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Master's in Nanoscience

Non-adiabatic effects in one-dimensional one- and two-electron systems:

the cases of H_2^+ and H_2

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nano-bio spectroscopy group

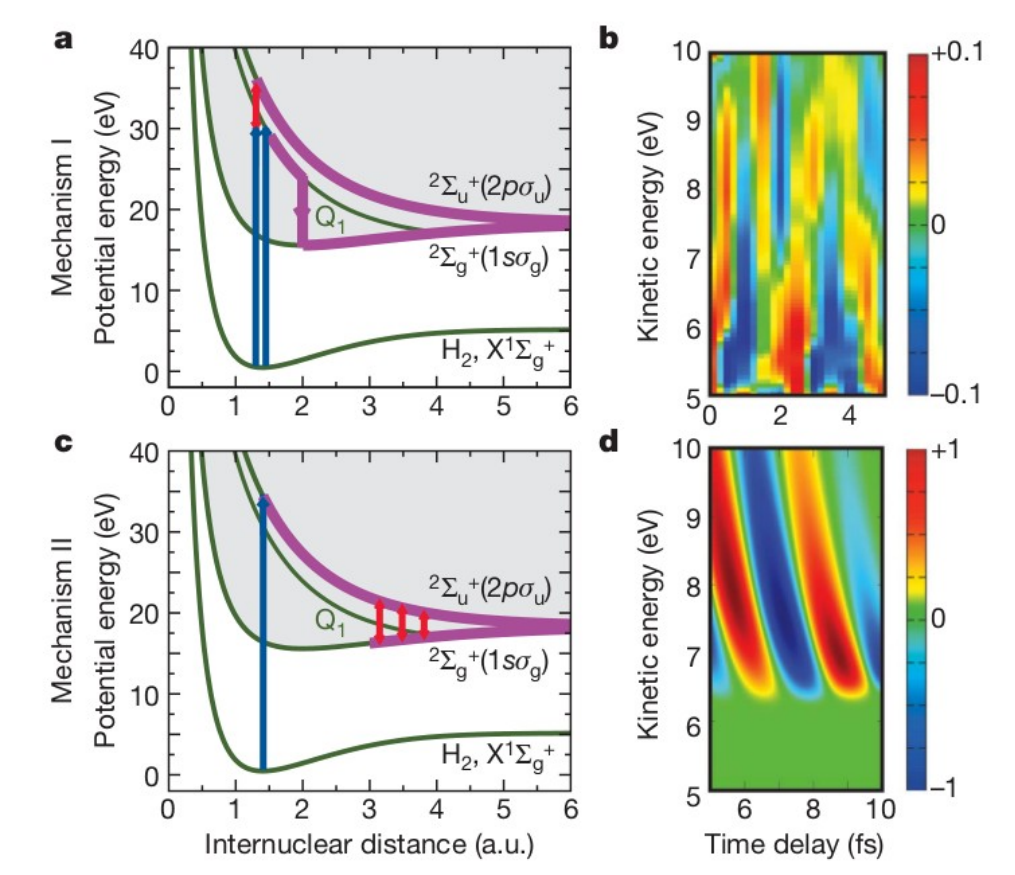
fundación D.I.P.C.

Outline

- Motivations
- Model systems: one-dimensional H_2^+ and H_2
- Results:
  - Validity of the Born Oppenheimer Approximation
  - Optical spectra from frozen ion calculations
  - Optical spectra from dynamic ion calculations
- Conclusions
- Future work

Motivations

- Interpret pump-probe attosecond experiments beyond the Born Oppenheimer Approximation

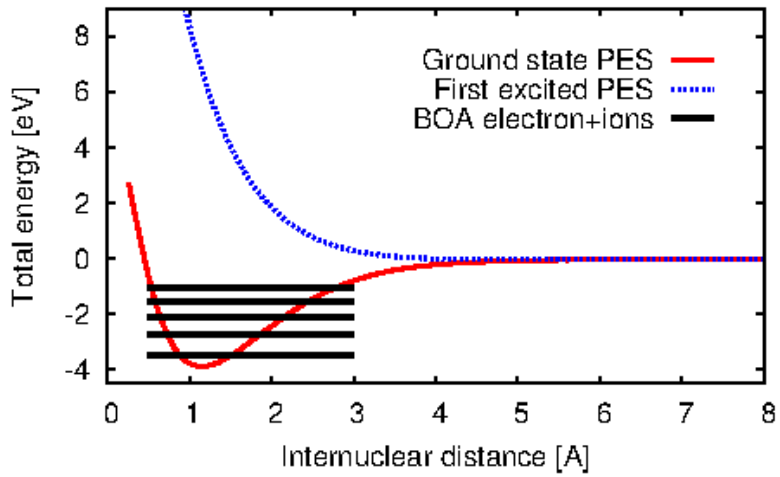


*G. Sansone et al., Nature Letters **465** (2010), 763–767.*

The Born Oppenheimer Approximation

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

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



Potential Energy Surfaces (PES's)

- If $\frac{m_e}{m_I}$ << 1, the kinetic energy of the ions is negligible: "frozen ions"

- Fictitiously vary the electron-ion mass ratio $\frac{m_e}{m_I}$ to change the "electron-ion coupling"

