Photoelectron angular distributions

From p. 4; assuming energy normalization

$$\frac{d\sigma_{a\to E}}{dE} = \frac{4\pi^2}{c\,\omega_{Ea}} \left| M_{Ea}(\omega_{Ea})\right|^2$$

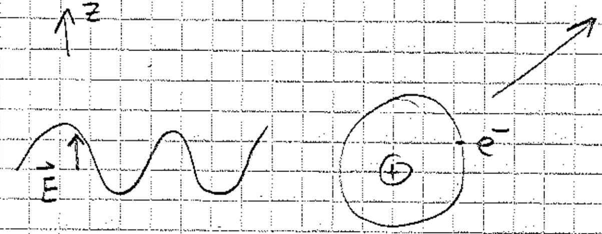
$$= \frac{4\pi^2}{c}\,\omega_{Ea} \left| D^{L}_{q=0} \right|^2 \quad \text{for } \hat{\epsilon} = \hat{z}$$

($\vec{E}$ polarized linearly along z axis)

Use spherical coordinates for initial & final state,

$$\langle \vec{r}\,|\,a\rangle = \langle \vec{r}\,|\,n\,\ell\,m\rangle = \frac{R_{n\ell}(r)}{r}\,Y_{\ell m}(\theta,\varphi)$$

$$\langle \vec{r}\,|\,b\rangle = \langle \vec{r}\,|\,E\,\ell' m'\rangle = \frac{R_{E\ell'}(r)}{r}\,Y_{\ell' m'}(\theta,\varphi)$$



(θ_d, φ_d) emission / detection direction

Partial-wave composition of final state with asymptotic momentum in direction (θ_d, φ_d)

$$\langle \vec{r}\,|\,E, \theta_d, \varphi_d\rangle = \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} \underbrace{i^{\ell'} e^{-i\eta_{E\ell'}}\, Y_{\ell' m'}(\theta_d,\varphi_d)}_{\text{coeff.s of partial wave expansion: } C_{E\ell' m'}(\theta_d,\varphi_d)} \frac{u_{E\ell'}}{r}\, Y_{\ell m}(\theta,\varphi)$$

coeff.s of partial wave expansion: $C_{E\ell' m'}(\theta_d, \varphi_d)$

$\eta_{E\ell'}$: asymptotic phase shift

$\left(= \arg \Gamma\left(\ell'+1 - i\,Z/\sqrt{2E}\right) \quad \text{for } V = -\frac{Z}{r}\right)$

To get the photoemission cross section for emission to (asympt.) direction (θ_d, φ_d), we need dipole matrix elements with partial-wave contributions, given as D_q^L on page 6.

Then, we need to coherently add them up with coefficients $c_{E'l'm'}(\theta_d, \varphi_d)$.

From the second equation on page 7, we now obtain the energy- and emission-angle differential photoelectron-emission cross section:

$$\frac{d^2\sigma_{a \to E, \theta_d, \varphi_d}}{dE\, d\Omega_d} = \frac{16\pi^3}{3c}\, \omega_{Ea}$$

$$\int d\cos\theta\, d\varphi$$

$$\times \left| \sum_{l'm'} a^*_{l'm'}\, f_{l'} \, \langle Y_{l'm'} | Y_{10} | Y_{lm} \rangle \right|^2$$

using dipole selection rules and some tedious algebra:

$$= \frac{\sigma_{tot}}{4\pi} \left[1 + \beta \, \frac{3\cos^2\theta - 1}{2} \right],$$

where

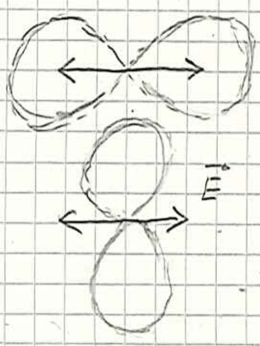
$$a_{l'm'} := i^{l'} e^{-i\eta_{El'}}\, Y_{l'm'}(\theta, \varphi), \quad f_{l'} := \langle R_{El'} | r | R_{nl} \rangle$$

$$\beta = \frac{l(l-1) f_{l-1}^2 + (l+1)(l+2) f_{l+1}^2 - 6l(l+1) f_{l+1} f_{l-1} \cos(\Delta_{El})}{(2l+1)\left[l f_{l-1}^2 + (l+1) f_{l+1}^2 \right]}$$

$$\Delta_{E,l} = \eta_{E,l+1} - \eta_{E,l-1}.$$

σ_{tot} is the total, angle-integrated cross section.

