Theoretical Spectroscopy and Electronic Excitations

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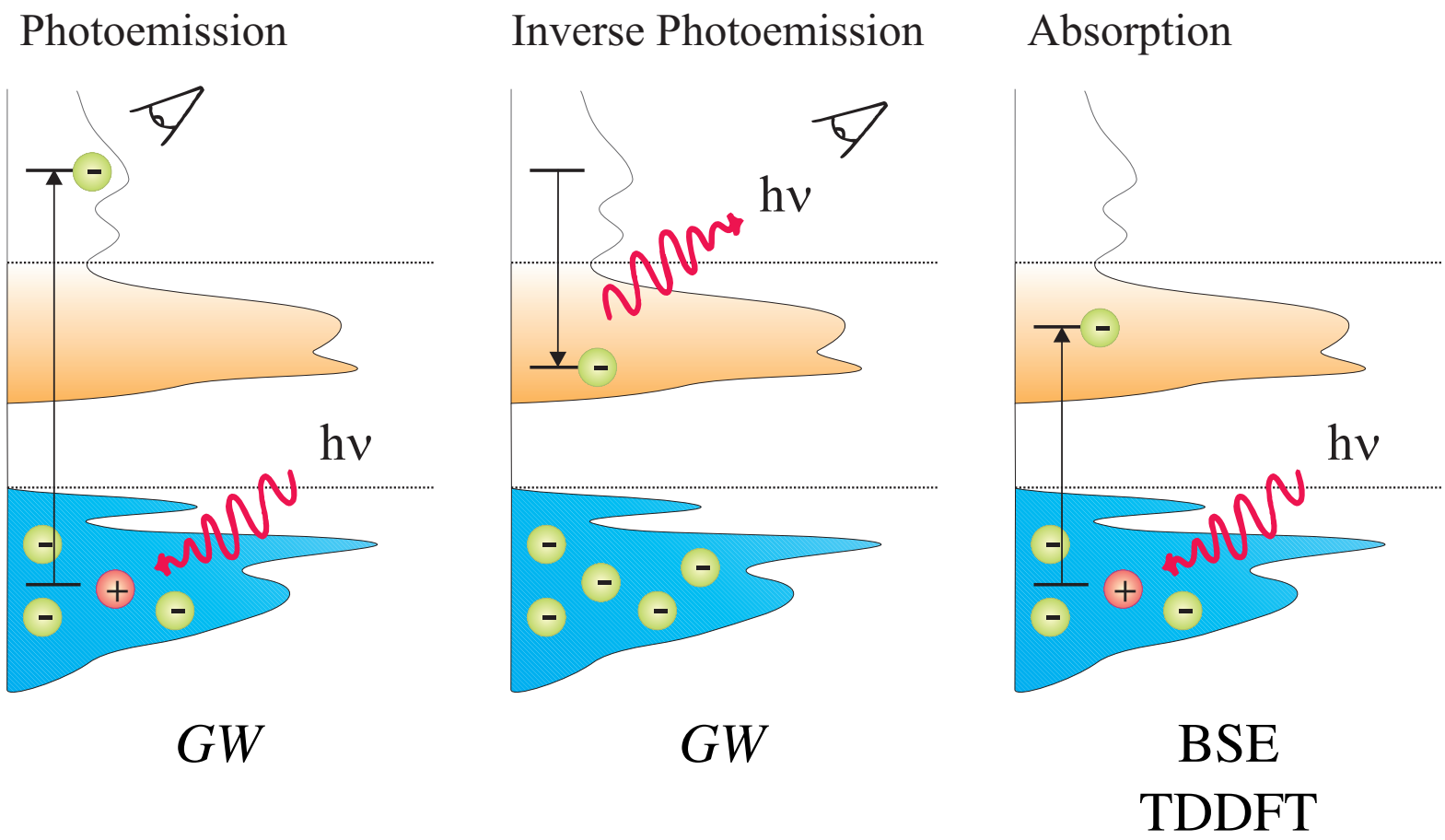
Electronic Structure Theory for Materials and (Bio)molecules
Tutorial 5 [Los Angeles 2014]

