Photoelectron Spectra Calculated From Absorption

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Introduction

- Simulating unbound quantum systems is computationally expensive
- If we use an absorber, some data will be lost
- Proposed solution:
  - Use density matrices to analyse what is absorbed

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- If we use an absorber, some data will be lost
- Proposed solution:
  - Use density matrices to analyse what is absorbed
- Articles
  - Selstø 2021: Absorption and analysis of unbound quantum particles one by one, DOI: 10.1103/PhysRevA.103.012812
  - Selstø 2022: Absorbers as detectors for unbound quantum systems, DOI: 10.1103/PhysRevA.106.042213
  - Dalen & Selstø 2025: Photoelectron Spectra Calculated from Absorption, DOI: 10.1103/PhysRevA.111.033116

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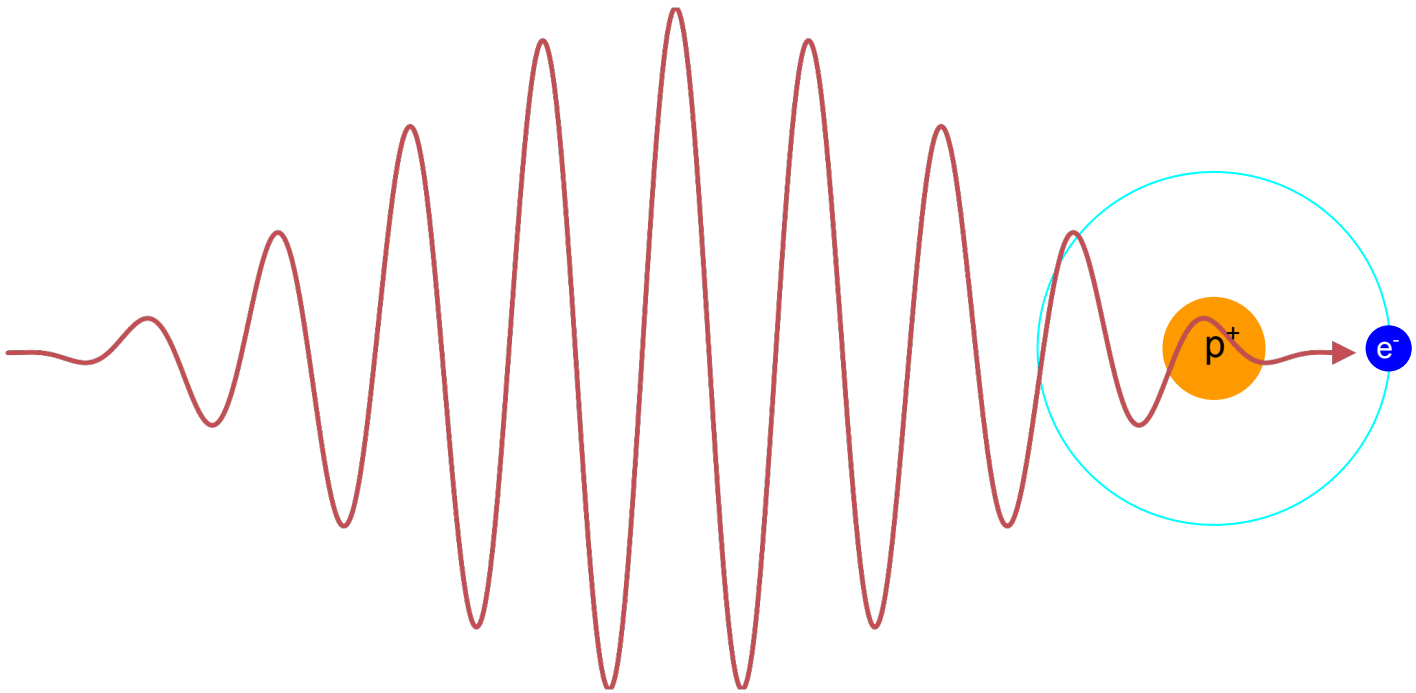
Case Example: Photoionisation



