Non-adiabatic contributions to the spectrum of simple molecular models:
the case of the one-dimensional dihydrogen cation

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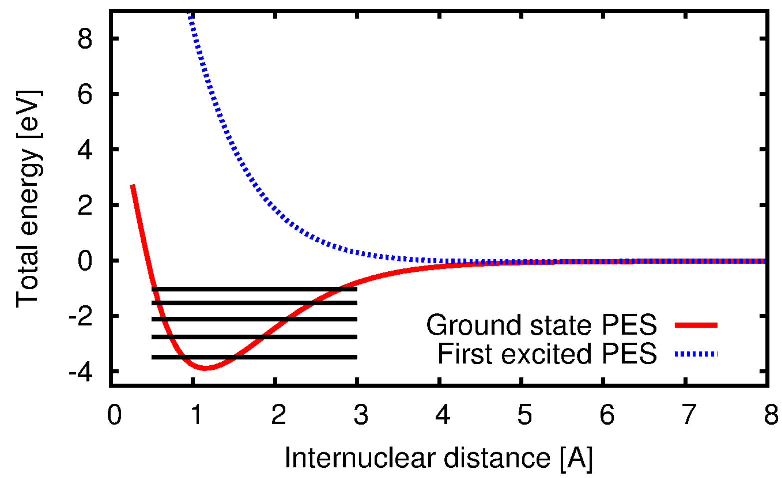
Outline

- Motivations
- Model system: one-dimensional (1-D) dihydrogen cation, H_2^+
- Results: optical spectra for frozen and dynamical ions using different ionic masses
- Conclusions
- Future work

Motivations

- Assess the accuracy of the Born-Oppenheimer Approximation (BOA)

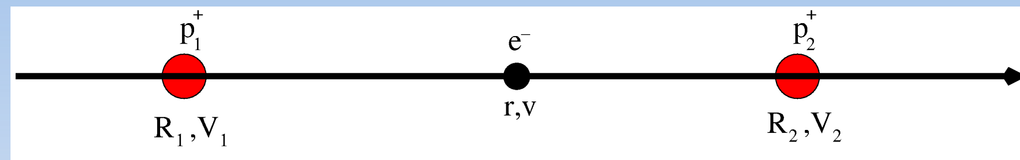
$$\psi_{total} = \psi_{electronic}\,\psi_{ionic}$$



H_2^+ adiabatic
Potential Energy Surfaces (PES)

- Fictitiously vary the electron-ion mass ratio $\frac{m_e}{m_I}$
- If $\frac{m_e}{m_I}$ << 1, the kinetic energy of the ions is negligible: "<u>frozen ions</u>"

Simple model: the one dimensional dihydrogen cation



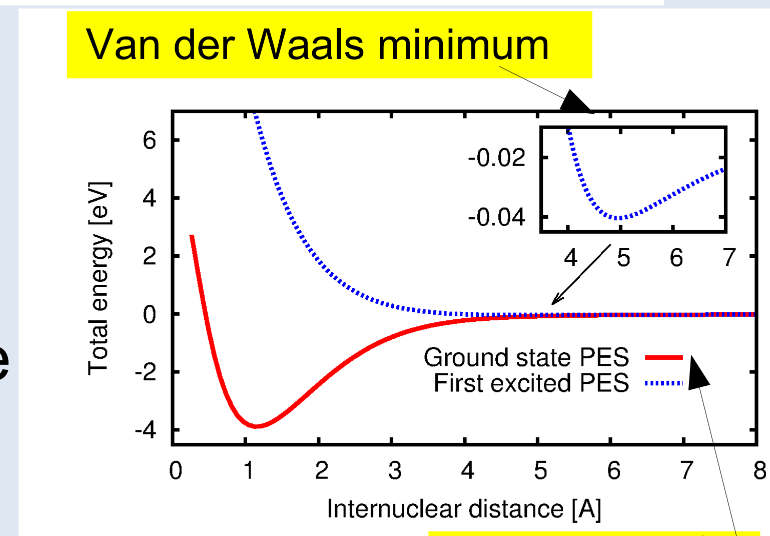
- Hamiltonian (centre of mass frame) in atomic units (a.u.)
  J. R. Hiskes, Phys. Rev. **122** (1960), 1207-1217

$$H_{internal}(R,\xi) = \boxed{-\frac{1}{2\mu_p}\frac{\partial^2}{\partial R^2}} - \frac{1}{2\mu_e}\frac{\partial^2}{\partial \xi^2} - \frac{1}{\sqrt{\left(\frac{R}{2}+\xi\right)^2 + 1}} - \frac{1}{\sqrt{\left(\frac{R}{2}-\xi\right)^2 + 1}} + \frac{1}{\sqrt{R^2+1}}$$

