The Particle-Hole Map: a computational tool to visualize electronic excitations

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September 22, 2016

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Outline

- Visualization/interpretation methods of electronic excitations
- The particle-hole map: definitions
- Examples and applications

Y. Li and C.A. Ullrich, submitted to JCP (2016)
Molecular optical spectroscopy

- Uses (weak) laser as Probe
- System Response has peaks at electronic excitation energies
- Spectra can be calculated using TDDFT

Vasiliev et al., PRB 65, 115416 (2002)

Real-time simulation of exciton dynamics

- Would like to visualize e-h pair motion in real time
- CT exciton creation, diffusion, dissociation at D-A interfaces
- Important for understanding organic photovoltaics systems
Real-time simulation of exciton dynamics

- Would like to visualize e-h pair motion in real time
- CT exciton creation, diffusion, dissociation at D-A interfaces
- Important for understanding organic photovoltaics systems
- Real D-A systems are complex, and require taking lattice relaxation into account.

- What should we be looking at?

Semiconducting polymer (donor) \[\text{e-}\] Fullerene (acceptor)
Charge-transfer excitations

Zinc bacteriochlorin-Bacteriochlorin complex (light-harvesting in plants and purple bacteria)

CT excitations are difficult with TDDFT: LDA and GGA fail.

*Dreuw and Head-Gordon, JACS (2004)*
Transition densities and difference densities


density (lowest excited state)

charge density difference
Visualization of electron dynamics: TDELF

\[ f_{\text{ELF}}(\mathbf{r},t) = \frac{1}{1 + [D_\sigma(\mathbf{r},t) / D_\sigma^0(\mathbf{r},t)]^2} \]

\[ D_\sigma(\mathbf{r},t) = \tau_\sigma(\mathbf{r},t) - \frac{\left| \nabla n_\sigma(\mathbf{r},t) \right|^2}{8n_\sigma(\mathbf{r},t)} - \frac{\left| j_\sigma(\mathbf{r},t) \right|^2}{2n_\sigma(\mathbf{r},t)} \]

Time-Dependent Electron Localization Function (TDELF)

- **Local** quantities like TDELF or the density itself show the motion of charges and ions or the breaking of bonds

- Charge fluctuations can be seen from transition densities or density differences, charge transfer can often be seen from MO’s

- But where do electrons and holes come from or go to? How do we identify electron-hole pairs or excitons? **Need nonlocal information.**
Electron-hole distributions for exciton

LiF

Erhart, Schleife, Sadigh and Aberg, PRB 89, 075132 (2014)

Obtained from solutions of the GW-Bethe-Salpeter eq.

Transition Density Matrix (TDM)

TDM associated with a specific excitation $\Psi_0 \rightarrow \Psi_n$:

$$\Gamma_n (r, r') = \langle \Psi_n | \hat{\rho}(r, r') | \Psi_0 \rangle$$

Many-body eigenstates:

$$\hat{H}_0 \Psi_n = E_n \Psi_n$$

1-body density matrix operator:

$$\hat{\rho}(r, r') = \psi^+(r')\psi(r)$$

R. McWeeny, RMP 32, 335 (1960)
F. Furche, JCP 114, 5982 (2001)

Excitation energies follow from eigenvalue problem (Casida 1995):

\[
\begin{pmatrix}
A & K \\
K^* & A^*
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \Omega^n
\begin{pmatrix}
-1 & 0 \\
0 & 1
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\]

\[
A_{ia,i'a'} = \delta_{ii'}\delta_{aa'}(\varepsilon_a - \varepsilon_i) + K_{ia,i'a'}
\]

\[
K_{ia,i'a'} = \int d^3r \int d^3r' \phi_i^*(r)\phi_a(r) \left[ \frac{1}{|r - r'|} + f_{xc}(r, r', \omega) \right] \phi_{i'}(r')\phi_{a'}(r')
\]

transition density:

\[
\delta n(r, \Omega_n) = \sum_{ia} \left[ \phi_i(r)\phi_a^*(r)X_{ia}(\Omega_n) + \phi_i^*(r)\phi_a(r)Y_{ia}(\Omega_n) \right]
\]
The diagonal elements are (in principle) exact transition densities:

\[
\Gamma_{n}^{KS} (\mathbf{r}, \mathbf{r}) = \Gamma_{n} (\mathbf{r}, \mathbf{r}) = \delta n(\mathbf{r}, \Omega_{n})
\]

The off-diagonal elements are in general not exact:

\[
\Gamma_{n}^{KS} (\mathbf{r}, \mathbf{r}') \neq \Gamma_{n} (\mathbf{r}, \mathbf{r}'), \quad \mathbf{r} \neq \mathbf{r}'
\]
Time-dependent TDM


\[ \Gamma(r, r', t) = \langle \Psi(t) \left| \hat{\rho}(r, r') \right| \Psi_0 e^{-iE_0 t} \rangle \]

