

# Theoretical Spectroscopy and Electronic Excitations

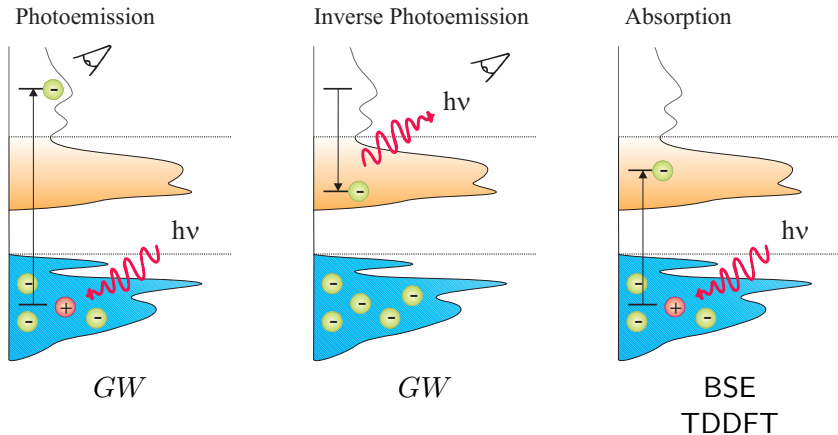
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Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

FHI Hands-On Workshop – Tutorial 6



# Band structures: photo-electron spectroscopy

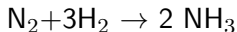


# In this tutorial

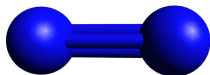
## Theoretical spectroscopy of N<sub>2</sub> (and H<sub>2</sub>O)

### Nitrogen:

- 78% of the earth's atmosphere
- strong triple bond
- ammonia (NH<sub>3</sub>) synthesis



- ▶ essential for production of fertilizers
- ▶ Nobel Prize for Fritz Haber in 1918



Haber, F.

# Photo-Electron Excitation Energies

## ● Photoemission

- ▶ electron removal

$$\psi_s(\mathbf{r}) = \langle N - 1, s | \hat{\psi}(\mathbf{r}) | N \rangle$$

- ▶ removal energy

$$\epsilon_s = E(N) - E(N - 1, s)$$

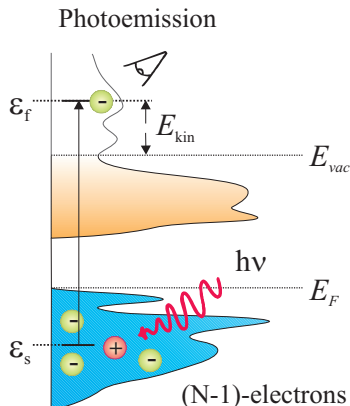
## ● Inverse Photoemission

- ▶ electron addition

$$\psi_s(\mathbf{r}) = \langle N | \hat{\psi}(\mathbf{r}) | N + 1, s \rangle$$

- ▶ addition energy

$$\epsilon_s = E(N + 1, s) - E(N)$$



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$ N\rangle$	:	$N$ -particle ground state
$ N - 1, s\rangle$	:	$(N - 1)$ -particle excited state $s$
$E(N, s)$	:	total energy in state $s$

# Ionisation Potential, Electron Affinity and (Band) Gaps

Could use total energy method to compute

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

Ionisation potential: *minimal energy to remove an electron*

$$I = E(N - 1) - E(N)$$

*Electron affinity: minimal energy to add an electron*

$$A = E(N) - E(N + 1)$$

*(Band) gap:  $E_{gap} = I - A$*

# Ionisation Potential, Electron Affinity and (Band) Gaps

Exercise:

- use HF and DFT-PBE total energies to compute  $I$  and  $A$  of  $N_2$

This procedure is often called  $\Delta$ SCF  
(difference of two self-consistent field calculations)

# $\Delta$ SCF versus eigenvalues

Hartree-Fock:

Koopmans' theorem: (Physica 1, 104 (1934))

$$E^*(N \pm 1, s) - E(N) = -\epsilon_s^{\text{HF}}$$

where the same orbitals are used in calculating  $E^*$  and  $E$   
(frozen orbitals)

but:

- orbital relaxations can be important
- correlations absent from HF

# $\Delta$ SCF versus eigenvalues

Density-functional theory:

- in exact KS-DFT: *ionization potential given by KS eigenvalue of highest occupied state*

$$I_{\text{KS}} = -\epsilon_N(N)$$

- otherwise **Janak's theorem**: (PRA 18, 7165 (1978)))

$$\frac{\partial E}{\partial n_s} = \epsilon_s$$

rearranging and making mid point approximation:

$$E(N + 1, s) - E(N) = \int_0^1 dn \epsilon_s(n) \approx \epsilon_s(0.5)$$

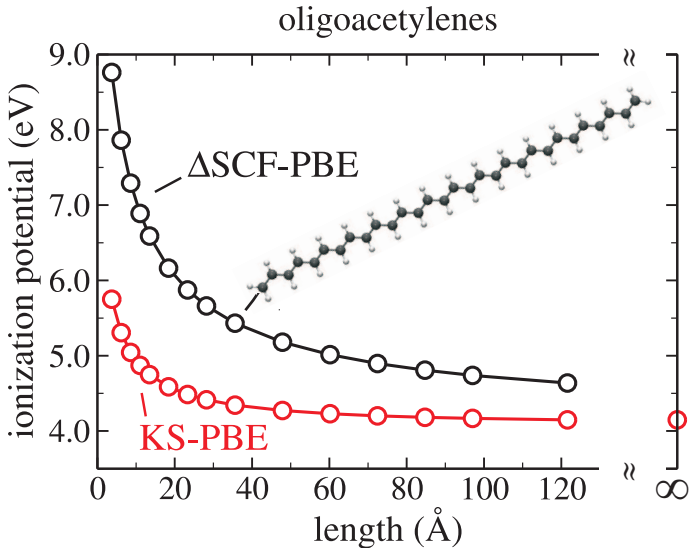


# $\Delta$ SCF versus eigenvalues

Exercise:

- calculate  $I$  and  $A$  of  $N_2$  using HF and DFT-PBE eigenvalues

# $\Delta$ SCF versus eigenvalues for finite systems



data courtesy of Max Pinheiro

# Single Particle Green's Functions

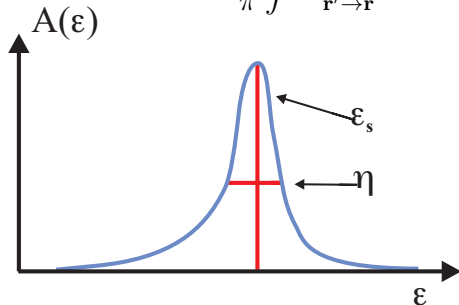
- Lehmann representation of single particle Green's function  $G$ :

$$G(\mathbf{r}, \mathbf{r}'; \epsilon) = \lim_{\eta \rightarrow 0^+} \sum_s \frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\epsilon - (\epsilon_s + i\eta \operatorname{sgn}(E_f - \epsilon_s))}$$

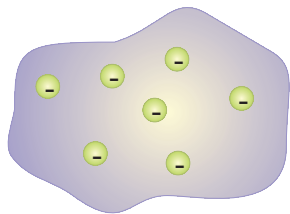
Excitation energies are poles of the Green's function!

- spectroscopically relevant quantity: spectral function  $A$ :

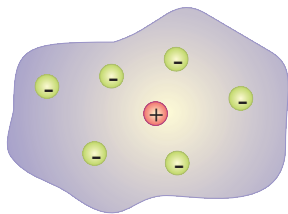
$$A(\epsilon) = -\frac{1}{\pi} \int d\mathbf{r} \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \operatorname{Im} G(\mathbf{r}, \mathbf{r}'; \epsilon)$$