Negligible if $\mu_p >> \mu_e$

- Soft Coulomb Potential:
  Coulomb potential ill-defined in 1-D
  R. Loudon, Am J. Phys. **27** (1959), 649-655

- The numerical diagonalisation is feasible



$$E_{gs}(R) \rightarrow \frac{1}{R^3}$$

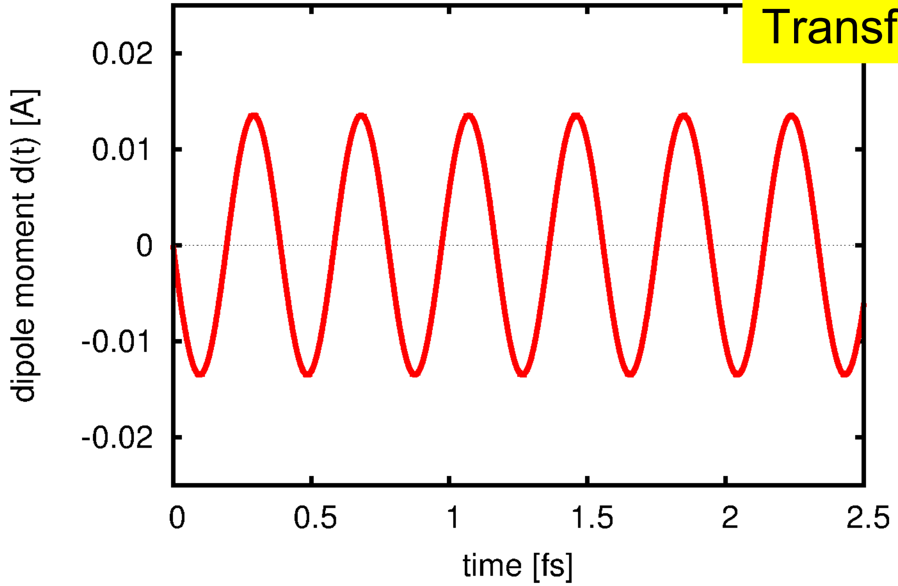
- We use the real-space code OCTOPUS
  A. Castro et al., phys. stat. Sol **243** (2006), 2465-2488
  http://www.tddft.org/programs/octopus/wiki/index.php/Main_page

Frozen Ion Optical Spectra

- The system is perturbed by a weak ”kick”
- Electric dipole d(t) response

Time domain

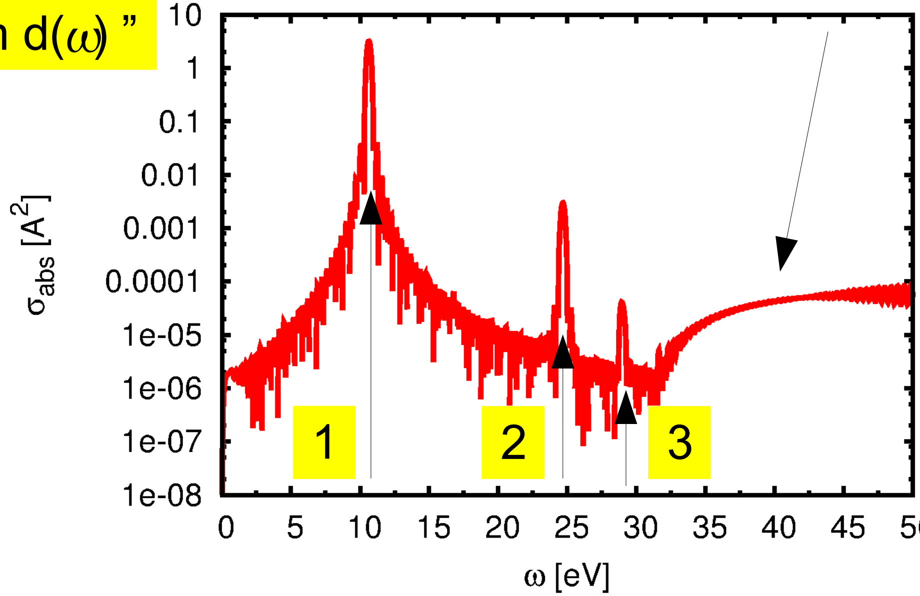
$$d(t)=\bar{d}\cos(\omega_{eq}t+\frac{\pi}{2})$$