KS Time-dependent TDM:

\[ \Gamma^{KS}(r, r', t) = \langle \Phi(t) \left| \hat{\rho}(r, r') \right| \Phi_0 e^{-iE_0^{KS} t} \rangle \]

Where \( \Phi(t), \Phi_0 \) are time-dependent and ground-state Kohn-Sham Slater determinants:

\[ \Phi(t) = \det \{ \varphi_j(r, t) \} \quad \chi(t) = -\frac{\nabla^2}{2} + v(t) + v_H(t) + v_{xc}(t) \varphi_j(t) = i \frac{\partial}{\partial t} \varphi_j(t) \]
**TDHF calculation**


Two characteristic length scales

Coherence Length $L_c$

Delocalization Length $L_d$
TDHF gives overbound excitons

No bound excitons in ALDA (e-h repulsion)

Hybrid functionals have bound excitons

Transition Density Matrix

- TDM is easy to compute and represent

- Allows to visualize excitonic character of an excitation (= electron-hole wave function)

- The TDM does not tell us where electron and hole are coming from: difficult to assess charge-transfer character of an excitation

- New visualization tool, complementary to TDM: the particle-hole map (PHM)
The time-dependent particle-hole map (I)

TDKS equation:

$$i\hbar \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_s(\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t)$$

where

$$\varphi_j(\mathbf{r}, t = 0) = \varphi_j^{(0)}(\mathbf{r}), \quad j = 1, \ldots, N$$

Consider the following sum of joint probabilities:

$$P(\mathbf{r}, \mathbf{r}', t) = \sum_{i=1}^{N} \left\{ \left| \varphi_i(\mathbf{r}', t) \right|^2 - \left| \varphi_i^{(0)}(\mathbf{r}') \right|^2 \right\} \left| \varphi_i^{(0)}(\mathbf{r}) \right|^2$$

density fluctuation of
ith time-dependent
KS orbital

ground-state
probability density
do ith KS orbital
at position \(\mathbf{r}\)
The time-dependent particle-hole map (II)

For small perturbation, we can linearize:

\[ | \varphi_i(r', t) |^2 - | \varphi_i^{(0)}(r') |^2 \]

\[ = \varphi_i^{(0)}(r') \delta \varphi_i(r', t) + c.c. \]

\[ = \varphi_i^{(0)}(r') \delta \varphi_{i,o}(r', t) + \varphi_i^{(0)}(r') \delta \varphi_{i,u}(r', t) + c.c. \]

where the orbital fluctuations involving initially unoccupied states are obtained by projection:

\[ \delta \varphi_{i,u}(r', t) = \varphi_i(r', t) - \sum_{i=1}^{N} \varphi_j^{(0)}(r') \int d^3 r'' \varphi_i(r'', t) \varphi_i^{(0)}(r'') \]

The orbital fluctuations involving occupied states don’t contribute to the linear density response are and hence discarded.
The time-dependent particle-hole map (III)

\[
\Xi(r, r', t) = \sum_{i=1}^{N} \left\{ \phi_{i}^{(0)}(r') \delta \phi_{i,u}(r', t) + c.c. \right\} |\phi_{i}^{(0)}(r)|^2
\]

Sum of joint probability densities that a KS particle originates at position \( r \) and moves, during the excitation process, to position \( r' \).

\( \Xi(r, r', t \leq 0) = 0 \) (starting from ground state)

\[ \int \Xi(r, r', t) d^3 r' = 0 \] (norm conservation)

\[ \int \Xi(r, r', t) d^3 r = \delta n(r', t) \] (exact density response)
The frequency-dependent particle-hole map

We expand

$$\delta \phi_{i,u}(\mathbf{r}, t) = \sum_{a=N+1}^{\infty} C_{ia}(t) \phi^{(0)}_a(\mathbf{r}) e^{i\omega_{ia} t}$$

If the system is in the electronic eigenmode of the nth excited state,

$$\delta n(\mathbf{r}, t) = e^{-i\Omega_n t} \delta n(\mathbf{r}, \Omega_n)$$

Using sum rule and comparing with the Casida equation from TDDFT,

$$\Xi(\mathbf{r}, \mathbf{r}', \Omega_n) =$$

$$\sum_{ia} \left[ \phi^{(0)}_i(\mathbf{r}') \phi^{(0)*}_a(\mathbf{r}') X_{ia}(\Omega_n) + \phi^{(0)*}_i(\mathbf{r}') \phi^{(0)}_a(\mathbf{r}') Y_{ia}(\Omega_n) \right] | \phi^{(0)}_i(\mathbf{r}) |^2$$
2\textsuperscript{nd}-order particle-hole transition density matrix between two Slater determinants:

\[
\gamma_{2}^{ph} (ia, 0; r_1, r_2; r'_1, r'_2) = \langle \Phi_{ia} | \hat{\psi}^+(r'_1)\hat{\psi}(r'_2)\hat{\psi}^+(r_2)\hat{\psi}(r_1) | \Phi_0 \rangle \\
= \varphi_i(r_1)\varphi^*_a(r'_1)\overline{\gamma}_1(r'_2, r_2) - \gamma_1(r_1, r'_1)\varphi_i(r'_2)\varphi^*_a(r_2) \\
+ \varphi_i(r_2)\varphi^*_a(r'_1)\gamma_1(r'_2, r'_1) + \gamma_1(r_1, r_2)\varphi_i(r'_2)\varphi^*_a(r'_1)
\]
Derivation from 2-particle RDM (II)