note: – $\beta \in [-1, 2]$ "β parameter"



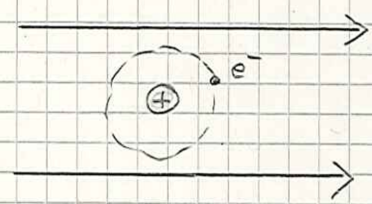
– $\beta = 2$: $\cos^2\theta$ distribution, aligned with light polarization

– $\beta = -1$: $\sin^2\theta$ distribution, aligned perpendicular to light polarization

– $\ell = 0$ (initial s state) $\Rightarrow \beta = 2$.

Lecture 2

A.2 Strong static fields



$\vec{E} = \vec{E}\, e_z$ in a.u. ($\hbar = m = e = 1$):

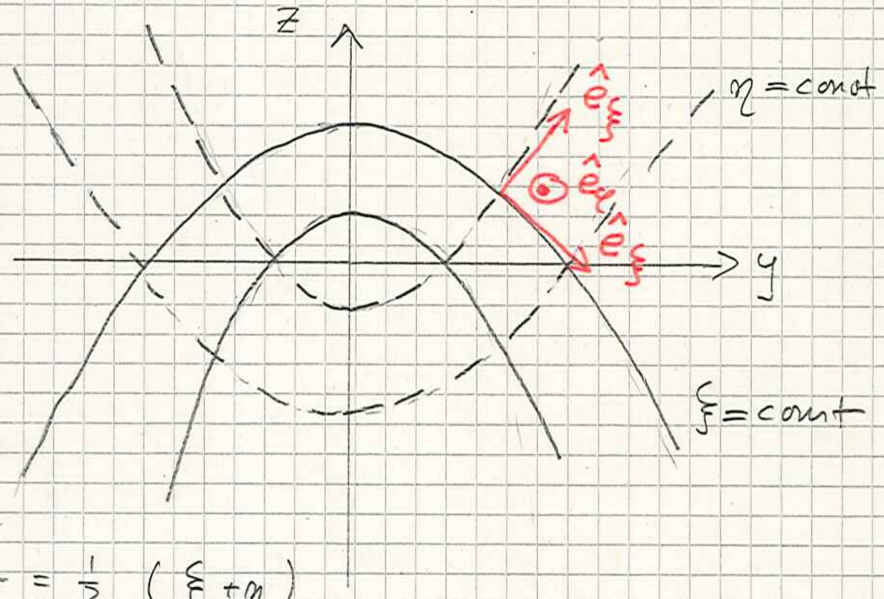
$$\left(-\frac{1}{2}\Delta - \frac{1}{r} + Ez\right)\psi = \varepsilon\psi \qquad (*)$$

– Separation of variables in parabolic coordinates (ξ, η, φ)

$\xi = r + z \quad \in [0, \infty]$

$\eta = r - z \quad \in [0, \infty]$

$\varphi = \tan^{-1}\frac{y}{x} \quad \in [0, 2\pi]$



or

$x = \sqrt{\xi\eta}\,\cos\varphi$

$y = \sqrt{\xi\eta}\,\sin\varphi$

$z = \frac{1}{2}(\xi - \eta)$, $\quad r = \frac{1}{2}(\xi + \eta)$

– Ansatz $\quad \psi = \frac{\chi_1(\xi)}{\sqrt{\xi}}\frac{\chi_2(\eta)}{\sqrt{\eta}}\, e^{im\varphi}$

separates $(*)$:
$$-\frac{1}{2}\frac{d^2\chi_1}{d\xi^2} + \left(U_1(\xi) - \frac{\varepsilon}{4}\right)\chi_1 = 0$$

