Theoretical Spectroscopy and Electronic Excitations

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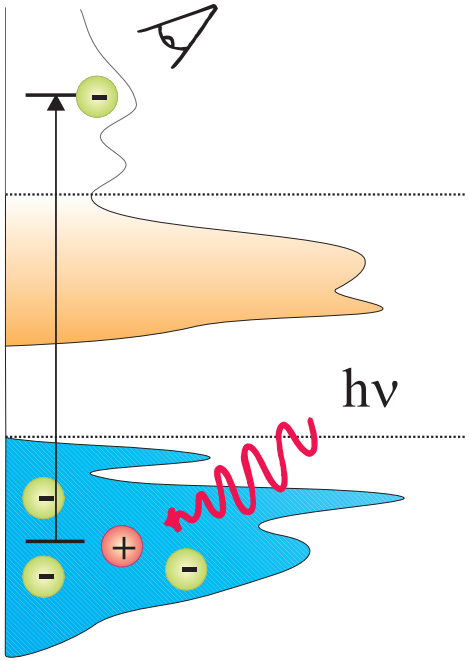
FHI Hands-On Workshop – Tutorial 5

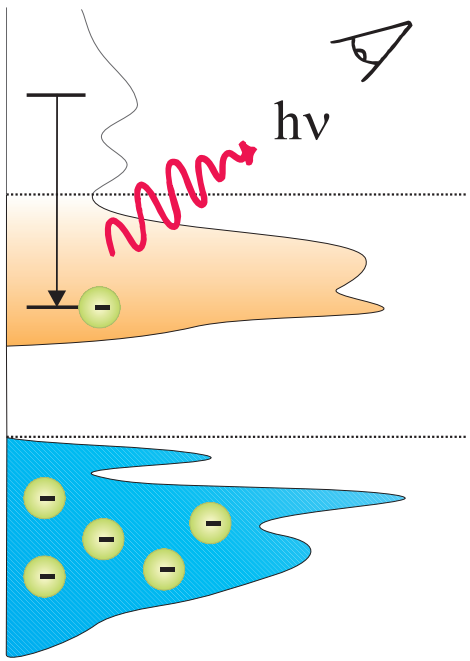
Band structures: photo-electron spectroscopy

Photoemission



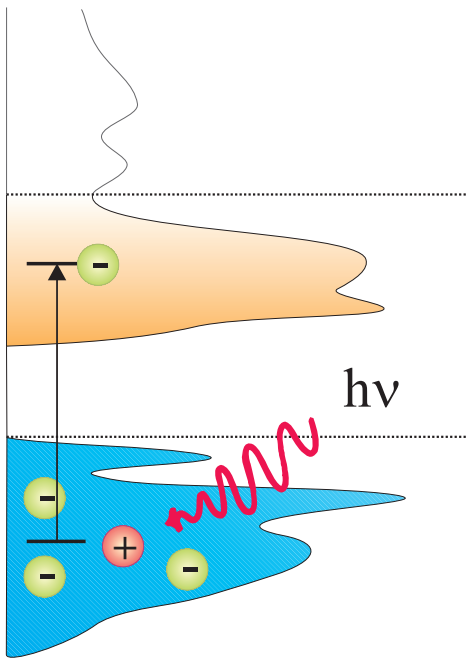
GW

Inverse Photoemission



GW

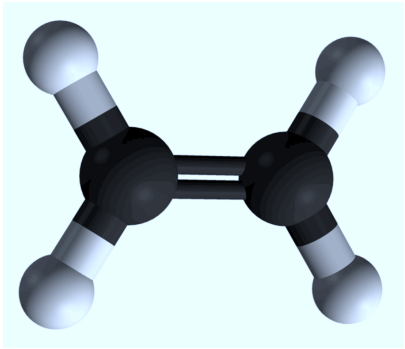
Absorption



BSE
TDDFT

In this tutorial

Theoretical spectroscopy of C_2H_4 (and H_20)



Ethylene:

- simplest unsaturated hydrocarbon (after acetylene (C_2H_2))
- key component of polyethylene
  - plastics (of any shape and form)
- 109 million tons produced worldwide (in 2006)
- plant hormone: induces fruit ripening

Photo-Electron Excitation Energies

- Photoemission
  - electron removal

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

  - removal energy

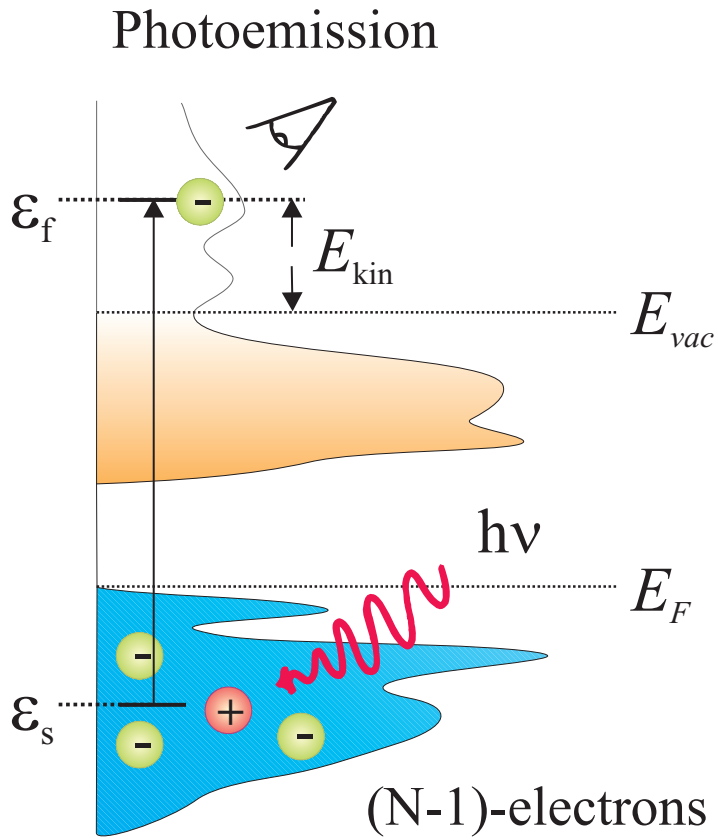
    $$\epsilon_s = E(N) - E(N-1, s)$$

- Inverse Photoemission
  - electron addition

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

  - addition energy

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



$\|N\rangle$	:	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 C_2H_4

This procedure is often called ΔSCF
(difference of two self-consistent field calculations)

