MARTIN-LUTHER-UNIVERSITÄT
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Time-dependent density functional theory

From the basic equations to applications

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Outline

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2. Basic theorems
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Standard density-functional theory

Most efficient and versatile computational tool for *ab initio* calculations.

Kohn-Sham (KS) equations:

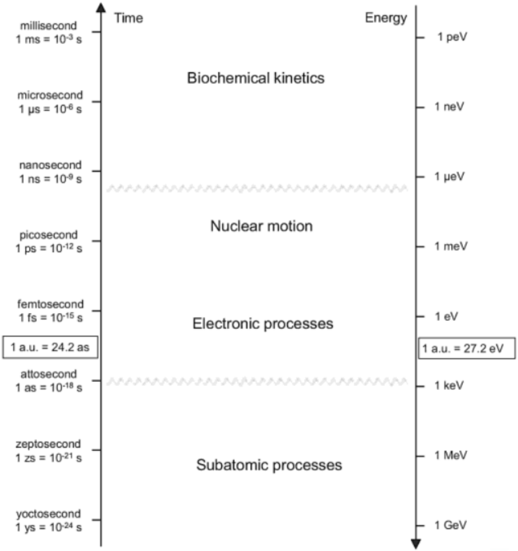
$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{ext}}\left(\boldsymbol{r}\right) + v_{\mathrm{H}}\left(\boldsymbol{r}\right) + v_{\mathrm{xc}}\left(\boldsymbol{r}\right)\right] \varphi_i\left(\boldsymbol{r}\right) = \varepsilon_i \varphi_i\left(\boldsymbol{r}\right)$$

Walter Kohn

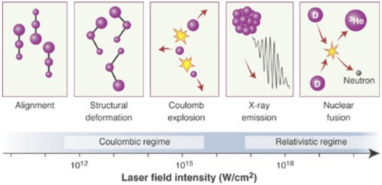
- ➜ DFT can yield excellent ground-state properties, such as structural parameters, formation energies, phonons, etc.
- ➜ But DFT is a ground-state theory and can not, in principle, yield excited-state properties, electron dynamics, or in general to study time-dependent problems.

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

Time-scales

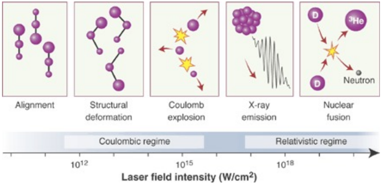

Time
Energy
millisecond
1 ms = 10^{-3} s
1 peV
Biochemical kinetics
microsecond
1 μs = 10^{-6} s
1 neV
nanosecond
1 ns = 10^{-9} s
1 μeV
Nuclear motion
picosecond
1 ps = 10^{-12} s
1 meV
femtosecond
1 fs = 10^{-15} s
1 eV
Electronic processes
1 a.u. = 24.2 as
1 a.u. = 27.2 eV
attosecond
1 as = 10^{-18} s
1 keV
zeptosecond
1 zs = 10^{-21} s
1 MeV
Subatomic processes
yoctosecond
1 ys = 10^{-24} s
1 GeV

Atto and femtosecond dynamics

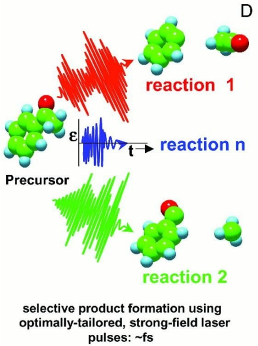


K. Yamanouchi, Science **295**, 1659 (2002)

Atto and femtosecond dynamics

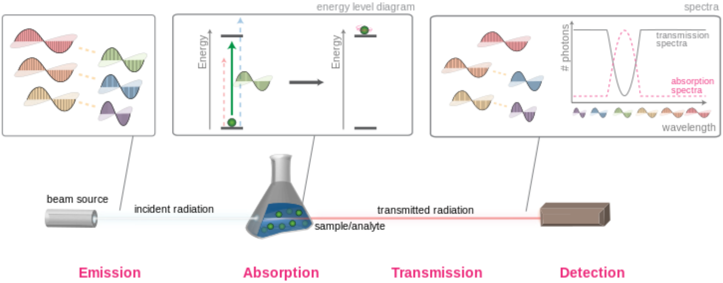


K. Yamanouchi, Science **295**, 1659 (2002)

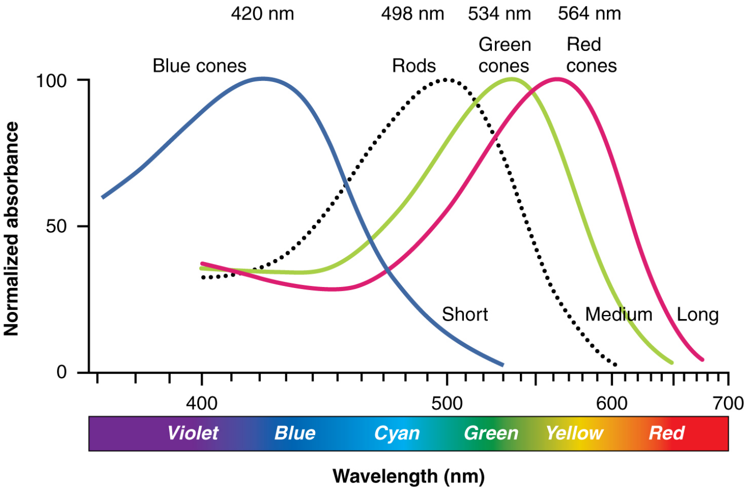


J. J. Levis, Science **292**, 709 (2001)

Linear response - absorption



Linear response - vision



TDDFT can explain why lobsters are blue!

Why are lobsters BLUE?

TDDFT can explain why lobsters are blue!

Why are lobsters BLUE?