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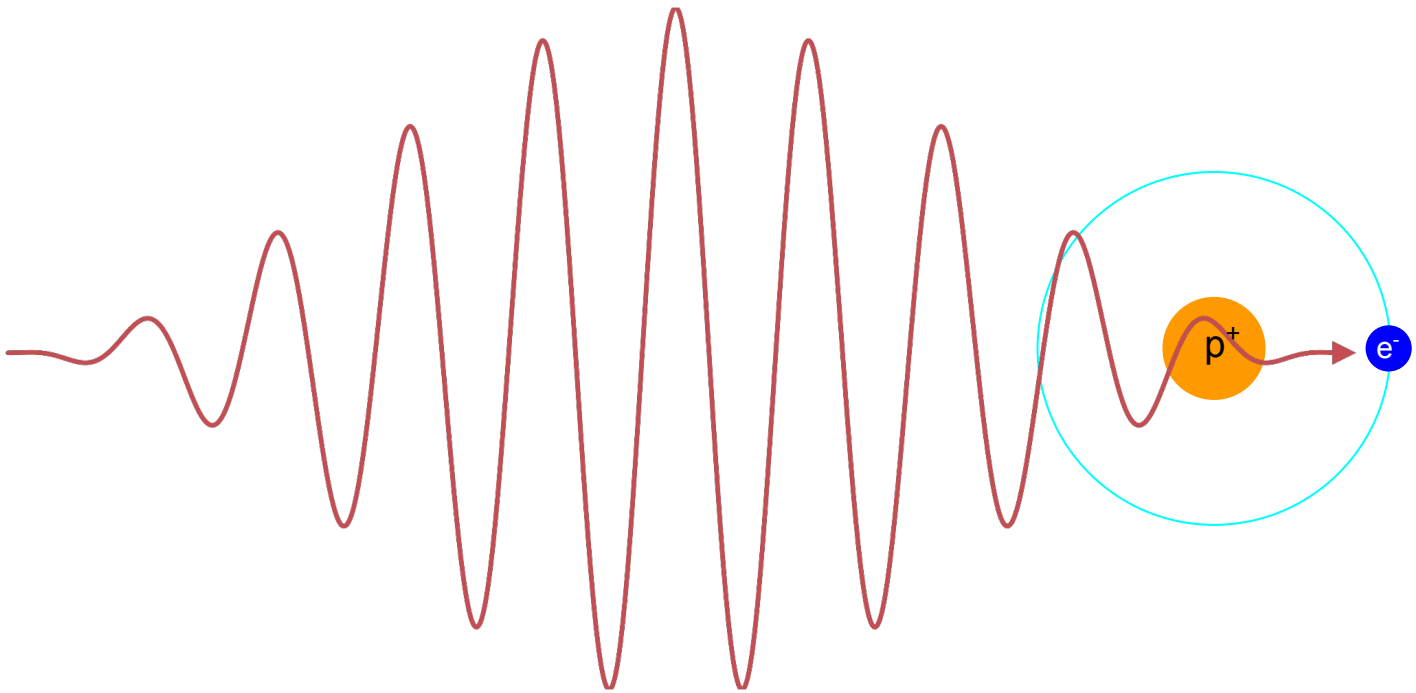


- Want to know:
  - How much of wavefunction is freed
  - Distribution in angle
  - Distribution in energy

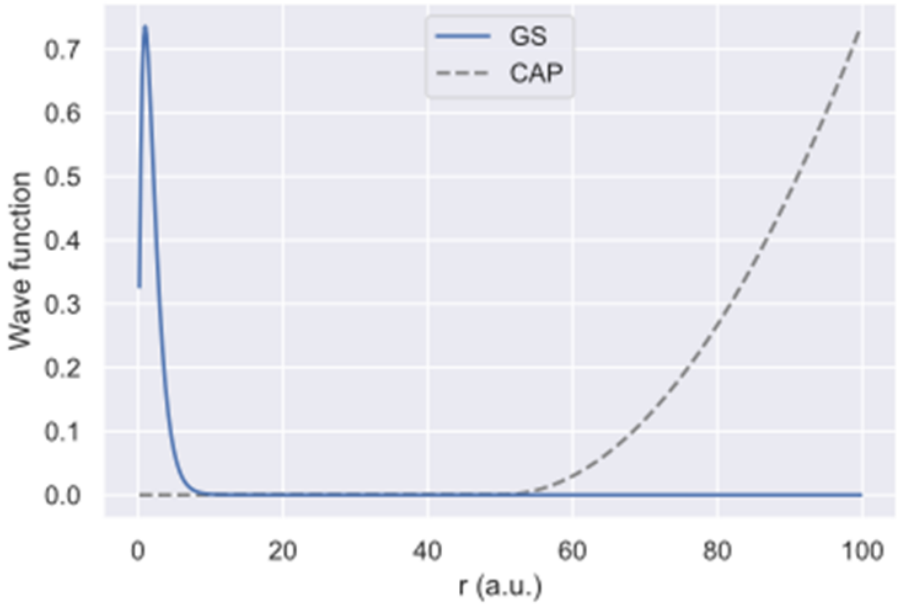
Assumptions

- $H = H_0 + H' = -\frac{1}{2}\mathbf{p}^2 - \frac{1}{r} + A(t)p_z$
- $A(t) = \begin{cases} \frac{E_0}{\omega}\sin^2\left(\frac{\pi}{T}\omega t\right)\cos(\omega t), & 0 \leqslant t \leqslant T \\ 0, & \text{otherwise} \end{cases}$
- Proton is unaffected
- Dipole approximation
  - $m = 0$ always $\longrightarrow$ Can ignore one dimension

