

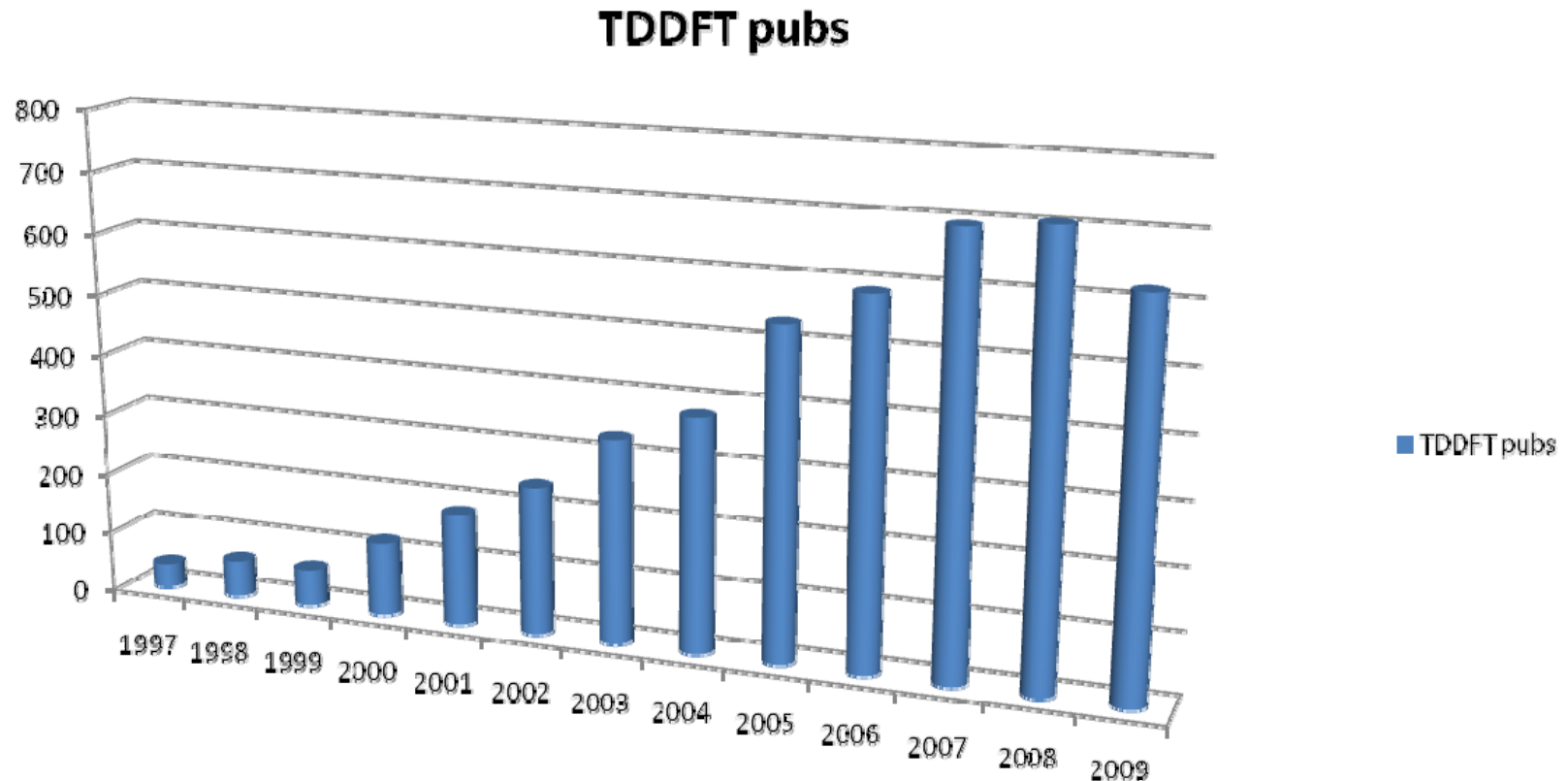
# TDDFT for finite systems: Tales from the dark side

Kieron Burke and friends  
UC Irvine Chemistry and Physics

<http://dft.uci.edu>

# TDDFT publications in recent years

Search ISI web of Science for topic 'TDDFT'



- Warning! By 2300, entire mass of universe will be TDDFT papers

# Recent reviews of TDDFT

PDF COPY 708522JCP

THE JOURNAL OF CHEMICAL PHYSICS 122, 1 (2005)

## Time-dependent density functional theory: Past, present, and future

Kieron Burke

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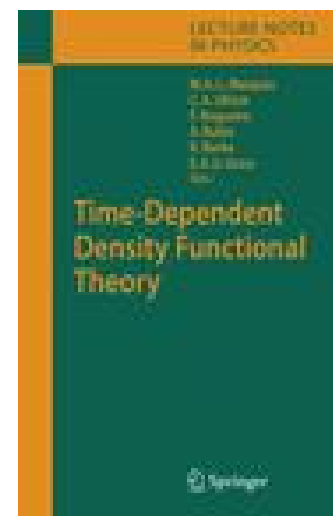
Jan Werschnik and E. K. U. Gross

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(Received 18 August 2004; accepted 17 March 2005)

Time-dependent density functional theory (TDDFT) is presently enjoying enormous popularity in quantum chemistry, as a useful tool for extracting electronic excited state energies. This article discusses how TDDFT is much broader in scope, and yields predictions for many more properties. We discuss some of the challenges involved in making accurate predictions for these properties.

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## Just appeared in Reviews of Computational Chemistry

Excited states from time-dependent density functional theory

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Kieron Burke

*Department of Chemistry, University of California, Irvine, CA 92697, USA*

Filipp Furche

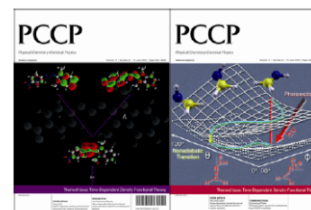
*Institut für Physikalische Chemie, Universität Karlsruhe, Kaiserstraße 12, 76128 Karlsruhe, Germany*

(Dated: March 21, 2007)

Time-dependent density functional theory (TDDFT) is presently enjoying enormous popularity in quantum chemistry, as a useful tool for extracting electronic excited state energies. This article explains what TDDFT is, and how it differs from ground-state DFT. We show the basic formalism, and illustrate with simple examples. We discuss its implementation and possible sources of error. We discuss many of the major successes and challenges of the theory, including weak fields, strong fields, continuum states, double excitations, charge transfer, high harmonic generation, multiphoton ionization, electronic quantum control, van der Waals interactions, transport through single molecules, currents, quantum defects, and, elastic electron-atom scattering.

## ● 2<sup>nd</sup> Gordon Research Conference, July 6

This paper is published as part of a PCCP Themed Issue on:  
[Time-Dependent Density-Functional Theory](#)



Guest Editors:

Miguel A. L. Marques and Angel Rubio

# Overview of ALL TDDFT

## 1. General Time-dependent Density Functional Theory

- Any  $e^-$  system subjected to any  $v_{\text{ext}}(\mathbf{r}t)$
- Only unknown:  $v_{\text{XC}}[\rho](\mathbf{r}t)$
- Treat atoms and molecules in **INTENSE** laser fields

## 2. TDDFT linear response to weak fields

- Linear response:  $\delta\rho(\mathbf{r}t) = \int d^3r' \int dt' \chi(\mathbf{r}\mathbf{r}', t-t') \delta v_{\text{ext}}(\mathbf{r}'t')$
- Only unknown:  $v_{\text{XC}}(\mathbf{r}t)$  **near** ground state  
$$v_{\text{XC}}[\rho_0 + \delta\rho](\mathbf{r}\omega) = v_{\text{XC}}[\rho_0](\mathbf{r}) + \int d^3r' f_{\text{XC}}[\rho_0](\mathbf{r}\mathbf{r}'\omega) \delta\rho(\mathbf{r}'\omega)$$
- Treat electronic excitations in atoms + molecules + solids

## 3. Ground-state Energy from TDDFT

- Fluctuation-dissipation theorem: Exc from susceptibility
- Van der Waals; seamless dissociation

Basic approximation: ALDA

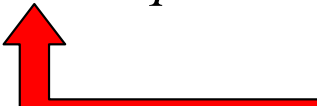
$$v_{\text{XC}}^{\text{unif}}(\rho(\mathbf{r}t))$$

# Eigenvalue equations

Casida's matrix formulation (1996)


$$\sum_{q'} \tilde{\Omega}_{qq'}(\omega) v_{q'} = \omega^2 v_q$$

True transition frequencies



$$\Omega_{qq'} = \delta_{qq'} \omega_q^2 + 4\sqrt{\omega_q \omega_{q'}} [q | f_{\text{HXC}}(\omega) | q']$$

KS transition frequencies

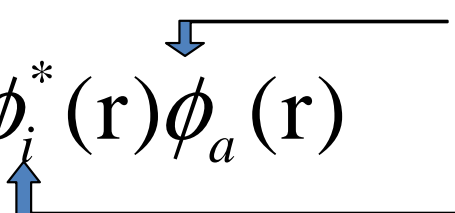


$$[q | f_{\text{HXC}}(\omega) | q] = \iint \Phi_q^*(\mathbf{r}') f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'; \omega) \Phi_q(\mathbf{r}) d\mathbf{r} d\mathbf{r}'$$

$$\Phi_q(\mathbf{r}) = \phi_j^*(\mathbf{r}) \phi_a(\mathbf{r})$$

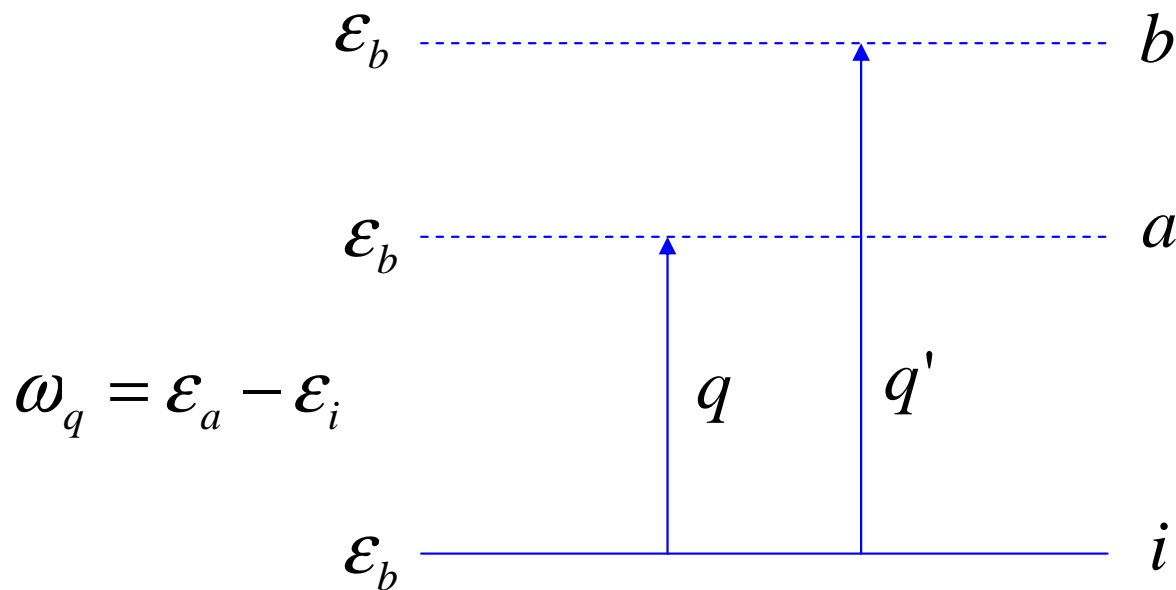
Unoccupied KS orbital

Occupied KS orbital



# Transitions in TDDFT response

In this equation,  $f_{\text{HXC}}$  is the Hartree-exchange-correlation kernel,  $1/|\mathbf{r}-\mathbf{r}'| + f_{\text{XC}}(\mathbf{r},\mathbf{r}',\omega)$ , where  $f_{\text{XC}}$  is the unknown XC kernel