# $\Delta$ SCF - the infinite time limit

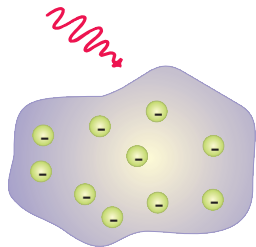


N electrons

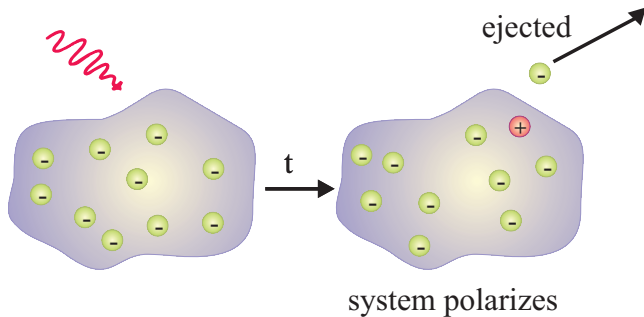


N-1 electrons

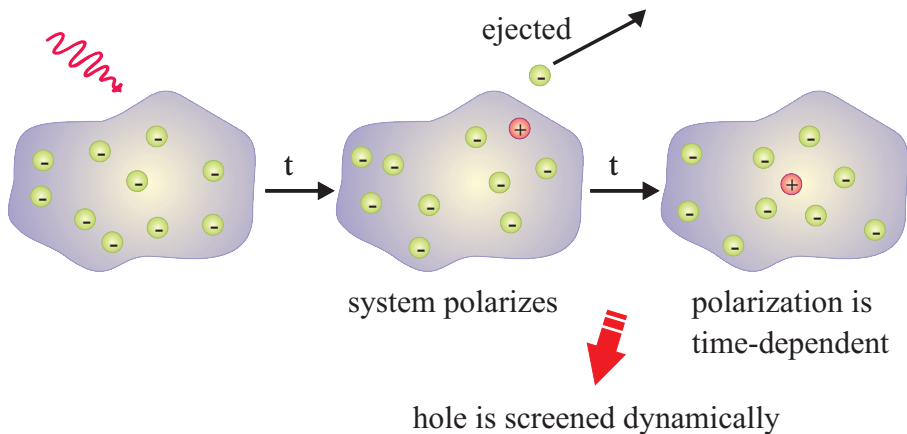
# Green's function and screening



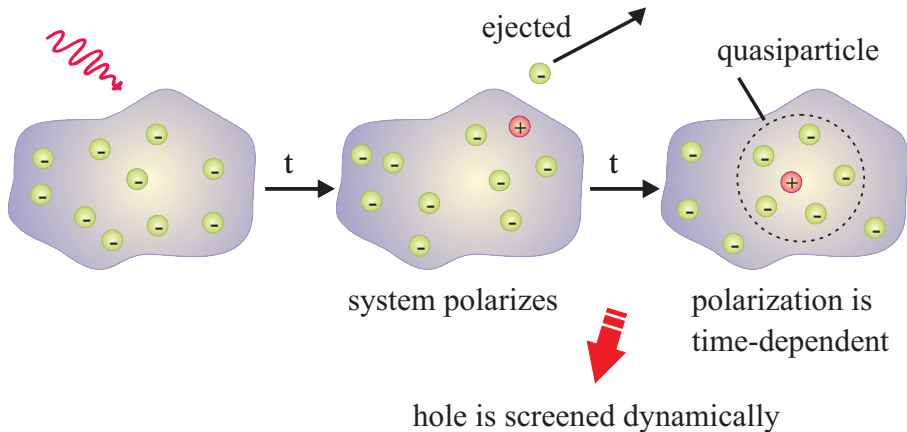
# Green's function and screening



# Green's function and screening

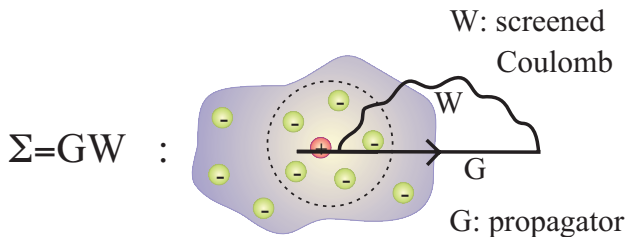


# Green's function and screening





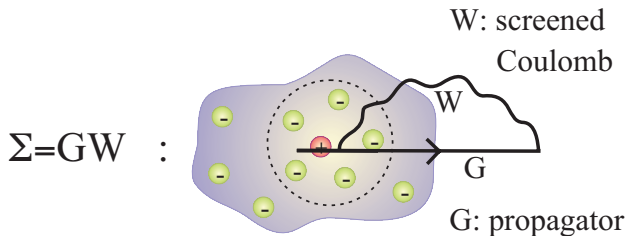
# GW Approximation - Screened Electrons



## Self-Energy

$$\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \omega) = -\frac{i}{2\pi} \int d\omega' e^{i\omega\eta} G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega')$$

# GW Approximation - Screened Electrons



Self-Energy:  $\Sigma = \Sigma_x + \Sigma_c$

- $\Sigma_x = iGv$ :
  - ▶ exact (Hartree-Fock) exchange
- $\Sigma_c = iG(W - v)$ :
  - ▶ correlation (screening due to other electrons)

# GW – The Issue of Self-Consistency

Hedin's  $GW$  equations:

$$G(1, 2) = G_0(1, 2) \quad \text{notation: } 1 = (\mathbf{r}_1, \sigma_1, t_1)$$

$$\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3)$$

$$P(1, 2) = -iG(1, 2)G(2, 1^+)$$

$$W(1, 2) = v(1, 2) + \int v(1, 3)P(3, 4)W(4, 2)d(3, 4)$$

$$\Sigma(1, 2) = iG(1, 2)W(2, 1)$$

# $G_0W_0$ quasiparticle energy corrections

- Quasiparticle equation:

$$\hat{h}_0(\mathbf{r})\psi_s(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_s^{qp})\psi_s(\mathbf{r}') = \epsilon_s^{qp}\psi_s(\mathbf{r})$$

- 1 solve for quasiparticle energies  $\epsilon_s^{qp}$  and wavefunctions  $\psi_s(\mathbf{r})$

- 2 perturbation theory:  $\psi_s(\mathbf{r}) = \phi_s^{\text{KS}}(\mathbf{r})$

$$\Rightarrow \epsilon_s^{qp} = \epsilon_s^{\text{KS}} + \langle s | \Sigma(\epsilon_s^{qp}) | s \rangle - \langle s | v_{xc} | s \rangle$$