Complex Absorbing Potentials (CAPs)

$$H \rightarrow H_{\text{eff}} = H - i\gamma(r)$$

$$\gamma(r) = \begin{cases} \gamma_0 (r - R_{\text{onset}})^2, & r > R_{\text{onset}} \\ 0, & \text{otherwise} \end{cases}$$



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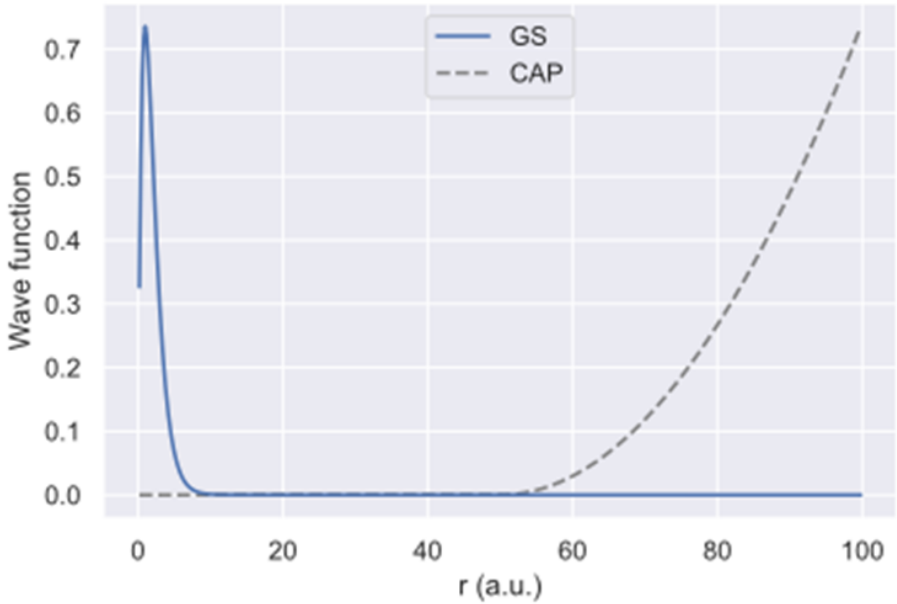

- Will remove parts of the wavefunction as it reaches the CAP
  - The norm will be reduced $\longrightarrow$ No longer Hermitian

CAP Continued

- Change in $|\Psi\rangle$
  - $|\Psi(t+\Delta t)\rangle = [1 - iH_{\text{eff}}(t)\Delta t]\,|\Psi(t)\rangle + \mathcal{O}(\Delta t^2) =$
    $[1 - iH(t)\Delta t - \gamma(r)\Delta t]\,|\Psi(t)\rangle + \mathcal{O}(\Delta t^2)$

CAP Continued

- Change in $|\Psi\rangle$
  - $|\Psi(t+\Delta t)\rangle = [1 - iH_{\text{eff}}(t)\Delta t]\,|\Psi(t)\rangle + \mathcal{O}(\Delta t^2) = [1 - iH(t)\Delta t - \gamma(r)\Delta t]\,|\Psi(t)\rangle + \mathcal{O}(\Delta t^2)$
- Norm loss
  - $-\left(\mathcal{N}^2(t+\Delta t) - \mathcal{N}^2(t)\right) = -\langle\Psi(t+\Delta t)|\Psi(t+\Delta t)\rangle + \langle\Psi(t)|\Psi(t)\rangle + \mathcal{O}(\Delta t^2) = 2\langle\Psi(t)|\gamma|\Psi(t)\rangle\,\Delta t + \mathcal{O}(\Delta t^2)$

CAP Continued

- Change in $|\Psi\rangle$
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- $|\Delta\Psi\rangle = \gamma\,|\Psi\rangle\,\Delta t$ has been removed

- Photoelectron Spectra Calculated From Absorption via the Density Operator
- Consider density operator: $\rho(t) = |\Psi\rangle\langle\Psi|$
- von Neumann equation
  - $i\frac{\partial}{\partial t}\rho = H_{\text{eff}}\rho - \rho H_{\text{eff}}^{\dagger} = [H, \rho] - i\{\gamma, \rho\}$

