TDDFT in Chemistry and Biochemistry IV

Dmitrij Rappoport

Department of Chemistry and Chemical Biology
Harvard University

TDDFT Winter School
Benasque, January 2010
Electronic Excitations

Response equations

\[
(\Lambda - n\omega\Delta)|X^{(n)}, Y^{(n)}\rangle = -|P^{(n)}, Q^{(n)}\rangle
\]

\[
\Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix}; \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

\[
(A + B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 2f^H_{iajb} + 2f^{xc}_{iajb} - c_x[f^H_{jaib} + f^H_{abij}]
\]

\[
(A - B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + c_x[f^H_{jaib} - f^H_{abij}]
\]

Excitation energies and transition matrix elements

Excitation energies are eigenvalues of \(\Lambda\) (Casida’s equations),

\[
(\Lambda - \Omega_k\Delta)|X^k, Y^k\rangle = 0; \quad \langle X^k, Y^k|\Delta|X^k, Y^k\rangle = 1
\]

Transition matrix elements are residues of the response equation at \(\Omega_k\),

\[
M^{(n)}_{0k} = \langle X^k, Y^k|P^{(n)}, Y^{(n)}\rangle.
\]
Variational formulation of excitation energies

Excitation energies $\Omega_k$ are stationary points of functional

$$G[X, Y, \Omega] = \langle X, Y | \Lambda | X, Y \rangle - \Omega (\langle X, Y | \Delta | X, Y \rangle - 1)$$

$$\frac{\partial G}{\partial |X, Y\rangle} = (\Lambda - \Omega \Delta) |X, Y\rangle = 0$$

$$\frac{\partial G}{\partial \Omega} = \langle X, Y | \Delta | X, Y \rangle - 1 = 0$$

- Total number of excitations $N_{occ} \cdot N_{virt}$;
- Usually only the low-energy part of the spectrum of interest;
- Solution of the eigenvalue equation (equivalently, minimization of $G[X, Y, \Omega]$) on iteratively expanded subspace most efficient.
Electronic Excitations

One-photon absorption spectrum of free-base porphin

BP86 functional / aug-SVP basis set

Experiment: M. Gouterman et al., J. Mol. Spectr., 1971, 38, 16;
Electronic Excitations

Two-photon absorption spectrum of 4-Dimethylamino-4’-nitrostilbene

Electronic Excitations

Accuracy of approximate TDDFT

- Typical accuracy of excitation energies in molecules: 0.3–0.5 eV

Molecular problem cases for approximate TDDFT

- Rydberg excitations, excitations close to the KS continuum
  \( \text{CH}_2\text{O}, \, 1B_2: \, \text{BP86: 5.97 eV, B3LYP: 6.45 eV, exp.: 7.13 eV} \)

- Excitations with strong charge-transfer character
  \( \text{DMABN}, \, 1A_2: \, \text{BP86: 1.76 eV, B3LYP: 2.69 eV, exp.: 3.05 eV} \)

- Excitations with significant double-excitation character
  \( \text{hexatriene}, \, 2A_g: \, \text{BP86: 5.05 eV, B3LYP: 5.65 eV, exp.: 5.21 eV} \)

- Triplet states
  \( \text{pyrazine}, \, 3B_{3u}: \, \text{BP86: 2.88 eV, B3LYP: 3.21 eV, exp.: 3.42 eV} \)
TDDFT and Nuclear Motion

Frequency-Domain Techniques

Linear Density Response
Polarizability $\alpha(\omega)$

Quadratic Density Response
Hyperpolarizability $\beta(\omega,\omega')$

Higher-Order Density Response

Excitation Energies $\Omega_n$

Derivatives w.r.t. Nuclear Displacements

Polarizability Derivatives
$\partial \alpha(\omega) / \partial \xi$

Hyperpolarizability Derivatives
$\partial \beta(\omega,\omega') / \partial \xi$

Excited State Gradients
$\partial \Omega_n / \partial \xi$

Raman Spectra

Hyper-Raman Spectra

Coherent Anti-Stokes Raman Spectra

Excited State Structures and Vibrations
### Excited State Properties

**Excited state properties as energy derivatives**

- Excited state wavefunction is unavailable from response theory;
- Need to define all excited state properties as derivatives of excited state energy $E_k = E_0 + \Omega_k$,

\[
\mu_k = \frac{\partial E_k}{\partial \xi} ;
\]

Dipole moment

\[
\rho_k(r) = \frac{\delta E_k}{\delta \nu_{\text{ext}}(r)} ;
\]

Electron density

\[
g_{k,A} = \frac{\partial E_k}{\partial R_A} .
\]

Gradient

- Variational formulation particularly suited for computation of derivatives ($\xi$ denotes derivative w.r.t. $\xi$),

\[
\frac{\partial}{\partial \xi} G[X, Y, \Omega] = \langle X, Y|\Lambda^\xi|X, Y \rangle .
\]
Excited State Properties