Homarus gammarus
(European lobster)

Astaxanthin (AXT)

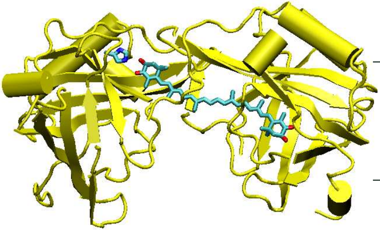
"The red comes from the molecule astaxanthin, a cousin of beta carotene, which gives carrots their orange color and is a source of vitamin A. Astaxanthin, which looks red because it absorbs blue light, also colors shrimp shells and salmon flesh. The blue pigment in lobster shells also comes from crustacyanin, which is astaxanthin clumped together with a protein."

(New York Times)

In solution: **In lobster shell:**

λ_{max} (AXT): 475-500 → 630 nm

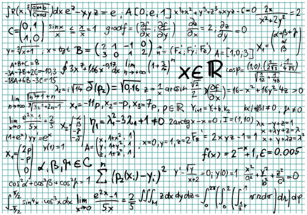
(orange-red) **(purple-blue)**



Molecule	CIS	TDDFT	ZINDO/S	Exp
AXT	394	579	468	488
AXTH+	582	780	816	840
AXT-His+			623	
AXT-His			473	

AXT in α-crustacyanin: 632 nm

B. Durbeej and L. A. Eriksson, Phys. Chem. Chem. Phys. **8**, 4053 (2006).



Time-dependent Schrödinger equation

The evolution of the wavefunction is governed by

$$\hat{H}(t)\Psi(t) = \left[\hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}\right]\Psi(t) = \mathrm{i}\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t}, \qquad \text{for a given } \Psi(0)$$

where

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 \qquad , \qquad \hat{V}_{\text{ee}} = \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$\hat{V}_{\text{ext}} = \sum_{i=1}^{N} v_{\text{ext}}(\boldsymbol{r}_i, t)$$

$v_{\text{ext}}(\boldsymbol{r}, t)$ contains an explicit time-dependence (e.g., a laser field) or an implicit time-dependence (e.g., the nuclei are moving).

Runge-Gross theorem

The (time-dependent) electronic density is

$$n(\boldsymbol{r},t) = N \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \, |\Psi(\boldsymbol{r},\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,t)|^2 \ ,$$

The Runge-Gross theorem proves a one-to-one correspondence between the density and the external potential

$$n(\boldsymbol{r},t) \longleftrightarrow v_{\text{ext}}(\boldsymbol{r},t)$$

Hardy Gross

The theorem states that the densities $n(\boldsymbol{r},t)$ and $n'(\boldsymbol{r},t)$ evolving from a common initial state $\Psi(t=0)$ under the influence of two potentials $v_{\text{ext}}(\boldsymbol{r},t)$ and $v'_{\text{ext}}(\boldsymbol{r},t)$ (both Taylor expandable about the initial time 0) eventually differ if the potentials differ by more than a purely time-dependent function:

$$\Delta v_{\text{ext}}(\boldsymbol{r},t) = v_{\text{ext}}(\boldsymbol{r},t) - v'_{\text{ext}}(\boldsymbol{r},t) \neq c(t)\,.$$

Erich Runge

Runge-Gross theorem: 1st step

The first part of the proof states that if the two potentials differ, then the current densities differ.

$$\boldsymbol{j}(\boldsymbol{r},t) = N\int \mathrm{d}^3r_2 \ldots \int \mathrm{d}^3r_N\, \Im\left\{\Psi(\boldsymbol{r},\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,t)\nabla\Psi^*(\boldsymbol{r},\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,t)\right\},$$

We also need the continuity equation:

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t} = -\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t)$$

Because the corresponding Hamiltonians differ only in their one-body potentials, the equation of motion for the difference of the two current densities is, at $t=0$:

$$\begin{aligned}
\frac{\partial}{\partial t}\left\{\boldsymbol{j}(\boldsymbol{r},t)-\boldsymbol{j}'(\boldsymbol{r},t)\right\}_{t=0} &= -\mathrm{i}\langle\Psi_0|\left[\hat{\boldsymbol{j}}(\boldsymbol{r},t),\hat{H}(0)-\hat{H}'(0)\right]|\Psi_0\rangle \\
&= -\mathrm{i}\langle\Psi_0|\left[\hat{\boldsymbol{j}}(\boldsymbol{r}),v_{\text{ext}}(\boldsymbol{r},0)-v'_{\text{ext}}(\boldsymbol{r},0)\right]|\Psi_0\rangle \\
&= -n_0(\boldsymbol{r})\nabla\left\{v_{\text{ext}}(\boldsymbol{r},0)-v'_{\text{ext}}(\boldsymbol{r},0)\right\},
\end{aligned}$$

Runge-Gross theorem: 1st step

If, at the initial time, the two potentials differ, the first derivative of the currents must differ. Then the currents will change infinitesimally soon thereafter. One can go further, by repeatedly using the equation of motion, and considering $t = 0$, to find

$$\frac{\partial^{k+1}}{\partial t^{k+1}} \left\{ \boldsymbol{j}(\boldsymbol{r},t) - \boldsymbol{j}'(\boldsymbol{r},t) \right\}_{t=0} = -n_0(\boldsymbol{r}) \nabla \frac{\partial^k}{\partial t^k} \left\{ v(\boldsymbol{r},t) - v'(\boldsymbol{r},t) \right\}_{t=0} .$$

If the potentials are Taylor expandable about $t = 0$, then there must be some finite k for which the right hand side of does *not* vanish, so that

$$\boldsymbol{j}(\boldsymbol{r},t) \neq \boldsymbol{j}'(\boldsymbol{r},t) .$$

For two Taylor-expandable potentials that differ by more than just a trivial constant, the corresponding currents must be different.