Exercise:

- calculate the quasiparticle excitations of  $N_2$  in  $G_0W_0$  starting from
  - ▶ DFT-PBE
  - ▶ HF
  - ▶ DFT-PBE0

# GW – The Issue of Self-Consistency

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$$\Sigma(1,2) = iG(1,2)W(2,1)$$

Dyson's equation:

$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

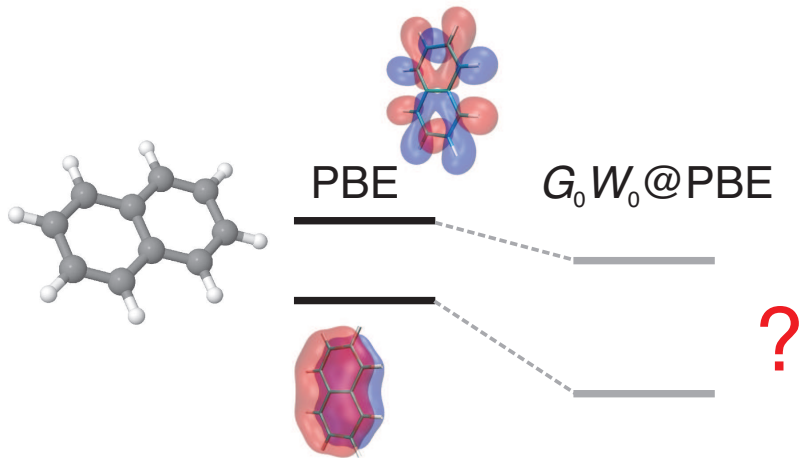
self-  
consistency

self-  
consistency

Exercise:

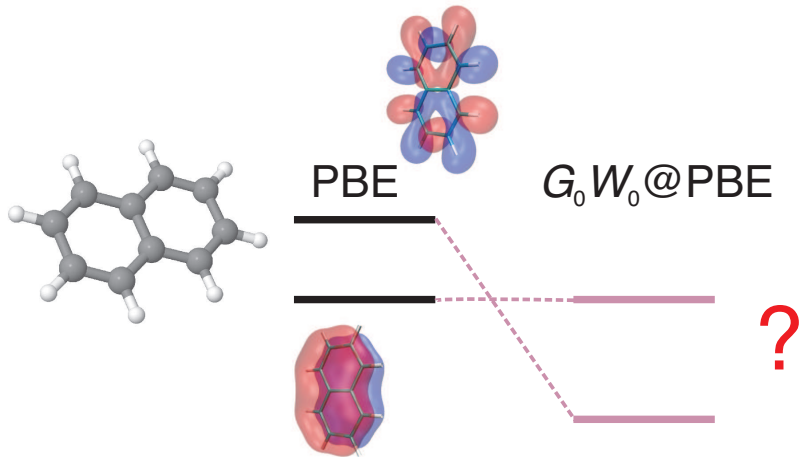
- calculate the quasiparticle spectrum of  $N_2$  in scGW
- extract  $I$  and  $A$  from the spectrum

# Naphtalene and the self-interaction error

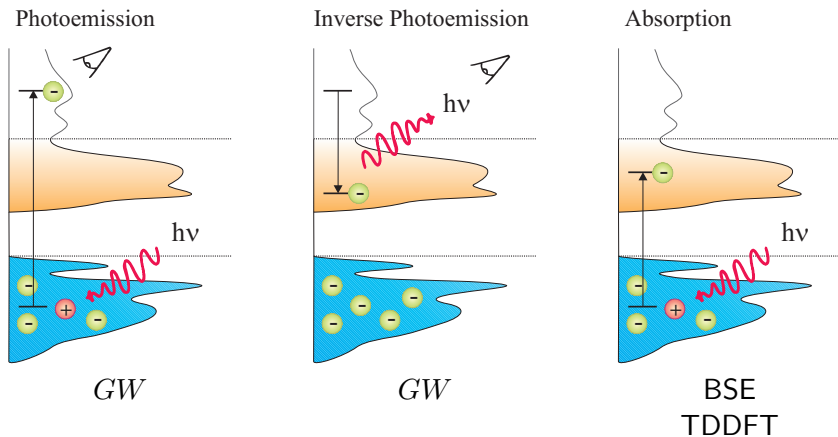




# Naphtalene and the self-interaction error



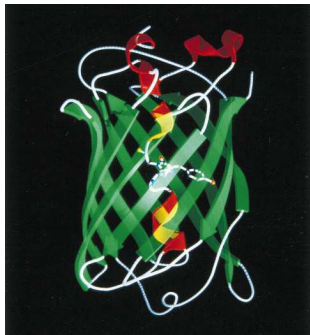
# Absorption spectroscopy



# Green fluorescent protein

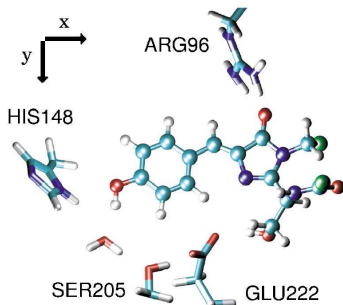
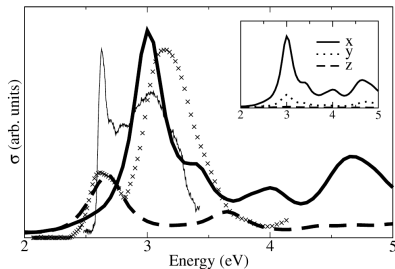