”Fourier Transform d(ω) ”

Frequency domain

Continuum states (ionization)

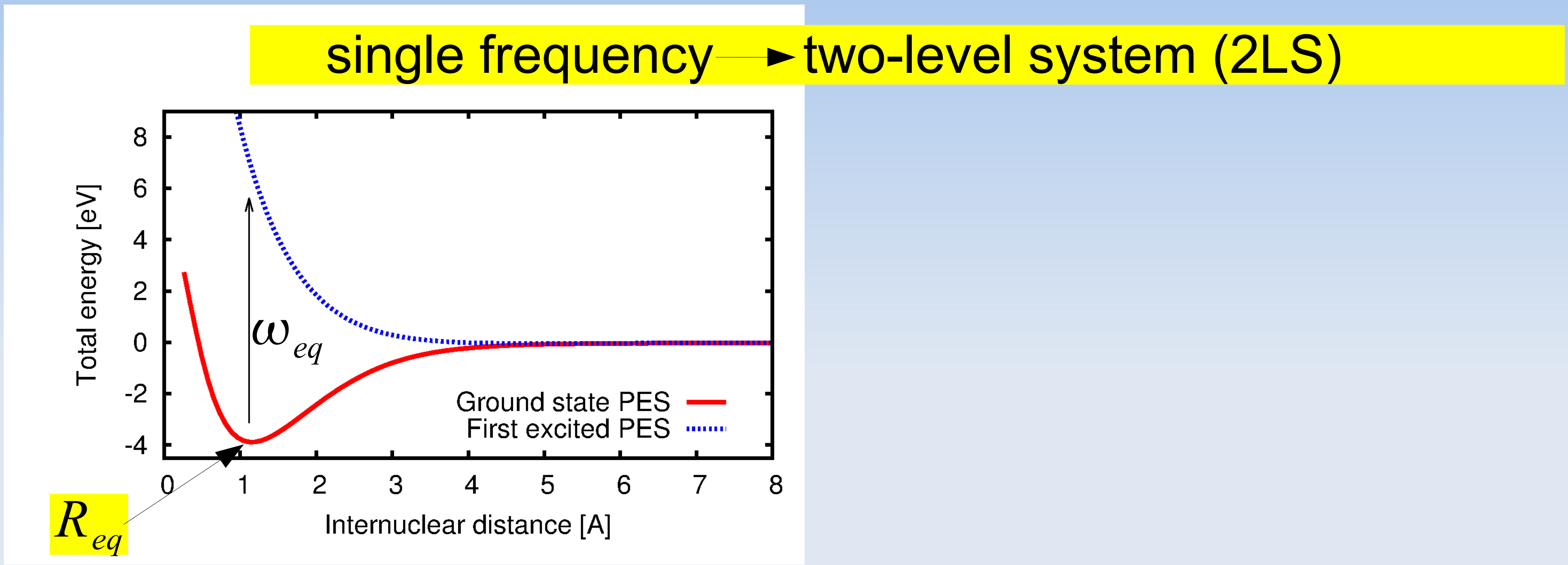


$$1: Ground\ State \rightarrow First\ Excited\ State\ (\omega_{eq})$$

$$2: Ground\ State \rightarrow Third\ Excited\ State$$

$$3: Ground\ State \rightarrow Fifth\ Excited\ State$$

Frozen Ion Optical Spectra



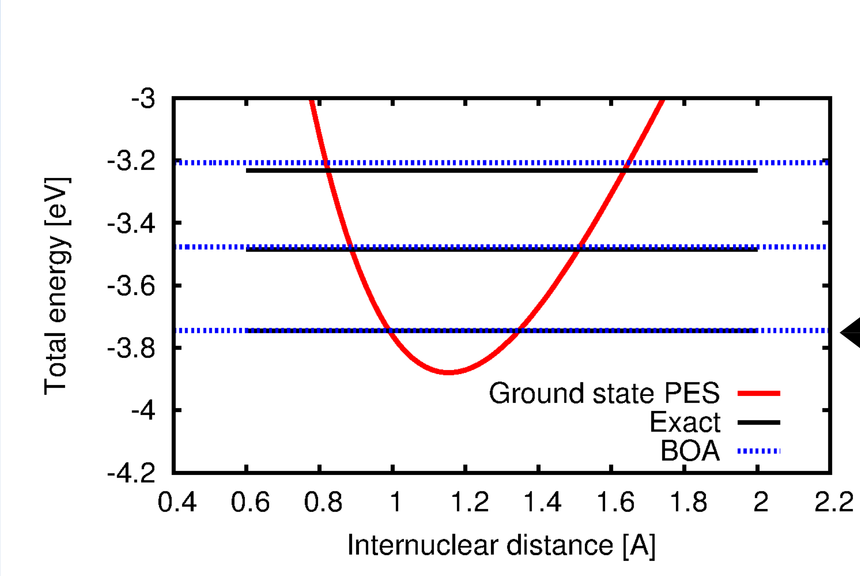
$\frac{m_e}{m_I}$	m_I	R_{eq} *fitted* $[A]$	$\omega_{eq}[eV]$
5.45×10^{-4}	**(proton)**	$1.1540(1)$	$10.6297192(5)$
4.84×10^{-3}	**(muon)**	$1.155(9)$	$10.6311886(8)$