Runge-Gross theorem: 2nd step

Taking the gradient of both sides of of the previous equation, and using continuity, we find

$$\frac{\partial^{k+2}}{\partial t^{k+2}}\left\{n(\boldsymbol{r},t)-n'(\boldsymbol{r},t)\right\}_{t=0}=\nabla\cdot\left[n_0(\boldsymbol{r})\nabla\frac{\partial^k}{\partial t^k}\{v_{\text{ext}}(\boldsymbol{r},t)-v'_{\text{ext}}(\boldsymbol{r},t)\}_{t=0}\right]$$

Now, if not for the divergence on the right-hand-side, we would be done, i.e., if

$$f(\boldsymbol{r})=\left.\frac{\partial^k\{v_{\text{ext}}(\boldsymbol{r},t)-v'_{\text{ext}}(\boldsymbol{r},t)\}}{\partial t^k}\right|_{(t=0)}$$

is nonconstant for some k, then the density difference must be nonzero. It turns out that the divergence can also be handled, thereby proving the Runge-Gross theorem.

Time-dependent Kohn-Sham equations

We define a fictious system of noninteracting electrons that satisfy time-dependent Kohn-Sham equations:

$$\mathrm{i}\frac{\partial \varphi_j(\boldsymbol{r},t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_{\mathsf{KS}}[n](\boldsymbol{r},t)\right]\varphi_j(\boldsymbol{r},t)\,,$$

whose density,

$$n(\boldsymbol{r},t) = \sum_{j=1}^{N} |\varphi_j(\boldsymbol{r},t)|^2\,,$$

is defined to be precisely that of the real system. By virtue of the one-to-one correspondence proven in the previous section, the potential $v_{\mathsf{KS}}(\boldsymbol{r},t)$ yielding this density is unique.

Kohn-Sham potential

We then define the exchange-correlation potential via:

$$v_{\mathsf{KS}}(\boldsymbol{r},t) = v_{\mathsf{ext}}(\boldsymbol{r},t) + v_{\mathsf{H}}(\boldsymbol{r},t) + v_{\mathsf{xc}}(\boldsymbol{r},t)\,,$$

where the Hartree potential has the usual form,

$$v_{\mathsf{H}}(\boldsymbol{r},t) = \int \mathrm{d}^3r'\,\frac{n(\boldsymbol{r}',t)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,,$$

The exchange-correlation potential is a functional of the entire history of the density, $n(\boldsymbol{r},t)$, the initial interacting wavefunction $\Psi(0)$, and the initial Kohn-Sham wavefunction, $\Phi(0)$. This functional is a very complex one, much more so than the ground-state case. Knowledge of it implies solution of all time-dependent Coulomb interacting problems.

Adiabatic approximation

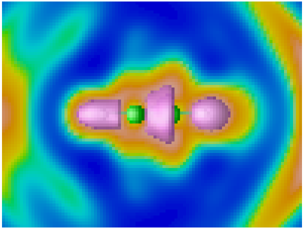
The adiabatic approximation is one in which we ignore all dependence on the past, and allow only a dependence on the instantaneous density:

$$v_{\mathsf{xc}}^{\mathrm{adia}}[n](\boldsymbol{r},t) = v_{\mathsf{xc}}^{\mathrm{approx}}[n(t)](\boldsymbol{r})\,,$$

i.e., it approximates the functional as being local in time. To make the adiabatic approximation exact for the only systems for which it can be exact, we require

$$v_{\mathsf{xc}}^{\mathrm{adia}}[n](\boldsymbol{r},t) = v_{\mathsf{xc}}^{\mathsf{GS}}[n_{\mathsf{GS}}](\boldsymbol{r})|_{n_{\mathsf{GS}}(\boldsymbol{r}')=n(\boldsymbol{r}',t)}\,,$$

where $v_{\mathsf{xc}}^{\mathsf{GS}}[n_{\mathsf{GS}}](\boldsymbol{r})$ is the *exact* ground-state exchange-correlation potential of the density $n_{\mathsf{GS}}(\boldsymbol{r})$. In practice, one uses for $v_{\mathsf{xc}}^{\mathsf{GS}}$ an LDA, GGA, metaGGA or hybrid functional.



Formulation of the problem

- The time-dependent Kohn-Sham equations are a set of coupled one-particle Schrödinger-like equations.
- The Hamiltonian is intrinsically time-dependent, which is obvious since it depends parametrically on the time-dependent density.
- This time dependence is not known *a priori*, since it is deduced from the solution density itself, $v_{\mathsf{KS}} = v_{\mathsf{KS}}[n]$.

The problem may then be formulated as follows: given $\varphi(\tau)$ and $\hat{H}(\tau)$ for $\tau \leq t$, calculate $\varphi(t + \Delta t)$ for some Δt.

The propagator

The Schrödinger equation may be rewritten in terms of its linear propagator $\hat{U}(t, t_0)$, which obeys the equation

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0)\,.$$

The solution of the time-dependent Schrödinger equation, for a given initial state $\varphi(t_0)$, is then written as $\varphi(t) = \hat{U}(t, t_0)\varphi(t_0)$. This differential equation may be rewritten as an integral equation

$$\hat{U}(t, t_0) = \hat{1} - \mathrm{i}\int_{t_0}^{t}\mathrm{d}\tau\;\hat{H}(\tau)\hat{U}(\tau, t_0)\,.$$

This equation has the formal solution

$$\hat{U}(t, t_0) = \hat{1} + \sum_{n=1}^{\infty}(-\mathrm{i})^n\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\ldots\int_{t_0}^{t_{n-1}}\mathrm{d}t_n\hat{H}(t_1)\ldots\hat{H}(t_n)\,.$$

Properties of the propagator - I

- For a Hermitian Hamiltonian, the evolution operator is unitary, i.e.

$$\hat{U}^{\dagger}(t+\Delta t, t) = \hat{U}^{-1}(t+\Delta t, t)\,.$$

  This mathematical property is linked to the conservation of probability of the wavefunction.