Band structures: photo-electron spectroscopy



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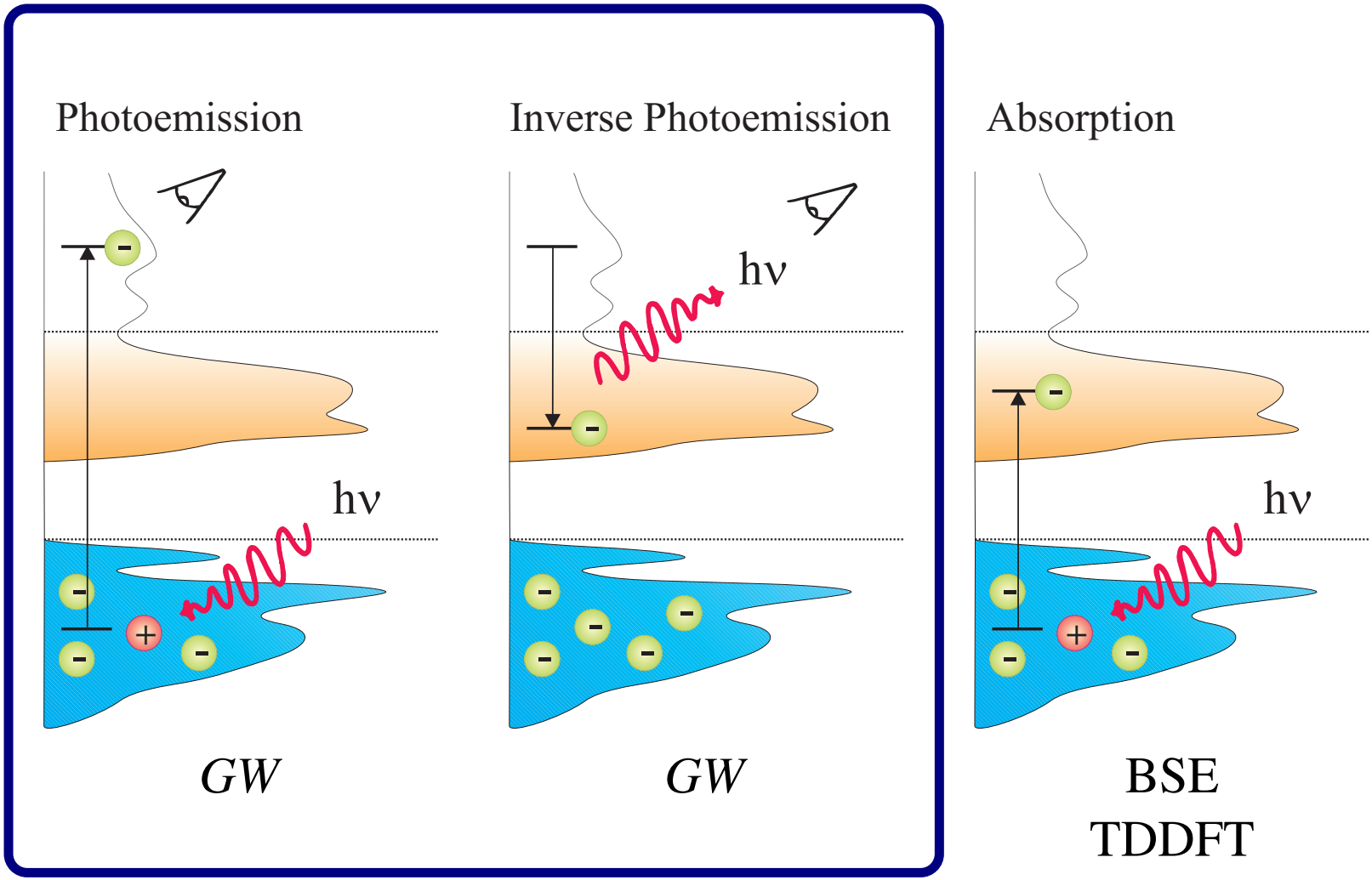
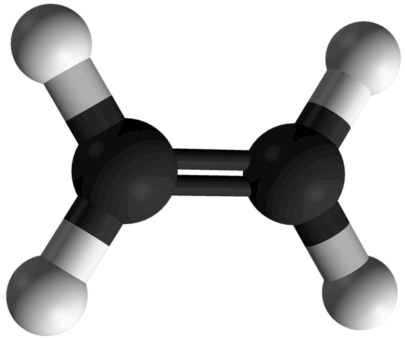