1.0	**(electron)**	$1.2709(1)$	$11.665466(1)$

As m_I decreases the R_{eq} and ω_{eq} increase

BOA accuracy

$\frac{m_e}{m_I}$ m_I	$E_{EXACT}[eV]$	$E_{BOA}[eV]$	$\Delta E[eV]$
5.45×10^{-4} **(proton)**	$-3.7454(3)$	$-3.7447(7)$	$0.0007(5)$
4.84×10^{-3} **(muon)**	$-3.4851(3)$	$-3.4791(4)$	$0.0060(4)$
1.0 **(electron)**	$-0.6052(2)$	$1.165(3)$	$1.770(3)$

Bottom ground state PES



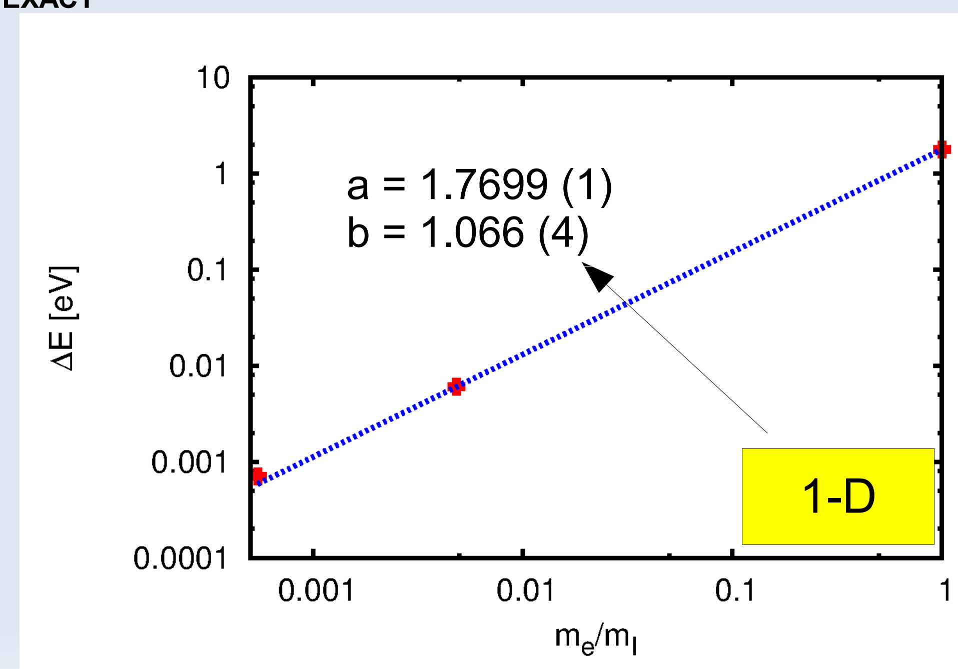
E$_{\mathbf{BOA}}$ = bottom PES + zero-point energy $\frac{1}{2}\hbar\omega$

E$_{\mathbf{EXACT}}$ (numerical)