PESCADO Continued

- Change in ρ
  - $\rho(t+\Delta t) = \rho(t) - i[H,\rho(t)]\Delta t - \{\gamma,\rho(t)\}\Delta t + \mathcal{O}(\Delta t^2)$
- Trace loss
  - $-\left(\mathrm{Tr}\rho(t+\Delta t) - \mathrm{Tr}\rho(t)\right) = \mathrm{Tr}\{\gamma,\rho(t)\}\,\Delta t + \mathcal{O}(\Delta t^2) = 2\langle\Psi(t)|\gamma|\Psi(t)\rangle\,\Delta t + \mathcal{O}(\Delta t^2)$
- $\Delta\rho(t) = \{\gamma,\rho(t)\}\,\Delta t = \{\gamma, |\Psi(t)\rangle\langle\Psi(t)|\}\,\Delta t$ has been removed

PESCADO Continued

- Gives increase of the momentum-differential ionization probability

$$\frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} \to \frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} + \Delta t \left\langle \varphi_{\mathbf{k}} \right| \left\{ \gamma, \rho(t) \right\} \left| \varphi_{\mathbf{k}} \right\rangle$$

$$\frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} = \int_0^t \langle \varphi_{\mathbf{k}} | \{ \gamma, \rho(t') \} | \varphi_{\mathbf{k}} \rangle \, dt'$$

PESCADO Continued

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$$\frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} = \int_0^t \langle \varphi_{\mathbf{k}} | \{\gamma, \rho(t')\} | \varphi_{\mathbf{k}} \rangle \, dt'$$

- If $\{\varphi_{\mathbf{k}}\}$ is time-independent

$$\frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} = \langle \varphi_{\mathbf{k}} | \int_0^t \{\gamma, \rho(t')\} dt' | \varphi_{\mathbf{k}} \rangle = 2\text{Re} \, \langle \varphi_{\mathbf{k}} | \eta | \varphi_{\mathbf{k}} \rangle$$

  - where $\eta \equiv \int_0^t \gamma |\Psi(t')\rangle\langle\Psi(t')| \, dt'$

PESCADO Continued

$$\frac{\partial^3 P_{\text{ion}}}{\partial^3 \mathbf{k}} = 2\text{Re}\,\langle \varphi_{\mathbf{k}} | \eta | \varphi_{\mathbf{k}} \rangle, \quad \text{where } \eta \equiv \int_0^t \gamma |\Psi(t')\rangle\langle\Psi(t')|\, dt' \tag{1}$$

- Scattering states of the form $\varphi_{\mathbf{k}}(\mathbf{r}; t) = \varphi_{\mathbf{k}}^{\text{stat}}(r) \cdot e^{iS_{\mathbf{k}}(t)}$, are phase independent when applied to eq. 1
  - Thus also time independent

Explicit Expressions for Differential Spectra

- Wave function in Spherical Harmonics

$$\Psi(r,\Omega;t) = \frac{1}{r}\sum_{\ell,m} f_{\ell,m}(r;t)\,Y_{\ell,m}(\Omega) = \frac{1}{r}\sum_{\ell} f_{\ell}(r;t)\,Y_{\ell}(\Omega)$$

- Approximate energy and ejection angle probabilities via

$$\varphi^{\mathrm{stat}}_{\varepsilon,\Omega_k} = \frac{1}{r}\sum_{\ell,m} i^{\ell} e^{i\sigma_\ell(\varepsilon)}\psi_{\varepsilon,\ell}(r)\,Y_{\ell,m}(\Omega)\,Y^{*}_{\ell,m}(\Omega_k), \tag{2}$$

Doubly Differential Spectra

$$\frac{\partial^2 P}{\partial \varepsilon \partial \Omega_k} \approx 2\mathrm{Re} \sum_{\ell} \sum_{\ell'} i^{\ell' - \ell} e^{i(\sigma_{\ell'}(\varepsilon) - \sigma_{\ell}(\varepsilon))}$$

$$\times\, Y_{\ell}(\Omega_k) Y^*_{\ell'}(\Omega_k)$$

$$\times \int \mathrm{d}r \int \mathrm{d}r' \psi^*_{\varepsilon,\ell}(r) \zeta_{\ell,\ell'}(r, r') \psi_{\varepsilon,\ell'}(r') \quad \text{where}$$

$$\zeta_{\ell,\ell'}(r, r') = \int_0^T \gamma(r) f_{\ell}(r; t) f^*_{\ell'}(r'; t)\, \mathrm{d}t$$