In this tutorial: Theoretical spectroscopy of C_2H_4

Ethylene:

- simplest unsaturated hydrocarbon (after acetylene (C_2H_2))



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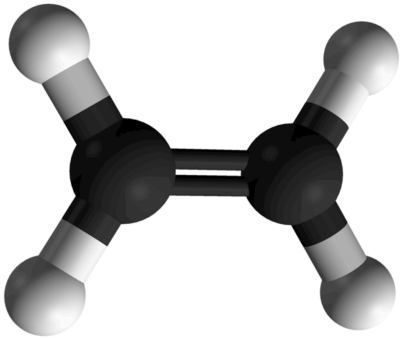
- key component of polyethylene (used for plastics of any shape and form)
- 109 million tonnes produced worldwide (in 2006)



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Ethylene:

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- plant hormone: induces fruit ripening

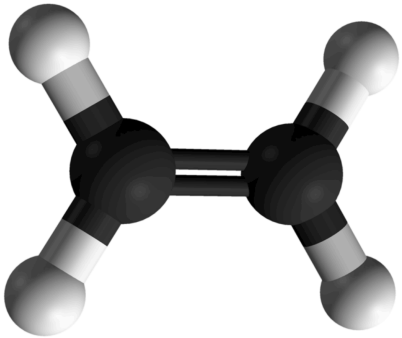
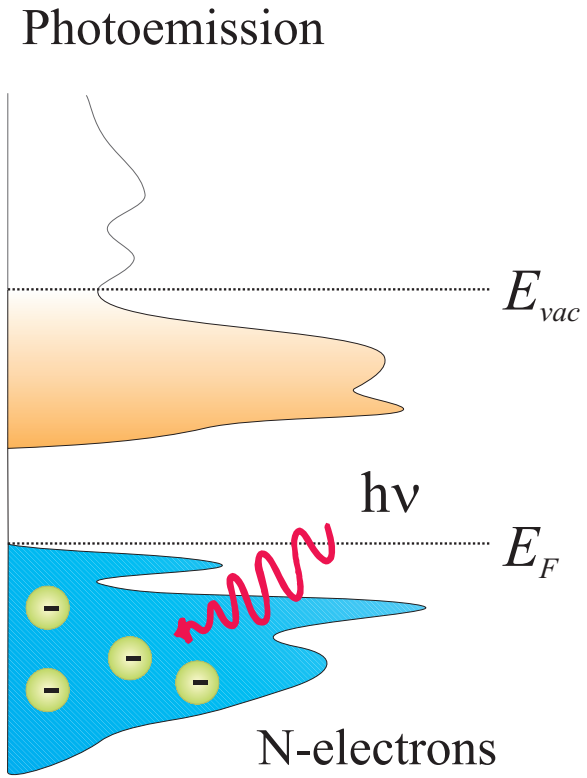


Photo-Electron Excitation Energies (Work in progress)