S. Takahashi and K. Takatsuka, J. Chem. Phys. ***124*** *(2006), 1–14.*

Model systems: H_2^+ and H_2 in 1D

- The exact numerical diagonalisation in real-space is feasible
- Exchange symmetry of the molecular wavefunction
  The spin part is directly determined (singlet, triplet)

$$\psi_{H_2^+}(R_1 S_1, R_2 S_2, r_1 s_1) = -\psi_{H_2^+}(R_2 S_2, R_1 S_1, r_1 s_1)$$

$$\psi_{H_2}(R_1 S_1, R_2 S_2, r_1 s_1, r_2 s_2) = -\psi_{H_2}(R_2 S_2, R_1 S_1, r_1 s_1, r_2 s_2)$$

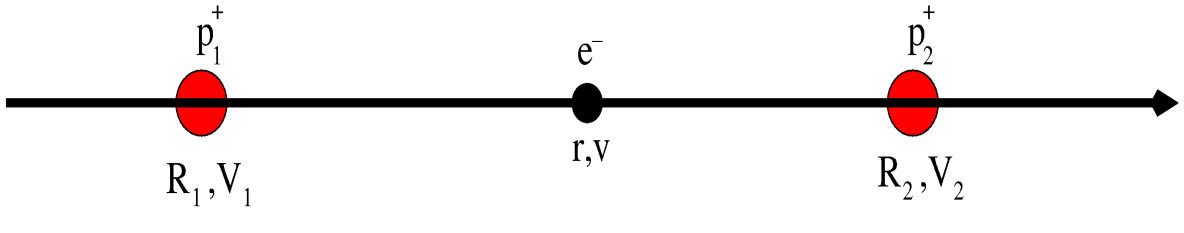
$$\psi_{H_2}(R_1 S_1, R_2 S_2, r_1 s_1, r_2 s_2) = -\psi_{H_2}(R_1 S_1, R_2 S_2, r_2 s_2, r_1 s_1)$$

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

$$V_{int}(x_i - x_j) = \frac{q_i q_j}{\sqrt{(x_i - x_j)^2 + a^2}}$$

- 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

The 1D dihydrogen cation H_2^+



$$R = R_2 - R_1$$

$$\xi = r - \frac{R_1 + R_2}{2}$$

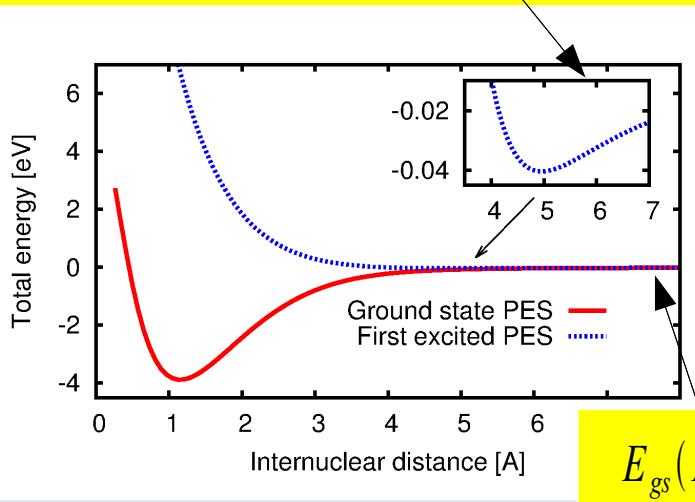
- Hamiltonian (centre of mass frame) in atomic units (a.u.)

J. R. Hiskes, Phys. Rev. ***122*** *(1960), 1207-1217*

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

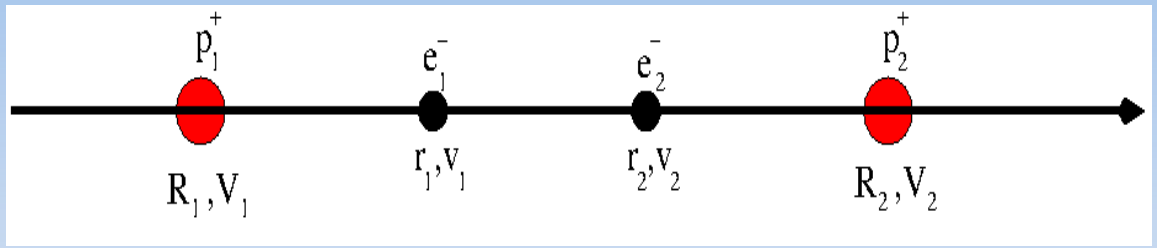
Negligible if $\mu_I >> \mu_e$

Non-covalent long range minimum (H^+ - H)