Aequorea victoria - crystal jelly



Ribbon diagram of the Green fluorescent protein (PNAS, 94, 2306 (1997)).

# Green fluorescent protein



TDDFT photoabsorption spectrum of neutral (thick solid line) and anionic (thick dashed line) green fluorescent protein chromophores (Marques, et. al., PRL, 90, 258101 (2003).)

# Photoabsorption cross section

- Frequency dependent polarizability

$$\alpha_{ij}(\omega) = -\frac{2}{E} \int \rho_1^{(i)}(\mathbf{r}, \omega) r_j d^3r \quad i, j = x, y, z$$

- Photoabsorption cross section

$$\sigma_{ij} = \frac{4\pi\omega}{c} \Im \alpha_{ij}(\omega)$$

- Van der Waals  $C_6$  coefficients from Casimir Polder formula

$$C_6(A, B) = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega) \alpha_B(i\omega) d\omega$$

# Standard linear response formalism

- Exact many-body eigenstates

$$\hat{H}(t = t_0)|m\rangle = E_m|m\rangle$$

- Lehmann representation of linear response function:

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \left( \frac{\langle 0 | \hat{\rho}(\mathbf{r}) | m \rangle \langle m | \hat{\rho}(\mathbf{r}) | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{\rho}(\mathbf{r}') | m \rangle \langle m | \hat{\rho}(\mathbf{r}') | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right)$$

Neutral excitation energies are poles of the linear response function!

- Exact linear density response to perturbation  $v_1(\omega)$

$$\rho_1(\omega) = \hat{\chi}(\omega)v_1(\omega)$$

# Linear response with TDDFT

- Dyson-type equation for response functions

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \chi_S(\mathbf{r}, \mathbf{r}'; \omega) + \int \int \chi_S(\mathbf{r}, \mathbf{r}'; \omega) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \right) \chi(\mathbf{r}, \mathbf{r}'; \omega) d^3 \mathbf{r} d^3 \mathbf{r}'$$

- Kohn-Sham linear response function:

$$\chi_S(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_{i,j} \frac{(f_j - f_k) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}') \phi_k^*(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

# Density response from real-time propagation

- Many-body TDSE

$$i\partial_t|\Psi(t)\rangle = (\hat{H}_0 + \alpha H_1(t))|\Psi(t)\rangle$$

- Density response

$$\begin{aligned}\rho(t) &= \langle\Psi(t)|\hat{\rho}|\Psi(t)\rangle \\ &= \rho_0 + \alpha\rho_1(t) + \alpha^2\rho_2(t) + \dots\end{aligned}$$

- Advantage: Allows to compute also nonlinear response



# Density response from TDDFT real-time propagation

- Time-dependent Kohn-Sham equation

$$i\partial_t|\Phi(t)\rangle = \hat{H}_{KS}(t)|\Phi(t)\rangle$$

- Kohn-Sham density response

$$\begin{aligned}\rho(t) &= \langle\Phi(t)|\hat{\rho}|\Phi(t)\rangle \\ &= \rho_0 + \alpha\rho_1(t) + \alpha^2\rho_2(t) + \dots\end{aligned}$$

- For the exact functional the time-dependent Kohn-Sham density is equivalent to the exact time-evolving many-body density.
- Need only to consider occupied states!

# Real-time evolution - Magnus expansion

- Time-ordered evolution operator

$$\hat{U}(t + \Delta t, t) = \hat{T} \exp \left( -i \int_t^{t+\Delta t} \hat{H}_{\text{KS}}(\tau) d\tau \right)$$

- Magnus expansion

$$\hat{U}(t + \Delta t, t) = \exp \left( \hat{\Omega}_1 + \hat{\Omega}_2 + \hat{\Omega}_3 + \dots \right)$$

- Magnus operators

$$\hat{\Omega}_1 = -i \int_t^{t+\Delta t} \hat{H}_{\text{KS}}(\tau) d\tau$$

$$\hat{\Omega}_2 = \int_t^{t+\Delta t} \int_t^{\tau_1} [\hat{H}_{\text{KS}}(\tau_1), \hat{H}_{\text{KS}}(\tau_2)] d\tau_2 d\tau_1$$