- Time-reversal symmetry:

$$\hat{U}(t+\Delta t, t) = \hat{U}^{-1}(t, t+\Delta t)\,.$$

  Note that this property does not hold if a magnetic field is present;

- For any three instants t_1, t_2, t_3, then

$$\hat{U}(t_1, t_2) = \hat{U}(t_1, t_3)\hat{U}(t_3, t_2)$$

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Properties of the propagator - II

This last property permits us to break the simulation into pieces. In practice, it is usually not convenient to obtain $\varphi(t)$ directly from φ_0 for a long interval $[0, t]$. Instead, one breaks $[0, t]$ into smaller time intervals:

$$\hat{U}(t, 0) = \prod_{i=0}^{N-1} \hat{U}(t_i + \Delta t_i, t_i)\,,$$

We then deal with the problem of performing the short-time propagation

$$\varphi(t + \Delta t) = \hat{\mathcal{T}} \exp\left\{-\mathrm{i}\int_t^{t+\Delta t} \mathrm{d}\tau\, \hat{H}(\tau)\right\} \varphi(t)\,.$$

There are many different methods for calculating this propagator. We will give only two examples, Crank-Nicholson and polynomial expansions.

Crank-Nicholson

We start by approximating the value of the operator $\hat{H}(t)$ by its central value in the interval $(t, t+\Delta t)$, i.e. $\hat{H}(t+\Delta t/2)$. We then write

$$\varphi(t+\Delta t) = \exp\left\{-\mathrm{i}\hat{H}(t+\Delta t/2)\Delta t\right\}\varphi(t)$$

which is equivalent to

$$\exp\left\{\mathrm{i}\hat{H}(t+\Delta t/2)\Delta t/2\right\}\varphi(t+\Delta t) = \exp\left\{-\mathrm{i}\hat{H}(t+\Delta t/2)\Delta t/2\right\}\varphi(t)$$

If we now expand the exponentials to first order

$$1 + \frac{\mathrm{i}}{2}\Delta t\hat{H}(t+\Delta t/2)\varphi(t+\Delta t) = 1 - \frac{\mathrm{i}}{2}\Delta t\hat{H}(t+\Delta t/2)\varphi(t)$$

This is a linear equation that can be solved by a multitude of linear algebra methods. The Crank-Nicholson propagator is

$$\hat{U}_{\mathrm{CN}}(t+\Delta t, t) = \frac{1 - \frac{\mathrm{i}}{2}\Delta t\hat{H}(t+\Delta t/2)}{1 + \frac{\mathrm{i}}{2}\Delta t\hat{H}(t+\Delta t/2)}\,.$$

Polynomial expansions

Again we start by approximating the propagator by its central value

$$\hat{U}_{\mathrm{EM}}(t+\Delta t, t) \equiv \exp\{-\mathrm{i}\Delta t \hat{H}(t+\Delta t/2)\}\,.$$

The (simple) exponential can then be expanded in, e.g., a Taylor series

$$\exp(\hat{A}) = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n\,,$$

or a Chebychev series

$$\exp(\hat{A}) = \sum_{n=0}^{k} c_n\, T_n(\hat{A})\,,$$

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\varepsilon_{a\sigma} - \varepsilon_{i\tau}) + (i_\sigma a_\sigma \mid j_\tau b_\tau)$$

$$-\delta_{\sigma\tau} c_{HF}(i_\sigma j_\sigma \mid a_\tau b_\tau) + (1 - c_{HF})(i_\sigma a_\sigma \mid f_{\sigma\tau} \mid j_\tau b_\tau)$$

$$B_{ia\sigma,jb\tau} = (i_\sigma a_\sigma \mid j_\tau b_\tau) - \delta_{\sigma\tau} c_{HF}(i_\sigma b_\sigma \mid a_\tau j_\tau)$$

$$+(1 - c_{HF})(i_\sigma a_\sigma \mid f_{\sigma\tau} \mid b_\tau j_\tau)$$

Response functions

In spectroscopic experiments, an external field $F(\boldsymbol{r},t)$ is applied to a sample. The sample, which is a fully interacting many-electron system from the theoretical point of view, responds to the external field. Then the response can be measured for some physical observable $\mathcal{P}$:

$$\Delta\mathcal{P} = \Delta\mathcal{P}_F[F].$$

If the external field is weak, the response can be expanded as a power series with respect to the field strength. The first-order response, also called the linear response of the observable,

$$\delta\mathcal{P}^{(1)}(\boldsymbol{r},t) = \int \mathrm{d}t' \int \mathrm{d}^3r'\, \chi^{(1)}_{\mathcal{P}\leftarrow F}(\boldsymbol{r},\boldsymbol{r'},t-t')\delta F^{(1)}(\boldsymbol{r'},t')$$

The linear response function is nonlocal in space and in time, but the above time convolution simplifies to a product in frequency space:

$$\delta\mathcal{P}^{(1)}(\boldsymbol{r};\omega) = \chi^{(1)}_{\mathcal{P}\leftarrow F}(\boldsymbol{r},\boldsymbol{r'},\omega)\delta F^{(1)}(\boldsymbol{r'},\omega).$$

Linear density response

the most important response function, from the TDDFT point of view, is the linear density response function

$$\chi(\boldsymbol{r}, \boldsymbol{r}', t-t') = \chi^{(1)}_{n \leftarrow v_{\text{ext}}}(\boldsymbol{r}, \boldsymbol{r}', t-t')$$

which gives the linear response of the density $\delta n^{(1)}(\boldsymbol{r}, t)$ to an external scalar potential $\delta v_{\text{ext}}(\boldsymbol{r}', t')$.
If the density response function $\chi(\boldsymbol{r}, \boldsymbol{r}', t-t')$ is obtained explicitly, it can then be used to calculate the first-order response of all properties derivable from the density with respect to any scalar field (e.g.,polarizability, magnetic susceptibility).