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

The 1D dihydrogen H_2



$$R = R_2 - R_1 \qquad r = r_2 - r_1$$

$$\xi = \frac{r_1 + r_2}{2} - \frac{R_2 + R_1}{2}$$

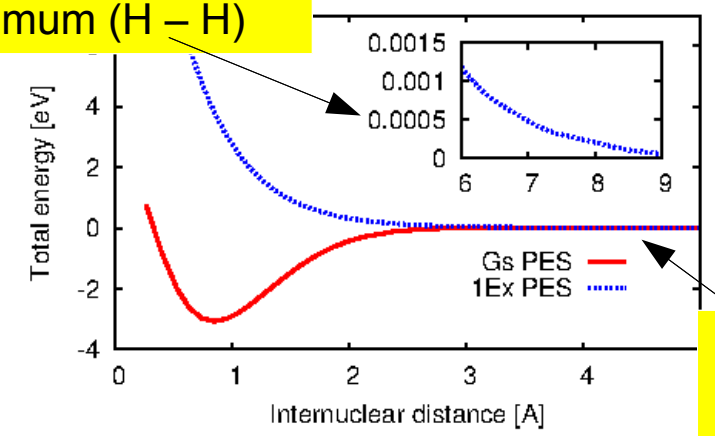
- Hamiltonian (centre of mass frame) in atomic units (a.u.)

$$H_{internal}(R, r, \xi) = -\frac{1}{2\mu_I}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_{eI}}\frac{\partial^2}{\partial \xi^2} - \frac{1}{2\tilde{\mu}_e}\frac{\partial^2}{\partial r^2} - \frac{1}{\sqrt{\left(\frac{R}{2} - \frac{r}{2} + \xi\right)^2 + 1}} - \frac{1}{\sqrt{\left(\frac{R}{2} - \frac{r}{2} - \xi\right)^2 + 1}}$$

Negligible if $\mu_I >> \tilde{\mu}_e$

$$- \frac{1}{\sqrt{\left(\frac{R}{2} + \frac{r}{2} + \xi\right)^2 + 1}} - \frac{1}{\sqrt{\left(\frac{R}{2} + \frac{r}{2} - \xi\right)^2 + 1}} + \frac{1}{\sqrt{R^2 + 1}} + \frac{1}{\sqrt{r^2 + 1}}$$

Non-covalent long range minimum (H – H)

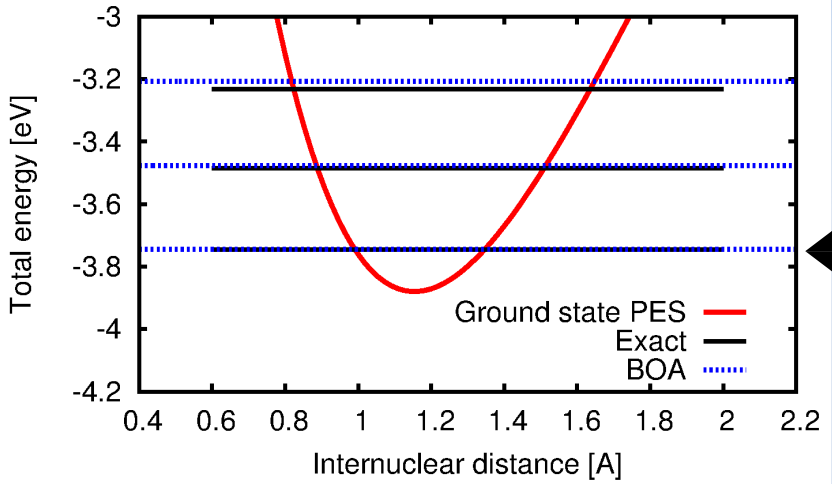


$$E_{gs}(R) \sim -\frac{1}{R^3}$$

BOA validity: H_2^+ case

$\frac{m_e}{m_I}$ 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)**	$-3.4851(3)$	$-3.4791(4)$	$0.0060(4)$
0.1 **(10 electron)**	$-2.2525(2)$	$-2.0936(9)$	$0.1589(6)$
1.0 **(electron)**	$-0.6052(2)$	$1.165(3)$	$1.770(3)$

Bottom of the ground state PES



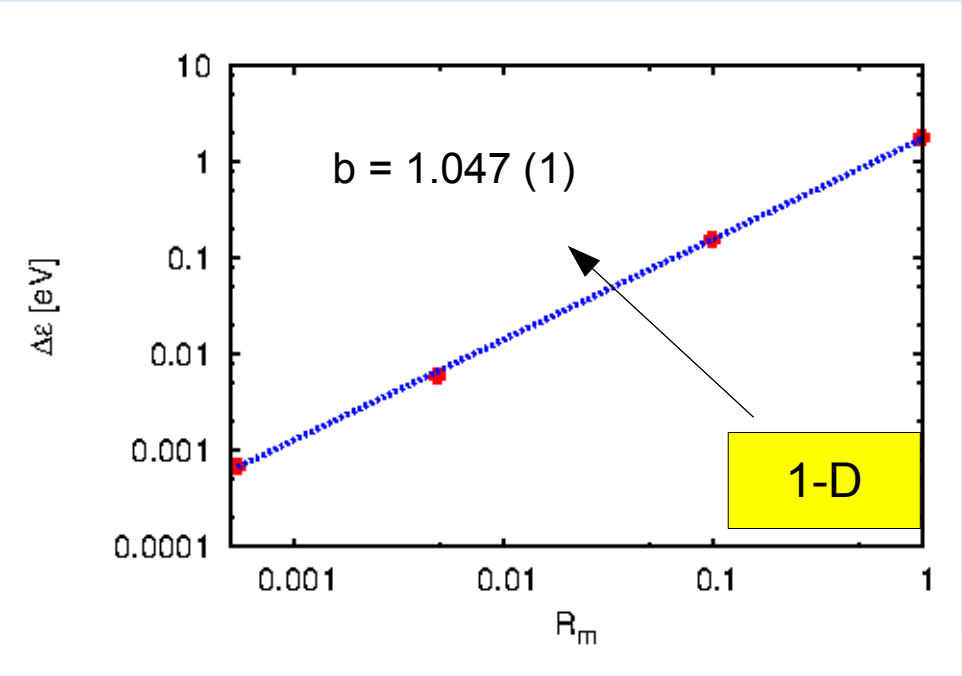
E_{BOA} = bottom PES + zero-point energy $\left(\frac{1}{2}\hbar\omega\right)$