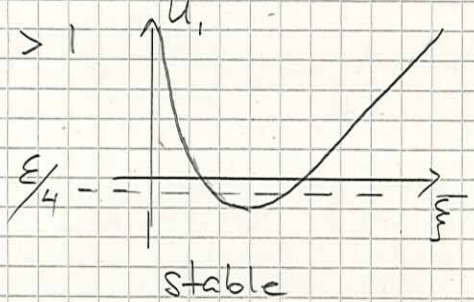
$$-\frac{1}{2}\frac{d^2\chi_2}{d\eta^2} + \left(U_2(\eta) - \frac{\varepsilon}{4}\right)\chi_2 = 0$$

where $$U_1 = -\frac{\beta_1}{2\xi} + \frac{m^2-1}{8\xi^2} + \frac{E}{8}\xi$$

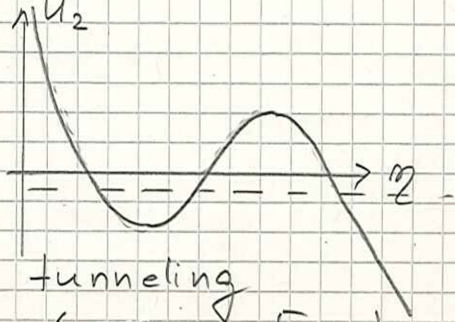
$$U_2 = -\frac{\beta_2}{2\eta} + \frac{m^2-1}{8\eta^2} - \frac{E}{8}\eta .$$

The separation constants satisfy : $\beta_1 + \beta_2 = 1$

For $m > 1$



stable



tunneling
(assume $E > 0$)

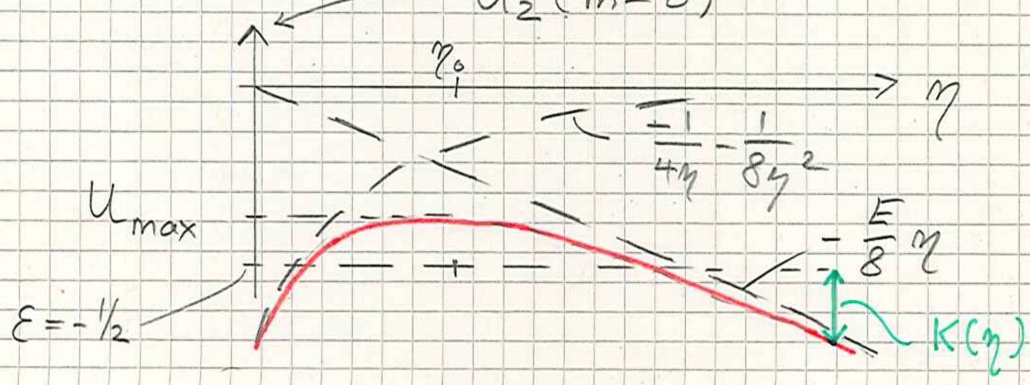
$\Rightarrow$ Ionization along η axis (negative z axis) for $E>0$

- Need ψ for large η

Ionization out of ground state : $\varepsilon = -1/2$, $m=0$, $\beta_2 = 1/2$

$$\psi_0 = \frac{1}{\sqrt{\pi}} \exp\left(-\frac{\xi+\eta}{2}\right)$$

$$-\frac{1}{2}\frac{\partial^2 \chi_2}{\partial \eta^2} - \underbrace{\left(\frac{1}{4\eta} + \frac{1}{8\eta^2} + \frac{E}{8}\eta - \frac{1}{8}\right)}_{U_2(m=0)} \chi_2 = 0$$



η_0 same value inside potential well.

Semi-classical solution (WKB Ansatz, cf. Landau-Lifschitz, QM, §50):

$$\chi_i = \text{Amplitude} \times \exp\left(i \int_{x_{i0}}^{x_i} dx_i' \, p(x_i')\right) \qquad x_1 = \xi, \quad x_2 = \eta$$

$\eta > \eta_0$

$$\psi(\xi,\eta) \simeq \left(\frac{\eta_0}{2\pi p \eta}\right)^{1/2} \exp\left(-\frac{\xi+\eta_0}{2} + i\int_{\eta_0}^{\eta} p(\eta)\, d\eta + i\frac{\pi}{4}\right)$$

$$p(\eta) := \sqrt{-\frac{1}{4} + \frac{1}{2\eta} + \frac{1}{4\eta^2} + E\frac{\eta}{4}}$$ (local momentum)