ΔSCF versus eigenvalues

Hartree-Fock:

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

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

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

but:

- orbital relaxations can be important
- correlations absent from HF

ΔSCF versus eigenvalues

Density-functional theory:

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

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

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

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

rearranging and making mid point approximation:

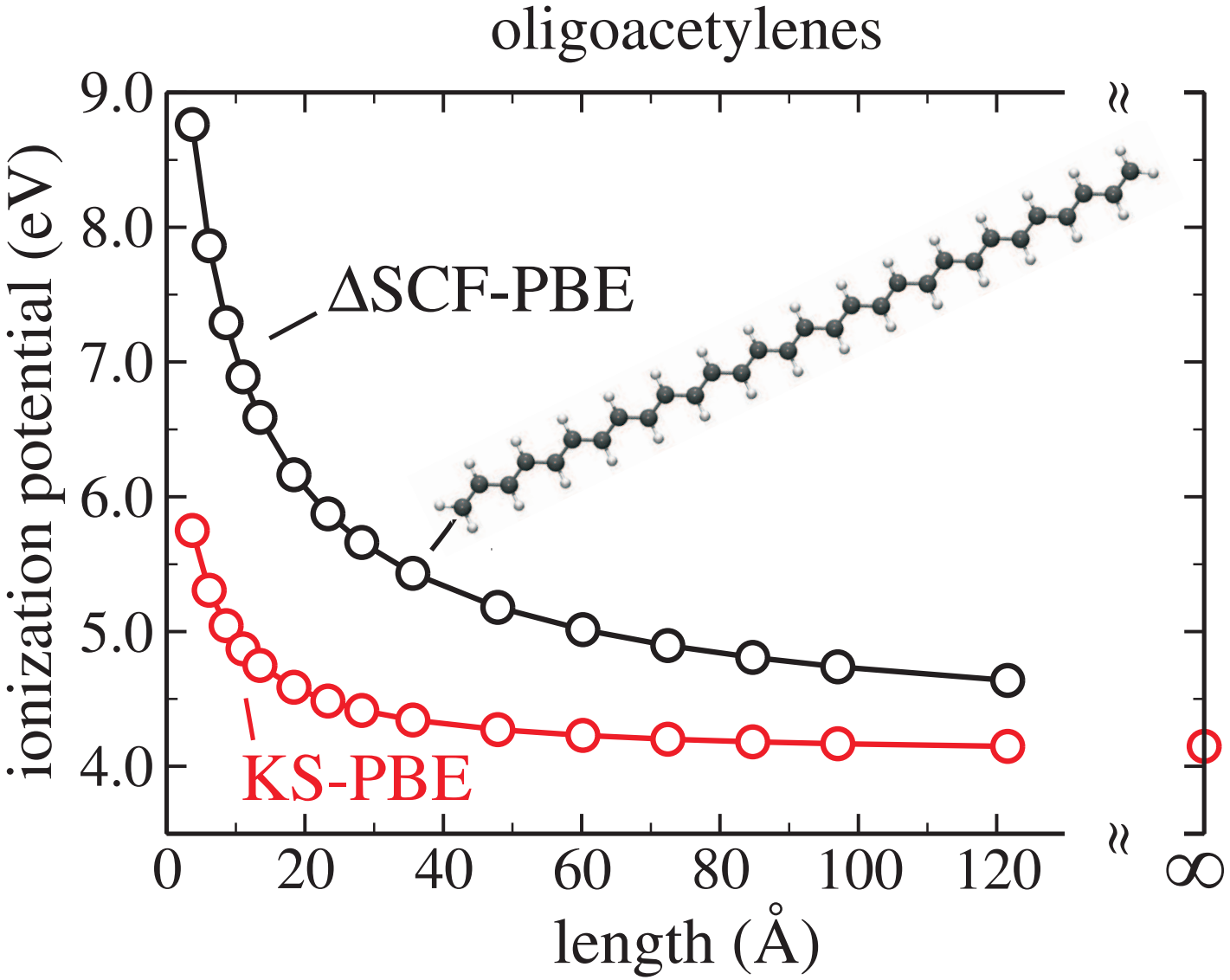
$$E(N+1,s) - E(N) = \int_0^1 dn\, \epsilon_s(n) \approx \epsilon_s(0.5)$$

ΔSCF versus eigenvalues

Exercise:

