/q^2$ behavior

\[
\varepsilon^{-1}(q, \omega) = 1 + \chi_S(q, \omega) \nu(q) \left[ 1 - \left( \nu(q) + f_{xc}^{\text{approx}}(q, \omega) \right) \chi_S(q, \omega) \right]^{-1}
\]
Bootstrap kernel (Sharma, Dewhurst, Sanna, EKUG, PRL 107, 186401 (2011))

\[
\begin{align*}
    f_{xc}^{\text{boot}}(q, \omega) &= \frac{\varepsilon^{-1}(q, \omega = 0)}{\tilde{\chi}^{00}(q, \omega = 0)} \\
    f_{xc}^{\text{appr}}(q, \omega) &= \frac{1}{\chi_S(q, \omega)} - \frac{1}{\tilde{\chi}(q, \omega)} + f_{xc}^{\text{boot}}(q)
\end{align*}
\]

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

\[
\varepsilon^{-1}(q, \omega) = 1 + \chi_0(q, \omega) \nu(q) \left[ 1 - \left( \nu(q) + f_{xc}^{\text{appr}}(q, \omega) \right) \chi_0(q, \omega) \right]^{-1}
\]
Bootstrap kernel  
(Sharma, Dewhurst, Sanna, EKUG, PRL 107, 186401 (2011))

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

\[ f_{xc}^{\text{appr}}(q, \omega) = \frac{1}{\chi_s(q, \omega)} - \frac{1}{\tilde{\chi}(q, \omega)} + f_{xc}^{\text{boot}}(q) \]

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

\[ \varepsilon^{-1}(q, \omega) = 1 + \chi_0(q, \omega) \nu(q) \left[ 1 - \left( \nu(q) + f_{xc}^{\text{appr}}(q, \omega) \right) \chi_0(q, \omega) \right]^{-1} \]

\[ \varepsilon^{-1}(q, \omega) = 1 + \tilde{\chi}(q, \omega) \nu(q) \left[ 1 - \left( \nu(q) + f_{xc}^{\text{boot}}(q, \omega) \right) \tilde{\chi}(q, \omega) \right]^{-1} \]
Bootstrap kernel  

\[ f_{xc}^{\text{boot}}(q, \omega) = \frac{\epsilon^{-1}(q, \omega = 0)}{\tilde{\chi}^{00}(q, \omega = 0)} \]

\[ \epsilon^{-1}(q, \omega) = 1 + \tilde{\chi}(q, \omega) \nu(q) \left[ 1 - \left( \nu(q) + f_{xc}^{\text{boot}}(q, \omega) \right) \tilde{\chi}(q, \omega) \right]^{-1} \]
Bootstrap kernel (Sharma, Dewhurst, Sanna, EKUG, PRL 107, 186401 (2011))

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

\[
\varepsilon^{-1} (q, \omega) = 1 + \tilde{\chi} (q, \omega) \nu (q) \left[ 1 - \left( \nu (q) + f_{xc}^{\text{boot}} (q, \omega) \right) \tilde{\chi} (q, \omega) \right]^{-1}
\]
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 $\rho_\sigma(r)$ is not useful!
- Orbitals are ambiguous (w.r.t. unitary transformations)
\[ D_\sigma (\bar{r}, \bar{r}') = \sum_{\sigma_3 \sigma_4 ... \sigma_N} \int d^3 r_3 ... \int d^3 r_N |\Psi (\bar{r}_\sigma, \bar{r'}_\sigma, \bar{r}_3 \sigma_3, ..., \bar{r}_N \sigma_N)|^2 \]

= diagonal of two-body density matrix

= probability of finding an electron with spin \( \sigma \) at \( \bar{r} \) and another electron with the same spin at \( \bar{r}' \).

\[ P_\sigma (\bar{r}, \bar{r}') := \frac{D_{\sigma\sigma} (\bar{r}, \bar{r}')}{\rho_\sigma (\bar{r})} \]

= conditional probability of finding an electron with spin \( \sigma \) at \( \bar{r}' \) if we know with certainty that there is an electron with the same spin at \( \bar{r} \).
Coordinate transformation

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

Spherical average

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

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

Expand in a Taylor series:

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

The first two terms vanish.
$C_\sigma(\mathbf{r})$ is a measure of electron localization.

Why? $C_\sigma(\mathbf{r})$, 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.

$C_\sigma(\mathbf{r})$ small means strong localization at $\mathbf{r}$
$C_\sigma$ is always $\geq 0$ (because $p_\sigma$ is a probability) and $C_\sigma(\vec{r})$ is not bounded from above.

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

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

where

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

is the kinetic energy density of the uniform gas.

**Advantage:** ELF is dimensionless and $0 \leq \text{ELF} \leq 1$
12-electron 2D quantum dot with four minima

Density

ELF

For a determinantal wave function one obtains

in the static case:

\[ C_{\sigma}^{\text{det}} \left( \mathbf{r} \right) = \sum_{i=1}^{N_{\sigma}} \left| \nabla \varphi_{i\sigma} \left( \mathbf{r} \right) \right|^2 - \frac{1}{4} \frac{\left( \nabla \rho_{\sigma} \left( \mathbf{r} \right) \right)^2}{\rho_{\sigma} \left( \mathbf{r} \right)} \]

\[(A.D. \; Becke, \; K.E. \; Edgecombe, \; JCP \; 92, \; 5397 \; (1990))\]

in the time-dependent case:

\[ C_{\sigma}^{\text{det}} \left( \mathbf{r}, t \right) = \sum_{i=1}^{N_{\sigma}} \left| \nabla \varphi_{i\sigma} \left( \mathbf{r}, t \right) \right|^2 - \frac{1}{4} \frac{\left( \nabla \rho_{\sigma} \left( \mathbf{r}, t \right) \right)^2}{\rho_{\sigma} \left( \mathbf{r}, t \right)} - j_{\sigma} \left( \mathbf{r}, t \right)^2 / \rho_{\sigma} \left( \mathbf{r}, t \right) \]

\[(T. \; Burnus, \; M. \; Marques, \; E.K.U.G., \; PRA \; (Rapid \; Comm) \; 71, \; 010501 \; (2005))\]
Acetylene in laser field
($\hbar \omega = 17.15$ eV, $I = 1.2 \times 10^{14}$ W/cm$^2$)
TDELF for acetylene in strong laser field

($\hbar \omega = 17.15$ eV, $I = 1.2 \times 10^{14}$ W/cm$^2$)