- Photoemission
  - electron removal
  - removal energy
    $E(N)$

$$|N\rangle$$



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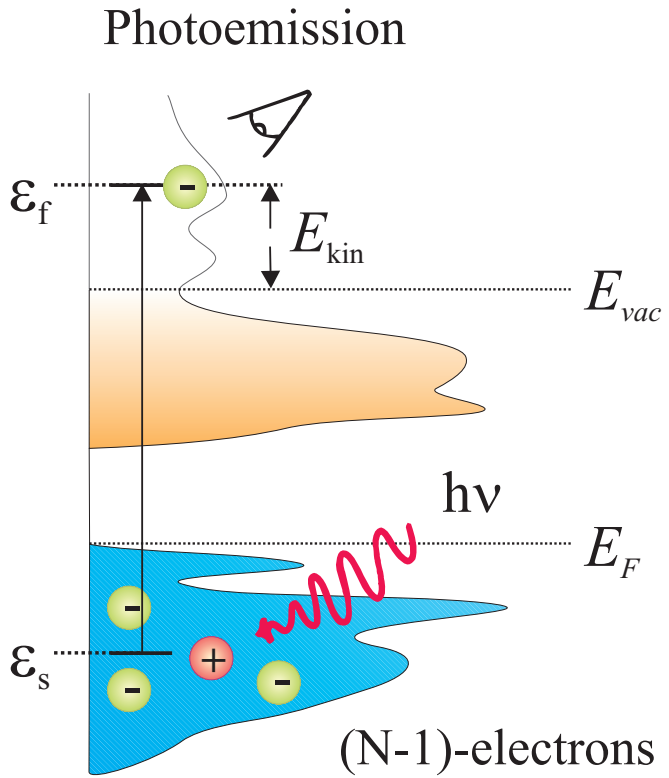

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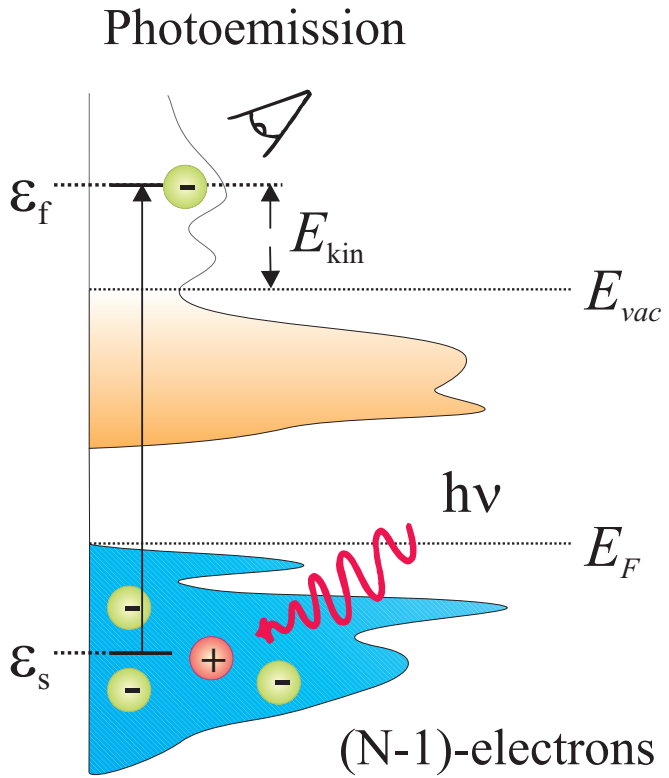
    $$E(N)-E(N-1,s)$$