⋮

# Real-time evolution - Magnus expansion

- Exponential midpoint rule

$$\hat{U}(t + \Delta t, t) = \exp\left(\hat{\Omega}_1\right) + O(\Delta t^3)$$
$$\hat{\Omega}_1 = -i\hat{H}(t + \Delta t/2) + O(\Delta t^3).$$

- Time-evolved state

$$|\Psi(t + \Delta t)\rangle \approx \exp\left(\hat{H}(t + \Delta t/2)\right) |\Psi(t)\rangle$$

- Task: Compute exponential of operator/matrix

# Approximate propagators

- Exact matrix exponential: Diagonalize matrix, exponentiate eigenvalues, transform with eigenvectors
- Taylor/Chebyshev expansion of exponential
- Pade approximation of exponential, e.g. lowest order (Crank-Nicholson)

$$\exp(-i\hat{H}\Delta t) \approx \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

$$(1 + i\hat{H}\Delta t/2)|\Psi(t + \Delta t)\rangle = (1 - i\hat{H}\Delta t/2)|\Psi(t)\rangle$$

- Time-reversal symmetry? Symplectic (phase-space preserving) properties?

# Properties of approximate real-time propagators

## Exercise 6: Getting familiar with real-time propagators

- Crank-Nicholson/Caley, Runge-Kutta 4th order (efficiency, stability)
- Coherent and squeezed states as initial state
- Spectra of autocorrelation functions
- Movies of wavepacket propagation

# Absorption spectra from TDDFT

## Exercise 7:

- Calculation of photoabsorption cross section for  $N_2$ ,  $H_2O$

# Part 1: Hands-on charged excitations

What you should do:

$N_2$	Exp	PBE	HF	$\Delta$ -SCF	$G_0W_0@PBE$	$G_0W_0@HF$	scGW
HOMO							
HOMO-1				***			
HOMO-3				***			

# How does DFT eigenvalues compare to experiments for charged excitation?

## Exercise 1:

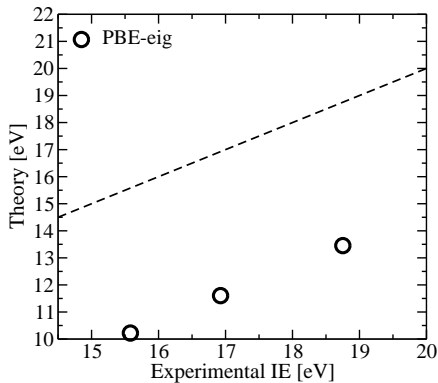
Perform a KS-DFT calculation, using the PBE exchange correlation functional for the  $N_2$  molecule (or optionally for  $H_2O$ ). Compare the first three non-degenerate DFT eigenvalue with the experimental ionization energies of  $N_2$  (see documentation),

- What is the average difference between the Kohn-Sham eigenvalues and experimental values?



# How does DFT eigenvalues compare to experiments for charged excitation?

## Exercise 1: RESULTS



# Hartree-Fock ionization energies: the Koopman theorem

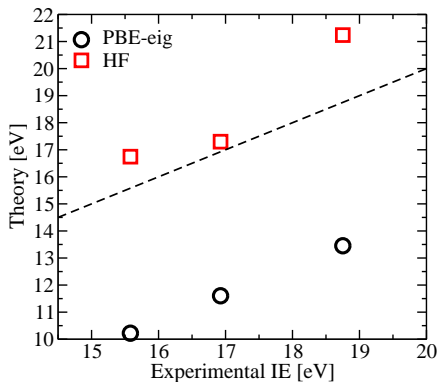
## Exercise 2:

Evaluate the first 3 ionization energies of  $N_2$  from an Hartree-Fock calculation. In Hartree-Fock, the Koopman theorem justifies the interpretation of the eigenvalues as addition and removal energies.

- What is the effect of neglecting the electron-electron correlation on ionization energies?

# Hartree-Fock ionization energies: the Koopman theorem

## Exercise 2: RESULTS



# Electron removal energies from the $\Delta$ -SCF approach

## Exercise 3:

Evaluate the first ionization energy  $I$  and the electron affinity  $A$  of  $N_2$  from KS-DFT and Hartree-Fock total energy differences using the formula:

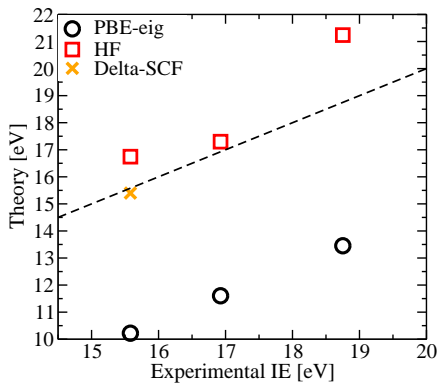
$$I = E(N - 1) - E(N) \quad (1)$$

$$A = E(N) - E(N + 1) \quad (2)$$

- Is the agreement with the first experimental ionization energy improved compared to those computed in Exercise 1?
- Is the Koopman theorem satisfied?