Projection onto occupied KS orbitals: \( P_{l}(r, r') = \phi_{l}(r)\phi_{l}^{*}(r') \)

\[
\sum_{occ} \langle P_{l} | \gamma_{2}^{ph} (ia,0) | P_{l} \rangle (r', r'; r, r) = \phi_{i}(r')\phi_{a}^{*}(r') | \phi_{i}(r) |^{2}
\]

\[
\Xi(r, r', \Omega_{n}) = \sum_{occ} \langle P_{l} | \gamma_{2}^{ph} (\Omega_{n}) | P_{l} \rangle (r'; r)
\]

\[
= \sum_{ia} \left[ \phi_{i}(r')\phi_{a}^{*}(r') X_{ia} (\Omega_{n}) + \phi_{i}^{*}(r')\phi_{a} (r') Y_{ia} (\Omega_{n}) \right] | \phi_{i}(r) |^{2}
\]

PHM: orbital-projected particle-hole 2-TDM
PHM: 1D examples

\[ N = 8 \]
PHM: 1D examples

Density response
Quantum wells

Orbital density response #1
Orbital density response #2
Orbital density response #3
Orbital density response #4

PHM

TDM
PHM: how to read it

integrates to $\delta n$ in this direction

(\text{where e/h is going to})

$x'$

integrates to zero in this direction

\begin{itemize}
  \item blue: electrons
  \item red: holes
\end{itemize}

(\text{where e/h is coming from})
PHM: 1D examples
1D example: time-dependent PHM

TDKS propagation, starting from ground state, with laser pulse at resonance

1DMol-dn.mp4

1DMol-outplane.mp4
The PHM in 3D: how to plot it

► Plot PHM for a fixed reference point: \( \Xi(r_0, r', \Omega_n) \)

► Atom-centered basis for KS orbitals: 
\[
\varphi_j(r) = \sum_{l=1}^{N_A} \sum_{k=1}^{M_l} \zeta_{jk} \eta_k^l(r)
\]

Assume zero overlap of basis functions on different atomic sites, and plot PHM similar to TDM as an array.

► For real-space grid, define a spatial coarse graining.

Each bin is numbered and we plot the average of the PHM over the bin. Can use boxes, slices, or Wigner-Seitz cells.
$\text{C}_2\text{H}_4 - \text{C}_2\text{F}_4$ charge transfer complex

$\Xi(r_0, r', \Omega_n)$
Both are donor-acceptor molecules, with very similar optical spectra. But TDPP has 20x bigger responsivity (photocurrent). Why?
PDPP-BBT versus TDPP-BBT: experiment

![Graph showing energy vs. responsivity for PDPP-BBT and TDPP-BBT](chart.png)

- **Responsivity (A/W)**
- **Energy (eV)**

The graph compares the responsivity of PDPP-BBT and TDPP-BBT as a function of energy. The PDPP-BBT curve is depicted in blue, and the TDPP-BBT curve is in black. The inset shows the absorption normalized to the area under the curve. Both curves are labeled with 'x20' indicating a scaling factor.

- **Axes:**
  - X-axis: Energy (eV)
  - Y-axis: Responsivity (A/W)

- **Key points:**
  - The PDPP-BBT curve peaks at lower energies compared to TDPP-BBT.
  - The inset graph provides a detailed view of the absorption characteristics at higher energies.
PDPP-BBT versus TDPP-BBT (monomers)
PDPP-BBT versus TDPP-BBT (dimers)
P3HT – $C_{60}$ charge transfer complex
Extensions & Generalizations

**Straightforward extensions:**

- Moving nuclei
- Spin-dependent
- Ultrafast time-dependent (weak intensity)
- Strong excitations: can use $P(r, r', t)$

Bound excitons in periodic systems

2-band tight-binding model

LiF
5x5 supercell

$|EWF|^2$

$|PHM|^2$
Summary

► TDM provides image of exciton wave function.

► PHM is ideal for charge-transfer processes. It can tell us
   • where electrons and holes are coming from and where
     they are going to
   • the role of individual chemical units in the excitation process

► Both are easy to apply as a post-TDDFT utilities, and provide
  complementary information

► Can be applied in real time to illustrate excitation dynamics.

► Applications in the ultrafast strong-field regime are possible

Y. Li and C.A. Ullrich, submitted to JCP (2016)