Energy Differential Spectra

- Integrate out Ω_k

$$\frac{\partial P}{\partial \varepsilon} \approx 2\mathrm{Re} \sum_{\ell} \int \mathrm{d}r \int \mathrm{d}r' \psi^*_{\varepsilon,\ell}(r) \zeta_\ell(r, r') \psi_{\varepsilon,\ell}(r') \quad \text{where}$$

$$\zeta_\ell(r, r') = \int_0^T \gamma(r) f_\ell(r; t) f^*_\ell(r'; t)$$

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Discretising a Truncated Wave Function

- A truncated wavefunction can be separated

$$\Psi(r,\Omega;t) = \frac{1}{r}\sum_{\ell,m} f_{\ell,m}(r;t)\,Y_{\ell,m}(\Omega)$$
$$= \frac{1}{r}\sum_{\ell,0} f_{\ell,0}(r;t)\,Y_{\ell,0}(\Omega) = \frac{1}{r}\sum_{\ell} f_{\ell}(r;t)\,Y_{\ell}(\theta)$$

  - Where $Y_{\ell,m}(\Omega)$ are the spherical harmonics, and $f_{\ell,m}(r;t)$ are the radial parts

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  - Where $Y_{\ell,m}(\Omega)$ are the spherical harmonics, and $f_{\ell,m}(r;t)$ are the radial parts
- We can represent the radial part as a matrix
- $$F(t) = \begin{pmatrix} f_0(r_1;t) & f_1(r_1;t) & \cdots & f_{\ell_{\max}}(r_1;t) \\ f_0(r_2;t) & f_1(r_2;t) & \cdots & f_{\ell_{\max}}(r_2;t) \\ \vdots & \vdots & \ddots & \vdots \\ f_0(r_N;t) & f_1(r_N;t) & \cdots & f_{\ell_{\max}}(r_N;t) \end{pmatrix}$$
  - N is the number of grid points and $\ell_{\max}$ is the maximum ℓ value in our truncated basis

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  - N is the number of grid points and $\ell_{\max}$ is the maximum ℓ value in our truncated basis
- Reduces computational cost

Discretising the Hamiltonian

- The action of the Hamiltonian is also separable, $H\Psi = H_0\Psi + H'(t)\Psi$, and is represented as matrix multiplications:

$$H_0\Psi \sim \frac{1}{2}\left(-D_2F + R^{-2}FS\right) - R^{-1}F$$
$$H'\Psi \sim -iA(t)\left(D_1FT_1 + R^{-1}FT_2\right)$$

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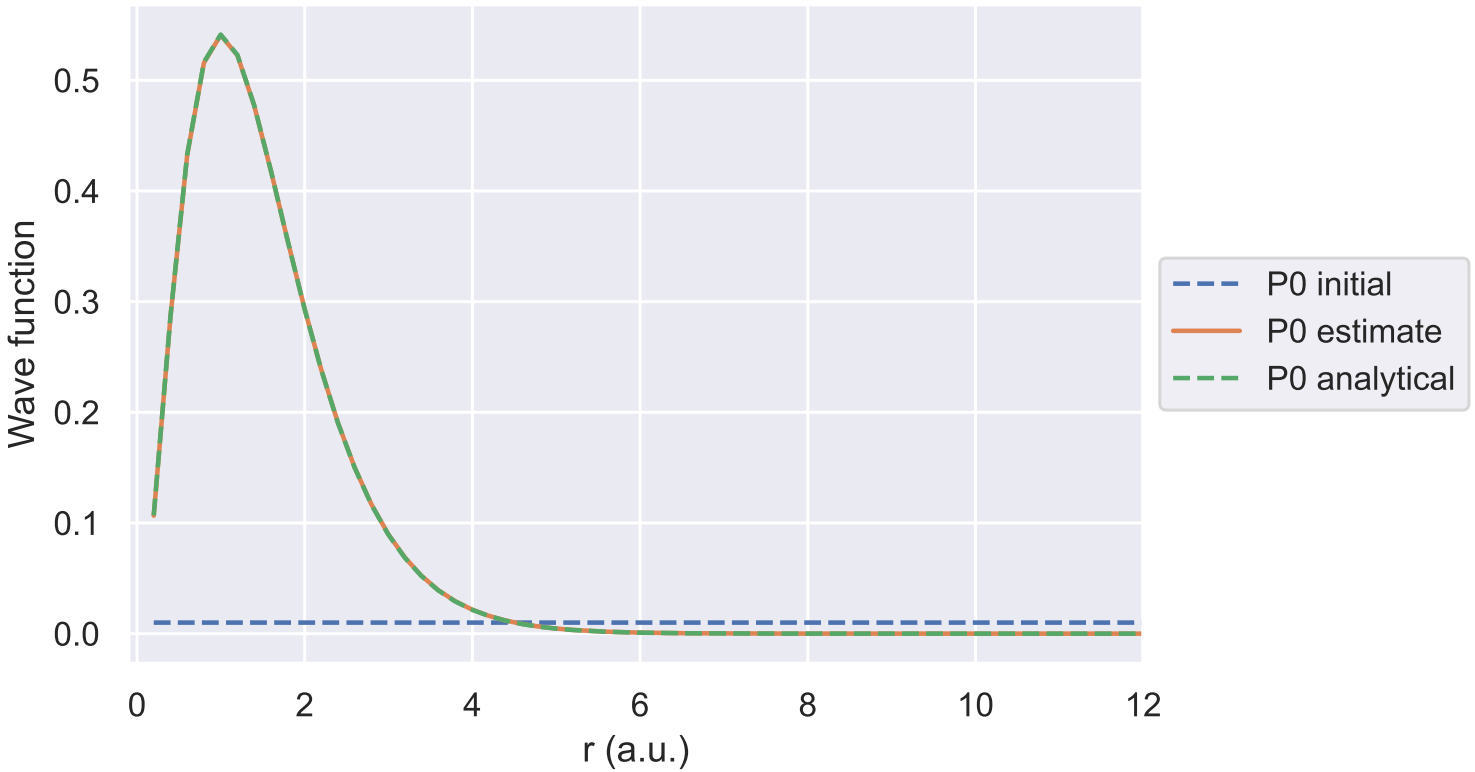
- Where
  - D_1 and D_2 are the finite difference approximations to the the first and second order derivatives in r
  - $A(t)$ is the potential from the laser pulse
- These matrices are also smaller