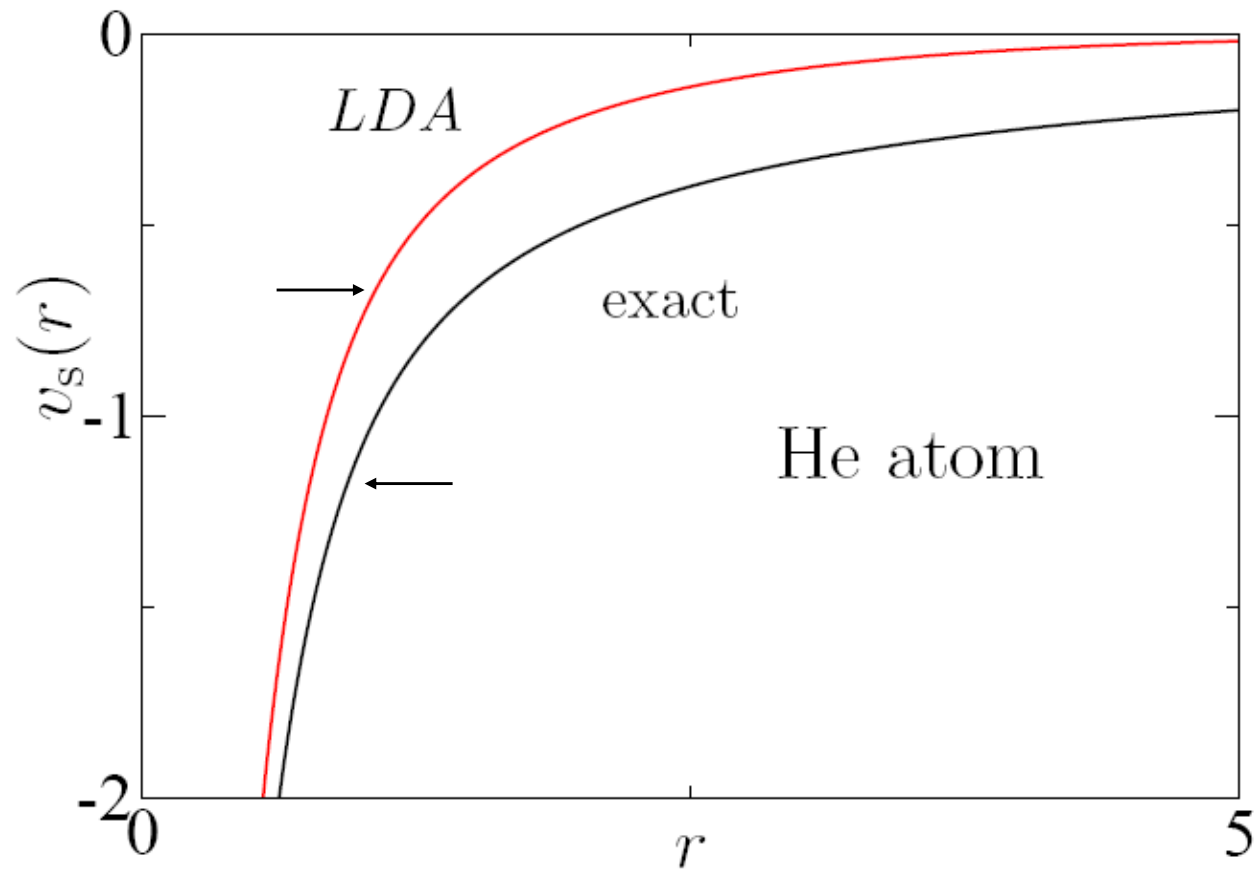
# Adiabatic approximation

$$v_{\text{xc}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) = v_{\text{KS}}[n, \Psi(0), \Phi(0)](\mathbf{r}, t) - v_{\text{ext}}(\mathbf{r}, t) - v_{\text{H}}[n](\mathbf{r}, t)$$

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

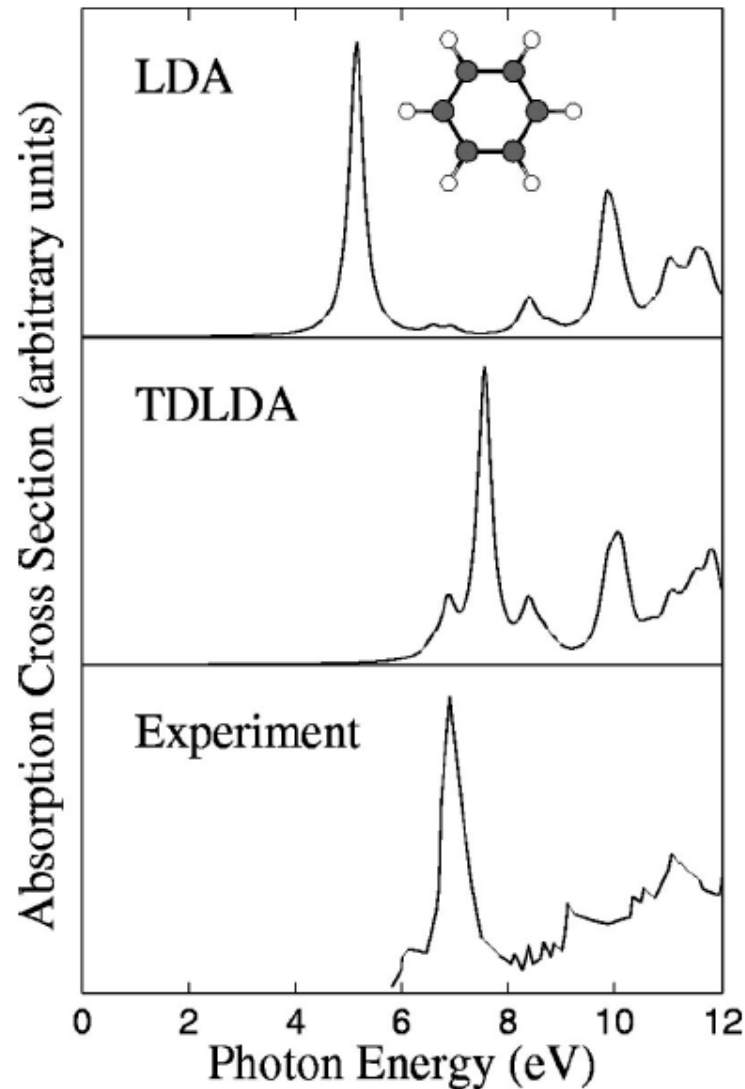
$$v_{\text{xc}}^{\text{adia}}[n](\mathbf{r}, t) = v_{\text{xc}}^{\text{approx}}[n(t)](\mathbf{r})$$

# KS potential in LDA





# Benzene: Fruitfly of TDDFT



*First-principles density-functional calculations for optical spectra of clusters and nanocrystals*

I. Vasiliev, S. Ogut, and J.R. Chelikowsky, Phys. Rev. B 65, 1 15416 (2002).

# Basic points

- TDDFT
  - is an addition to DFT, using a different theorem
  - allows you to convert your KS orbitals into optical excitations of the system
  - for excitations usually uses ground-state approximations that usually work OK
  - has not been very useful for strong laser fields
  - is in its expansion phase: Being extended to whole new areas, not much known about functionals
  - with present approximations has problems for solids
  - with currents is more powerful, but harder to follow
  - yields a new expensive way to get ground-state  $E_{xc}$ .

# Old Rutgers DFT group



# Students and postdocs in TDDFT

- **Paul** Hessler –high-school teacher



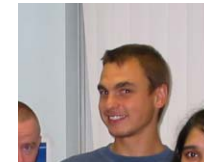
- **Heiko** Appel – postdoc with diVentra



- **Neepa** Maitra – Hunter college –talks Monday morning



- **Rene** Gaudoin – postdoc with Pitarke in San Sebastian



- **Adam** Wasserman – chem prof at Purdue



- **Fan** Zhang ?



- **Maxime** Dion ??



- **Meta** van Faassen



# *Finite systems for fundamentals*

- RG theorem requires a surface condition, so original theorem only proven for finite systems.
- Should always ask “what is case for finite systems, and then what are complications in thermodynamic limit?”

# Scaling relations in TDDFT

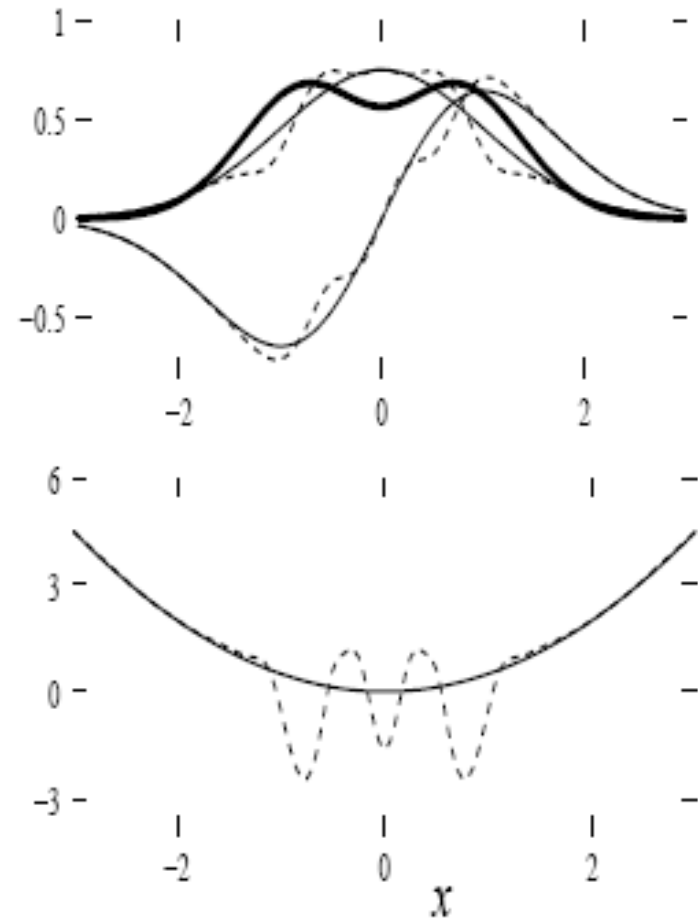
- Hessler, Park, (PRL 99): Scaling relations in TDDFT

$$v_{XC}^{\lambda}[n](\mathbf{r}t) = \lambda^2 v_{XC}[n_{1/\lambda}, 1/\lambda^2](\lambda\mathbf{r}, \lambda^2 t)$$

- Conservation of power
- Careful definition of adiabatic effects
- Complete breakdown of adiabatic approximation.
- Maxime Dion did current generalization, PRA 05.
- See also *Exact conditions* in TDDFT book.

# Does functional depend on initial state?

- Demonstration of initial-state dependence (Maitra, PRA 01).
- Also applies in Floquet formulation (Maitra, CPL 02, CPL 08).



# Can any initial-state dependence be written as memory?

- Relation between initial state and memory effects (Maitra, Woodward, PRL 02).

$$v_{\text{ext}}[n_{t'}, \Psi(t')](\mathbf{r}t) = v_{\text{ext}}[n_0, \Psi(0)](\mathbf{r}t) \quad \text{for } t \geq t', \quad (3)$$

where

$$n_{t'}(\mathbf{r}t) = n(\mathbf{r}t) \quad \text{for } t \geq t', \quad (4)$$

and  $n_{t'}(\mathbf{r}t)$  is undefined for  $t < t'$ . To see why this trivial

- Difficulties with pumping to excited states:  
 $1s^2 \rightarrow 1s2p$  in singlet He!



# Demo: Memory effects

- Memory in time-dependent Hooke's atom, see Hessler, Maitra, JCP 02.

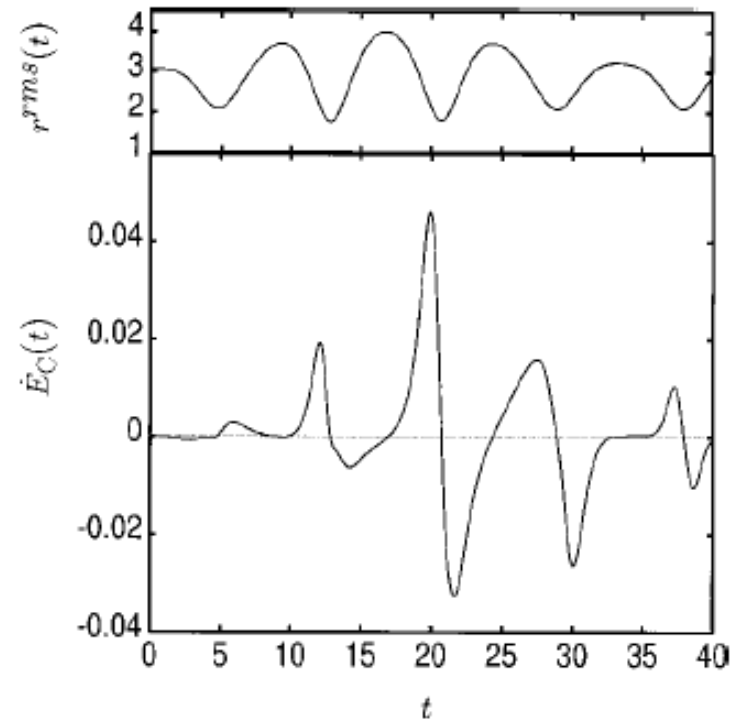


FIG. 7. A measure of the nonlocality of  $\dot{E}_C$  with respect to time for the nonresonant run (NR): Contrast the very similar density profiles implied in the top panel near times  $t=4.8$  and  $28.9$  with the very different values of  $\dot{E}_C$  there in the graph above. Similar comparisons may be made near  $t=9.35$  and  $t=24.3$ .

# *Excitations in real molecules*

- Very large systems, mostly closed shells
- Usefulness is when there are many excitations of same symmetry in same region of spectrum.

# Challenges for static DFT of excitations

- Rene Gaudoin, PRL 03.