E_{EXACT} (numerical)

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

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

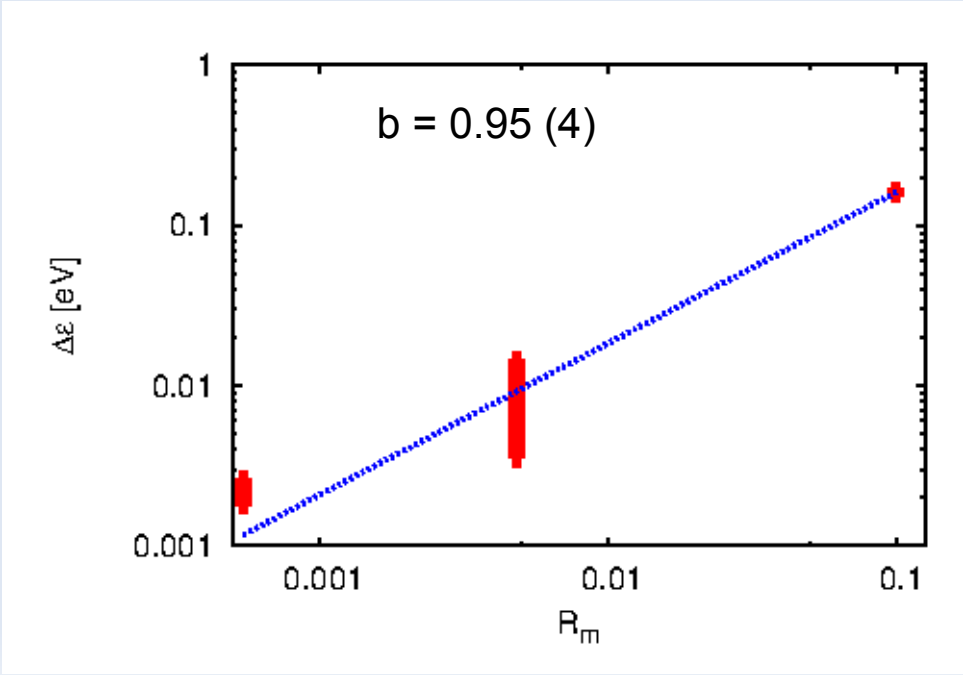
- 3-D → b=1.5
- 1-D → b=1 (There are no contributions from rotations)



BOA validity: H_2 case

$\frac{m_e}{m_I}$ m_I	$E_{EXACT}[eV]$	$E_{BOA}[eV]$	$\Delta E[eV]$
5.45×10^{-4} **(proton)**	$-2.89071(3)$	$-2.8885(5)$	$0.0022(3)$
4.84×10^{-3} **(muon)**	$-2.53937(2)$	$-2.530(1)$	$0.009(1)$
0.1 **(10 electron)**	$-1.11145(2)$	$-0.94962(3)$	$0.16183(3)$

- No bound states for $\frac{m_e}{m_I} = 1$ (**electron**)

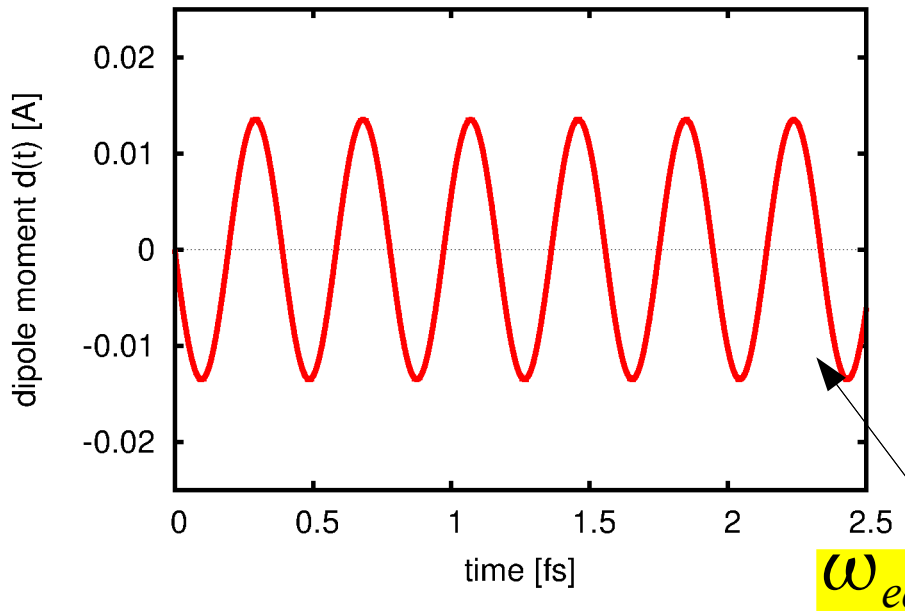


Frozen Ion Optical Spectra H_2^+

- The system is perturbed by a weak "kick" $|\psi(r, t=0)\rangle = e^{ikr}|\psi_{gs}\rangle$
- Dipole response d(t)