- BOA, expansion E_{gs} in terms $(\frac{m_e}{m_I})^{\frac{1}{4}}$

$$\Delta E = E_{BOA} - E_{EXACT} = a\left(\frac{m_e}{m_I}\right)^b$$

- 3-D → b=1.5
- 1-D → b=1 (There are no contributions from rotations)



Electron+Ions Optical Spectra

$\frac{m_e}{m_I}$

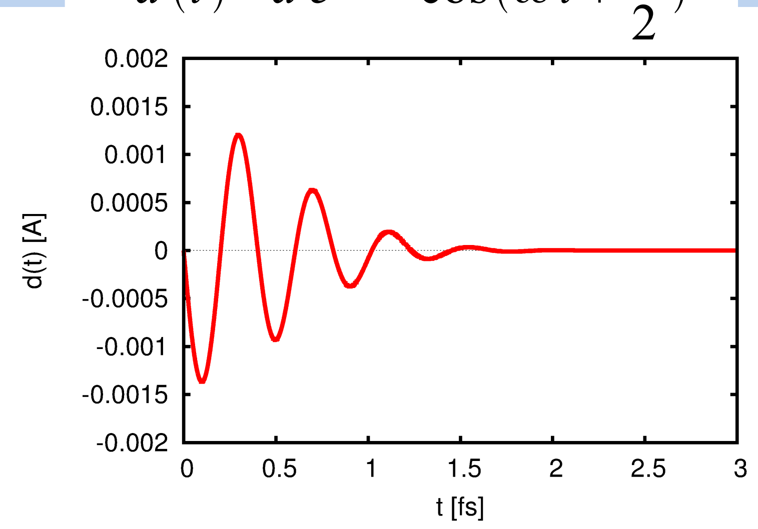
Time domain

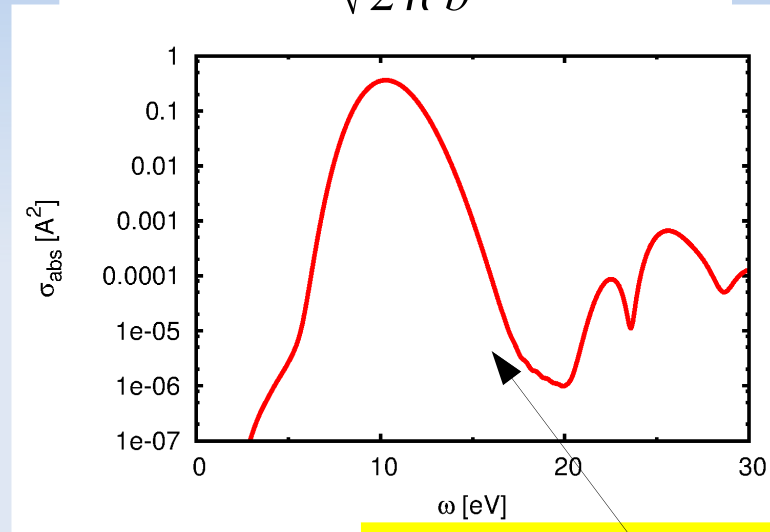
$$d(t) = \bar{d}\, e^{-\frac{b^2 t^2}{2}} \cos(\bar{\omega} t + \frac{\pi}{2})$$

Frequency domain

$$d(\omega) = \frac{a}{\sqrt{2\pi b^2}} e^{-\frac{(\omega-\omega_0)^2}{2b^2}}$$

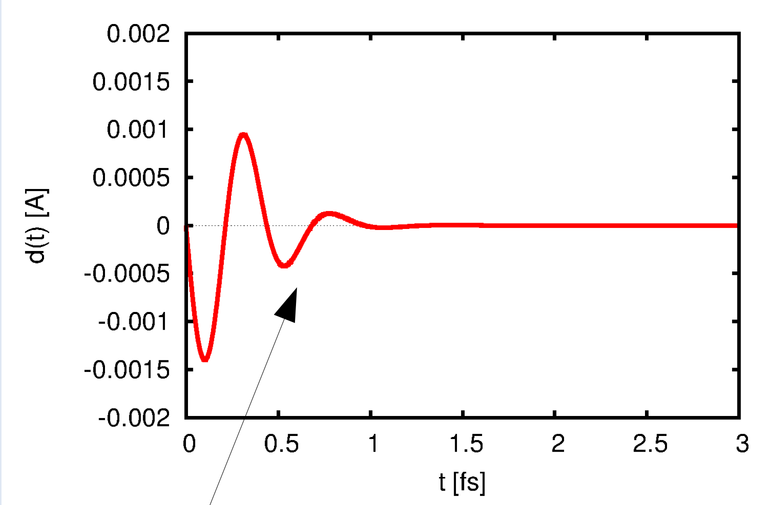
5.45×10^{-4} (proton)