# The GW approximation: self-consistent *GW*

## Exercise 3: RESULTS



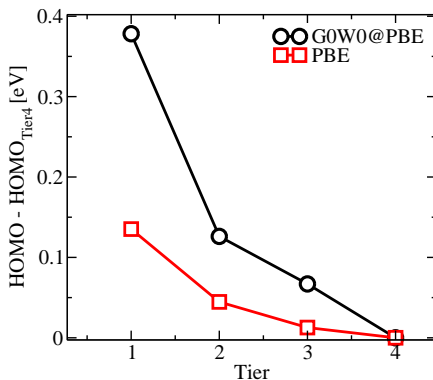
# The GW approximation: one-shot $G_0W_0$

## Exercise 4:

- Perform a  $G_0W_0$ @PBE calculation for  $N_2$ . How do the quasi-particle energies compare with experiments?
- Basis set convergence: plot the convergence of the quasi-particle HOMO level of  $N_2$  for Tier 1, 2, 3 and 4.
- **Optional:** Dependence on the starting point. Perform a  $G_0W_0$ @HF and a  $G_0W_0$ @PBE0 calculation of the ionization energies and compare with  $G_0W_0$ @PBE the obtained values.

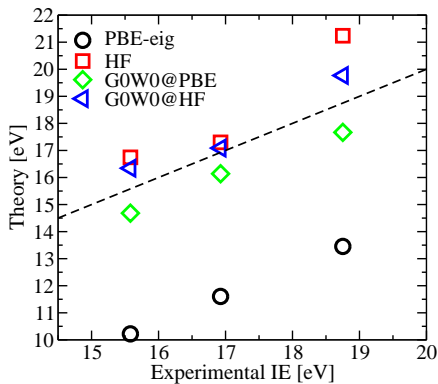
# The GW approximation: one-shot $G_0W_0$

## Exercise 4: RESULTS - Basis set convergence



# The GW approximation: one-shot $G_0W_0$

## Exercise 4: RESULTS - Ionization energies





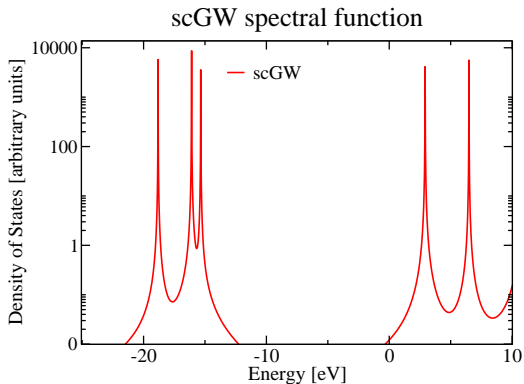
# The GW approximation: self-consistent $GW$

## Exercise 5:

- Perform a self-consistent  $GW$  calculation for  $N_2$  (**Tier 1** basis set) and plot the  $GW$  spectral function.
- Extract the ionization energies from the spectral function (gnuplot, xmgrace, ...).
- Compare the density obtained from the self-consistent Green's function and  $PBE$ .
- **Optional:** Try sc- $GW$  with a Hartree-Fock starting point.

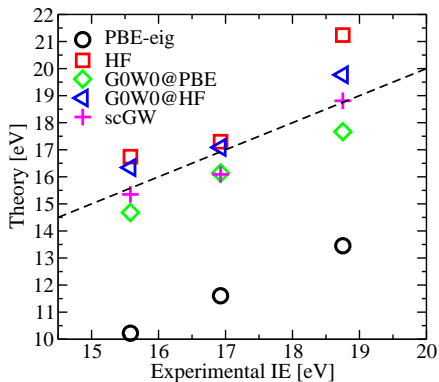
# The GW approximation: self-consistent $GW$