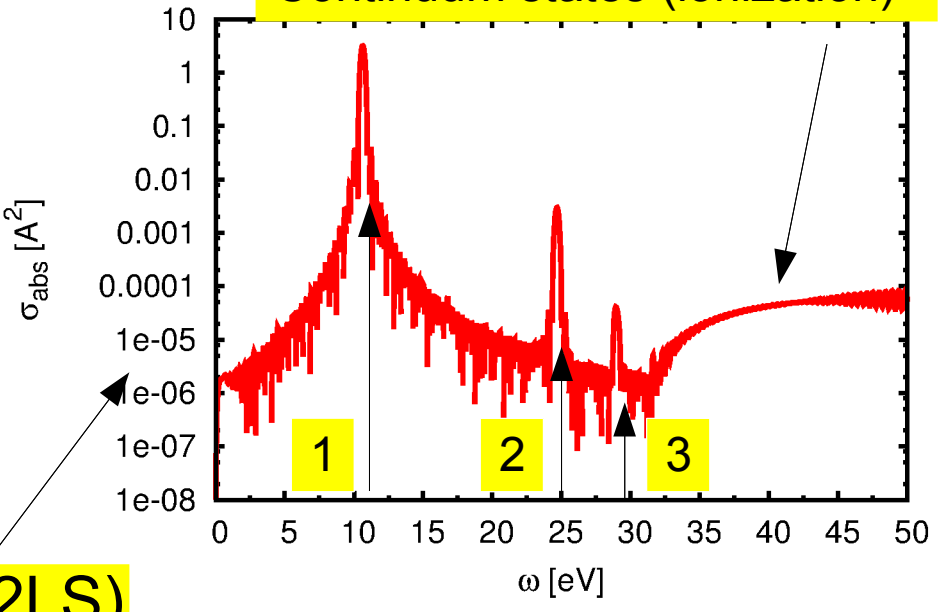
$$d(t) = -\bar{d}\sin(\omega_{eq} t)$$

$$\sigma_{abs} = 4\pi\omega\alpha\,\mathrm{Im}\left[\frac{1}{k}\int_0^t dt\, e^{-i\omega t} f\left(\frac{t}{T}\right) d(t)\right]$$



ω_{eq} (2LS)

Continuum states (ionization)



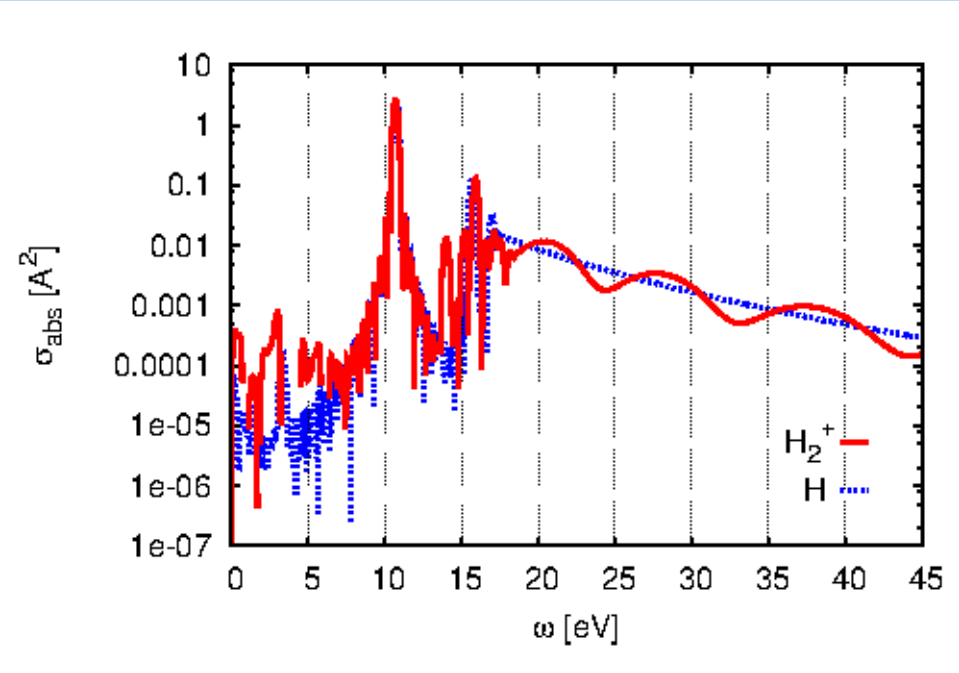
1 : *Ground State → First Excited State* (ω_{eq})