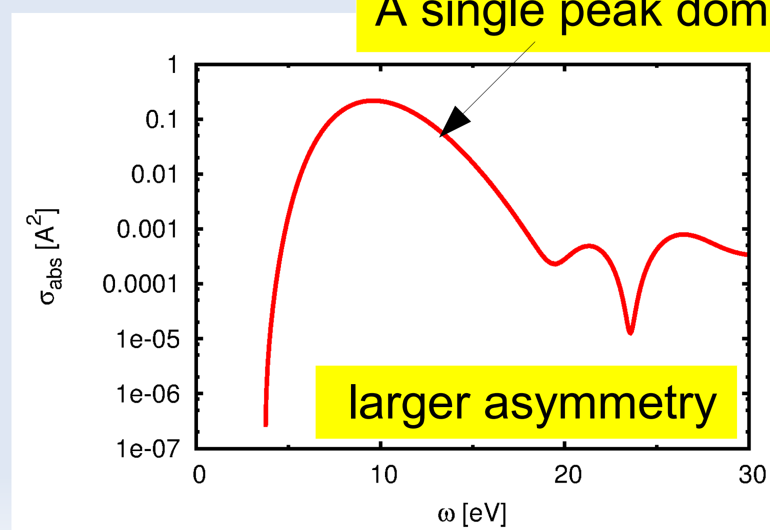




A single peak dominates

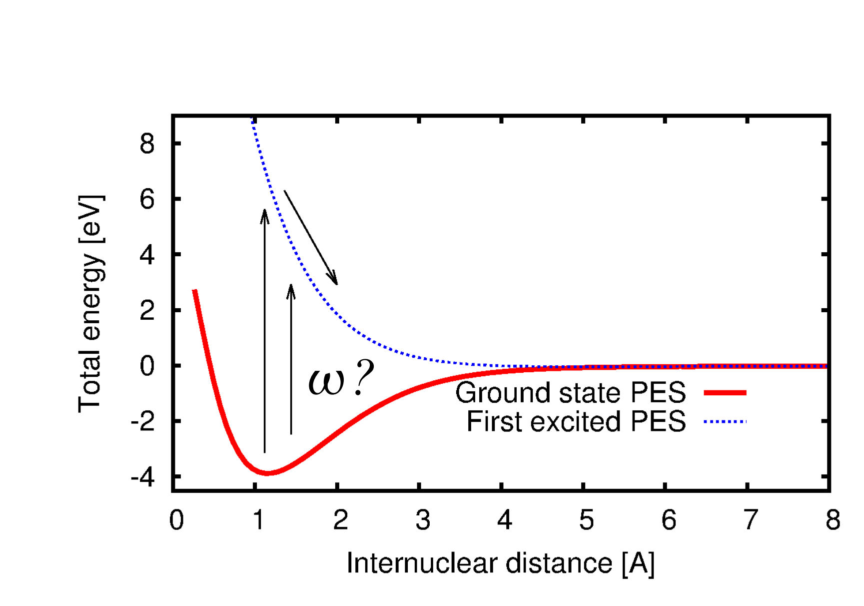
4.84×10^{-3} (muon)





Quicker energy transfer

Electron+Ions Optical Spectra



Time domain

$$d(t)=\bar{d}\, e^{-\frac{b^2 t^2}{2}} \cos\left(\bar{\omega} t + \frac{\pi}{2}\right)$$

