



Extension of LCAO to excited states

Peter Koval, Dietrich Foerster

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Extension of LCAO to excited states: Summary

Application to excitation spectra within TDDFT linear response.

Peter Koval and Dietrich Foerster

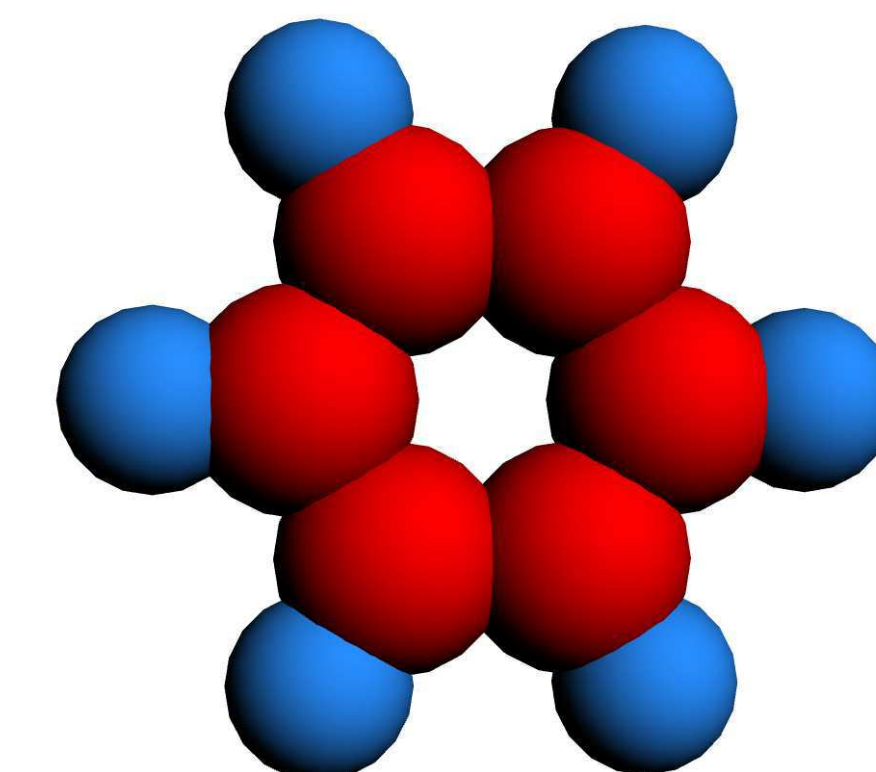
INRIA Sud Ouest, Bordeaux; CPMOH, University of Bordeaux 1