- calculate I and A of C_2H_4 using HF and DFT-PBE eigenvalues

ΔSCF versus eigenvalues for finite systems



data courtesy of Max Pinheiro

Single Particle Green's Functions

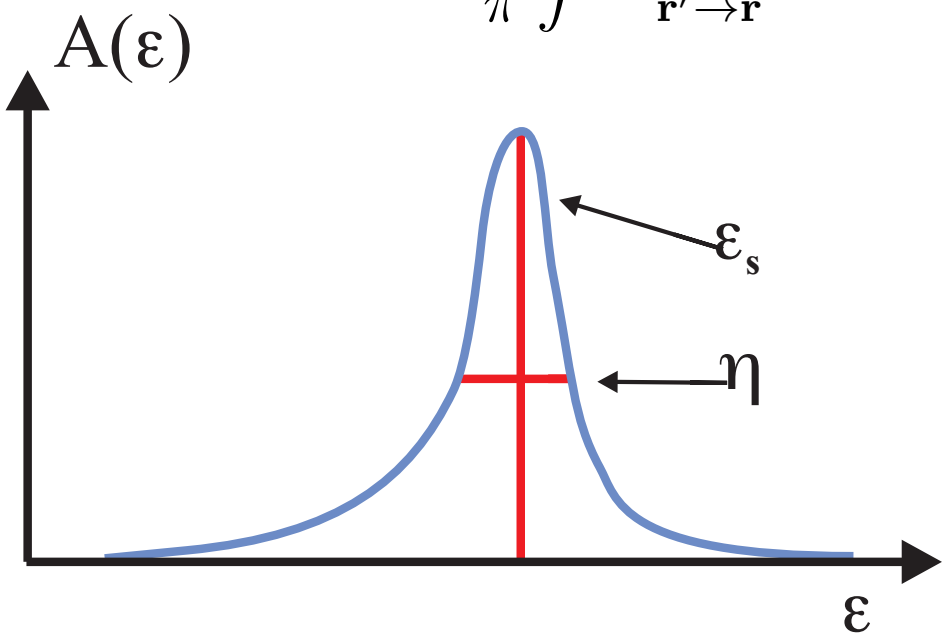
- Lehmann representation of single particle Green's function G:

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

Excitation energies are poles of the Green's function!

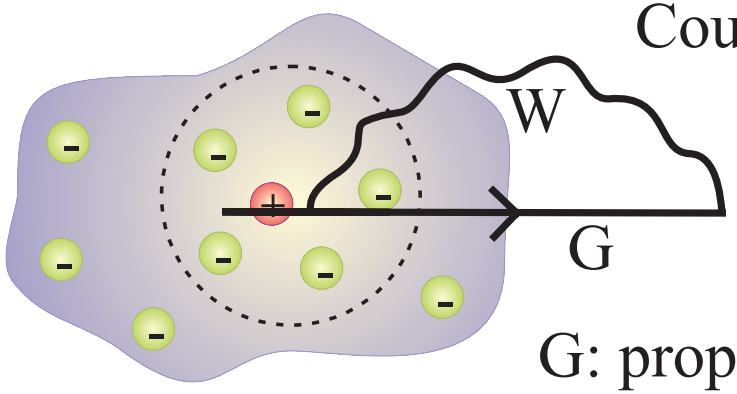
- spectroscopically relevant quantity: spectral function A:

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



GW Approximation - Screened Electrons

Σ=GW :



W: screened Coulomb

G: propagator

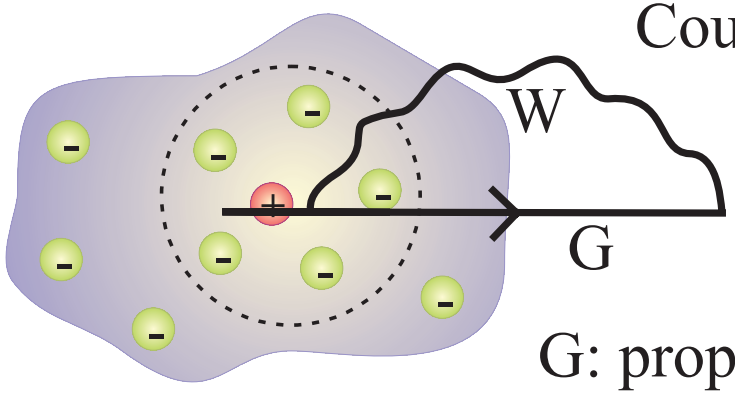
Self-Energy

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

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

GW Approximation - Screened Electrons

Σ=GW :



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)

G_0W_0 exercise

Exercise:

- calculate the quasiparticle excitations of C_2H_4 in G_0W_0 starting from
  - DFT-PBE
  - HF
  - DFT-PBE0

GW – The Issue of Self-Consistency

Hedin's GW equations:

$$
\begin{aligned}
G(1,2) &= G_0(1,2) \qquad \text{notation:} \quad 1 = (\mathbf{r}_1, \sigma_1, t_1) \\
\Gamma(1,2,3) &= \delta(1,2)\delta(1,3) \\
P(1,2) &= -iG(1,2)G(2,1^+) \\
W(1,2) &= v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4) \\
\Sigma(1,2) &= iG(1,2)W(2,1)
\end{aligned}
$$

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\end{aligned}
$$

self-consistency

self-consistency

Dyson's equation:

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

scGW exercise

Exercise:

- calculate the quasiparticle spectrum of C_2H_4 in scGW
- extract I and A from the spectrum

Convergence of G_0W_0 and GW

- single particle Green's function G_0:

$$G^0_\sigma(\mathbf{r},\mathbf{r}',\omega) = \sum_n \frac{\psi_{n\sigma}(\mathbf{r})\psi^*_{n\sigma}(\mathbf{r}')}{\omega - \epsilon_{n\sigma} - i\eta\ \mathrm{sgn}(\epsilon_\mathrm{F} - \epsilon_{n\sigma})}$$

- polarizability:

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

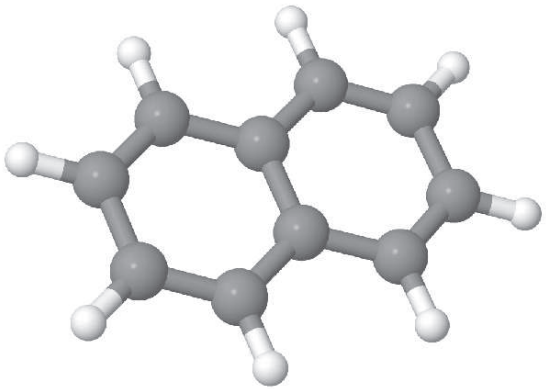
where c.c. denotes "complex conjugate"

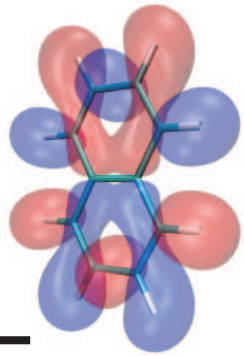
Convergence of G_0W_0 and scGW with basis size

Exercise:

- calculate the quasiparticle spectrum of C_2H_4 in G_0W_0 and scGW for Tier 1 to Tier 3.