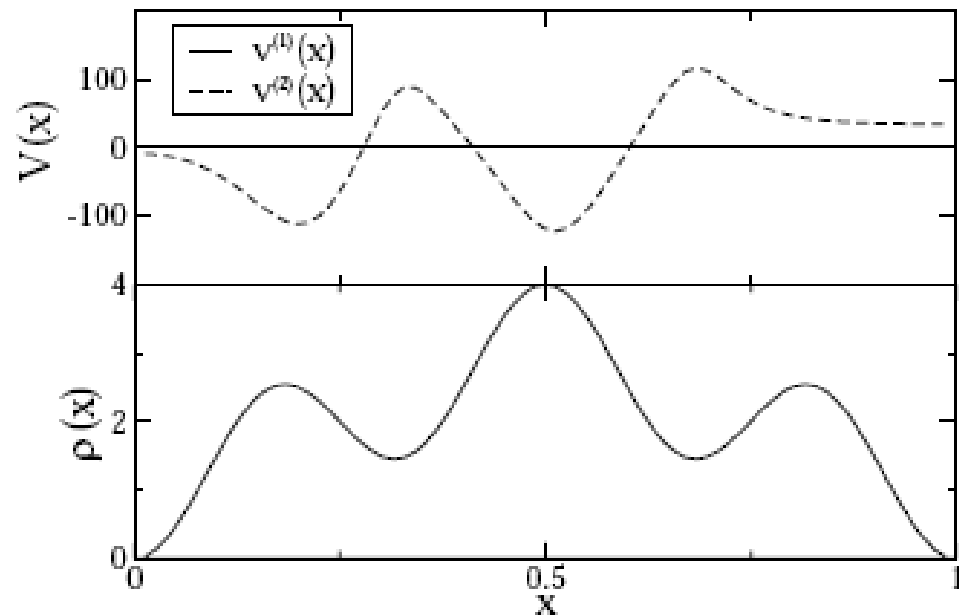


FIG. 1. Two potentials (upper panel) yielding the same first excited-state density (lower panel).

# Success of TDDFT for excited states

- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5%
- Vibrational frequencies good to 5%
- Cost scales as  $N^2$ , vs  $N^5$  for CCSD
- Available now in your favorite quantum chemical code

TABLE III: Performance of various density functionals for the first six singlet excitation energies (in eV) of naphthalene. An aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used. The “best” estimates of the true excitations were from experiment and calculations, as described in text.

Method	$1^1B_{3u}$	$1^1B_{2u}$	$2^1A_g$	$1^1B_{1g}$	$2^1B_{3u}$	$1^1A_u$
Pure density functionals						
LSDA	4.191	4.026	5.751	4.940	5.623	5.332
BP86	4.193	4.027	5.770	4.974	5.627	5.337
PBE	4.193	4.031	5.753	4.957	5.622	5.141
Hybrids						
B3LYP	4.393	4.282	6.062	5.422	5.794	5.311
PBE0	4.474	4.379	6.205	5.611	5.889	5.603
“best”.	4.0	4.5	5.5	5.5	5.5	5.7

TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

Method	$1^1B_{3u}$	$1^1B_{2u}$	$2^1A_g$	$1^1B_{1g}$	$2^1B_{3u}$	$1^1A_u$
CIS	5.139	4.984	7.038	6.251	6.770	5.862
CC2	4.376	4.758	6.068	5.838	6.018	5.736
CASPT2	4.03	4.56	5.39	5.53	5.54	5.54
expt.	3.97, 4.0	4.45, 4.7	5.50, 5.52	5.28, 5.22	5.63, 5.55 5.89	
“best”.	4.0	4.5	5.5	5.5	5.5	5.7

TDDFT results for vertical singlet excitations in Naphthalene

*Elliot, Furche, KB, Reviews Comp Chem, sub. 07.*

*Note: For valence excitations, variations in  $v_{xc}(r)$  comparable to those in  $f_{xc}(r, r')$*

# *Understanding TDDFT response*

- Staring at response equations, how they work, and what they mean, tells us much about what is going on.

# Eigenvalue equations

Casida's matrix formulation (1996)

$$\sum_{q'} \tilde{\Omega}_{qq'}(\omega) v_{q'} = \omega^2 v_q$$

True transition frequencies

$$\Omega_{qq'} = \delta_{qq'} \omega_q^2 + 4 \sqrt{\omega_q \omega_{q'}} [q | f_{\text{HXC}}(\omega) | q']$$

KS transition frequencies

$$[q | f_{\text{HXC}}(\omega) | q] = \iint \Phi_q^*(\mathbf{r}') f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'; \omega) \Phi_q(\mathbf{r}) d\mathbf{r} d\mathbf{r}'$$

$$\Phi_q(\mathbf{r}) = \phi_j^*(\mathbf{r}) \phi_a(\mathbf{r})$$

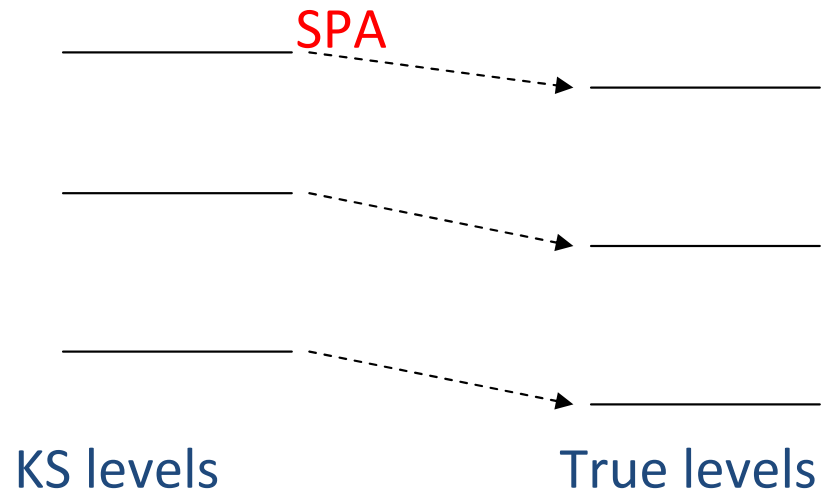
Unoccupied KS orbital

Occupied KS orbital

# First, a little technology: SPA- when excitations are well separated

The single pole approximation (SPA)

$$\omega = \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q]$$



$$[q|f_{\text{HXC}}(\omega_q)|q] = \iiint \Phi_q^*(\mathbf{r}') f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'; \omega_q) \Phi_q(\mathbf{r}) d\mathbf{r} d\mathbf{r}'$$

H. Appel, E.K.U. Gross and K. Burke, Phys. Rev. Lett. **90**, 043005 (2003)



# Understanding TDDFT response

- Consider matrix in equations:
- Appel, Gross, PRL 03.
- If diagonal, just get KS oscillator strengths, but shifted excitations (small matrix approx)
- Include off-diagonal, but assume small:
  - Change in oscillator strengths is first-order
  - Change in transition frequencies is second-order

TABLE I. Exact results for the He and Be atoms, using numerically exact ground-state Kohn-Sham potentials.

Atom	Transition	Frequency (eV)			Oscillator strength	
		KS <sup>a</sup>	SMA <sup>b</sup>	Exact	KS	Exact <sup>c</sup>
He	$1s \rightarrow 2p$	21.15	21.23	21.22	0.3243	0.2762
	$1s \rightarrow 3p$	23.06	23.10	23.09	8.47(-2)	7.34(-2)
	$1s \rightarrow 4p$	23.73	23.75	23.75	3.41(-2)	2.99(-2)
	$1s \rightarrow 5p$	24.04	24.05	24.05	1.71(-2)	1.50(-2)
	$1s \rightarrow 6p$	24.21	24.22	24.22	9.8(-3)	8.6(-3)
Be	$2s \rightarrow 2p$	3.61	4.95	5.28	2.5422	1.3750
	$2s \rightarrow 3p$	7.33	7.39	7.46	3.79(-2)	9.01(-3)
	$2s \rightarrow 4p$	8.29	8.31	8.33	2.06(-2)	2.3(-4)
	$2s \rightarrow 5p$	8.69	8.70	8.69	1.08(-2)	8.1(-4)
	$2s \rightarrow 6p$	8.90	8.90	8.90	6.3(-3)	7.5(-4)

<sup>a</sup>Exact values published previously [17].

<sup>b</sup>Hybrid SPA results from Ref. [9], converted to SMA.

<sup>c</sup>He numbers are from Ref. [23] and Be numbers from Ref. [24].

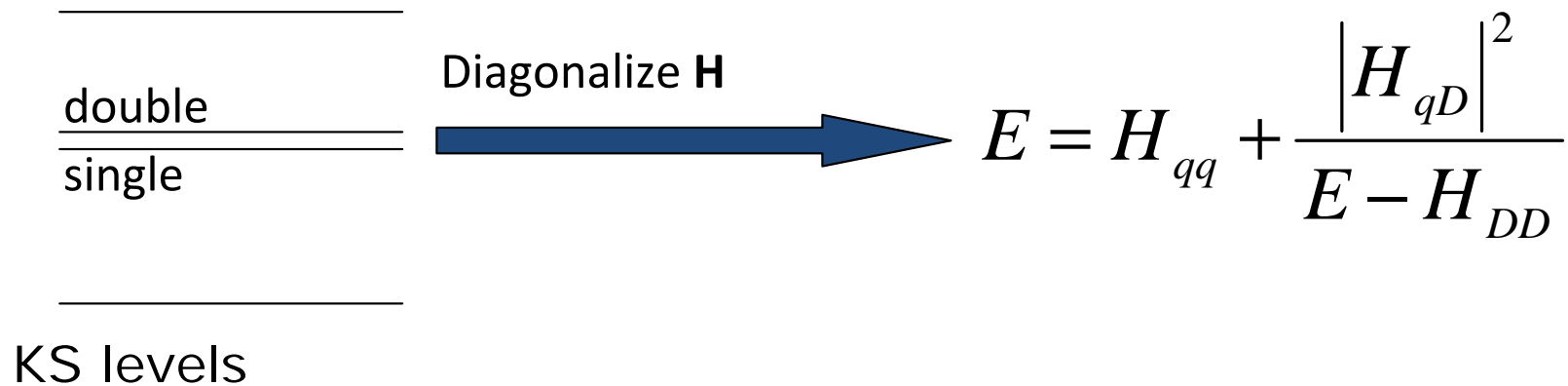
# Double excitations

- Counting argument: Number of excitations = number of singles
- In special case of single + double strongly coupled: Can reverse engineer and solve 2x2 matrix
- Maitra kernel, JCP 04.
- Butadiene and hexatriene with Bob Cave (CPL 04).
- 1d quantum well with Fan Zhang (PRA, 04)

# Recapturing the double excitations

What frequency-dependent is needed in  $f_{HXC}$ ?

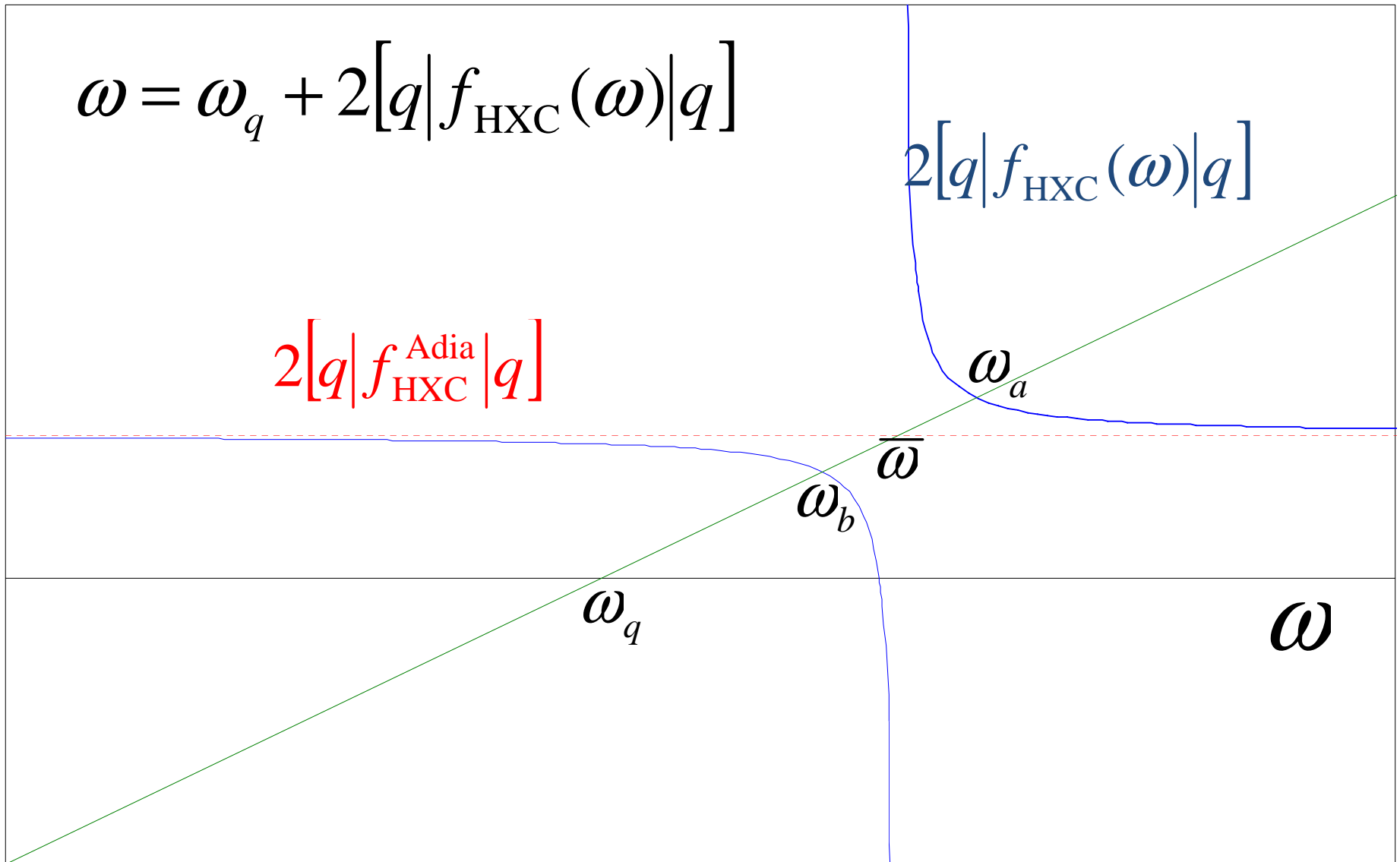
Consider a double excitation, close to a single, and separated from all others