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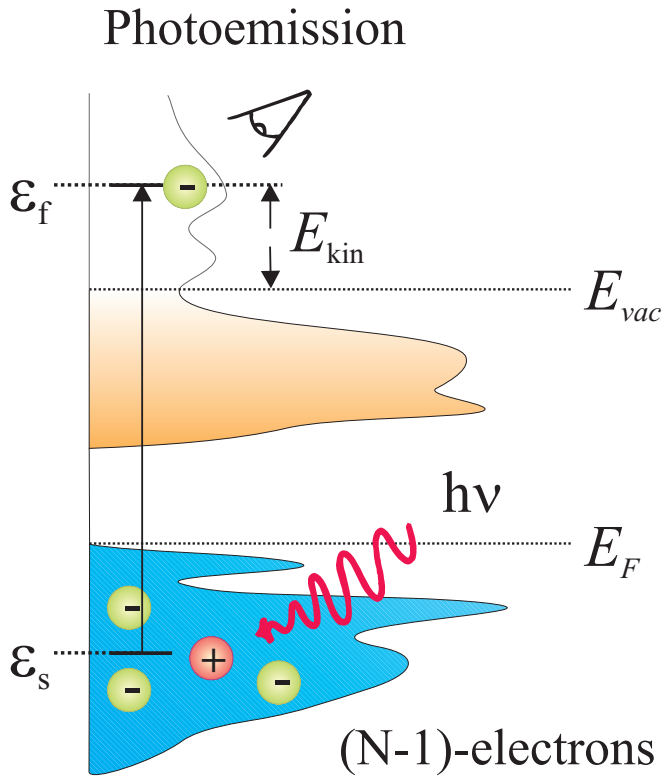

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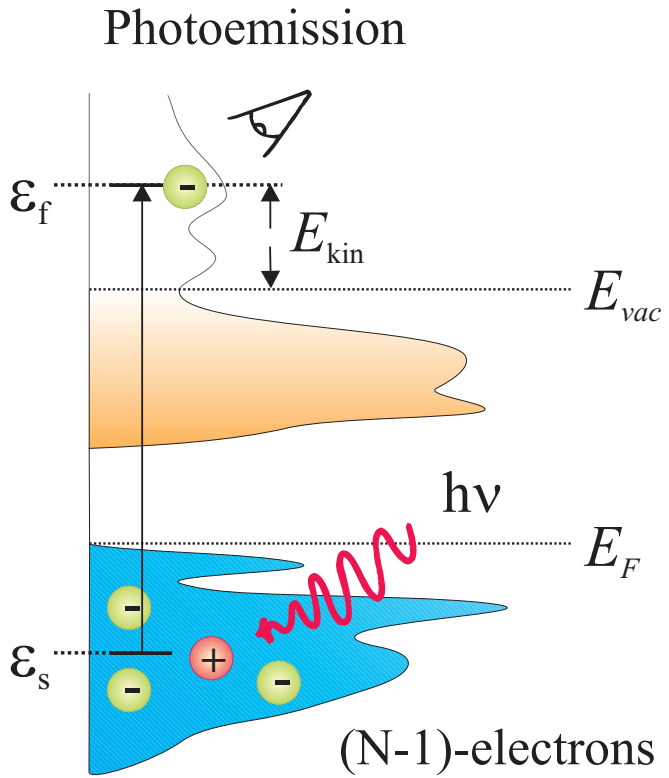
- Inverse Photoemission
  - electron addition
    $\psi_s(\mathbf{r}) = \left\langle N+1, s \middle| \hat{\psi}(\mathbf{r})^\dagger \middle| N \right\rangle$
  - addition energy
    $\epsilon_s = E(N+1, s) - E(N)$



Ionisation Potential, Electron Affinity and (Band) Gaps

We could use a total energy method to compute excitation energies:

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Band Gap energy difference between HOMO and LUMO

$$E_{gap} = I - A$$

What about Hartree-Fock eigenvalues?

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

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

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Problems with this approach:

- orbital relaxations can be important
- correlations absent from HF

Janak's theorem (PRA 18, 7165 (1978)))

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rearranging and making mid point approximation:

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In exact KS-DFT the ionization potential is given by the KS eigenvalue of highest occupied state.