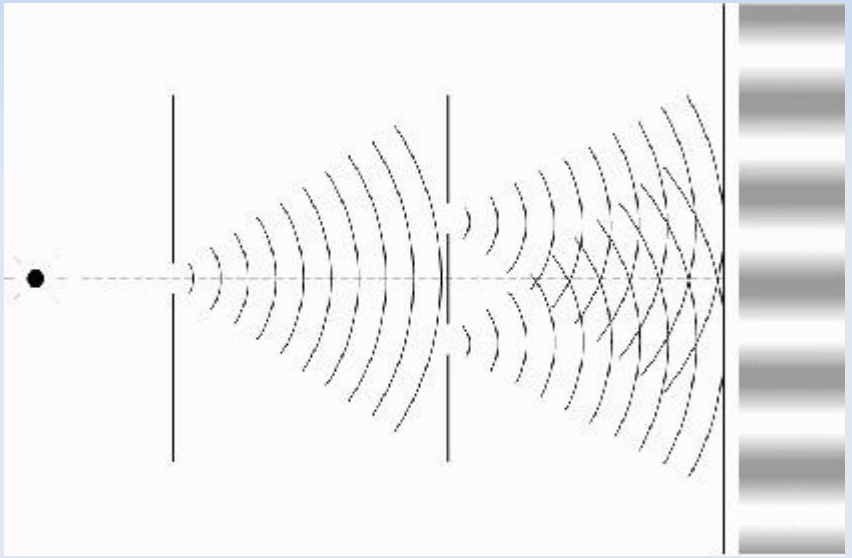
2 : *Ground State → Third Excited State*

3 : *Ground State → Fifth Excited State*

Frozen Ion Optical Spectra H_2^+

- For large R: H_2^+ vs H





http://www.physics.uiowa.edu/~umallik/adventure/quantumwave.html

H H^+ + H^+ H

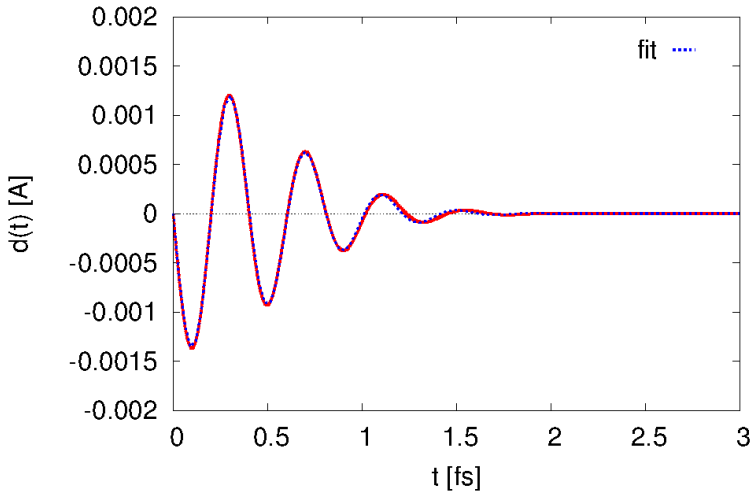
Dynamic Ion Optical Spectra H_2^+

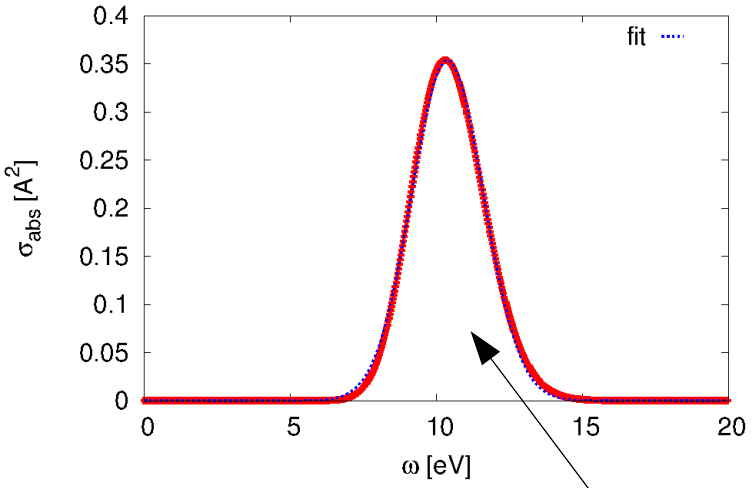
$\frac{m_e}{m_I}$

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

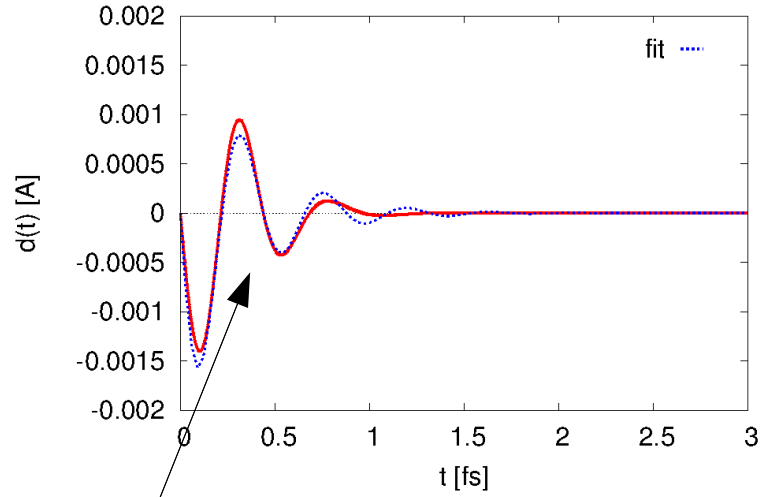
$$\sigma_{abs} = \frac{a\,\omega}{\sqrt{2\pi b^2}} e^{-\frac{(\omega-\omega_0)^2}{2b^2}}$$