Discretising the Hamiltonian

- We also have
  - $R = \mathrm{diag}\{r_1, r_2, ...\} \quad S = \mathrm{diag}\{0, ..., \ell(\ell+1), ..., \ell_{\max}(\ell_{\max}+1)\}$
  - $T_1 = \begin{pmatrix} 0 & b_1 & 0 & \cdots \\ b_1 & 0 & b_2 & \cdots \\ 0 & b_2 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad T_2 = \begin{pmatrix} 0 & -1b_1 & 0 & \cdots \\ 1b_1 & 0 & -2b_2 & \cdots \\ 0 & 2b_2 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$
  - $b_\ell = \frac{\ell}{\sqrt{(2\ell-1)(2\ell+1)}}$
  - Here we have used that:
    - $\cos\theta\, Y_{\ell,0} = b_{\ell+1} Y_{\ell+1,0} + b_\ell Y_{\ell-1,0}$
    - $\sin\theta \frac{\partial}{\partial\theta} Y_{\ell,0} = \ell b_{\ell+1} Y_{\ell+1,0} - (\ell+1) b_\ell Y_{\ell-1,0}$

Initial State

- Found using imaginary time
  - $t \to \tau = -it$
  - $\Psi(t) = e^{-iH_0 t}\Psi_0 \to e^{-H_0 \tau}\Psi_0$
  - Will approach the ground sate as imaginary time passes



Calculating Time Evolution

- Use Magnus propagator
  - $\Psi(\vec{x}, t + \Delta t) \approx \exp[-iH(t + \Delta t/2)\Delta t]\Psi(\vec{x}, t)$
- Lanczos method is used to speed up exponentiation
  - Project Ψ into the sub-space
    - $\Psi_k(t) = V^T \Psi(t)$
  - Substitute the Hamiltonian with T
    - $\Psi_k(\vec{x}, t + \Delta t) \approx \exp[-iT\Delta t]\Psi_k(\vec{x}, t)$
  - Project back
    - $\Psi(t + \Delta t) = V\Psi_k(t + \Delta t)$
- Repeat every timestep

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Energy Distribution ($\frac{\partial P}{\partial \epsilon}$)