Kohn-Sham response

The Kohn-Sham response is

$$\delta n(\boldsymbol{r},t) = \int \mathrm{d}t' \int \mathrm{d}^3 r' \, \chi_{\mathsf{KS}}(\boldsymbol{r},\boldsymbol{r}',t-t')\delta v_{\mathsf{KS}}(\boldsymbol{r}',t').$$

but the variation of the KS potential includes several contributions

$$\delta v_{\mathsf{KS}}(\boldsymbol{r}',t') = \delta v_{\mathsf{ext}}(\boldsymbol{r}',t') + \delta v_{\mathsf{H}}[n](\boldsymbol{r}',t') + \delta v_{\mathsf{xc}}[n](\boldsymbol{r}',t'),$$

The Hartree term is very easy to derive

$$\delta v_{\mathsf{H}}[n](\boldsymbol{r}',t') = \int \mathrm{d}t'' \int \mathrm{d}^3 r'' \, \frac{\delta(t'-t'')}{|\boldsymbol{r}'-\boldsymbol{r}''|} \delta n(\boldsymbol{r}'',t'').$$

The xc kernel

The exchange-correlation term is a bit harder. We will use the chain rule for functional derivatives

$$\frac{\delta F}{\delta f(\boldsymbol{r})} = \int \mathrm{d}^3 r' \, \frac{\delta F}{\delta g(\boldsymbol{r}')} \frac{\delta g(\boldsymbol{r}')}{\delta f(\boldsymbol{r})}$$

and write

$$\delta v_{\mathsf{xc}}[n](\boldsymbol{r}', t') = \int \mathrm{d}t'' \int \mathrm{d}^3 r'' \, f_{\mathsf{xc}}[n_{\mathrm{GS}}](\boldsymbol{r}', \boldsymbol{r}'', t' - t'') \delta n(\boldsymbol{r}'', t'').$$

where

$$f_{\mathsf{xc}}[n_{\mathrm{GS}}](\boldsymbol{r}', \boldsymbol{r}'', t' - t'') = \left. \frac{\delta v_{\mathsf{xc}}[n](\boldsymbol{r}', t')}{\delta n(\boldsymbol{r}'', t'')} \right|_{n = n_{\mathrm{GS}}}$$

The response equation - I

The variation of the density must be equal in the interacting and Kohn-Sham systems. We obtain therefore

$$
\begin{aligned}
&\int \mathrm{d}t' \int \mathrm{d}^3 r' \, \chi(\boldsymbol{r}, \boldsymbol{r}', t-t') \delta v_{\mathsf{ext}}(\boldsymbol{r}', t') = \\
&\int \mathrm{d}t' \int \mathrm{d}^3 r' \, \chi_{\mathsf{KS}}(\boldsymbol{r}, \boldsymbol{r}', t-t') \delta v_{\mathsf{ext}}(\boldsymbol{r}', t') + \int \mathrm{d}t' \int \mathrm{d}^3 r' \, \chi_{\mathsf{KS}}(\boldsymbol{r}, \boldsymbol{r}', t-t') \\
&\qquad \times \int \mathrm{d}t'' \int \mathrm{d}^3 r'' \left[\frac{\delta(t'-t'')}{|\boldsymbol{r}'-\boldsymbol{r}''|} + f_{\mathsf{xc}}[n_{\mathrm{GS}}](\boldsymbol{r}', \boldsymbol{r}'', t'-t'') \right] \\
&\qquad\qquad \times \int \mathrm{d}t''' \int \mathrm{d}^3 r''' \, \chi(\boldsymbol{r}'', \boldsymbol{r}''', t''-t''') \delta v_{\mathsf{ext}}(\boldsymbol{r}''', t''').
\end{aligned}
$$

As this equation is valid for every $\delta v_{\mathsf{ext}}(\boldsymbol{r}', t')$, we obtain

$$
\begin{aligned}
\chi(\boldsymbol{r}, \boldsymbol{r}', \omega) = \chi_{\mathsf{KS}}(\boldsymbol{r}, \boldsymbol{r}', \omega) &+ \int \mathrm{d}^3 r'' \int \mathrm{d}^3 r''' \chi_{\mathsf{KS}}(\boldsymbol{r}, \boldsymbol{r}'', \omega) \\
&\times \left[\frac{1}{|\boldsymbol{r}''-\boldsymbol{r}'''|} + f_{\mathsf{xc}}[n_{\mathrm{GS}}](\boldsymbol{r}'', \boldsymbol{r}''', \omega) \right] \chi(\boldsymbol{r}''', \boldsymbol{r}', \omega).
\end{aligned}
$$

The response equation - II

The Kohn-Sham density response function $\chi_{\mathsf{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega)$ is straightforward to obtain from first-order perturbation theory:

$$\chi_{\mathsf{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \lim_{\eta\to 0^+} \sum_{a,i} (n_i - n_a) \left[\frac{\varphi_i^*(\boldsymbol{r})\varphi_a(\boldsymbol{r})\varphi_i(\boldsymbol{r}')\varphi_a^*(\boldsymbol{r}')}{\omega - (\varepsilon_a - \varepsilon_i) + \mathrm{i}\eta} - \frac{\varphi_i(\boldsymbol{r})\varphi_a^*(\boldsymbol{r})\varphi_a(\boldsymbol{r}')\varphi_i^*(\boldsymbol{r}')}{\omega - (\varepsilon_i - \varepsilon_a) + \mathrm{i}\eta} \right],$$

where $\varphi_i(\boldsymbol{r})$ and $\varphi_a(\boldsymbol{r})$ are occupied and unoccupied KS orbitals, respectively.
This equation can be formally written as

$$\chi = \left(1 - \chi_{\mathsf{KS}} f_{\mathsf{Hxc}}\right)^{-1} \chi_{\mathsf{KS}},$$

where all terms on the right-hand-side are known from a ground-state Kohn-Sham calculation.

Higher-order response - I

Sometimes we need to consider the reponse to higher orders in the perturbing field. This can be done in the same way as for the linear term. For example, in second order

$$\delta n^{(2)}(\boldsymbol{r},t) = \frac{1}{2}\int \mathrm{d}t' \int \mathrm{d}t'' \int \mathrm{d}^3r' \int \mathrm{d}^3r''\, \chi^{(2)}(\boldsymbol{r},t,\boldsymbol{r}',t',\boldsymbol{r}'',t'')\delta v^{(1)}_{\mathsf{ext}}(\boldsymbol{r}',t')\delta v^{(1)}_{\mathsf{ext}}(\boldsymbol{r}'',t'') + \int \mathrm{d}t' \int \mathrm{d}^3r'\, \chi^{(1)}(\boldsymbol{r},t,\boldsymbol{r}',t')\delta v^{(2)}_{\mathsf{ext}}(\boldsymbol{r}',t').$$

And the Kohn-Sham reponse (too large to fit in this slide!)