351 Cours de la Liberation, 33405 Talence, France



Motivation

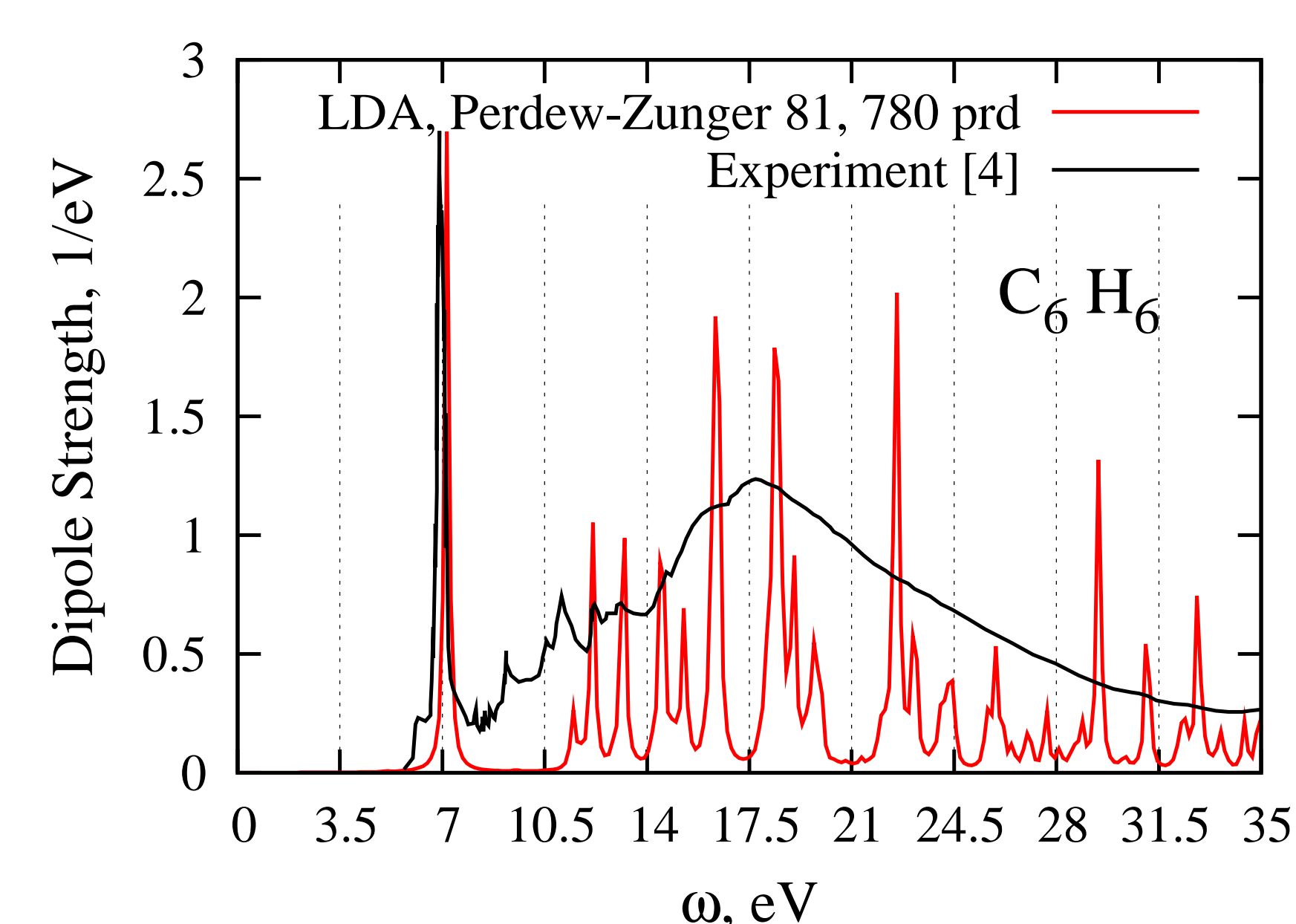
- Electronic excitation spectra within TDDFT linear response.
- Excitonic effects, where interaction between electrons and holes (excitons) requires density-density correlator χ_0 in GW and BSE.
- Need a simple basis in space of orbital products for observables.



Benzene: 108 LCAO in DZP basis
5832 original products.
780 products after compression

Difficulties to be solved for molecules

- **Too many products:**
In LCAO approach density is expanded in products of (atom-centered) orbitals $f_a(\mathbf{r})f_b(\mathbf{r})$.
Traditional solution: expand products in Gaussians.
- **Bad scaling in kernel:**
Coulomb interaction $\Sigma_{Coulomb}$ in basis of eigenstates requires 4-center integrals.
Number of these integrals grows like N^4
Traditional solution: fit the density with auxiliary functions.



Collective resonance in benzene acquires right position

Our resolution of these difficulties

- **Small basis in space of products:**
Products of orbitals are strongly linear-dependent. We analyse the space of products and construct an orthogonal basis.
Due to strong linear dependence of the original products, they are spanned by only few “dominant” products.
- **Basis in space of products needs only 2-center integrals:**
4-center integrals naturally disappear if we work in a product basis set.