Implement in a dressed SPA

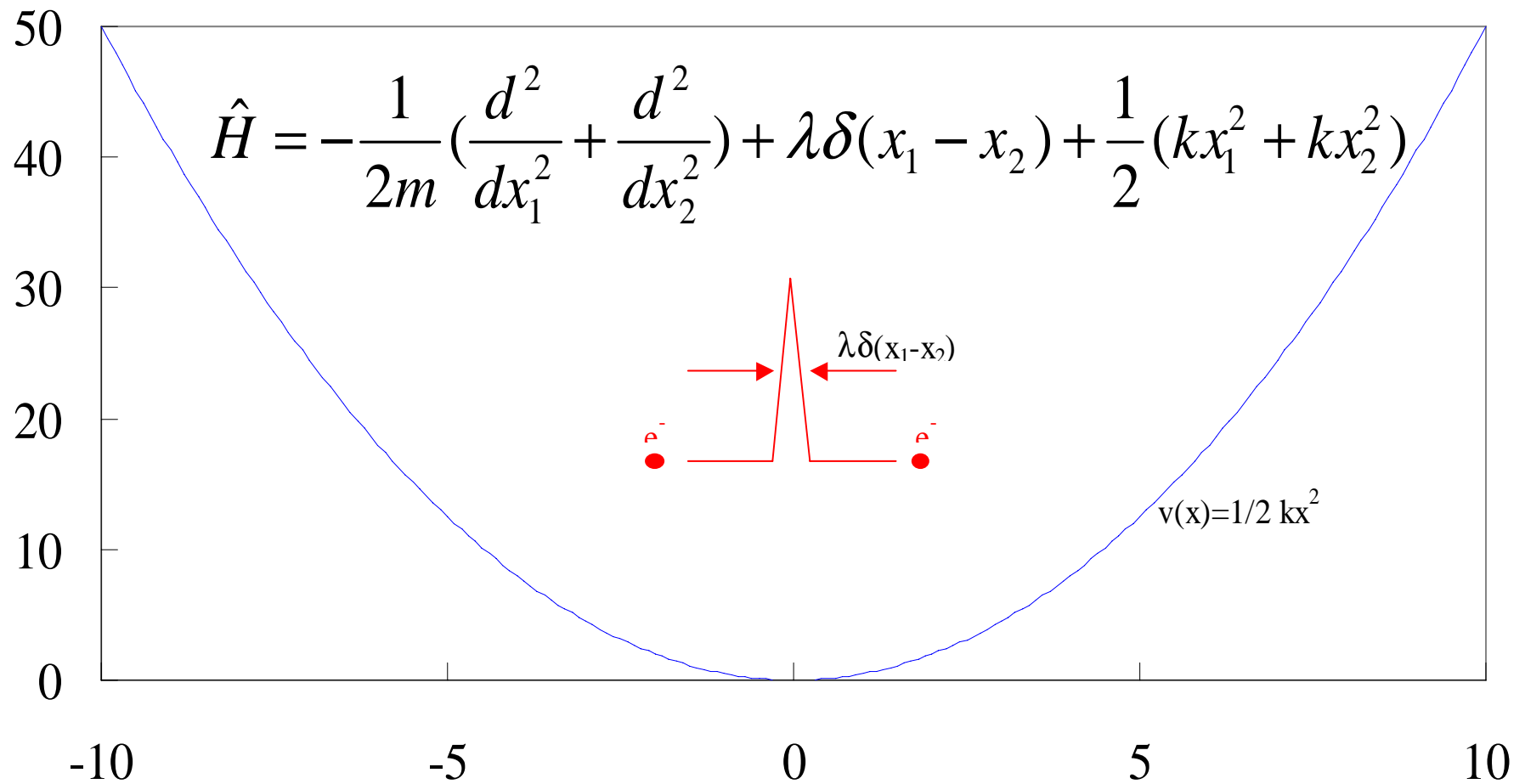
$$2[q|f_{HXC}(\omega)|q] = 2[q|f_{HXC}^{Adia}|q] + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{00})}$$