In this tutorial (Part I)

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- compute the ionization potential and electron affinity using the Δ-SCF method

Δ-SCF method

- compute the DFT ground state energy of the neutral system
- compute the DFT ground state energy of the charged system
- compute the ionization potential / electron affinity as the energy difference between the two charge states

Single Particle Green's Functions

- single particle Green's function G

$$iG(\mathbf{r},\mathbf{r}';t-t') = \left\langle \psi_0^N \middle| \hat{T}\left[\psi(\mathbf{r},t)\psi(\mathbf{r}',t')^\dagger\right] \middle| \psi_0^N \right\rangle$$

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- Lehmann Representation of the Green's function:

$$iG(\mathbf{r},\mathbf{r}';\omega) = \sum_k \frac{\left\langle \Psi_0^N \middle| \psi(\mathbf{r}) \middle| \Psi_k^{N+1} \right\rangle \left\langle \Psi_k^{N+1} \middle| \psi(\mathbf{r})^\dagger \middle| \Psi_0^N \right\rangle}{\omega - (E_k^{N+1} - E_0^N) + i\eta} + \sum_k \frac{\left\langle \Psi_0^N \middle| \psi(\mathbf{r})^\dagger \middle| \Psi_k^{N-1} \right\rangle \left\langle \Psi_k^{N-1} \middle| \psi(\mathbf{r}) \middle| \Psi_0^N \right\rangle}{\omega + (E_k^{N-1} - E_0^N) - i\eta}$$

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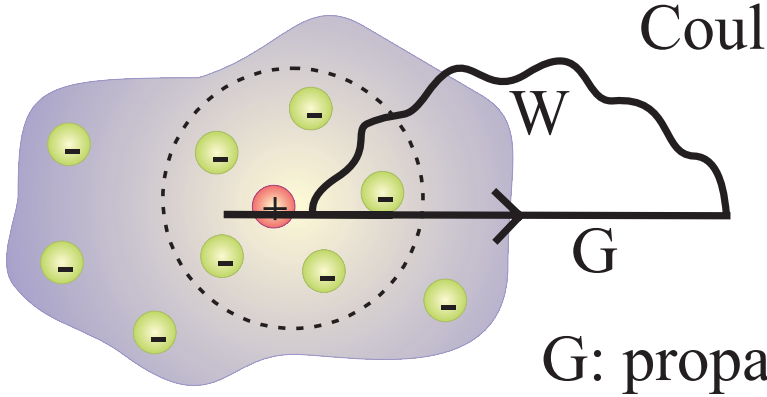
GW Approximation - Screened Electrons

Σ=GW :



W: screened Coulomb

G: propagator

Self-Energy

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

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

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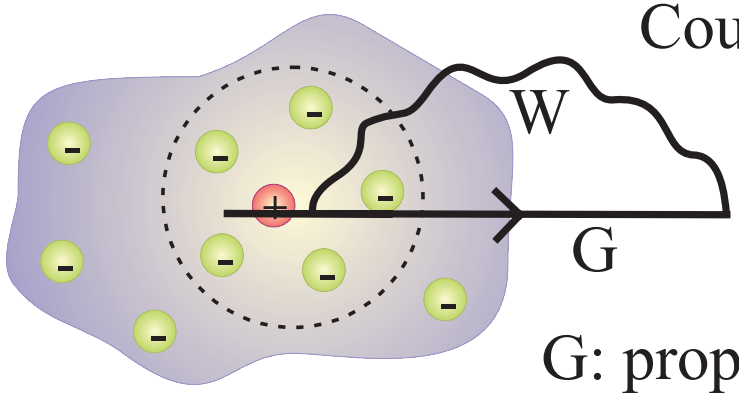

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$\Sigma_x = iGv$ exact (Hartree-Fock) exchange

$\Sigma_c = iG(W-v)$ correlation (screening due to other electrons)