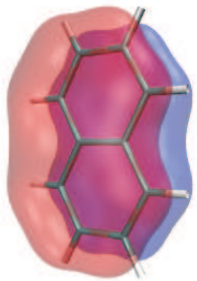
Naphtalene and the self-interaction error





PBE

G_0W_0@PBE



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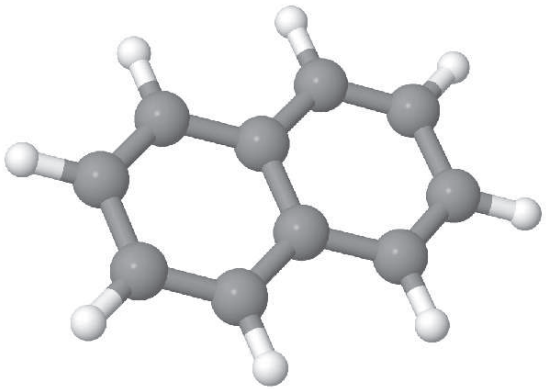
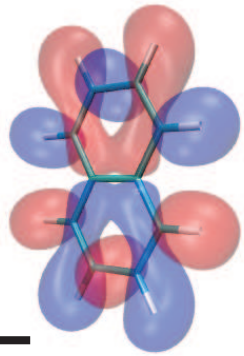
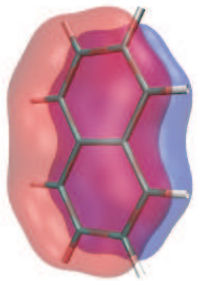
Naphtalene and the self-interaction error





PBE

G_0W_0@PBE



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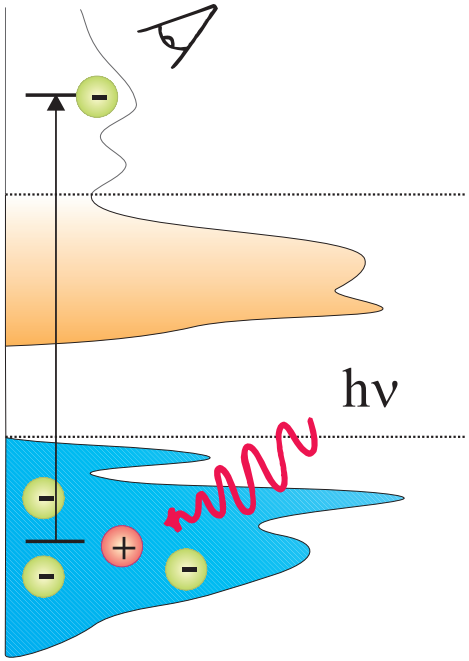
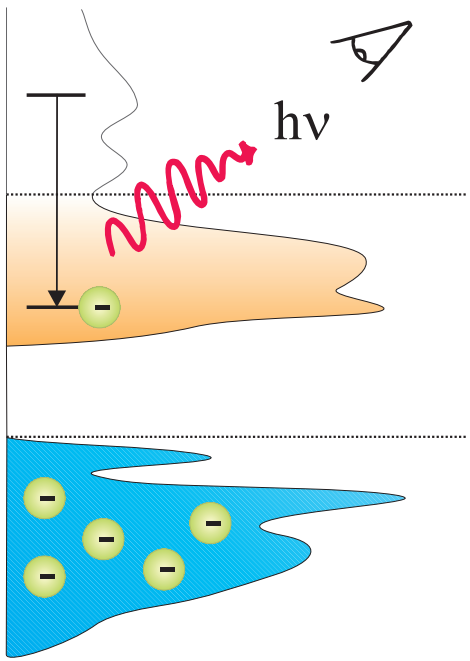
Absorption spectroscopy

Photoemission



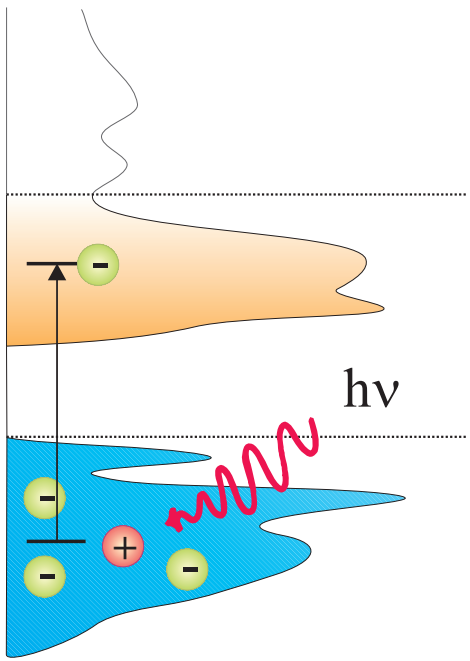
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

Casida equation

- (Non-linear) eigenvalue equation for excitation energies

$$\Omega \mathbf{F}_j = \omega_j^2 \mathbf{F}_j$$

with

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma,\tau}\delta_{i,j}\delta_{a,b}(\epsilon_a - \epsilon_i)^2 + 2\sqrt{(\epsilon_a - \epsilon_i)}K_{ia\sigma,jb\tau}\sqrt{(\epsilon_b - \epsilon_j)}$$

and

$$K_{ia\sigma,jb\tau}(\omega) = \int d^3r \int d^3r' \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}) \times \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},\mathbf{r}',\omega)\right]\phi_{k\tau}(\mathbf{r})\phi_{l\tau}(\mathbf{r})$$

- Eigenvalues ω_j are exact vertical excitation energies
- Eigenvectors can be used to compute oscillator strength

Absorption spectroscopy and excited states

Exercise 6:

- Vertical Franck-Condon absorption spectrum for C_2H_4 using the Casida implementation in FHI-aims

Exercise 7:

- Excited state Born-Oppenheimer surfaces for C_2H_4

Real-time evolution - Magnus expansion

- Time-ordered evolution operator

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

- Magnus expansion

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

- Magnus operators

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

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

$$\vdots$$

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
  $\rightarrow$ Taylor series, Chebyshev polynomials, (Krylov) subspace diagonalization, ...

