TDDFT Excitation Energies: An Evaluation and a Diagnostic Test

David J Tozer www.dur.ac.uk/d.j.tozer





Vertical excitation energies from TDDFT



Typical DFT errors:

Local	$0.2 - 0.3 \ eV$
Rydberg	$1.0-2.0~\mathrm{eV}$
Charge transfer (CT)	????



DMABN J. Chem. Phys. **116** 8761 (2002)

... when are CT excitations reliable with TDDFT?

Aims of the present work

Are there any new XC functionals that yield improved CT and Rydberg excitations, whilst maintaining accurate local excitations?

Can we understand/predict when conventional DFT functionals will fail?

Molecules



- 59 Excitations, comprising 32 Local; 13 Rydberg; 14 CT
- Compare with gas phase expt. or CASPT2/CC2 at same geometry

Results: PBE GGA functional



- Local excitations generally fine
 Rydberg significantly underestimated
 CT significantly underestimated
 DMABN is the exception!
- ${}^{1}B_{2u}$ too low in acenes
- ${}^{1}B_{2u}/{}^{1}B_{3u}$ order incorrect for n=1
- PP local excitations underestimated
- Error increases with chain length for PA
- $\bullet~{\rm Error}>1~{\rm eV}$ for 25/59

Mean & Mean abs. errors, in eV

	PBE
Local	
ME	-0.31
MAE	0.33
Rydberg	ξ
ME	-1.84
MAE	1.84
СТ	
ME	-2.60
MAE	2.60

Results: B3LYP hybrid functional



- Energies increase relative to PBE
- Local excitations generally fine
- Rydberg improve, still underestimate
- CT improve but still underestimate
- DMABN CT still accurate!
- ${}^{1}B_{2u}$ improves slightly
- ${}^{1}B_{2u}/{}^{1}B_{3u}$ order still incorrect
- PP improves
- Still large PA errors for longer chains
- $\bullet~{\rm Error}>1~{\rm eV}$ for 16/59

Mean & Mean abs. errors, in eV

	PBE	B3LYP
Local		
ME	-0.31	-0.15
MAE	0.33	0.22
Rydberg		
ME	-1.84	-1.11
MAE	1.84	1.11
СТ		
ME	-2.60	-1.35
MAE	2.60	1.36

Can we do any better?

Much current interest in 'Coulomb Attenuated' or 'Long-Range Corrected' or 'Range Separated Hybrid' XC functionals ...



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A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP)

Takeshi Yanai ^{a,*}, David P. Tew ^b, Nicholas C. Handy ^b

^a Oak Ridge National Laboratory, P.O. Box 2008, MS6367, Oak Ridge, TN 37831, USA ^b Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK

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Results: CAM-B3LYP coulomb attenuated functional



- Further increase in energies
- Local excitations generally fine
- Rydbergs improve, still too low; AC
- \bullet No CT underestimation; just 2 $> 0.5 \mbox{ eV}$
- DMABN CT still accurate!
- ${}^{1}B_{2u}$ improved
- ${}^{1}B_{2u}/{}^{1}B_{3u}$ order correct!
- PP and PA well described
- $\bullet~{\sf Error}>1~{\sf eV}$ for 0/59

Mean & Mean abs. errors, in eV

	PBE	B3LYP	CAM
Local			
ME	-0.31	-0.15	0.02
MAE	0.33	0.22	0.20
Rydberg			
ME	-1.84	-1.11	-0.50
MAE	1.84	1.11	0.50
СТ			
ME	-2.60	-1.35	-0.18
MAE	2.60	1.36	0.27

Can we understand/predict when conventional functionals fail?



No spatial overlap between occupied & virtual orbitals involved in the excitation

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

$$\omega^{\text{local}} = \epsilon^{\text{A}}_{\text{LUMO}} - \epsilon^{\text{D}}_{\text{HOMO}}$$
$$\omega^{\text{exact}} = \text{IP}^{\text{D}} - \text{EA}^{\text{A}}$$

Local functional excitation energies too low by many eV!

COMMUNICATIONS

Relationship between long-range charge-transfer excitation energy error and integer discontinuity in Kohn–Sham theory

David J. Tozer Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE UK (Received 29 September 2003; accepted 23 October 2003)

For local functionals,

$$\epsilon_{\text{HOMO}} pprox -\text{IP} + rac{\Delta_{\text{XC}}}{2}$$

 $\epsilon_{\text{LUMO}} pprox -\text{EA} - rac{\Delta_{\text{XC}}}{2}$

where Δ_{XC} is the integer discontinuity of PRL **49** 1691 (1982). Hence,

$$\omega^{\mathsf{local}} - \omega^{\mathsf{exact}} \approx -\frac{1}{2} \left(\Delta_{\mathsf{XC}}^{\mathsf{A}} + \Delta_{\mathsf{XC}}^{\mathsf{D}} \right)$$

which explains the significant underestimation.

Do our errors (general excitations) correlate with spatial orbital overlap?

For a given occupied-virtual pair, degree of overlap can be measured using

$$O_{ia} = \left< |arphi_i| \left| |arphi_a| \right> = \int |arphi_i(\mathbf{r})| |arphi_a(\mathbf{r})| \, d\mathbf{r}$$

But, many occ-virt pairs contribute; contribution from each pair measured by

$$\kappa_{ia} = X_{ia} + Y_{ia}$$
 where $\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} I & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}$

 \rightarrow

This leads us to consider the quantity

$$\Lambda = \frac{\sum_{i,a} \kappa_{ia}^2 O_{ia}}{\sum_{i,a} \kappa_{ia}^2}$$

which takes the value $0\leqslant\Lambda\leqslant 1.$

Small $\Lambda \rightarrow$ long-range excitation Large $\Lambda \rightarrow$ short-range excitation





Poor GGA description of CT in the tripeptide can be attributed to the **small** overlap between the occupied and virtual orbitals involved in the excitation.

 $n_1 \rightarrow \pi_3^*~$ CT , error =~-5.04 eV, $\Lambda=0.06$



Good GGA description of CT in DMABN can be attributed to the large overlap.

CT, error = -0.26 eV, $\Lambda = 0.72$



Tripeptide/DMABN results highlight ambiguous nature of term charge-transfer





B3LYP



CAM-B3LYP



CAM-B3LYP is therefore recommended for excitation energy calculations

But, if wish to use PBE or B3LYP, then use above observations to propose a diagnostic test:





PBE excitation with $\Lambda < 0.4$ likely to be in significant error

B3LYP excitation with $\Lambda < 0.3$ likely to be in significant error

Expect analogous observations for other GGAs/Hybrids

 Λ is not unique and its diagnostic value is qualitative rather than quantitative. However, it captures the essential physics of the problem and may prove useful in practical calculations. Implemented in DALTON. Further investigation necessary....

Conclusions J. Chem. Phys. 128 044118 (2008)

 \bullet CAM-B3LYP provides best quality excitation energies; no correlation between error and orbital overlap, $\Lambda.$ Reflects presence of long-range, non-local exact orbital exchange.

• Clear correlation between error and Λ for PBE and B3LYP.

• Allows us to propose simple diagnostic test. If Λ below prescribed threshold, errors likely to be very significant. Further investigation required.

• Results highlight ambiguous nature of term "charge transfer". Wide range of Λ values for the CT excitations – correlation between Λ and error provides simple explanation as to why tripeptide (small Λ) is poor with GGA/hybrid, but DMABN (large Λ) is well-described.

• Inappropriate to say that GGA/hybrids *fail for CT excitations*. Must quantify degree of orbital overlap before making judgment.

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