Higher-order response - II

$$\delta n^{(2)}(\boldsymbol{r},t) =$$

$$\frac{1}{2}\int \mathrm{d}t' \int \mathrm{d}t'' \int \mathrm{d}^3r' \int \mathrm{d}^3r''\, \chi^{(2)}_{\mathsf{KS}}(\boldsymbol{r},t,\boldsymbol{r}',t',\boldsymbol{r}'',t'')\delta v^{(1)}_{\mathsf{ext}}(\boldsymbol{r}',t')\delta v^{(1)}_{\mathsf{ext}}(\boldsymbol{r}'',t'')$$

$$+\int \mathrm{d}t' \int \mathrm{d}^3r'\, \chi^{(1)}_{\mathsf{KS}}(\boldsymbol{r},t,\boldsymbol{r}',t')\delta v^{(2)}_{\mathsf{ext}}(\boldsymbol{r}',t')$$

$$+\frac{1}{2}\int \mathrm{d}t' \int \mathrm{d}t'' \int \mathrm{d}t''' \int \mathrm{d}^3r' \int \mathrm{d}^3r'' \int \mathrm{d}^3r'''\, \chi^{(1)}_{\mathsf{KS}}(\boldsymbol{r},t,\boldsymbol{r}',t')$$

$$\times\, k_{\mathsf{xc}}(\boldsymbol{r}',t',\boldsymbol{r}'',t'',\boldsymbol{r}''',t''')\delta n^{(1)}(\boldsymbol{r}'',t'')\delta n^{(1)}(\boldsymbol{r}''',t''')$$

$$+\int \mathrm{d}t' \int \mathrm{d}t'' \int \mathrm{d}^3r' \int \mathrm{d}^3r''\, \chi^{(1)}_{\mathsf{KS}}(\boldsymbol{r},t,\boldsymbol{r}',t')$$

$$\times\left(\frac{\delta(t'-t'')}{|\boldsymbol{r}'-\boldsymbol{r}''|} + f_{\mathsf{xc}}(\boldsymbol{r}',t',\boldsymbol{r}'',t'')\right)\delta n^{(2)}(\boldsymbol{r}'',t''),$$

where

$$k_{\mathsf{xc}}(\boldsymbol{r}',t',\boldsymbol{r}'',t'',\boldsymbol{r}''',t''') = \frac{\delta^2 v_{\mathsf{xc}}(\boldsymbol{r}',t')}{\delta n(\boldsymbol{r}'',t'')\delta n(\boldsymbol{r}''',t''')}\Bigg|_{n=n_{\mathrm{GS}}}.$$

Alternative methods for response

One can explicitly calculate the response-functions. However, this is seldom the most efficient method to calculate response. There are many alternatives

- ➜ Response in real time
- ➜ Sternheimer equation
- ➜ Casida method
- ➜ ...

Time-evolution method

In this method, we apply a small perturbing external potential, $\delta v_{\mathsf{ext}}(\boldsymbol{r},t)$, and solve the time-dependent Kohn-Sham equations. We can choose the form of the perturbation, but a particularly convenient form is:

$$\delta v_{\mathsf{ext}}(\boldsymbol{r},t) = -e\boldsymbol{r}\cdot\boldsymbol{K}\delta(t) = -e\boldsymbol{r}\cdot\boldsymbol{K}\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\,\exp(\mathrm{i}\omega t),$$

With this form we can propagate from $t = 0^-$ to $t = 0^+$ analytically

$$\begin{aligned}\varphi_k(\boldsymbol{r},t=0^+) &= \exp\left\{-\frac{\mathrm{i}}{\hbar}\int_{0^-}^{0+}\mathrm{d}t\left[\mathsf{H}_{\mathsf{KS}}^{(0)}(t) - e\boldsymbol{r}\cdot\boldsymbol{K}\delta(t)\right]\right\}\varphi_k(\boldsymbol{r},t=0^-)\\ &= \exp\left(\mathrm{i}e\boldsymbol{r}\cdot\boldsymbol{K}/\hbar\right)\varphi_k(\boldsymbol{r},t=0^-),\end{aligned}$$

and then we propagate the free oscillations in time.

Dynamic polarizability

The time-dependent dipole moment

$$\boldsymbol{\mu}(t) = -e \int \mathrm{d}^3r\, \boldsymbol{r} n(\boldsymbol{r}, t)$$

can be used to extract the dynamic polarizability tensor $\alpha(\omega)$

$$\alpha_{\gamma\delta}(\omega) = \frac{1}{K_\delta} \int_0^\infty \mathrm{d}t \left[\mu_\gamma(t) - \mu_\gamma(0^-)\right] \mathrm{e}^{-\mathrm{i}\omega t} + \mathcal{O}(K_\delta).$$

The imaginary part of the diagonal component of the dynamic polarizability $\mathcal{I}[\alpha_{\delta\delta}(\omega)]$ is proportional to the absorption spectrum. Note that in practice we have to add an artificial lifetime to the equation by introducing a decay $\mathrm{e}^{-\eta t}$.

Sternheimer method

In the Sternheimer method we expand the wave-function as a power series with respect to the perturbation strength λ.

$$\varphi_k(\boldsymbol{r},t) = \varphi_k^{(0)}(\boldsymbol{r},t) + \lambda\varphi_k^{(1)}(\boldsymbol{r},t) + \lambda^2\varphi_k^{(2)}(\boldsymbol{r},t) + \ldots$$

after a few pages of algebra we obtain the frequency-dependent Sternheimer equation

$$\left[\hat{H}_{\mathsf{KS}}^{(0)} - \varepsilon_k^{(0)} \pm \omega\right] \varphi_{k,\pm\omega}^{(1)}(\boldsymbol{r}) = -\left(v_{\mathsf{Hxc},\pm\omega}^{(1)} + v_{\mathsf{ext},\pm\omega}^{(1)} - \varepsilon_{k,\pm\omega}^{(1)}\right)\varphi_k^{(0)}(\boldsymbol{r})$$

Note that the Sternheimer method looks like a set of linear equations, but in reality it is a nonlinear set of equations as the right-hand side depends on the solution.