# Cartoon of missing freq dep

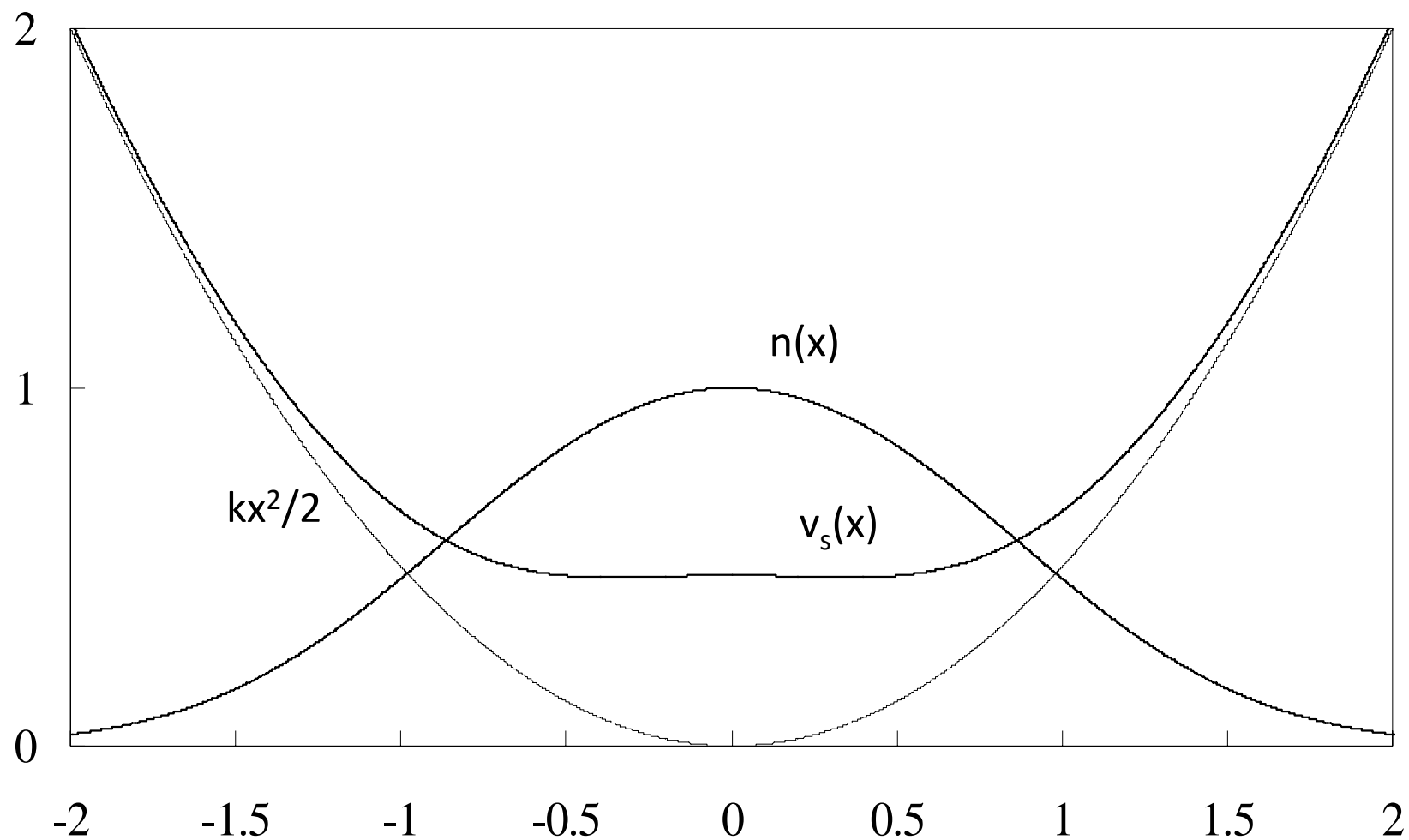


# Example: a toy model

2 Fermions in Harmonic Well

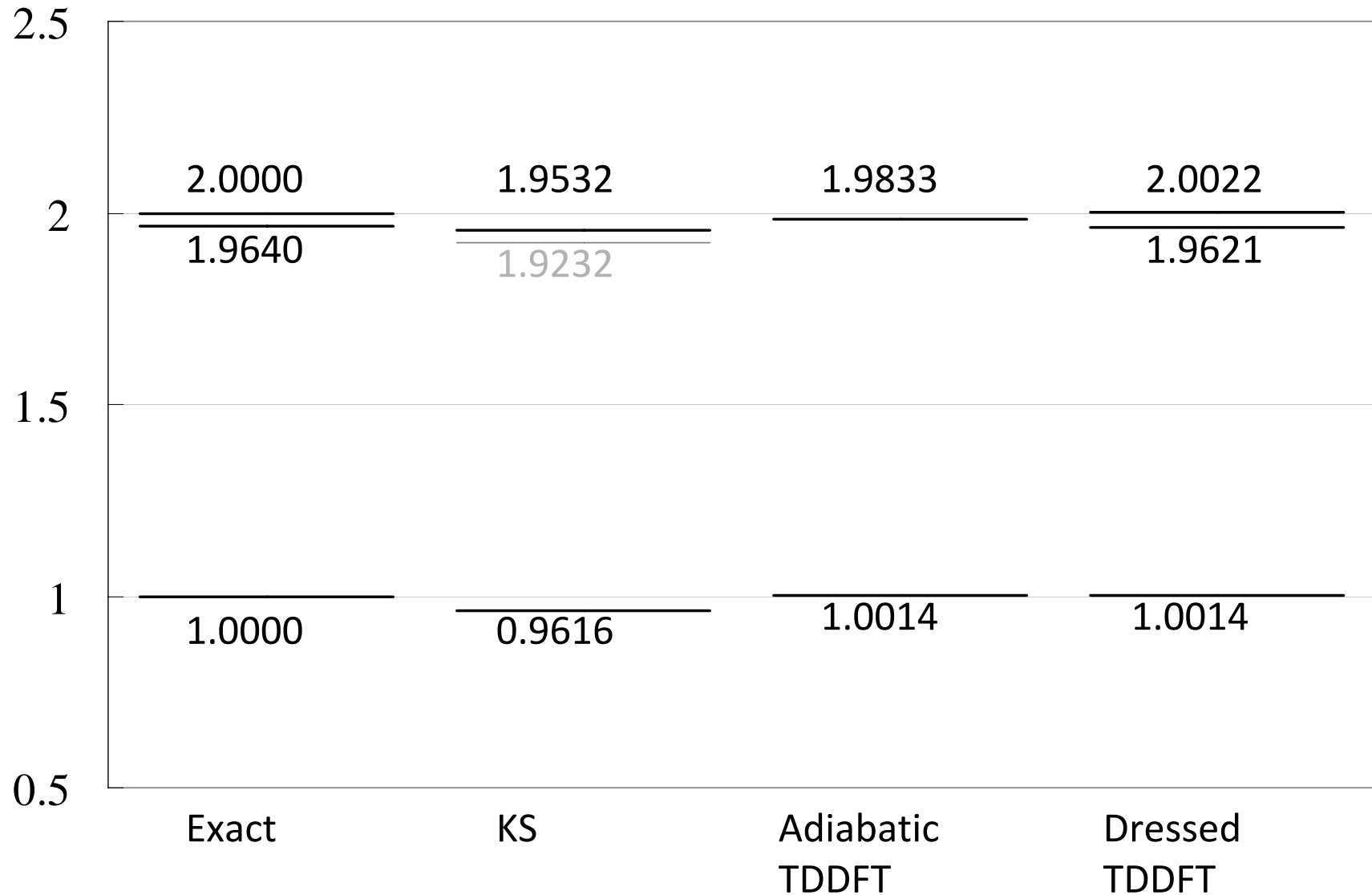


# Exact Kohn-Sham potential

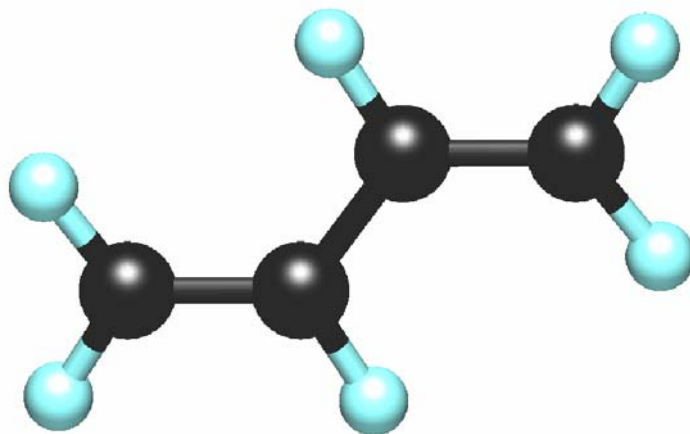
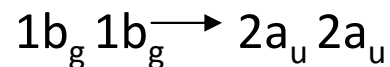
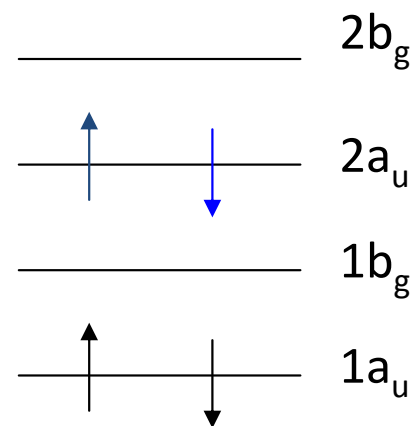
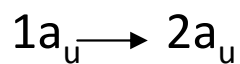
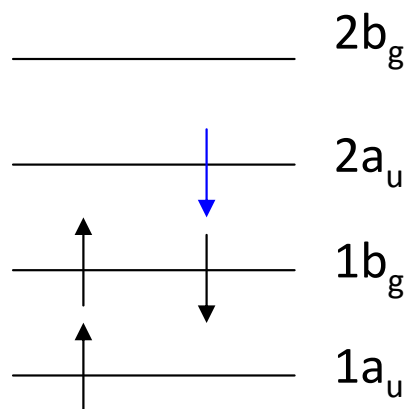
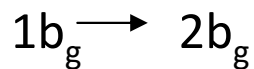
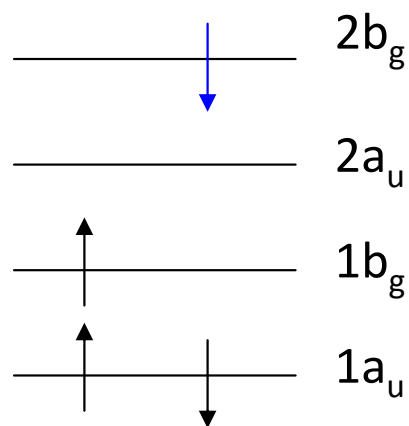


# Results for toy model

## Transition frequencies ( $\lambda=0.2$ )



# Real-life Example: $2^1A_g$ state of butadiene





# Dressed TDDFT equations

The Dressed TDDFT-AB response matrix

$$\begin{pmatrix} A + X_{dress} & B + X_{dress} \\ B + X_{dress} & A + X_{dress} \end{pmatrix}$$

$$X_{dress} = \begin{pmatrix} \frac{|\langle 1b_g \rightarrow 2b_g | H | Double \rangle|^2}{E - E_{double}} & \frac{\langle 1b_g \rightarrow 2b_g | H | Double \rangle \langle Double | H | 1a_u \rightarrow 2a_u \rangle}{E - E_{double}} \\ \frac{\langle 1a_u \rightarrow 2a_u | H | Double \rangle \langle Double | H | 1b_g \rightarrow 2b_g \rangle}{E - E_{double}} & \frac{|\langle 1a_u \rightarrow 2a_u | H | Double \rangle|^2}{E - E_{double}} \end{pmatrix}$$

# Dressed TDDFT results

The Dressed TDDFT-AB response matrix

$$A = \begin{pmatrix} \omega_{a_u} + 2[a_u | f_{HXC} | a_u] & 2[a_u | f_{HXC} | b_g] \\ 2[b_g | f_{HXC} | a_u] & \omega_{b_g} + 2[b_g | f_{HXC} | b_g] \end{pmatrix}$$

$2^1A_g$  Excitation energies

Molecule	Adiabatic TDDFT	Dressed TDDFT	CASPT2
Butadiene	7.22	6.29	6.27
Hexatriene	6.03	5.06	5.20

# X-ray absorption

Measuring the kernel of time-dependent density functional theory with X-ray absorption spectroscopy of 3d transition metals

A. Scherz,\* E.K.U. Gross, H. Appel, C. Sorg, K. Baberschke,<sup>†</sup> and H. Wende  
*Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany.*

K. Burke  
*Department of Chemistry and Chemical Biology,  
Rutgers University, 610 Taylor Rd, Piscataway, NJ 08854  
(Dated: July 5, 2005)*

- Analyze TDDFT results for absorption in bulk transition metals
- Shows novel core-hole interaction.
- PRL 2005.

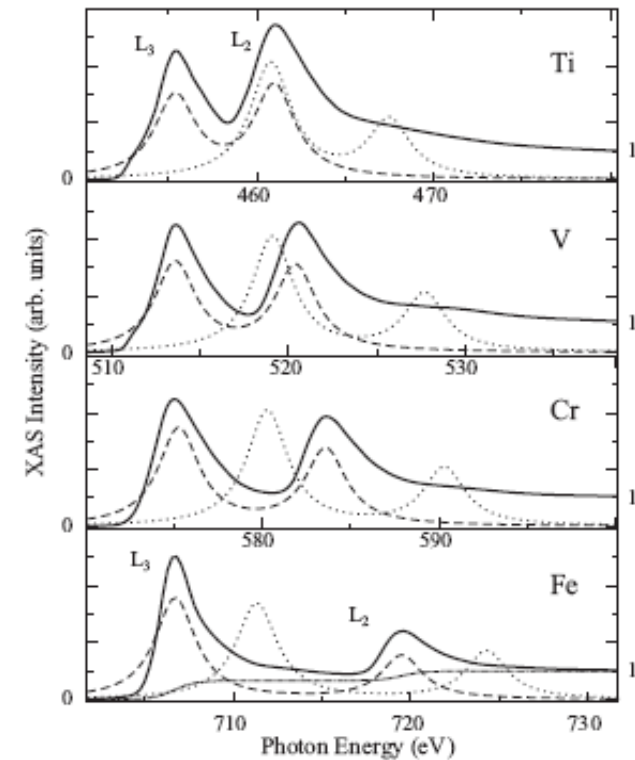
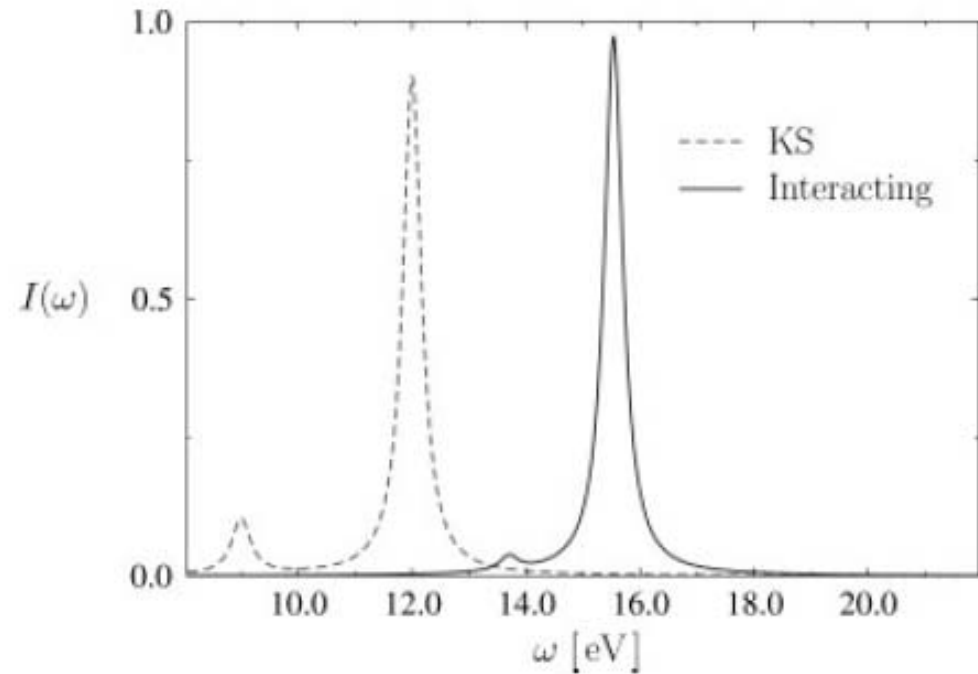


FIG. 2: The experimental isotropic absorption spectra (solid line) at the  $L_{2,3}$  edges are shown for the early 3d TMs Ti, V, and Cr versus Fe. The edge jumps are normalized to unity for direct comparison. The continuum in the experimental spectrum is simulated by a two-step function as shown for Fe (dashed-dotted line). The treatment of the core hole redshifts the independent particle spectrum (dotted line) and changes the statistical branching ratio in the correlated spectrum (dashed line) as revealed by the DPA model.

# Double pole approximation

- Appel, Gross,  
Int J  
Quantum  
Chem 2006.

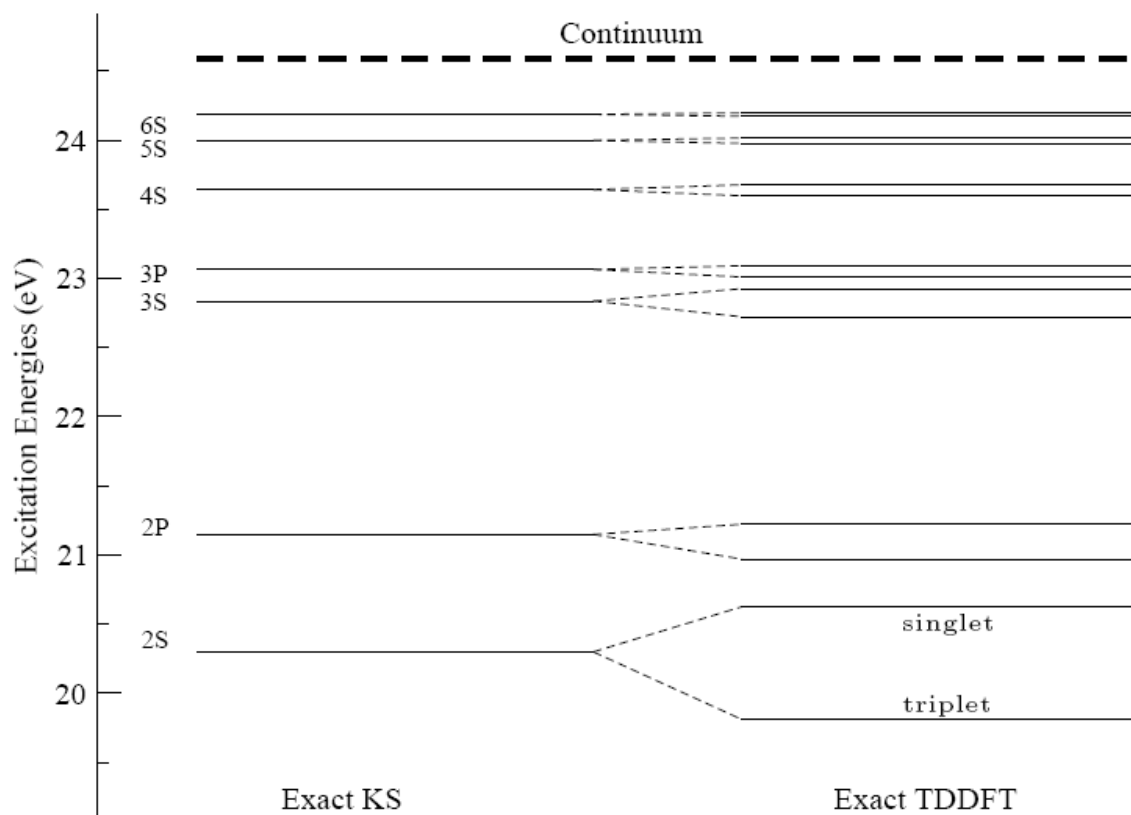


**FIGURE 1.** Interacting and Kohn–Sham spectra as function of frequency ( $\omega_1 = 9$  eV,  $M_{12} = 0.2$  eV).

# *Does TDDFT really work?*

- Given exact ground-state Kohn-Sham potential, what does TDDFT actually give you?
- Does it give you more than RPA?