Real-time evolution - Crank-Nicholson/Cayley propagator

- Padé approximation of exponential, e.g. lowest order (Crank-Nicholson)

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

- Need only action of operator on a state vector

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

- (Non-)Linear system of equations at each time-step

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

Real-time evolution - Operator splitting methods

- Typically, the Hamiltonian has the form $\hat{H} = \hat{T} + \hat{V}$
- $\hat{T}$ is diagonal in momentum space, $\hat{V}$ in position space
- Baker-Campbell-Hausdorff relation

$$e^{\hat{A}} e^{\hat{B}} = \exp(\hat{A} + \hat{B} + \frac{1}{2}[\hat{A}, \hat{B}] + \ldots)$$

- Split-Operator

$$\exp(-i\Delta t(\hat{T} + \hat{V})) \approx \exp(-i\Delta t\hat{T}/2) \exp(-i\Delta t\hat{V}) \exp(-i\Delta t\hat{T}/2)$$

Use FFT to switch between momentum space and real-space.

Real-time evolution - Enforced time reversal symmetry

- Enforced time-reversal symmetry

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

- Propagator with time-reversal symmetry

$$\hat{U}^{\mathrm{ETRS}}(t+\Delta t,t) = \exp(-i\frac{\Delta t}{2}\hat{H}(t+\Delta t))\exp(-i\frac{\Delta t}{2}\hat{H}(t))$$

Properties of approximate real-time propagators

Exercise 8: 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

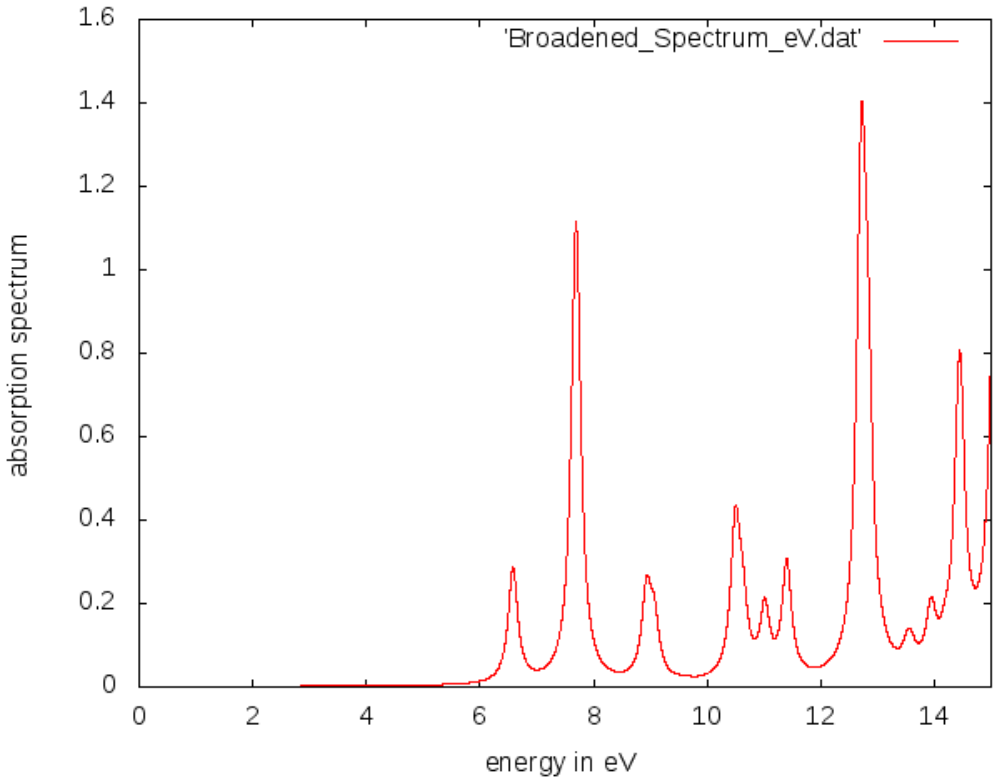
Nuclear wavepacket dynamics

Exercise 9: Nuclear wavepacket dynamics on coupled BO surfaces

- Combining excited state BO surfaces from excercise 7 and real-time propagation from excercise 8.