## Exercise 5: RESULTS

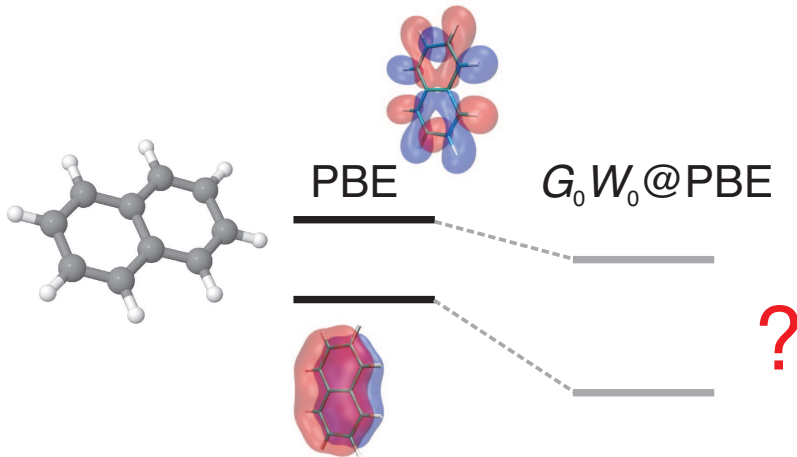


# The GW approximation: self-consistent $GW$

## Exercise 5: RESULTS



# Naphtalene and the self-interaction error



# Self-interaction error in Naphatalene

## Bonus Exercise:

- Perform a  $G_0W_0@PBE$  calculation of Naphtalene.
- Determine which orbitals are energetically swapped in  $G_0W_0@PBE$  compared to PBE.
- Visualize the orbital 27 and 28. Is the shape of the orbitals consistent with the self-interaction error picture?

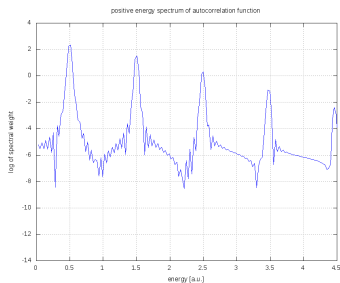
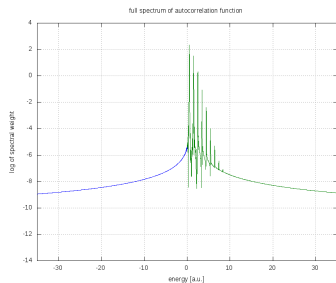
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## Exercise 6: Getting familiar with real-time propagators

- Crank-Nicholson/Caley, Runge-Kutta 4th order (efficiency, stability)
- Coherent and squeezed states as initial state
- Spectra of autocorrelation functions
- Movies of wavepacket propagation

# Properties of approximate real-time propagators

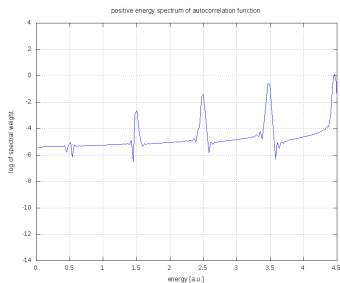
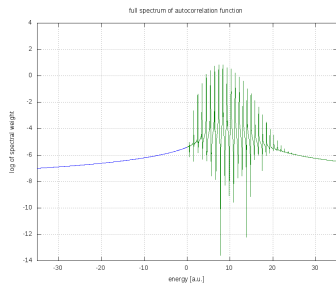
## Exercise 6: RESULTS - autocorrelation function



$x_{\min} = 1.0$ ,  $\text{squeeze} = 1.2$ , 9 spectral peaks

# Properties of approximate real-time propagators

## Exercise 6: RESULTS - autocorrelation function

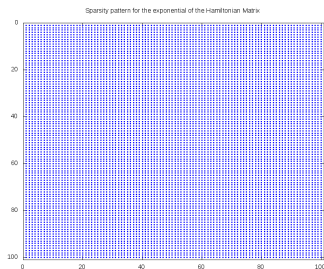
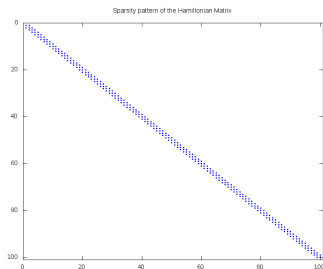


$x_{\min} = 4.0$ ,  $\text{squeeze} = 1.2$ , 28 spectral peaks



# Properties of approximate real-time propagators

## Exercise 6: RESULTS - sparsity of matrices



# Properties of approximate real-time propagators

## Exercise 6: RESULTS - Runge-Kutta 4th order

```
rk1 = -sqrt(-1) * dt * Hm_t * (psi);  
rk2 = -sqrt(-1) * dt * Hm_t_dt2 * (psi + rk1/2);  
rk3 = -sqrt(-1) * dt * Hm_t_dt2 * (psi + rk2/2);  
rk4 = -sqrt(-1) * dt * Hm_t_dt * (psi + rk3);  
psi = psi + (rk1 + 2*rk2 + 2*rk3 + rk4)/6;
```

# Properties of approximate real-time propagators

## Exercise 6: RESULTS - Quiz time

- Which method allows for the largest time step?
  - ▶ Crank-Nicholson/Caley
- Which method allows for the fastest time stepping?
  - ▶ Runge-Kutta 4th order, Taylor expansion
- How is the grid spacing related to the time step?
  - ▶ The spacings appear in the ratio  $\Delta t/\Delta x^2$  in the exponential

# Absorption spectra from TDDFT

## Exercise 7:

- Calculation of photoabsorption cross section for  $N_2$ ,  $H_2O$