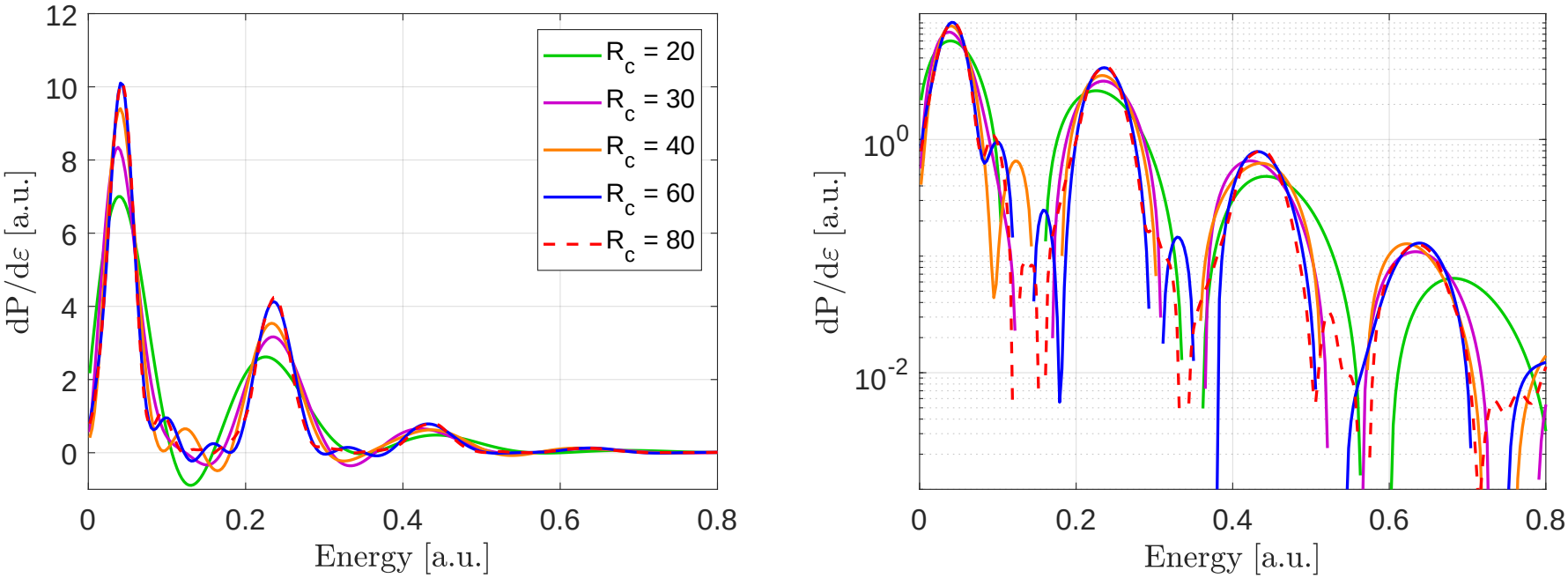

Figure: Energy probability distribution ($\frac{\partial P}{\partial \Omega}$), with different values for CAP onset.

Energy Distribution ($\frac{\partial P}{\partial \epsilon}$)