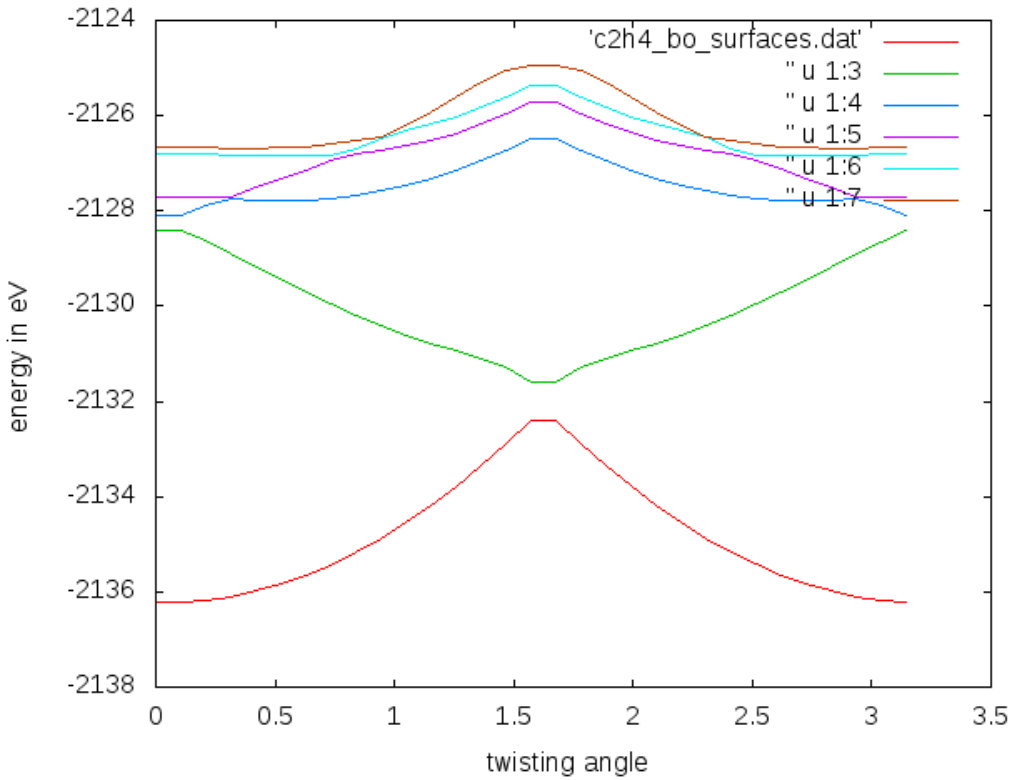
Vertical Frank-Condon transitions

Exercise 6: RESULTS - Vertical Frank-Condon transitions



Ground state and excited state Born-Oppenheimer surfaces

Exercise 7: RESULTS - Ground and excited state Born-Oppenheimer surfaces for C_2H_4



Properties of approximate real-time propagators

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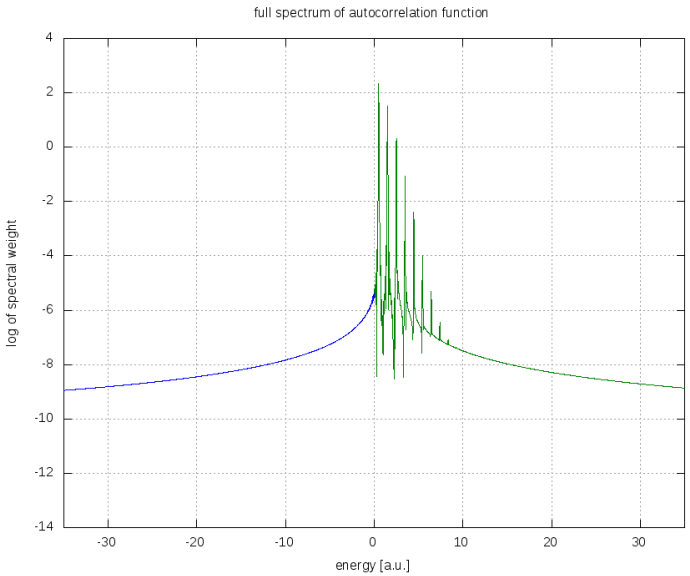
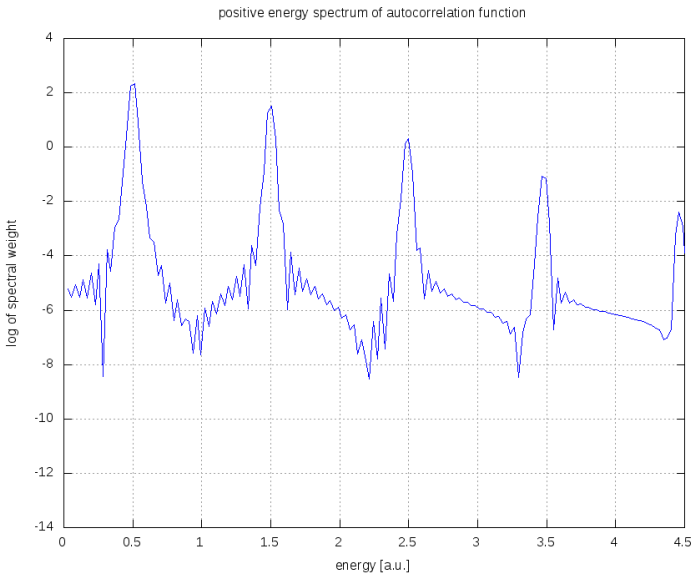
Properties of approximate real-time propagators