GW -- How to obtain the self energy

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Convergence of *GW*-methods

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$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \sum_\sigma \sum_m^{\text{occ}} \sum_a^{\text{unocc}} \frac{\psi^*_{m\sigma}(\mathbf{r})\psi_{a\sigma}(\mathbf{r})\psi^*_{a\sigma}(\mathbf{r}')\psi_{m\sigma}(\mathbf{r}')}{i\omega - \epsilon_{a\sigma} + \epsilon_{m\sigma}} + \text{c.c.},$$

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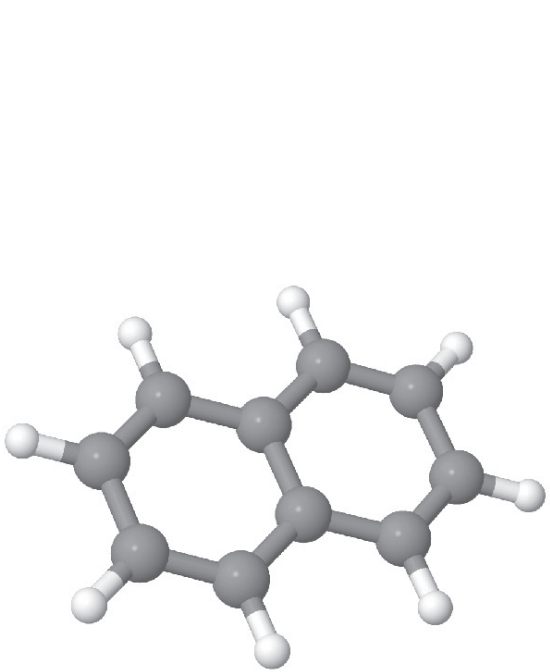
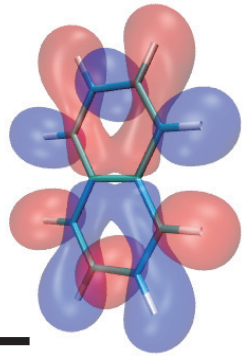
- check the starting point independence of scGW

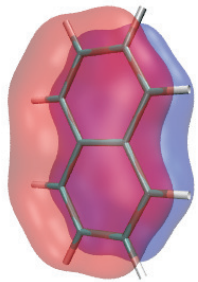
Naphtalene and the self-interaction error





PBE

G_0W_0@PBE



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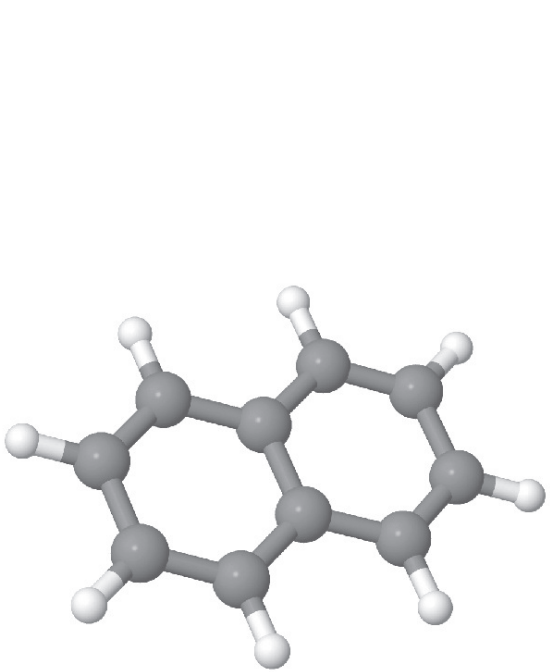

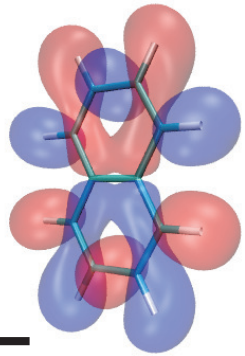

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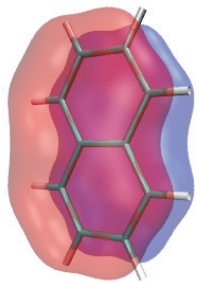