Frequency domain

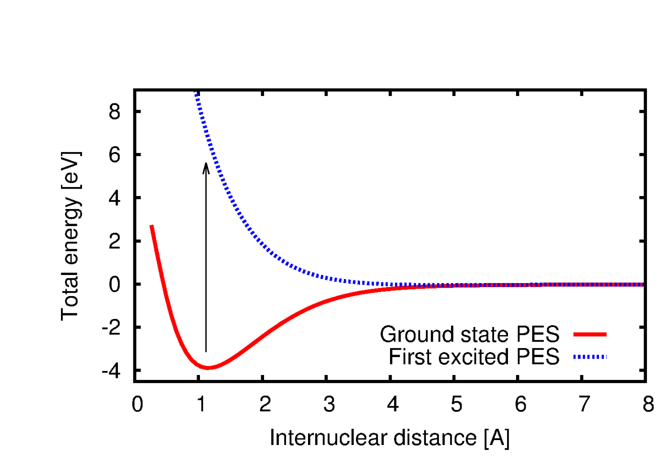
$$d(\omega)=\frac{a}{\sqrt{2\pi b^2}}\, e^{-\frac{(\omega-\omega_0)^2}{2b^2}}$$

$\frac{m_e}{m_I}$ m_I	$\hbar b[eV]$	$\hbar\bar{\omega}[eV]$	$b[eV]$	$\omega_0[eV]$
5.45×10^{-4} **(proton)**	$1.1687(2)$	$10.3984(5)$	$1.228(3)$	$10.385(3)$
4.84×10^{-3} **(muon)**	$1.890(1)$	$9.918(3)$	$2.003(9)$	$9.875(9)$

Conclusions

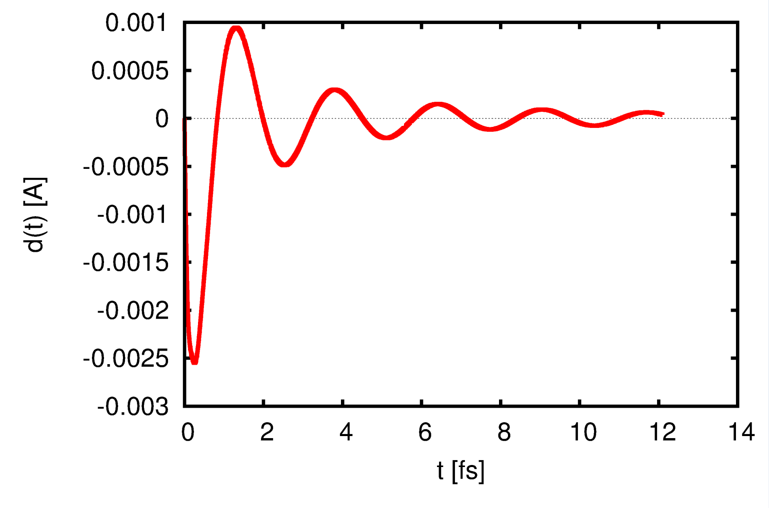
- <u>Static case</u>, we find a BOA power law exponent b$\approx$1 (1-D)

- <u>Dynamic case</u>, single frequency → two-level system (2LS) dynamics for small $\frac{m_e}{m_I}$ (proton,muon)

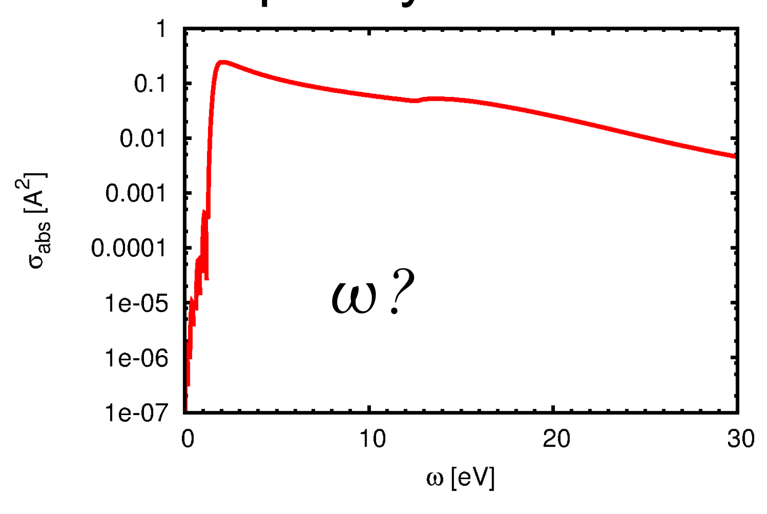


- 2LS is not good for $\frac{m_e}{m_I} = 1$

Time domain



Frequency domain



Future Work

- Same analysis for molecular hydrogen H_2 (e-e correlation included)
- Compare with TDDFT and Ehrenfest calculations
- Consider more realistic electromagnetic pulses (e.g. attosecond XUV pulse) for molecular photodissociation

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THE END