Casida's method

Casida's equations can be written as

$$\Delta E^2 + 2\Delta E^{\frac{1}{2}} N^{\frac{1}{2}} K N^{\frac{1}{2}} \Delta E^{\frac{1}{2}} = \omega^2 I,$$

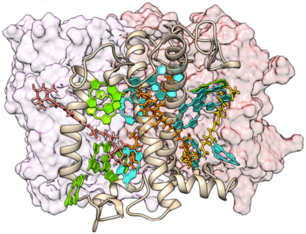
where

$$\begin{aligned} \Delta E_{bk,b'k'} =& \delta_{k,k'} \delta_{b',b'} (\varepsilon_b - \varepsilon_k) \\ N_{bk,b'k'} =& \delta_{k,k'} \delta_{b,b'} n_{k'}, \end{aligned}$$

and K the Hartree-exchange-correlation kernel matrix.

This is by far the most used method in Quantum-Chemistry!

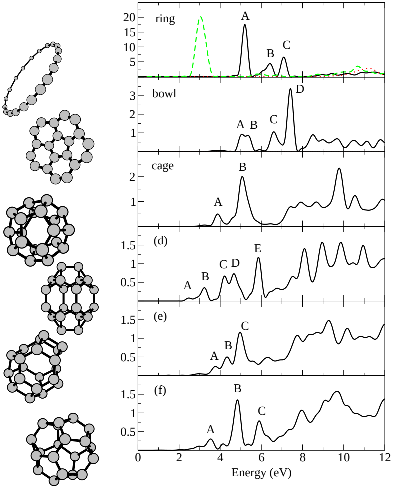
Mark Casida



Discriminating the C_{20} isomers

- ➜ Real-space, real-time TDLDA yields reliable photo-absorption spectra of carbon clusters
- ➜ Spectra of the different C_{20} are significantly different
- ➜ Optical spectroscopy proposed as an experimental tool to identify the structure of the cluster

J. Chem Phys **116**, 1930 (2002)



Aequorea victoria

Aequorea victoria is an abundant jellyfish in Puget Sound, Washington State, from which the luminescent protein aequorin and the fluorescent molecule GFP have been extracted, purified, and eventually cloned. These two products have proved useful and popular in various kinds of biomedical research in the 1990s and 2000s and their value is likely to increase in coming years.

`http://faculty.washington.edu/cemills/Aequorea.html`

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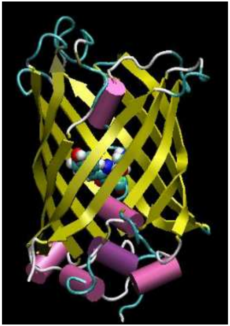
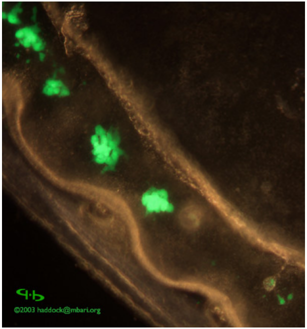
Data Sheet

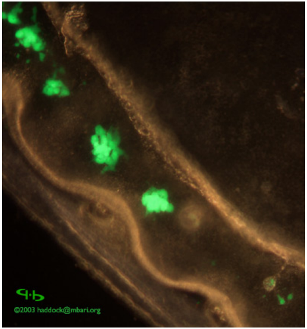
- 238 AA protein forming a β-barrel or β-can
- Chromophore located inside the β-barrel (shielded)
- Info to create the chromophore contained entirely in the gene
- High stability: wide pH, T, salt
- Long half life: $\approx$20 years
- Resistant to most proteases
- Active after peptide fusions: reporter protein
- Availability of chromophores variants