# How good the KS response is

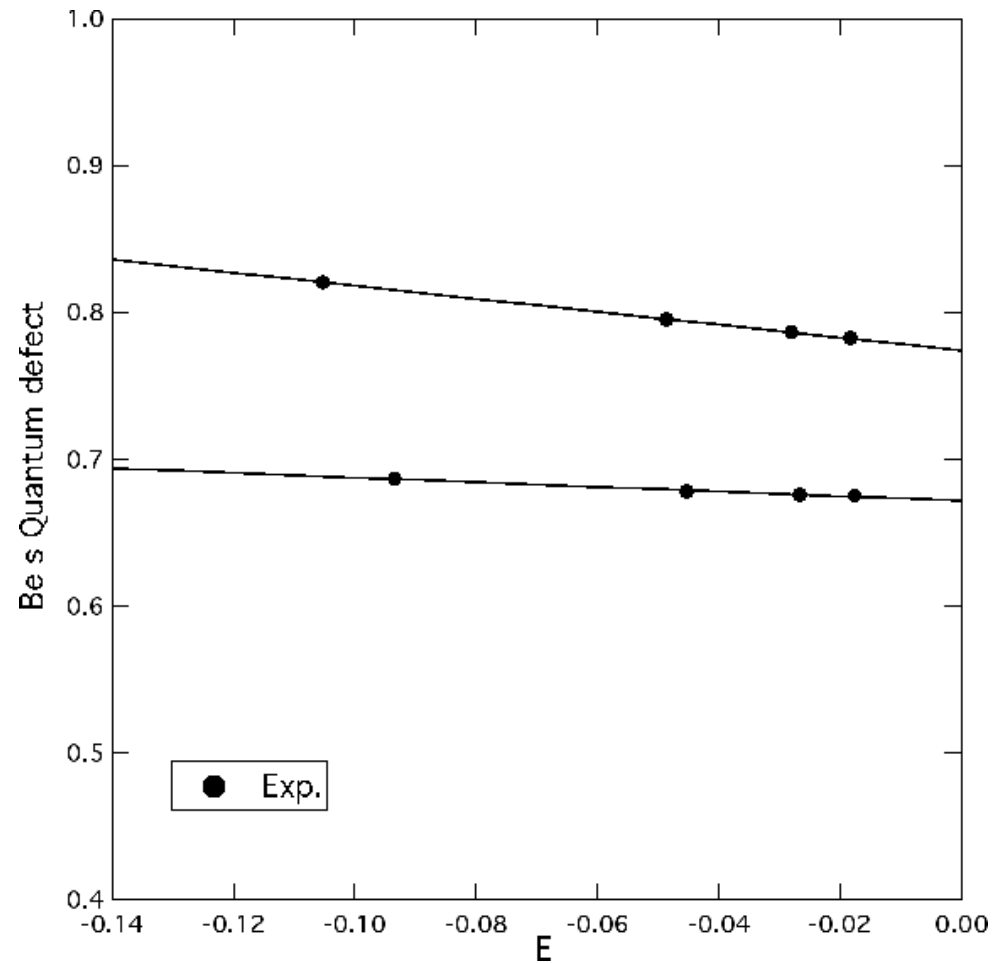


## Quantum defect of Rydberg series

$$\omega_{nl} = I - \frac{1}{2(n - \mu_{nl})^2}$$

- $I$ =ionization potential,  $n$ =principal,  $l$ =angular quantum no.s
- Due to long-ranged Coulomb potential
- Effective one-electron potential decays as  $-1/r$ .
- Absurdly precise test of excitation theory, and very difficult to get right.