/ asymptotic expansion (in $1/\eta$) for <u>large η</u>:

i) in pre exponential factor : $p(\eta) \simeq \frac{1}{2}\sqrt{E\eta - 1}$

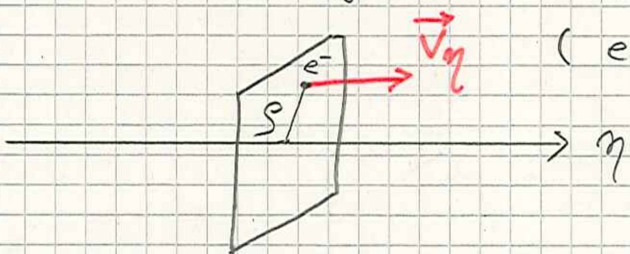
ii) in exponent (include next order in $1/\eta$)

$$p(\eta) \simeq \underbrace{\frac{1}{2}\sqrt{E\eta-1}}_{p|_{1/\eta \to 0}} + \underbrace{\frac{1}{\eta}\frac{1}{\sqrt{E\eta}}\left(1 - \frac{1}{2}E\eta^2\right)}_{\frac{dp}{dw}|_{w\to 0}} \qquad w = \frac{1}{\eta} \to 0$$

evaluate $\int_{\eta_0}^{\eta} p(\eta)\, d\eta$, assume $\eta_0 E \ll 1$

$$\Rightarrow \quad |\psi(\xi,\eta)|^2 \simeq \frac{4}{\pi E \sqrt{E\eta - 1}\;\eta} \exp\left(-\xi - \frac{2}{3E}\right)$$

/ probability current along z (i.e. η) axis , $\eta \gg \eta_0$:



(e^- velocity)

from bottom diagram on p 10 :

$$K(\eta) \simeq \frac{E}{4} - \left(-\frac{E}{8}\eta\right) = \frac{1}{8}(E\eta - 1) \stackrel{!}{=} \frac{V_\eta^2}{2}$$

$$V_\eta = \frac{1}{2}\sqrt{E\eta - 1}$$

$\Rightarrow$ tunneling rate

$$\Gamma(E) = \int_0^\infty \underbrace{d\rho\, 2\pi\rho}_{\text{area}} \; \underbrace{|\psi(\xi,\eta)|^2 \cdot v_\eta}_{\text{prob. current density}}$$

$$d\rho \approx \frac{1}{2}\sqrt{\frac{\eta}{\xi}}\, d\xi \quad \text{for large (fixed) } \eta$$

$$\Rightarrow \boxed{\begin{aligned} \Gamma(E) &= \frac{4}{E}\exp\left(-\frac{2}{3E}\right) \quad \text{in a.u.} \\ &= 8\,\frac{I_{1s}}{\hbar}\cdot\frac{E_{1s}}{E}\exp\left(-\frac{2}{3}\frac{E_{1s}}{E}\right) \end{aligned}}$$

$$I_{1s} = 13.6\,\text{eV} = \tfrac{1}{2}\ \text{a.u.}, \quad E_{1s} = 5.14\cdot 10^9\ \text{V/cm} = 1\,\text{a.u}$$

- Generalization for arbitrary central potential states

$$I_{n^*\ell} = \frac{Z^2}{2n^{*2}} \quad \text{binding energy}$$

$$n^* = n - \delta_\ell \quad \text{effective quantum no.}$$

δ_ℓ : quantum defect

asymptotic wavefunction for $r \gg \frac{1}{p} = \frac{1}{\sqrt{2 I_{n^*\ell}}}$

(assumed field free, to get $C_{n^*\ell}$ only!) typical momentum

$$\psi_{n^*\ell m}(\vec{r}) = C_{n^*\ell}\left(\frac{Z}{n^*}\right)^{n^*+\frac{1}{2}} \exp\left(-\frac{Zr}{n^*}\right) Y_{\ell m}(\hat{r})$$

note : - for ionization of neutral atoms $Z = 1$

- $C_{n\ell} = 2^{2n}\left[\, n\,\Gamma(n+\ell+1)\,\Gamma(n-\ell)\,\right]^{-1}$ known analytically for H atoms only