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Ground state properties from Green's functions

- The Green's Function also gives access to ground state properties.
- Galitskii-Migdal formula for total energy

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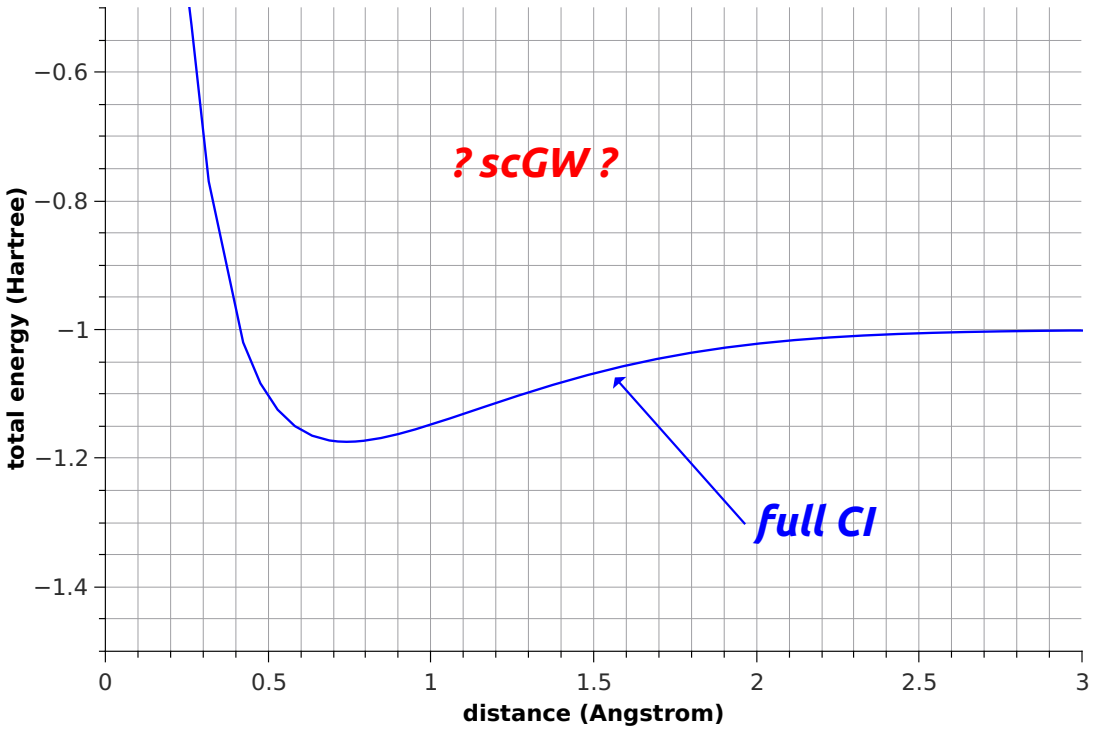
- In this tutorial: application to H_2 binding curve

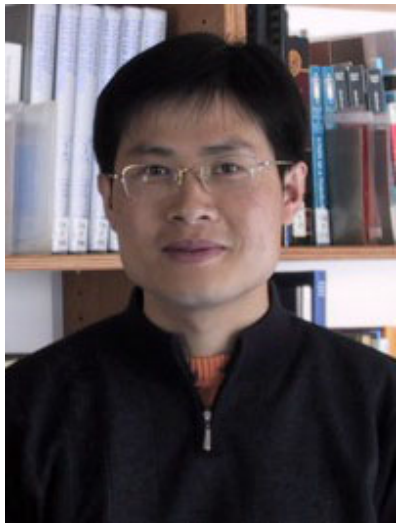


Your tutors this afternoon

Patrick Rinke

Arvid Ihrig

Björn Bienek



Xinguo Ren

Daniel Berger

Your tutors this evening

Oliver Hofmann

Mariana Rossi