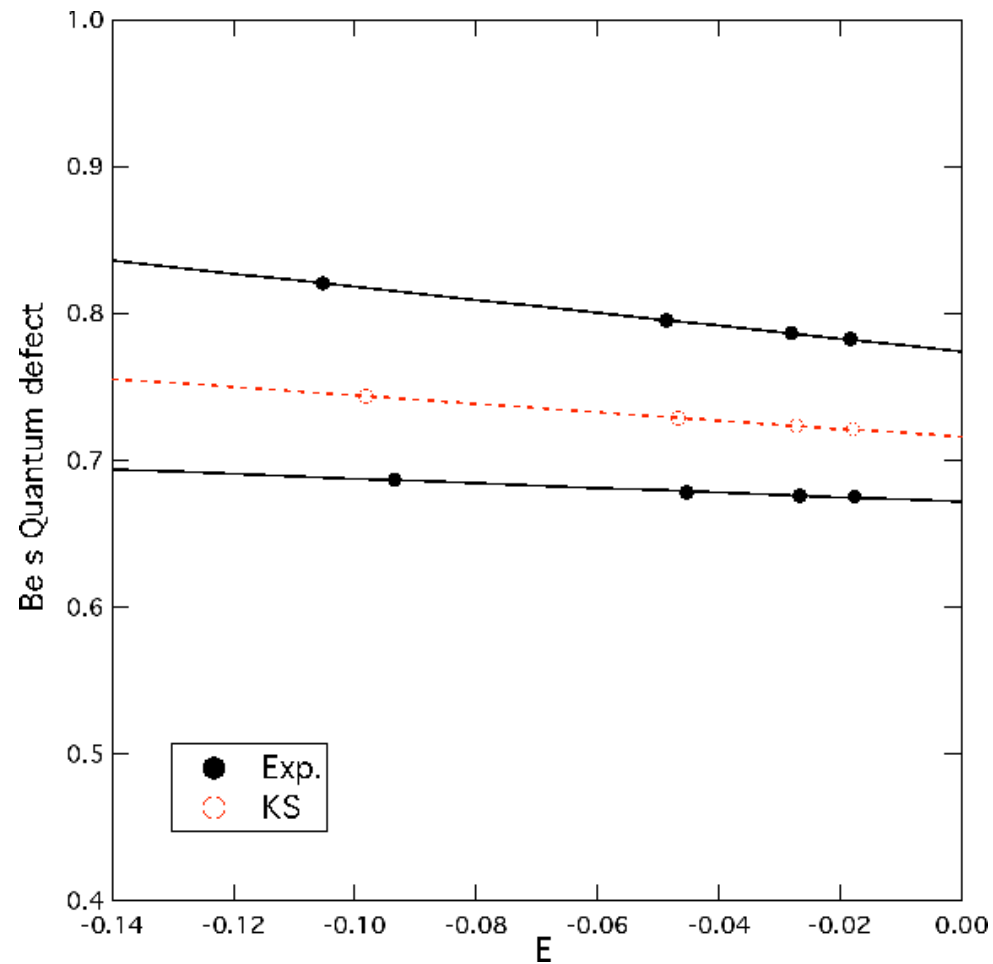
# Be s quantum defect: expt



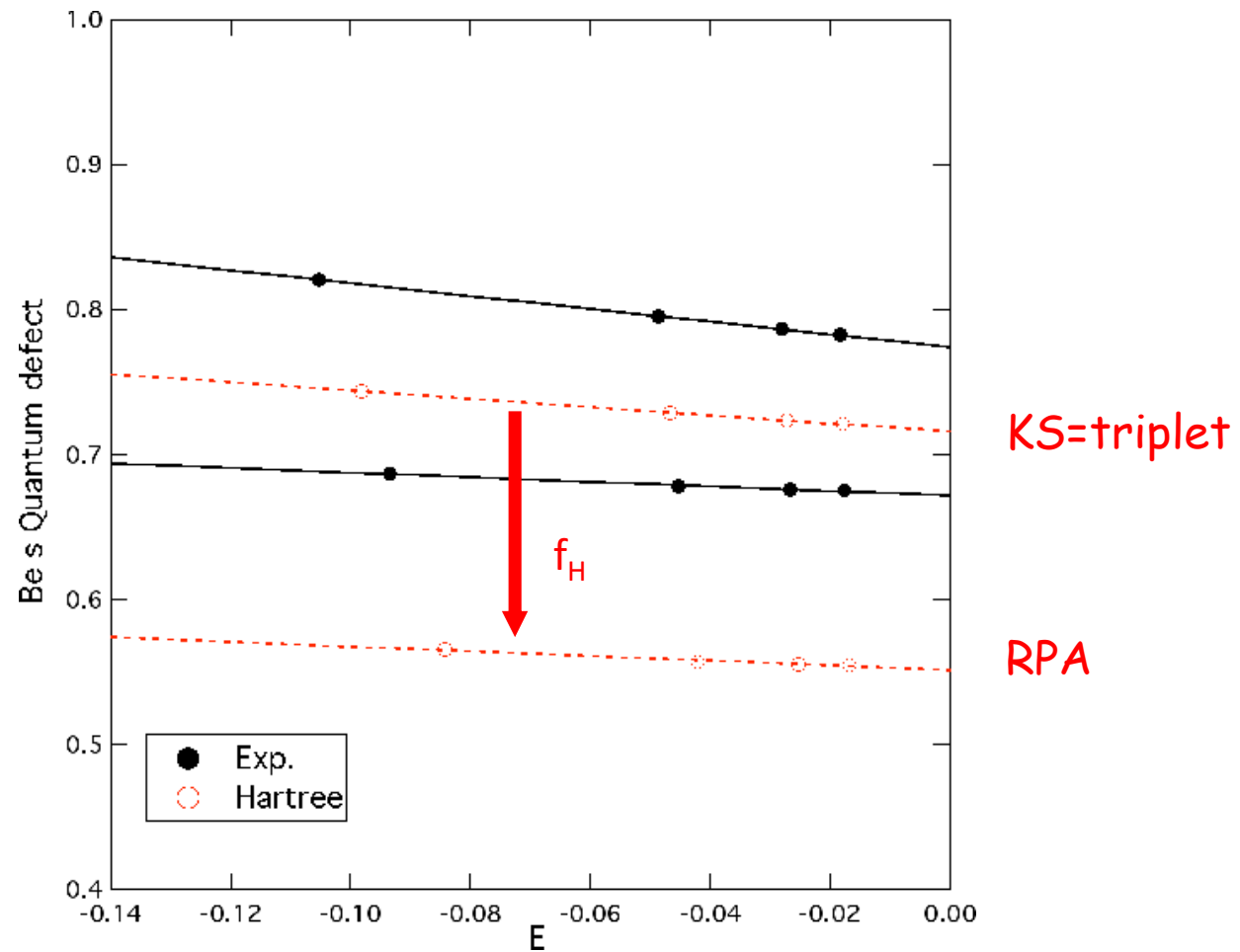
Top: triplet,  
bottom:  
singlet



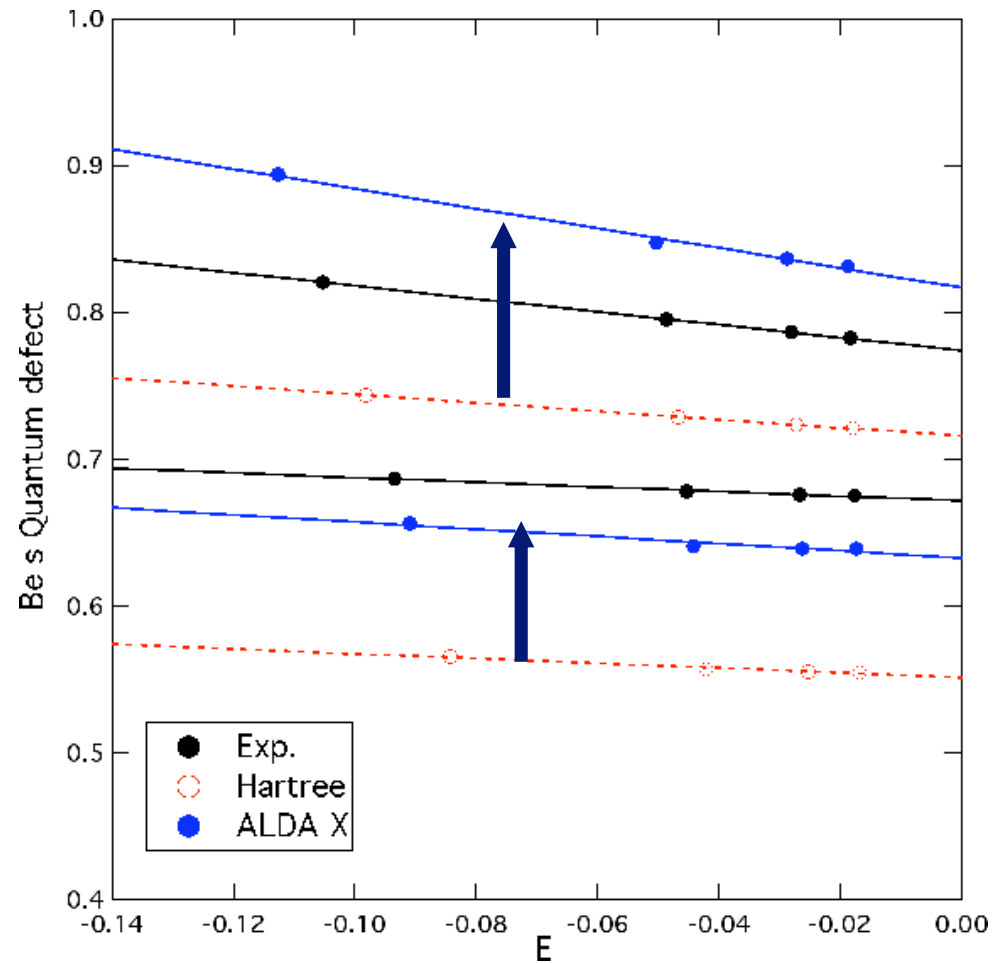
# Be s quantum defect: KS



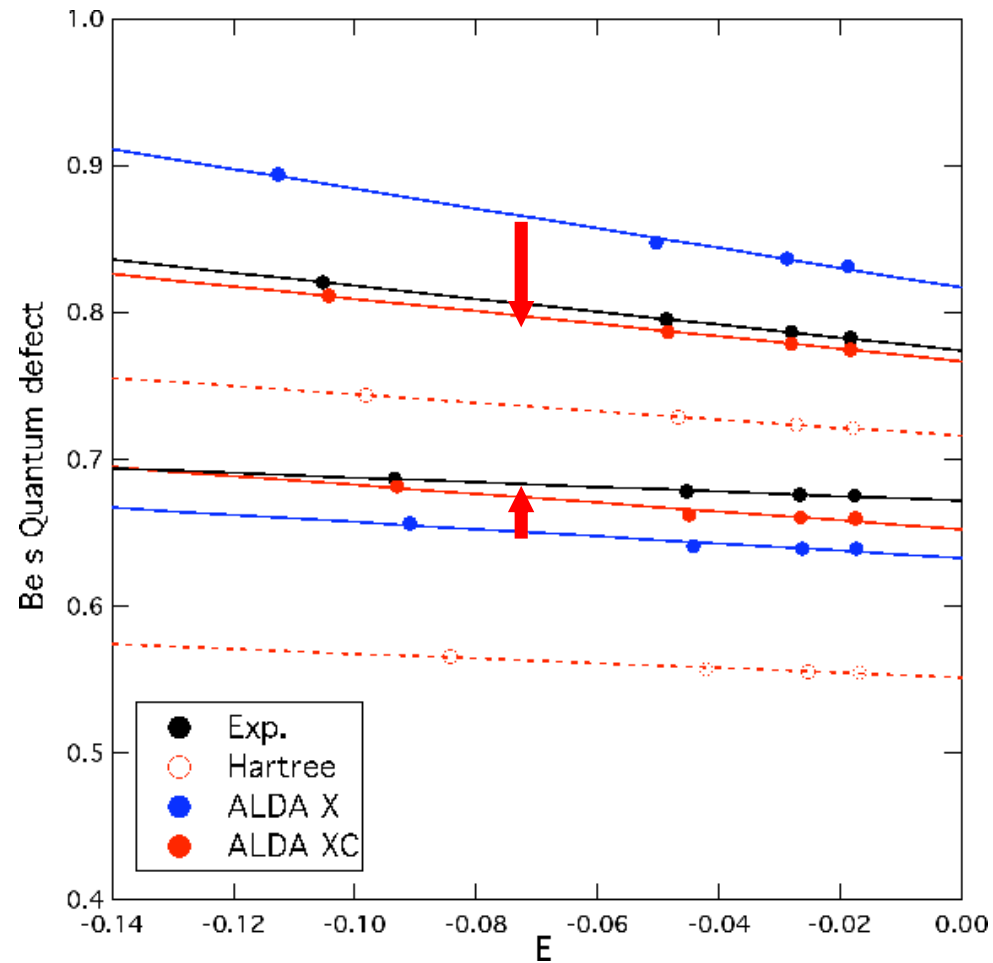
# Be s quantum defect: RPA



# Be s quantum defect: ALDAX



# Be s quantum defect: ALDA



# *Problems with approximate ground-state potential*

- Folklore:
  - Biggest errors come from error in ground-state potential
  - Unbound states are meaningless
  - You cannot get Rydberg series from LDA/GGA/hybrid potentials

# Good oscillator strengths from LDA

- Wasserman and Maitra show how to get accurate oscillator strengths from LDA (PRL 03)

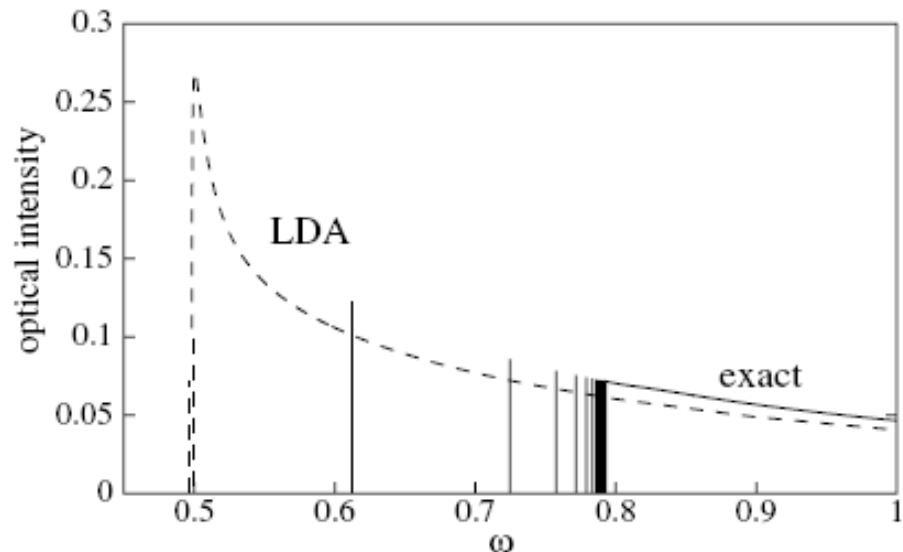


FIG. 1. Oscillator strengths (in inverse Hartrees) for the  $2p \rightarrow ns$  transitions in Ne as a function of photon energy (in Hartrees), from the exact KS potential, and from the LDA one. The discrete spectrum has been multiplied by the density-of-states factor (see text).

# More about LDA osc str

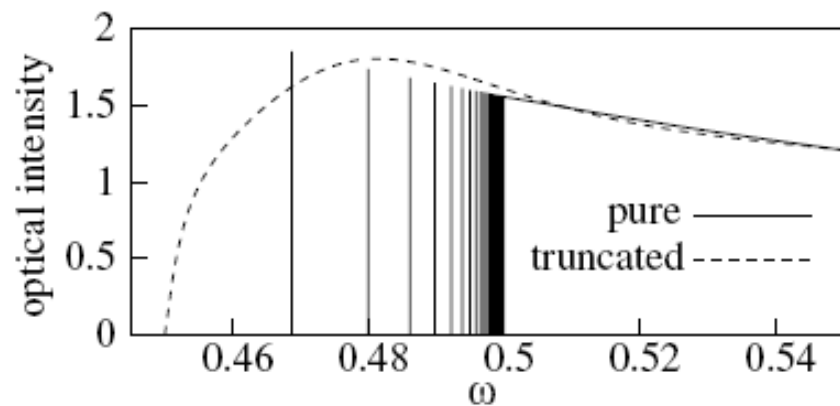


FIG. 2. Oscillator strengths (in inverse Hartrees) corresponding to  $1s \rightarrow np$  transitions (only shown for  $n \geq 4$ ) for a pure Coulomb and the truncated-Coulomb potential given by Eq. (1) with  $1/C = 20$ .

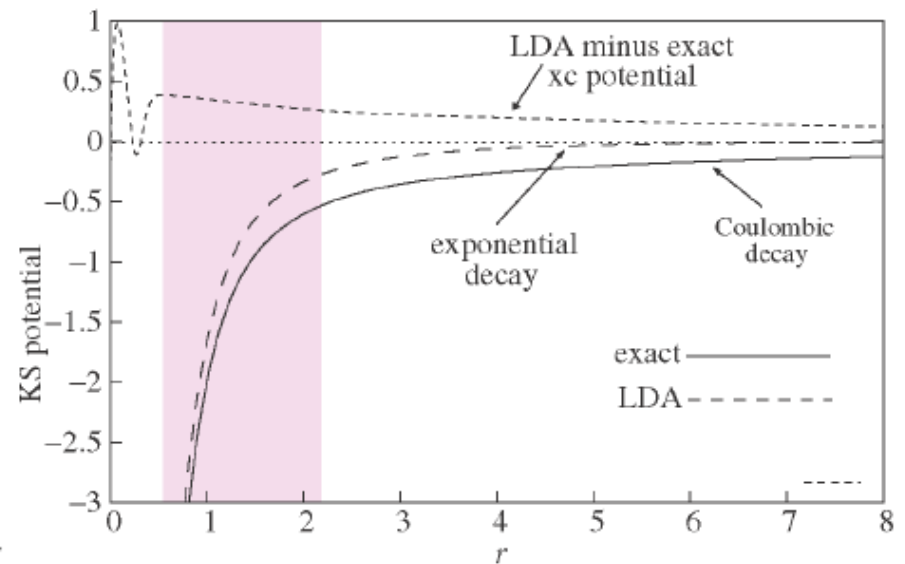


FIG. 3 (color online). Ne atom: the top curve shows the difference between the LDA and exact XC potential. The bottom curves show  $v_s^{\text{exact}}$  and  $v_s^{\text{LDA}}$ . In the valence region (shaded) the two potentials run almost parallel.

# Rydberg series in He atom

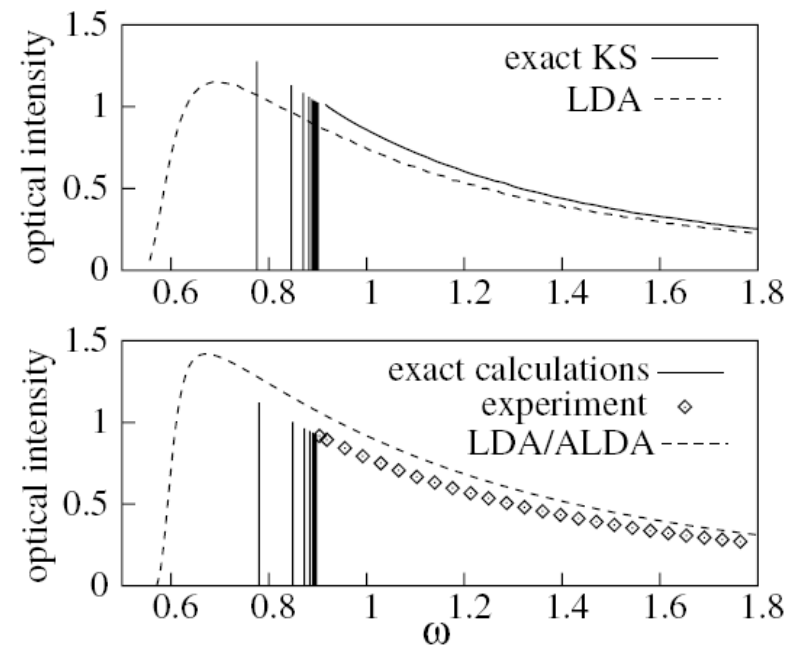


FIG. 6. He atom: The top panel shows the bare exact KS and LDA spectra, and the lower panel shows the TDDFT corrected spectra, LDA/ALDA results are from [29] but unshifted; the exact calculations are from [30], multiplied by the density of states factor (see text), and the experimental results are from [31]



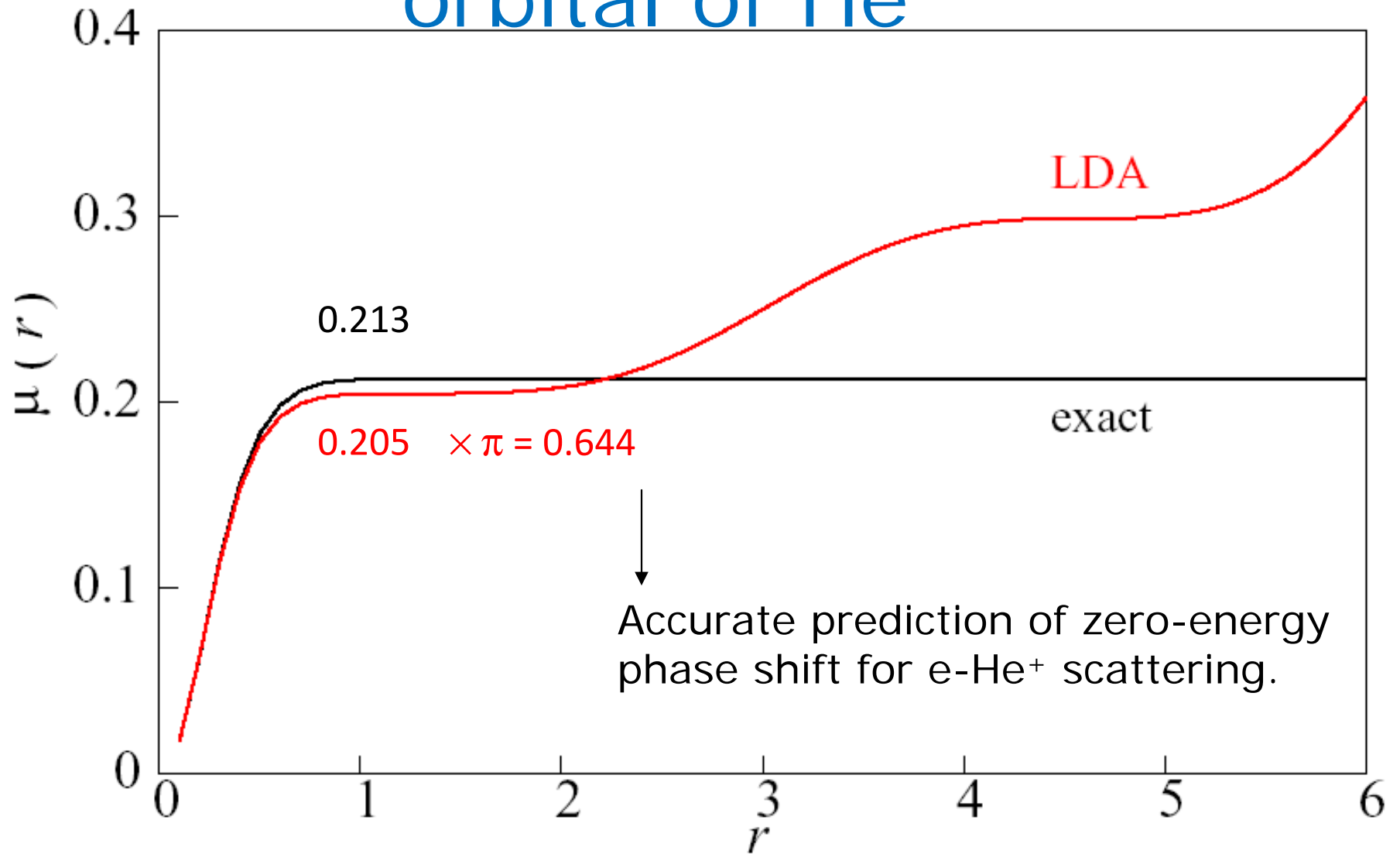
# Truncation tricks II

- Wasserman shows how to get accurate Rydberg transition frequencies from LDA potentials (PRL 05)