$$\Rightarrow \boxed{\begin{aligned} &\Gamma_{n^*\ell m}(E) = |C_{n^*\ell}|^2 \left(\frac{3E}{\pi p}\right)^{1/2} I_{n^*\ell m} \cdot G_{\ell m} \left(\frac{2p}{E}\right)^{2n^*-|m|-1} \\ &\qquad \times \exp\left(-\frac{2}{3}\frac{p}{E}\right) \\ &p = \sqrt{2 I_{n^*\ell m}}\,, \quad G_{\ell m} := \frac{(2\ell+1)(\ell+|m|)!}{2^{|m|}\, m!\, (\ell-|m|)!} \end{aligned}}$$

Adiabatic approximation for time-dependent fields

- quasi-static external (laser) fields
- field assumed constant during ionization

(one optical cycle $T \gg$ (ionization rate)$^{-1}$)

replace : $E \longrightarrow E(t)$

special case : $E(t) = E_0 \cos \omega t$:

$$\Gamma_{ADK} = \overline{\Gamma_{n^*\ell m}} = \frac{1}{T}\int_{-T/2}^{T/2} dt\; \Gamma_{n^*\ell m}(E(t)) \quad , \quad T = \frac{2\pi}{\omega}$$

(cycle average)

$$= |C_{n^*\ell}|^2 G_{\ell m} I_{n^*\ell m}\, D^{2n^*-|m|-1} e^{-D/3}$$

$$D := \frac{2^{5/2} I_{n^*\ell m}^{3/2}}{E_0}$$

Ammosov, Delone, Krainov, Sov. Phys. JETP 64, 1191 (1986)
(includes elliptical polarization, special case $n \gg \ell$)

Corkum, Phys. Rev. Lett 71, 1994 (1993) assumes ADK tunneling model for first step in rescattering model for atomic ionization

Note: For shorter optical cycles or more weakly bound (slower) electrons, the adiabatic ADK model eventually breaks down.

A.3 Strong cw fields

- Floquet Ansatz for monochromatic fields

Laser-matter interaction

$$H_{int}(t) = H_{int}(t+T) \quad , \quad T = \frac{2\pi}{\omega}$$

e.g.: $H_{int} = -i\vec{A}\cdot\vec{\nabla}$, $\vec{A}(t) = \vec{A}_0 \cos\omega t$

periodicity implies discrete Fourier expansion

$$H_{int}(t) = \sum_{n=-\infty}^{\infty} H_{int}^{(n)} e^{-in\omega t} \qquad (*)$$

TDSE

$$\underbrace{\left(H_0 + H_{int}(t)\right)}_{H(t)} \psi(t) = i\frac{\partial}{\partial t}\psi \qquad (**)$$

periodicity motivates Ansatz

$$\psi(t) = e^{-i\varepsilon t} \underbrace{\sum_{n=-\infty}^{\infty} F_n e^{-in\omega t}}_{=:\, u_\varepsilon(t)}$$

note: $\boxed{\text{energy} = \varepsilon + n\omega}$

"Quasi energies" ε: cast TDSE in TISE form

$$H\psi = i\frac{\partial}{\partial t}\psi \iff \left(H - i\frac{\partial}{\partial t}\right) u_\varepsilon = \varepsilon\, u_\varepsilon$$

(**) $\iff$ system of time-independent coupled equations:

$$\boxed{\begin{aligned} &\left[\varepsilon + n\omega - H_0\right] F_n(\xi) = \sum_{k=-\infty}^{\infty} H_{int}^{(n)} F_k(\xi) \\ &\text{or } \left[\underline{\underline{H}}_{Floquet} - \varepsilon\right] \vec{F}(\xi) = 0 \end{aligned}}$$

all spatial coordinates

matrix

$$\begin{pmatrix} F_{-\infty} \\ \vdots \\ F_{\infty} \end{pmatrix}$$

(cf. extra sheet)

14a

$$\underset{D_2}{(+ \overset{R}{—} +)} \xrightarrow{\text{pump}} \underset{D_2^+}{(+ \quad +)} \nearrow e^- \xrightarrow{\text{probe}} D + d + \text{kin. energy}$$