Results

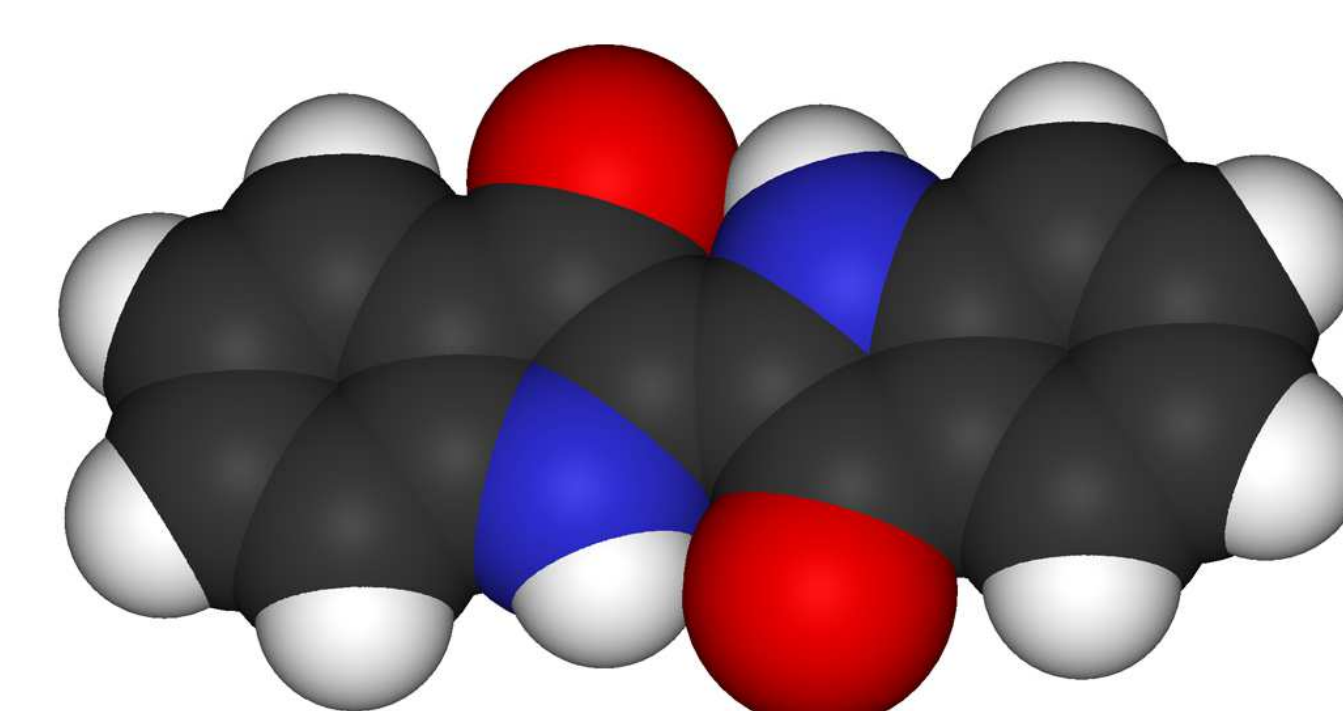
- ✓ Basis of dominant products: $O(N)$ (8 s for benzene).
- ✓ The non-interacting response χ_0 : $O(N^2N_\omega)$ (480 s for benzene).
- ✓ Matrix elements of interaction: $O(N^2)$ (180 s for benzene).
- ✓ Interacting polarizability: $O(N^2N_\omega)$ (110 s for benzene).