Lagrangian of the excited state energy

\[ L[X, Y, \Omega, C, Z, W] = E_0 + G[X, Y, \Omega] + \sum_{ia} Z_{ia} H_{ia}^{(0), KS} \]
\[ - \sum_{pq} W_{pq} (S_{pq} - \delta_{pq}) \]

- \( Z, W \) Lagrange multipliers for orbital coefficients \( C_{\mu p \sigma} \)
- \( E_0 \) Ground state energy functional
- \( S \) Overlap matrix of KS orbitals

- At stationary point
  \[ \delta L = 0 \iff L = E_k \]
- Lagrange multipliers \( Z, W \) follow from stationarity w.r.t. \( C_{\mu p \sigma} \).

Excited State Properties

Computation of excited state gradients

1) Compute excitation energies and excitation vectors,

\[(\Lambda - \Omega_k \Delta)|X_k, Y_k\rangle = 0\];

2) Determine Lagrange multipliers \(Z, W\),

\[\sum_{jb} (A + B)_{iajb} Z_{jb} = -R_{ia};\]

3) Evaluate the excited state energy gradient,

\[L^\xi = \sum_{\mu\nu\sigma} h_{\mu\nu\sigma}^\xi P_{k,\mu\nu\sigma} - \sum_{\mu\nu\sigma} S_{\mu\nu}^\xi W_{k,\mu\nu\sigma} + \sum_{\mu\nu\sigma\kappa\lambda\sigma'} (\mu\nu|\kappa\lambda)^\xi \Gamma_{k,\mu\nu\sigma\kappa\lambda\sigma'}^\xi\]

\[+ \sum_{\mu\nu\sigma} v_{\mu\nu\sigma}^{xc(\xi)} P_{k,\mu\nu\sigma} + \sum_{\mu\nu\sigma\kappa\lambda\sigma'} f_{\mu\nu\sigma\kappa\lambda\sigma'}^{xc(\xi)} (X + Y)_{k,\mu\nu\sigma} (X + Y)_{k,\kappa\lambda\sigma'}\]
Excited State Properties

Excited state optimizations

Chlorophyll $a$, $2^1A$

$T_e = 1.98 \text{ eV}$

GS energy 0:33 h

ES energy, grad. 1:44 h

opt. cycles 13

BP86 functional/RI-J/SVP basis set

**TURBOMOLE, Ver. 5.7**

- Excited state optimizations with TDDFT are similar in computational cost to ground state DFT optimizations.

Azulene, $1^1B_1$

$T_0$ (theor.) = 1.99 eV

$T_0$ (exp.) = 1.78 eV

B3LYP func./TZVP basis set

Excited State Properties

Excited state potential energy surfaces of DMABN

LE state: \( \Delta E_{em} \text{ (theor.)} = 3.76 \text{ eV}, \quad \Delta E_{em} \text{ (exp.)} = 3.76 \text{ eV} \)

CT state: \( \Delta E_{em} \text{ (theor.)} = 2.69 \text{ eV}, \quad \Delta E_{em} \text{ (exp.)} = 3.05 \text{ eV} \)

B3LYP functional/TZVPP basis set

## Excited State Properties

### Excited state vibrational frequencies of DMABN

<table>
<thead>
<tr>
<th>Mode</th>
<th>CT state</th>
<th>LE state</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(C≡N)</td>
<td>-103</td>
<td>-11</td>
</tr>
<tr>
<td>ν(C≡N)</td>
<td>-124, -102</td>
<td>-38, -33</td>
</tr>
<tr>
<td>ν(C=O) 8a</td>
<td>-7</td>
<td>-503</td>
</tr>
<tr>
<td>ν(C=O) 19a</td>
<td>-94</td>
<td>-41</td>
</tr>
<tr>
<td>ν(Ph–N)</td>
<td>-72</td>
<td>-107</td>
</tr>
<tr>
<td>ν(C≡N)</td>
<td>-169, -104</td>
<td>-61, -68</td>
</tr>
<tr>
<td>ν(Ph–N)</td>
<td>-96</td>
<td>-45, -36</td>
</tr>
<tr>
<td>ν(Ph–CN)</td>
<td>-5</td>
<td>-59</td>
</tr>
<tr>
<td>δ(C–H) 18a</td>
<td>-60</td>
<td>-19, -57</td>
</tr>
<tr>
<td>ring br. 1</td>
<td>-42</td>
<td>-59, -53</td>
</tr>
</tbody>
</table>

Excited state vibrational frequencies are accurate to 30–50 cm$^{-1}$; Excited state properties are often significantly more accurate than excitation energies.
Excited State Properties