Floquet picture:
Application to identify light-induced molecular dissociation pathways

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Quantum-beat imaging of the nuclear dynamics in D_2^+: Dependence of bond softening and bond hardening on laser intensity, wavelength, and pulse duration

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(Received 30 January 2009; published 18 March 2009)

Based on a quantum-mechanical model, we calculate the time evolution of an initial nuclear vibrational wave packet in D_2^+ generated by the rapid ionization of D_2 in an ultrashort pump-laser pulse. By Fourier transformation of the nuclear probability density with respect to the time delay between the pump pulse and the instant destructive Coulomb-explosion imaging of the wave packet at the high-intensity spike of an intense probe-laser pulse, we provide two-dimensional internuclear-distance-dependent power spectra that serve as a tool for visualizing and analyzing the nuclear dynamics in D_2^+ in an intermittent external laser field. The external field models the pedestal to the central ultrashort spike of a realistic probe pulse. Variation in the intensity, wavelength, and duration of this probe-pulse pedestal (i) allows us to identify the optimal laser parameters for the observation of field-induced bond softening and bond hardening in D_2^+ and (ii) suggests a scheme for quantitatively testing the validity of the "Floquet picture" that is commonly used for the interpretation of short-pulse laser-molecule interactions, despite its implicit "continuum wave" (*infinite* pulse length) assumption.

Fragmentation mechanisms

Coulomb explosion

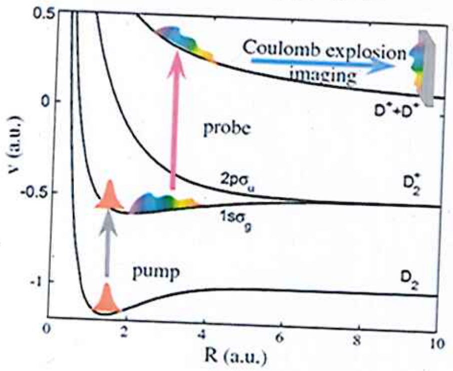

FIG. 1. (Color online) Schematic of the simulated KER measurement underlying the frequency-resolved investigation of the nuclear dynamics in D_2^+ discussed in this work. The pump-laser pulse launches a nuclear wave packet onto the D_2^+ $1s\sigma_g^+$ potential curve by ionizing D_2 and starts the molecular clock. After an adjustable time delay, an intense short probe pulse promotes the nuclear wave packet onto the $2D^+$ repulsive $1/R$ Coulomb-explosion curve and allows for the detection of the fragment-kinetic-energy distribution.

Bond-softening dissociation; Floquet channels

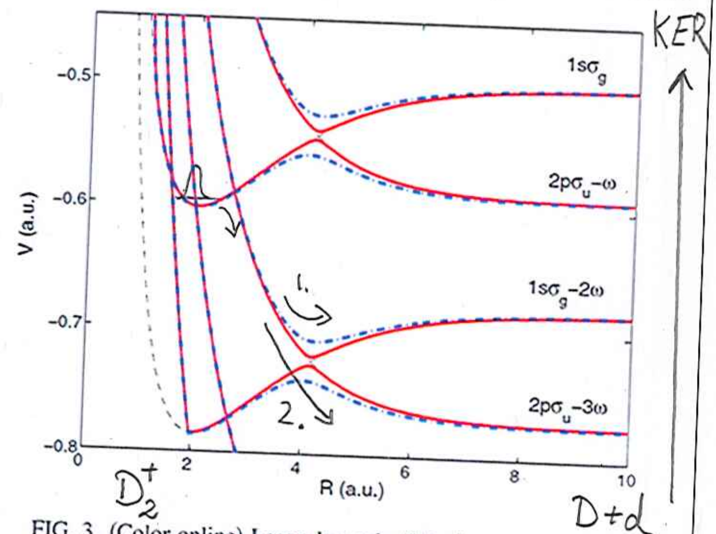

FIG. 3. (Color online) Laser-dressed adiabatic molecular potential curves for D_2^+ and a 500 nm cw laser field with an intensity of 5×10^{11} (solid red lines) and 10^{13} W/cm^2 (dashed-dotted blue lines). Thin black dashed lines show field-free BO potential curves.

KER : fragment kinetic energy release