$$\frac{d \ln \phi_{>r_0}}{dr} = \frac{1}{n^*} - \frac{n^*}{r} - \frac{1}{r} \frac{U(-n^*; 2; 2r/n^*)}{U(1 - n^*; 2; 2r/n^*)}. \quad (3)$$

Here  $k$  was written as  $k = (n^*)^{-1}$ , with  $n^* = (n - \mu_n)$ ,

# QDE applied to LDA scattering orbital of He



# Rydberg series of LDA in Ne

TABLE I: Transition frequencies (in eV) for the first six discrete  $2p \rightarrow ns$  transitions in Ne, from the exact and LDA KS potentials.

trans.	transition frequency	
	LDA	exact
$2p \rightarrow 3s$	16.468	16.604
$2p \rightarrow 4s$	19.603	19.666
$2p \rightarrow 5s$	20.534	20.561
$2p \rightarrow 6s$	20.931	20.945
$2p \rightarrow 7s$	21.135	21.143
$2p \rightarrow 8s$	21.255	21.260

From Wasserman and KB, PRL 05.

# *Electron scattering from TDDFT*

- Huge interest in low energy scattering from biomolecules, since resonances can lead to cleavage of DNA
- Traditional methods cannot go beyond 13 atoms
- Can we use TDDFT? Yes!

# Review of scattering work

PERSPECTIVE

www.rsc.org/pccp | Physical Chemistry Chemical Physics

## Time-dependent density functional theory of high excitations: to infinity, and beyond<sup>†</sup>

Meta van Faassen<sup>\*a</sup> and Kieron Burke<sup>b</sup>

*Received 22nd January 2009, Accepted 17th February 2009*

*First published as an Advance Article on the web 13th March 2009*

DOI: 10.1039/b901402k

We review the theoretical background for obtaining both quantum defects and scattering phase shifts from time-dependent density functional theory. The quantum defect on the negative energy side of the spectrum and the phase shift on the positive energy side merge continuously at  $E = 0$ , allowing both to be found by the same method. We illustrate with simple, one-dimensional examples: the spherical well and the delta well potential. As an example of a real system, we study in detail elastic electron scattering from the  $\text{He}^+$  ion. We show how the results are influenced by different approximations to the unknown components in (time-dependent) density functional theory: the ground state exchange–correlation potential and time-dependent kernel. We also revisit our previously obtained results for  $e\text{-H}$  scattering. Our results are remarkably accurate in many cases, but fail qualitatively in others.

# Simple scheme for spherical case

- Eg e- scattering from H.
- Put H- into spherical box, and consider  $E > 0$  states.
- Old formula due to Fano (1935):

$$\delta_{\alpha} = -k_{\alpha} R_b + \alpha\pi \quad (l = 0)$$

- Exact for any  $R_b$  beyond potential.

# Is KS a good starting place?

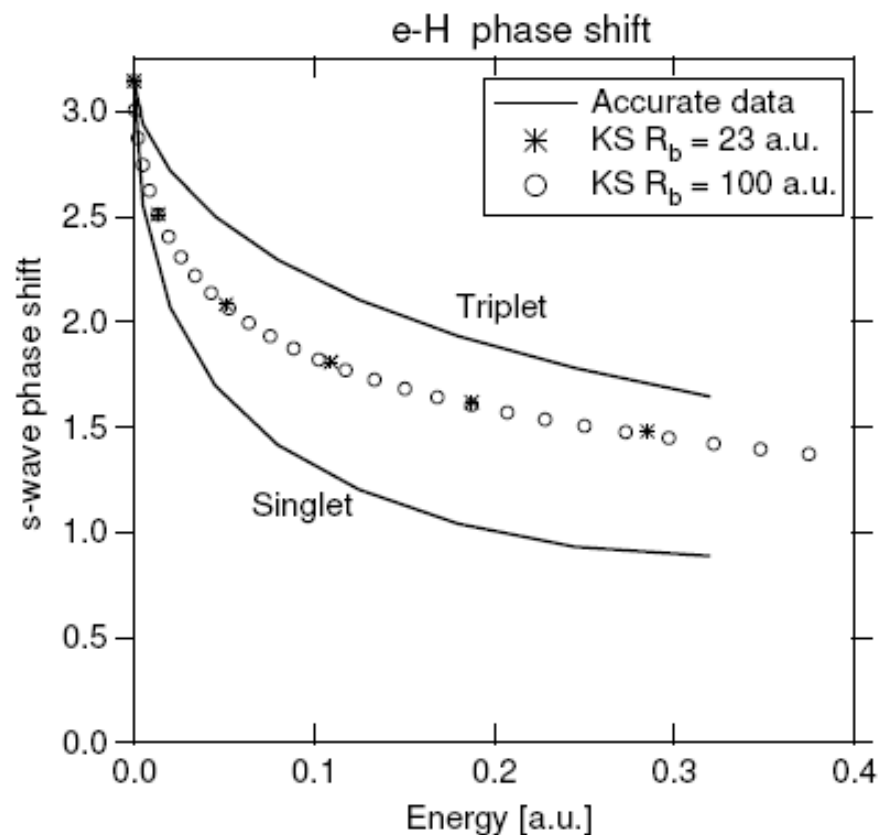


FIG. 1: Accurate quantum chemical singlet and triplet s-phase shifts [19], together with the KS values, calculated with a wall at 15 a.u. and at 100 a.u..

# Is the LDA potential good enough?

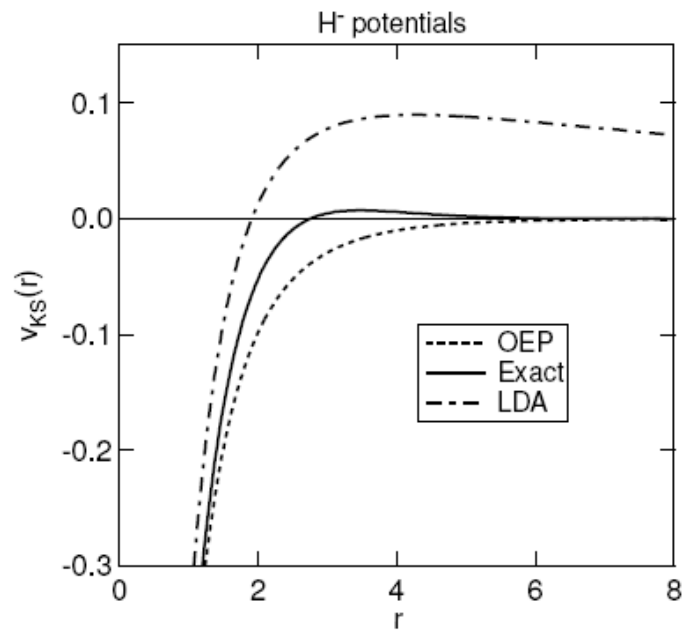
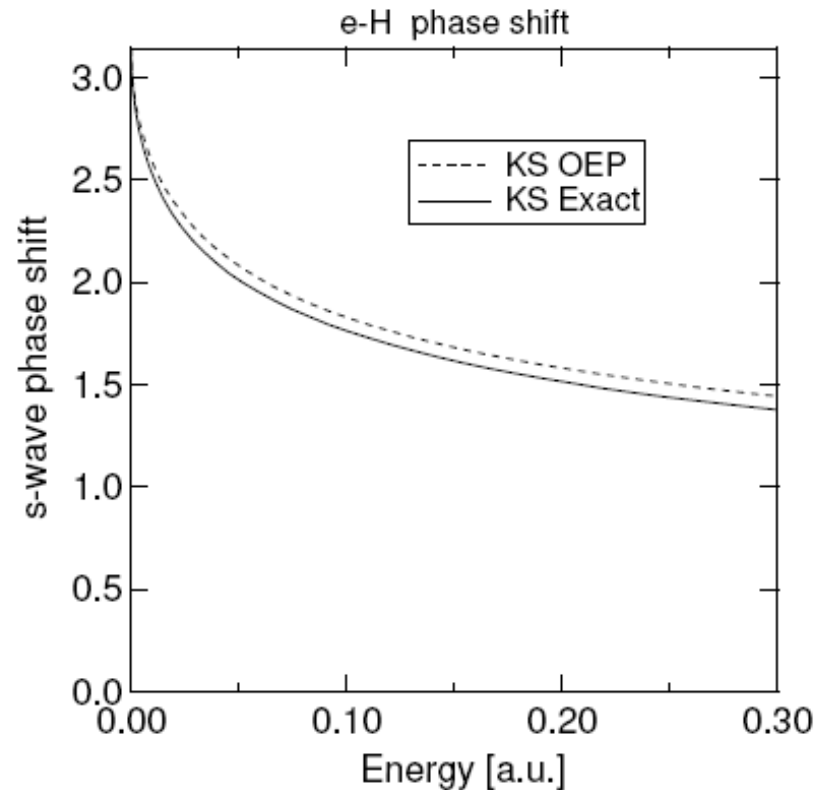


FIG. 2: The exact, exact-exchange, and LDA KS-potentials for  $H^-$ .





# TDDFT corrections

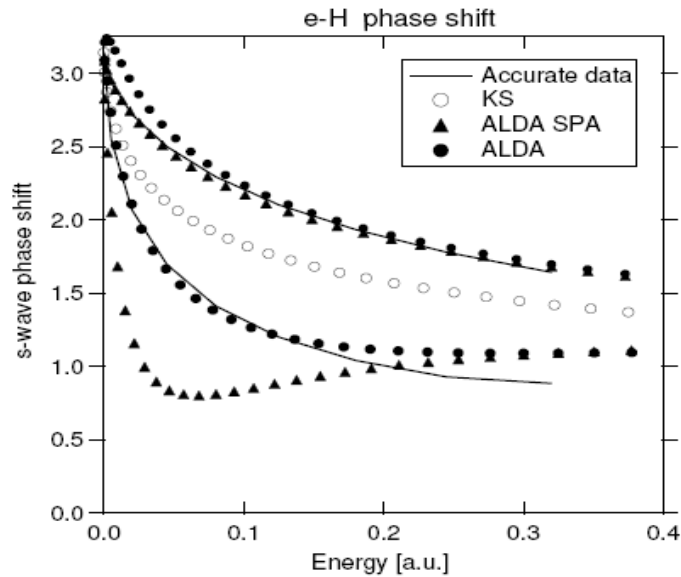


FIG. 4: Singlet and triplet TDDFT curves from an SPA and full ALDA calculation, together with the KS values and accurate quantum chemical data from Ref. [19]. The ground state KS potential is exact-exchange. The wall location in all calculations is at 100 a.u.

$$k^{2l+1} \cot \delta_l(k) \Big|_{k \rightarrow 0} = -\frac{1}{a_l} + \frac{1}{2} r_{el} k^2 + O(k^4)$$

TABLE I: TDDFT scattering lengths.

	Singlet $a$	Triplet $a$
Accurate data <sup>a</sup>	5.97	1.77
ALDA SPA	9.7	1.8
ALDA	5.6	2.0 <sup>b</sup>

<sup>a</sup>Accurate variational calculations from [19]

<sup>b</sup>This is the value as obtained from our tangent approximation as explained in the text

# Summary

- Finite systems good for establishing principles.
- Much to understand of a single-body nature.
- Scattering important inside solids
- Thanks to NSF and all students.