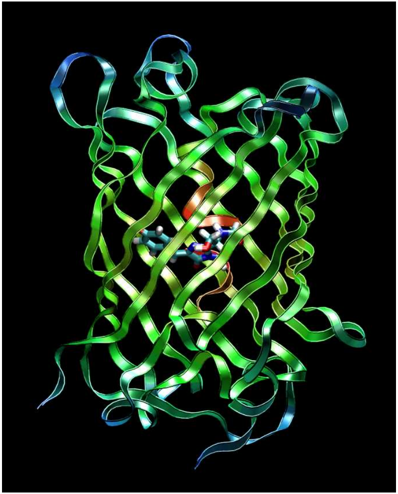


Chromophore

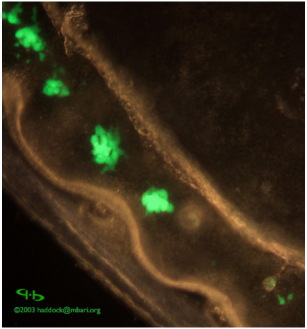


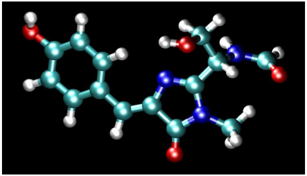
Chromophore

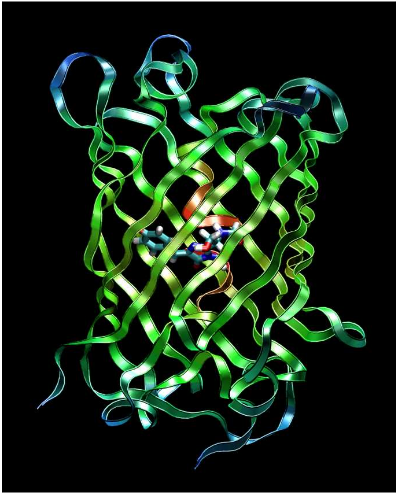




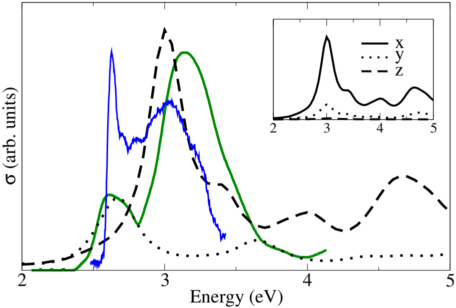
Chromophore







Optical Absorption



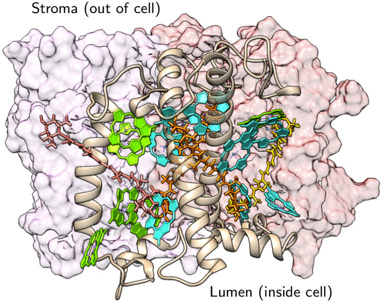
[exp1, exp2, neutral (dashes), anionic (dots)]

- Excellent agreement with experimental spectra
- Clear assignment of neutral and anionic peaks
- We extract an *in vivo* neutral/anionic ratio of 4 to 1

GFP: Phys. Rev. Lett. **90**, 258101 (2003)

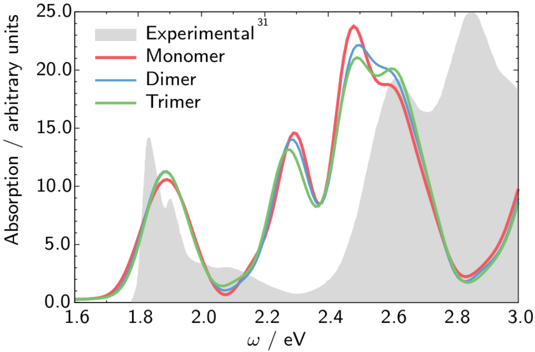
What can we do in 2015?

The light-harvesting complex II



The simplified LHC–II chromophore network contains 6075 atoms (corresponding to 31200 electrons). Each monomer contain contains 14 chlorophyll molecules (the key functional units in the light–harvesting process) and four secondary carotenoid chromophores.

What can we do in 2015?

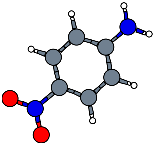


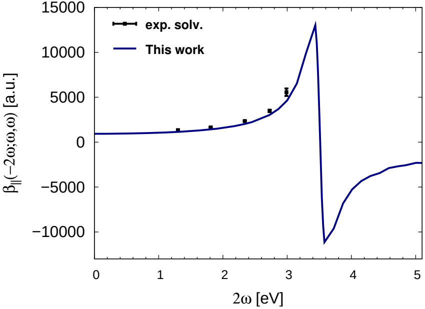
Performing an analysis based on the time-dependent density, we can, e.g., find which chlorophyll unit contributes to which peak.

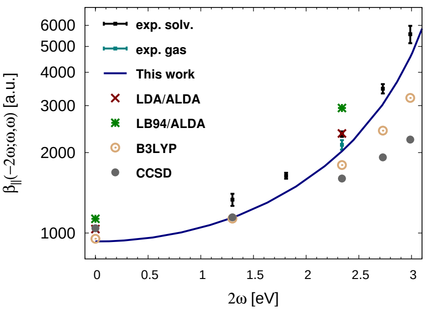
Jornet-Somoza et al, submitted (2015)

Non-linear response: SHG

Second harmonic generation of paranitroaniline:
$\beta(-2\omega, \omega, \omega)$



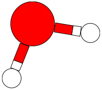


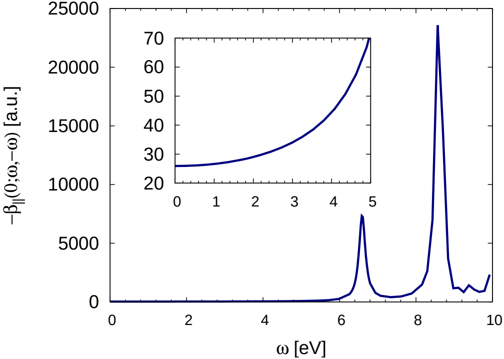


JCP **126**, 184106 (2007)

Non-linear response: optical rectification

Optical rectification of H_2O: $\beta(0,\omega,-\omega)$





JCP **126**, 184106 (2007)

Van der Waals coefficients

Non-retarded regime – Casimir-Polder formula ($\Delta E = -C_6/R^6$):

$$C_6^{AB} = \frac{3}{\pi}\int_0^\infty \mathrm{d}u\, \alpha^{(A)}(\mathrm{i}u)\, \alpha^{(B)}(\mathrm{i}u)\,,$$

Retarded regime ($\Delta E = -K/R^7$):

$$K^{AB} = \frac{23c}{8\pi^2}\alpha^{(A)}(0)\, \alpha^{(B)}(0)$$

The polarizability is calculated from

$$\alpha_{ij}(\mathrm{i}u) = \int \mathrm{d}r\, n_j^{(1)}(\boldsymbol{r}, \mathrm{i}u) r_i$$

Alternative – Time Propagation

Apply explicitly the perturbation:

$$\delta v_{\rm ext}(\boldsymbol{r}, t) = -x_j \kappa \delta(t - t_0)$$

The dynamic polarizability reads, at imaginary frequencies:

$$\alpha_{ij}(\mathrm{i}u) = -\frac{1}{\kappa} \int \mathrm{d}t \int \mathrm{d}r \, x_i \, \delta n(\boldsymbol{r}, t) \mathrm{e}^{-ut}$$

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It turns out:

- ➜ Both Sternheimer and time-propagation have the same scaling
- ➜ Only a few frequencies are needed in the Sternheimer approach, but ...
- ➜ 2 or 3 fs are sufficient for the time-propagation
- ➜ In the end, the pre-factor is very similar

C_6 - Polycyclic Aromatic Hydrocarbons