Exercise 8: RESULTS - autocorrelation function

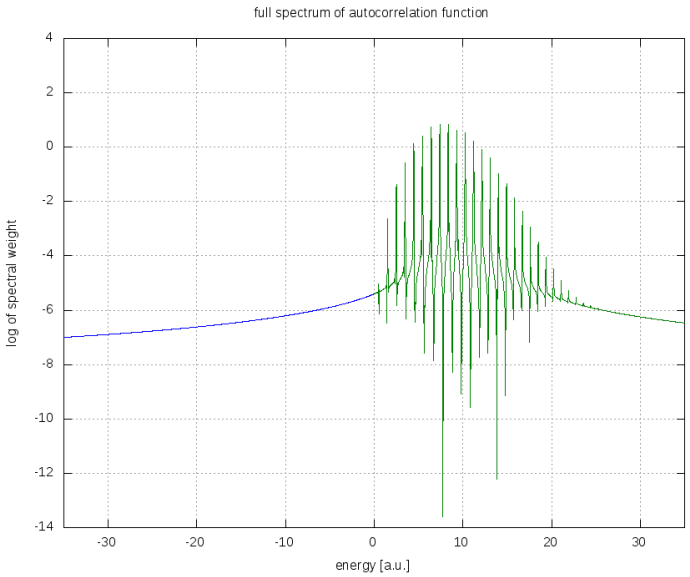


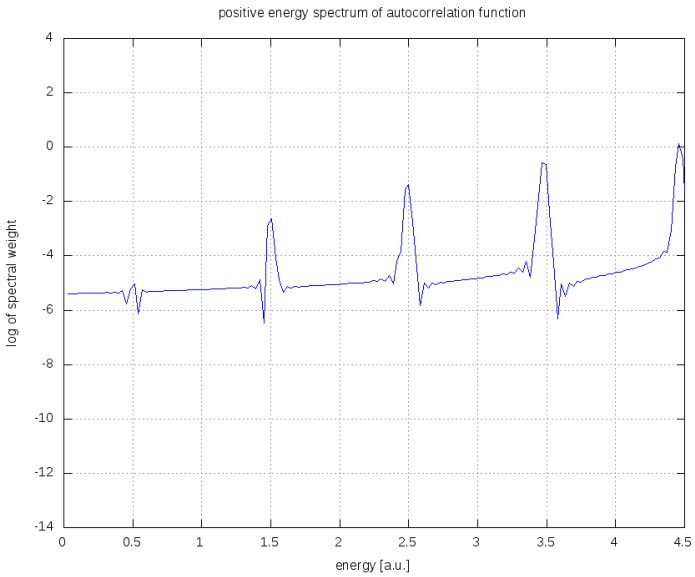


`xmin = 1.0, squeeze = 1.2`, 9 spectral peaks

Properties of approximate real-time propagators

Exercise 8: RESULTS - autocorrelation function

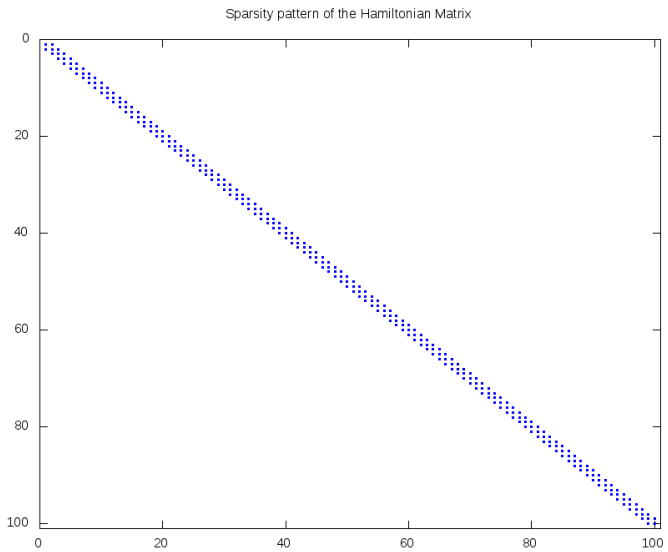


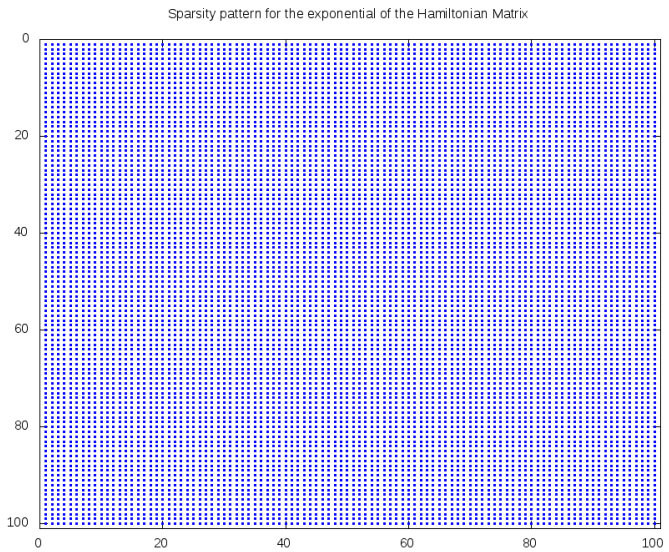


`xmin = 4.0, squeeze = 1.2`, 28 spectral peaks

Properties of approximate real-time propagators

Exercise 8: RESULTS - sparsity of matrices





Properties of approximate real-time propagators

Exercise 8: 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;