Conclusion and outlook

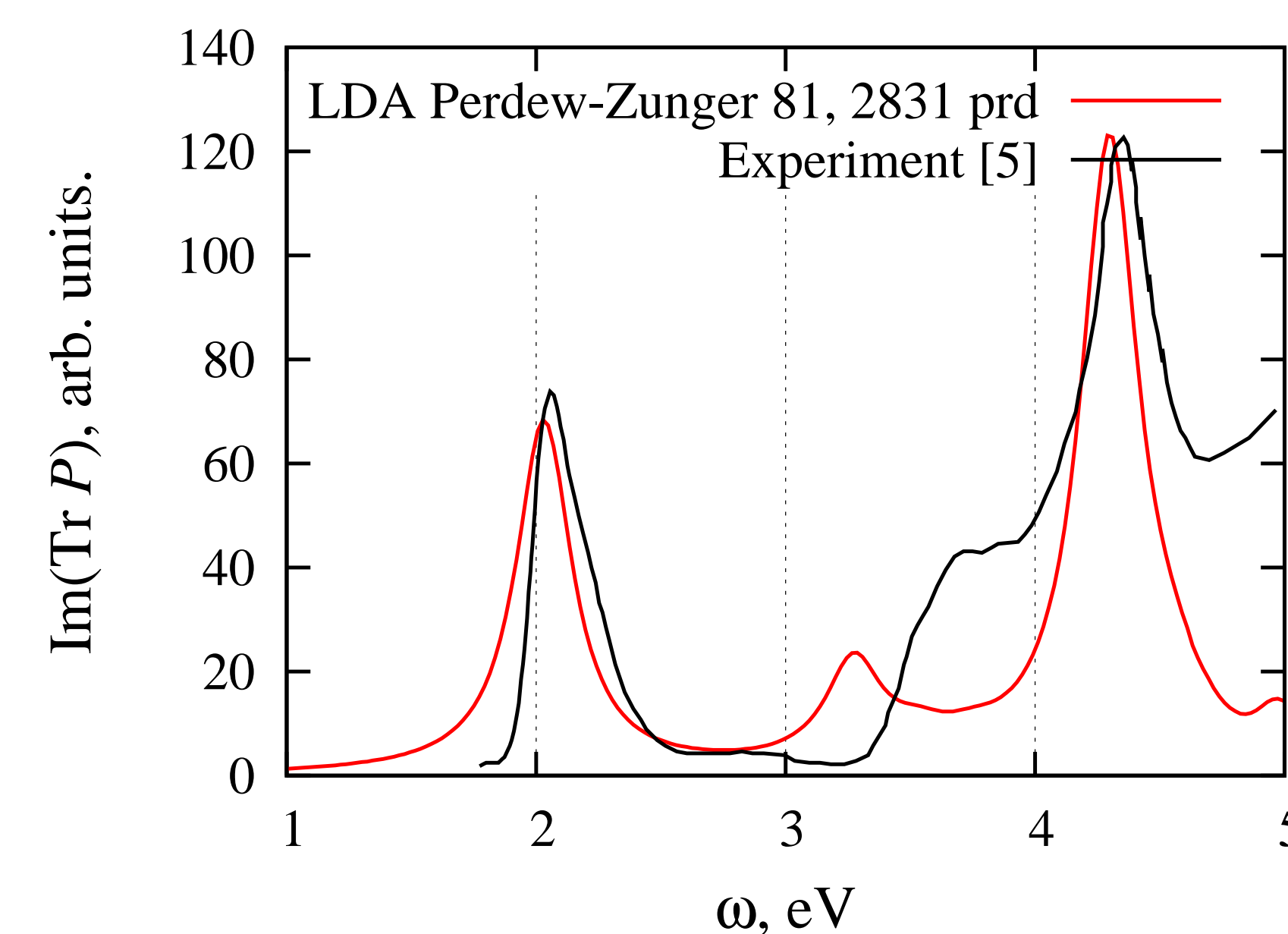
- Small basis of dominant products has been constructed.
- The algorithm for χ_0 is fast and exact up to discretization of the spectral density.
- Complexity for interacting polarizability scales as $O(N^2N_\omega)$.
- Problem solved: true excitation spectra within TDDFT linear response
- Applications to spectra of dyes on surfaces (ANR NOSSI).
- Application to screened Coulomb interaction between particles and holes in GW and BSE.
- Application to charge-hole dynamics and current generation in photovoltaics.

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Nouveaux Outils pour la Simulation de Surfaces et Interfaces



Indigo blue: 310 LCAO in DZP basis
48050 original products
2831 products after compression



SIESTA's basis of short support is able to reproduce experimental data for indigo blue molecule