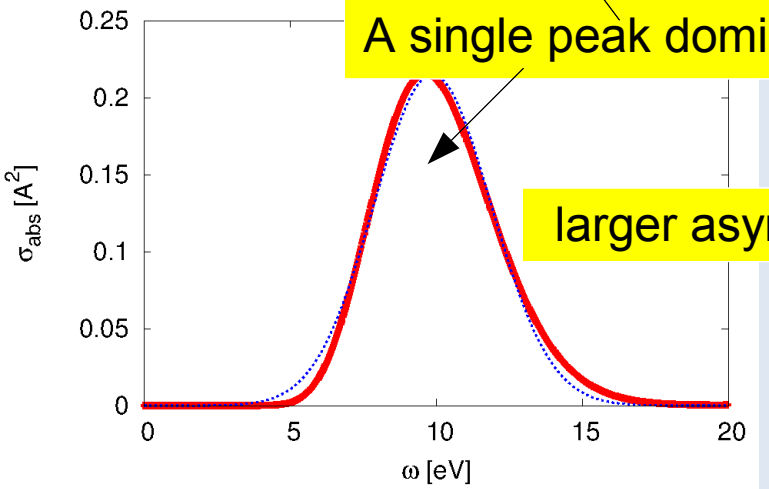
5.45×10^{-4} (proton)





4.84×10^{-3} (muon)





A single peak dominates

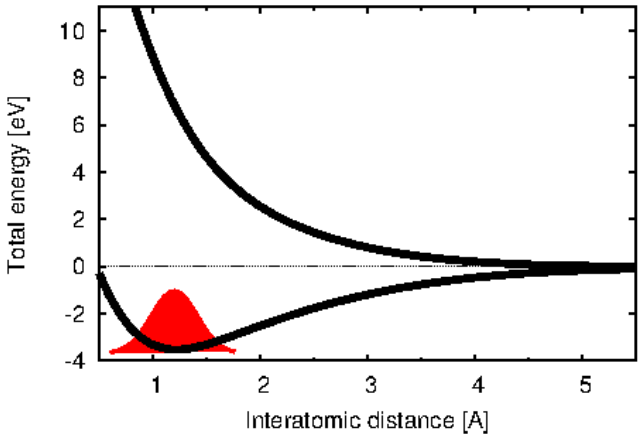
larger asymmetry

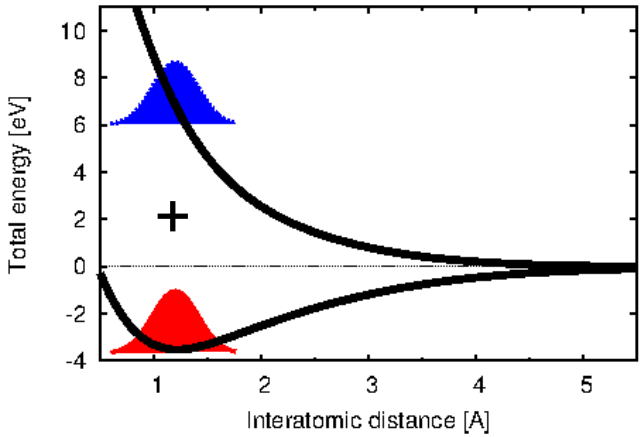
Quicker energy transfer

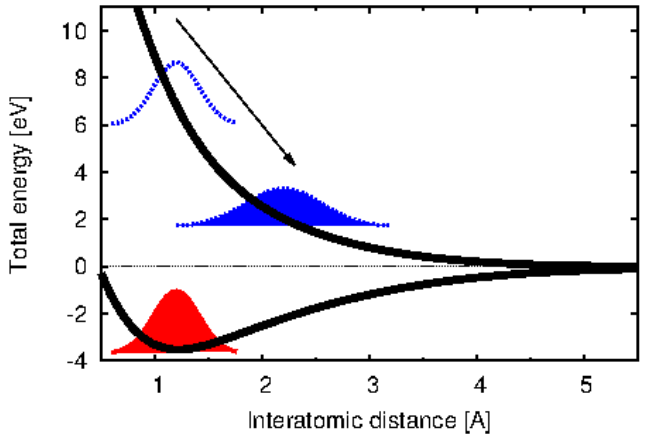
*J. Mauritsson et al., PRL **105** (2010), 1–4.*

Dynamic Ion Optical Spectra H_2^+

- Gaussian qualitative analysis (2LS)