```

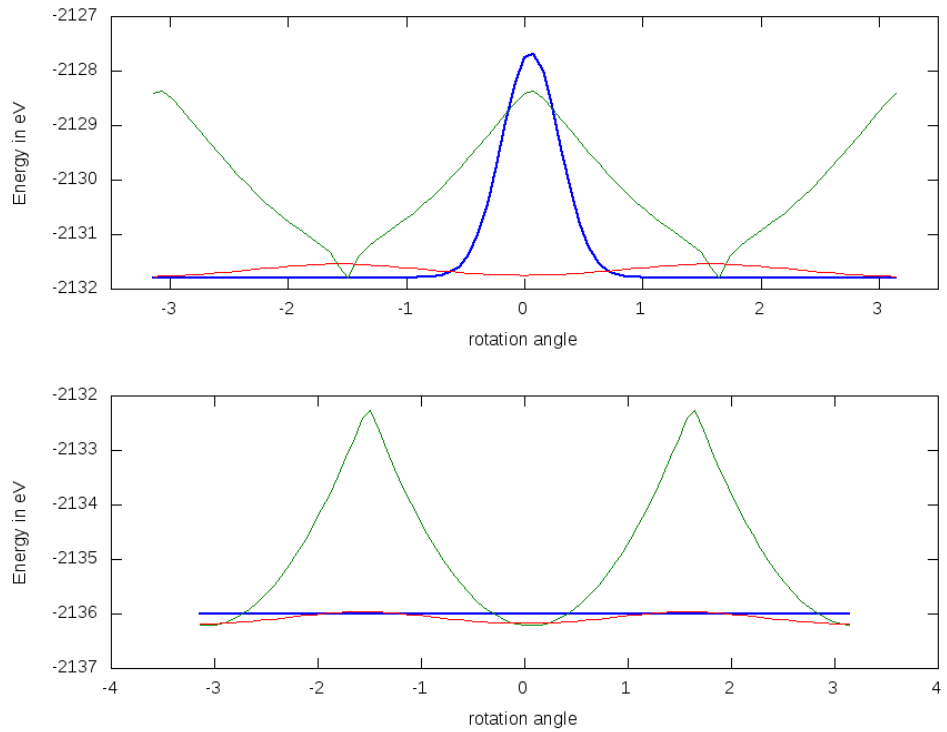
Properties of approximate real-time propagators

Exercise 8: 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

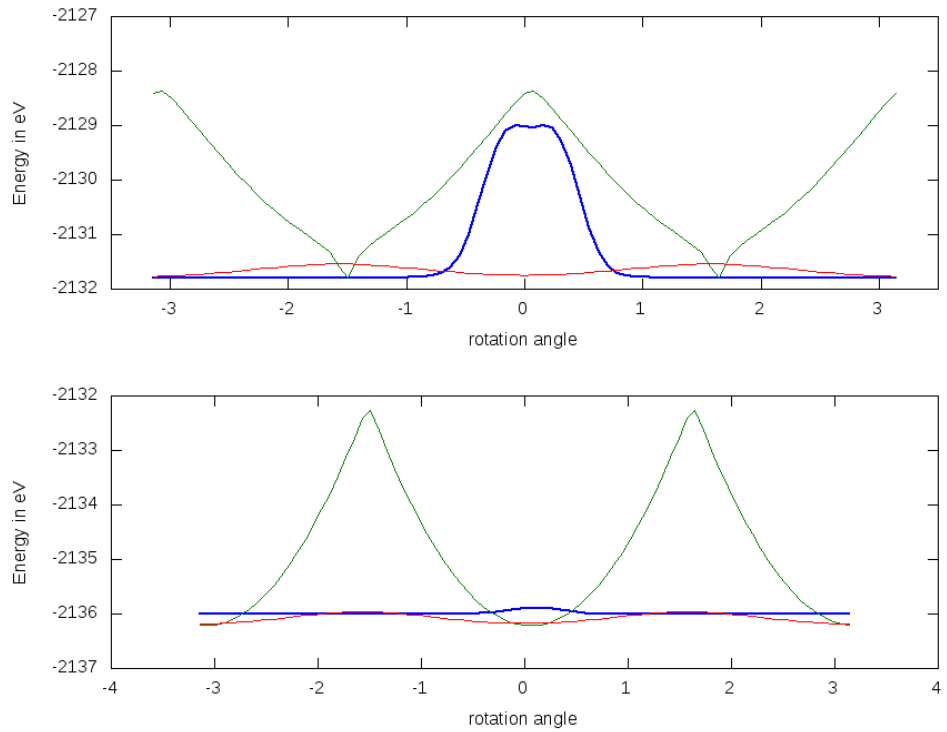
Wavepacket dynamics on coupled BO surfaces

Exercise 9: RESULTS - Wavepacket dynamics on coupled Born-Oppenheimer surfaces



Wavepacket dynamics on coupled BO surfaces

Exercise 9: RESULTS - Wavepacket dynamics on coupled Born-Oppenheimer surfaces



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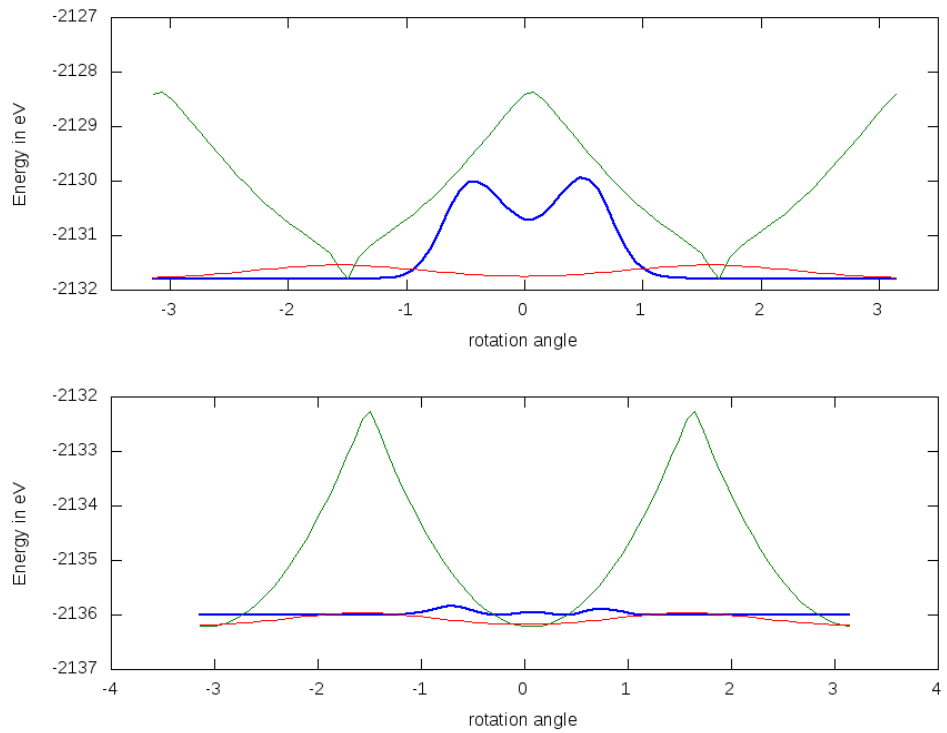

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