### Accuracy of TDDFT for excited state properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Exp. Mean</th>
<th>CIS</th>
<th>LDA</th>
<th>BP86</th>
<th>PBE</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>34 adiab. exc. en. (eV)</td>
<td>4.5</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>40 bond len. (pm)</td>
<td>142.2</td>
<td>3.5</td>
<td>1.5</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>10 dipole mom. (D)</td>
<td>1.3</td>
<td>0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>80 vib. freq. (cm(^{-1}))</td>
<td>1258</td>
<td>169</td>
<td>62</td>
<td>49</td>
<td>49</td>
<td>61</td>
</tr>
</tbody>
</table>

- Excludes the \(1^2\Sigma^+\) state of NO (instability).
- Excludes the \(1^1B_1\) state of CCl\(_2\) and the \(1^2\Sigma^+\) state of NO (instabilities).
- Excludes the \(1^2\Sigma^+\) state of NO (instability) and the \(\nu_{13}(1a_2)\) frequency of the \(1^1B_2\) state of pyridine (saddle point).

Raman Intensities

Raman scattering cross sections in double-harmonic approximation

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_Q = \frac{(\omega - \omega_Q)^4}{2\omega_Q c^4} \left| \langle \sigma_Q^{mn}(\omega) \rangle \right|^2
\]

\[
\sigma_Q^{mn}(\omega) = \frac{\partial \alpha^{mn}}{\partial Q}(\omega) = \sum_{\xi} \frac{\partial \alpha^{mn}}{\partial \xi}(\omega) \ell_{Q\xi}
\]

- $\xi$ – Cart. nuclear displ.
- $\omega_Q$ – Vib. freq. of $Q$
- $\ell_{Q\xi}$ – Normal mode of $Q$
- $\omega$ – External frequency
- $m, n \in \{x, y, z\}$

[Diagram showing energy levels for Rayleigh, Stokes Raman, and Anti-Stokes Raman transitions]
Raman Intensities

Lagrangian for frequency-dependent polarizability

\[ L_{mn}[X^m, Y^m, X^n, Y^n, C, Z^{mn}, W^{mn}](\omega) = \langle X^m, Y^m | \Lambda - \omega \Delta | X^n, Y^n \rangle + 2\langle X^m, Y^m | \mu^n, \mu^n \rangle + 2\langle \mu^m, \mu^m | X^n, Y^n \rangle + \sum_{ia} Z_{ia}^{mn} H_{ia}^{(0),KS} - \sum_{pq} W_{pq}^{mn} (S_{pq} - \delta_{pq}) \]

Stationarity conditions for \( L_{mn}(\omega) \)

\[ \frac{\partial L_{mn}}{\partial |X^m, Y^m\rangle} = (\Lambda - \omega \Delta) |X^n, Y^n\rangle + |\mu^n, \mu^n\rangle = 0 \]

\[ \frac{\partial L_{mn}}{\partial |X^n, Y^n\rangle} = (\Lambda - \omega \Delta) |X^m, Y^m\rangle + |\mu^m, \mu^m\rangle = 0 \]

- Computation of \( \frac{\partial \alpha_{mn}(\omega)}{\partial \xi} \) analogous to excited state gradients.

Raman Intensities

Comparison of computed Raman scattering activities $S_Q$

$$S_Q = g_Q \left( 45 \left( \text{tr} \, \sigma_Q^{mn}(\omega) \right)^2 + 7 \chi \left( \text{anis} \, \sigma_Q^{mn}(\omega) \right)^2 \right)$$

<table>
<thead>
<tr>
<th>Vib.</th>
<th>Freq.</th>
<th>PBE0</th>
<th>HF</th>
<th>LDA</th>
<th>BP</th>
<th>PBE0</th>
<th>CCSD</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>2484</td>
<td>26.9</td>
<td>21.2</td>
<td>22.0</td>
<td>22.2</td>
<td>18.8</td>
<td>20.2±0.4</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2239</td>
<td>14.7</td>
<td>15.0</td>
<td>15.7</td>
<td>15.1</td>
<td>20.0</td>
<td>17.4±1.1</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>1713</td>
<td>46.2</td>
<td>11.2</td>
<td>12.7</td>
<td>15.2</td>
<td>13.5±0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₁</td>
<td>3046</td>
<td>253</td>
<td>277</td>
<td>264</td>
<td>250</td>
<td>241</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td>ν₃</td>
<td>3167</td>
<td>171</td>
<td>164</td>
<td>168</td>
<td>157</td>
<td>145</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>Mean Dev. (40)</td>
<td>11.5</td>
<td>20.4</td>
<td>17.8</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Abs. (40)</td>
<td>21.1</td>
<td>24.1</td>
<td>21.0</td>
<td>16.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Excitation frequency $\omega = 19435 \text{ cm}^{-1}$ (514 nm), TZVPP/aug-TZVPP Basis
Raman Intensities

Raman spectrum of endohedral fullerene Eu@C\textsubscript{74}

Raman Intensities

Raman excitation profiles of PhS–Ag_{10} complex

PBE0 functional/SV(P)/TZVP basis sets