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

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

$\frac{m_e}{m_I}$ m_I	$\hbar b[eV]$	$\hbar\bar{\omega}[eV]$	$b[eV]$	$\omega_0[eV]$
5.45×10^{-4} **(proton)**	$1.052(2)$	$10.228(7)$	$1.237(3)$	$10.237(3)$
4.84×10^{-3} **(muon)**	$2.02(1)$	$9.428(6)$	$2.051(9)$	$9.44(1)$

Conclusions

- Static case H_2^+ and H_2, we find b $\approx$ 1 (1-D)

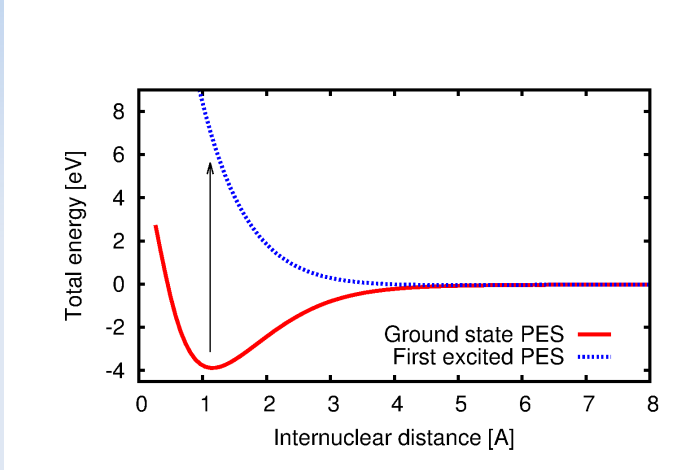
$$E_{BOA} - E_{EXACT} = a\left(\frac{m_e}{m_I}\right)^b$$

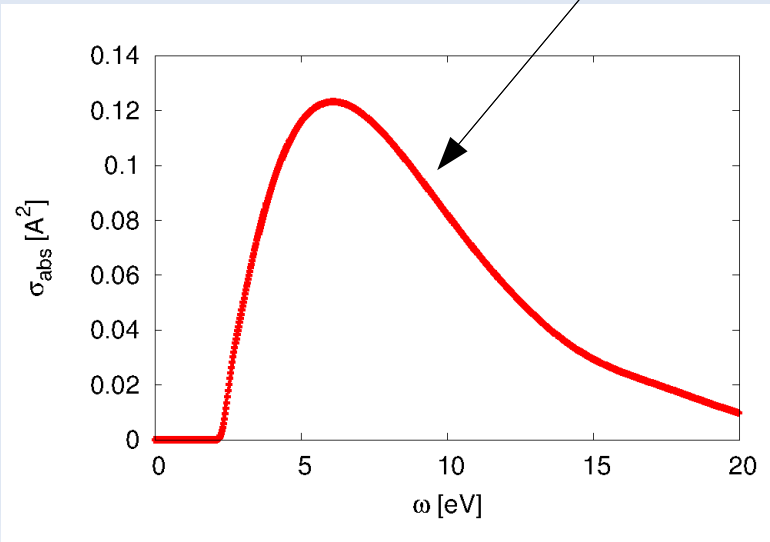
- Dynamic case H_2^+, single frequency → two-level system (2LS)

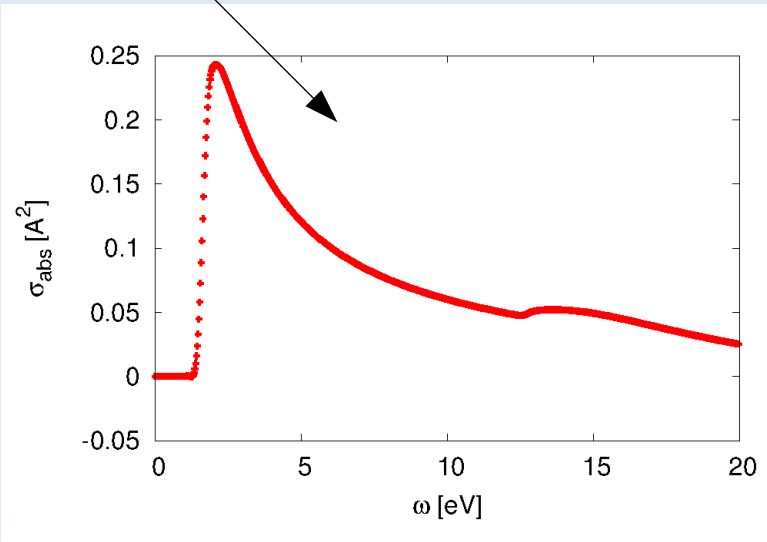
  dynamics for small $\frac{m_e}{m_I}$ (proton,muon)

- 2LS is not accurate for $\frac{m_e}{m_I} = 0.1; \frac{m_e}{m_I} = 1$

  (yet to be fully understood)







Future Work

- Dihydrogen H_2 optical spectra from frozen and dynamic ion calculations
- Improve theoretical model for the dynamic ion calculations (asymmetry, gaussian)
- Perform TDDFT and Ehrenfest dynamics calculations and compare to the exact calculations
- Consider more realistic systems and electromagnetic pulses (pulse shapes) to interpret the experiments

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THANK YOU

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