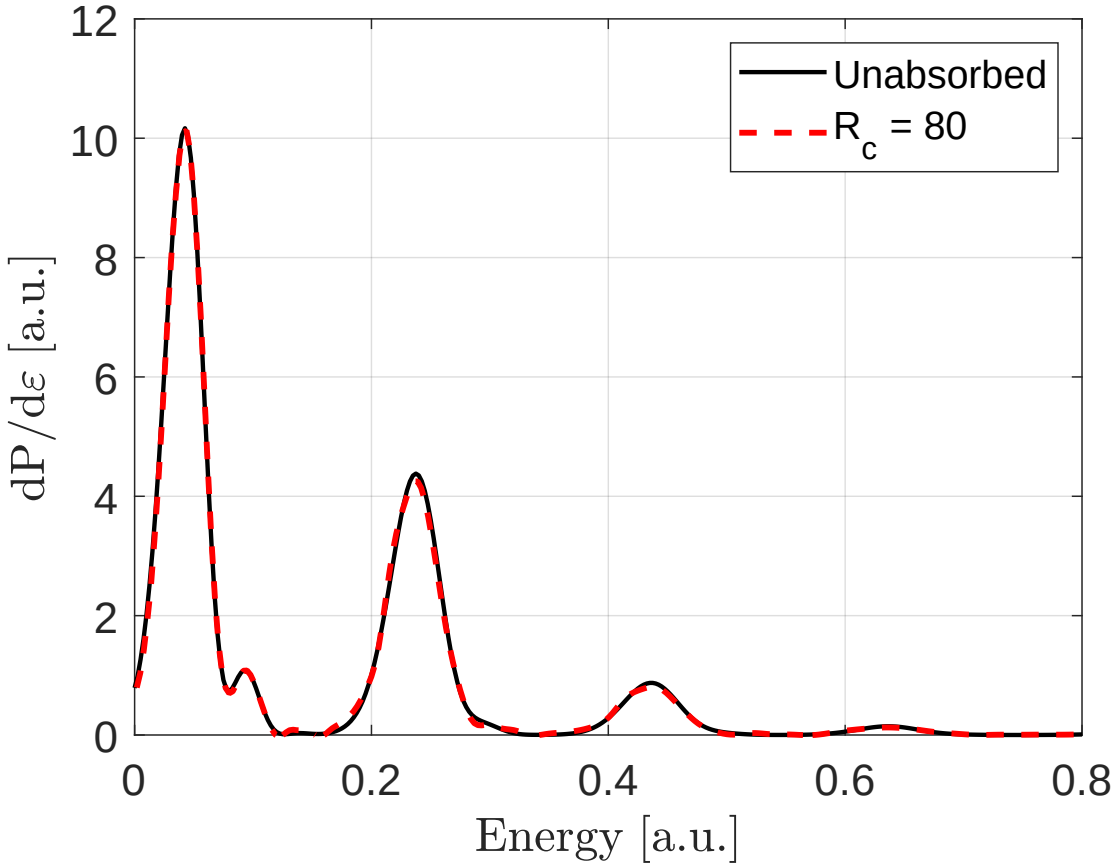

Figure: Energy probability distribution ($\frac{\partial P}{\partial \Omega}$), compared with unabsorbed.

Norm

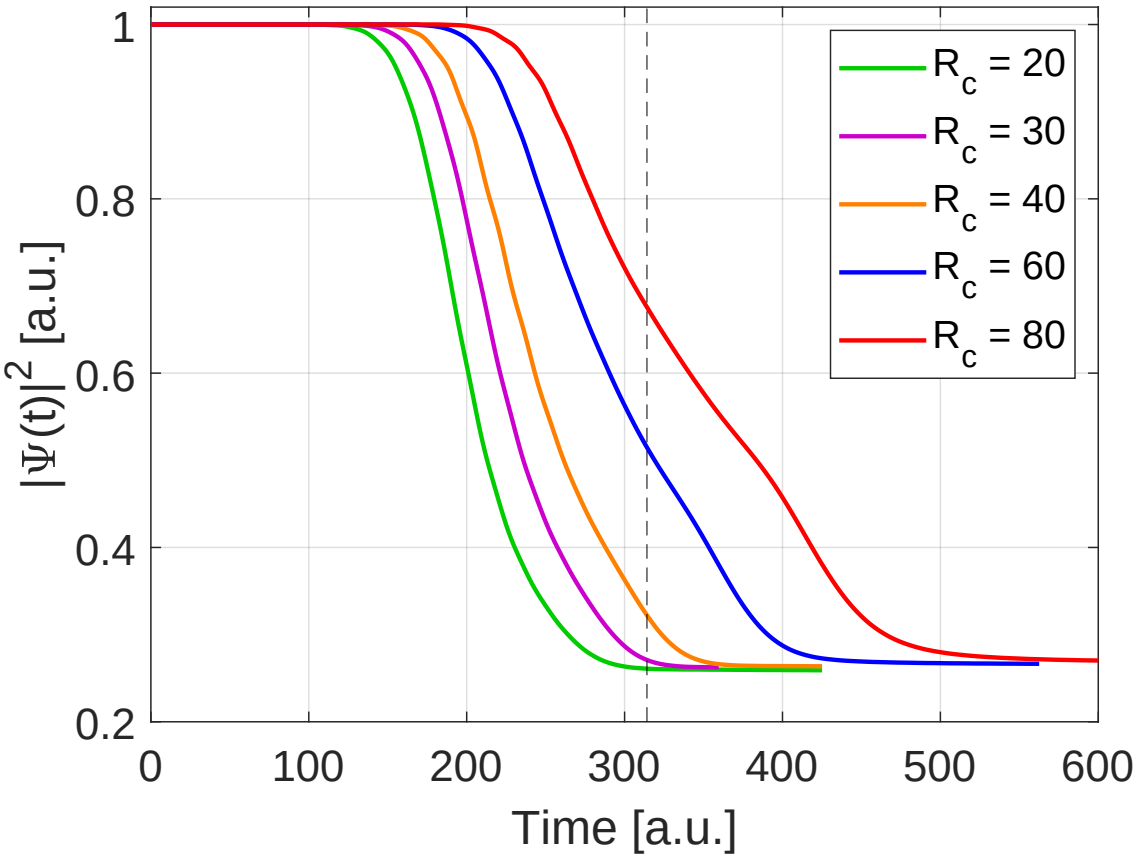

Figure: The final norm of Ψ as a function of time, with different values for CAP onset.

Comparison with Mask and tSURFF

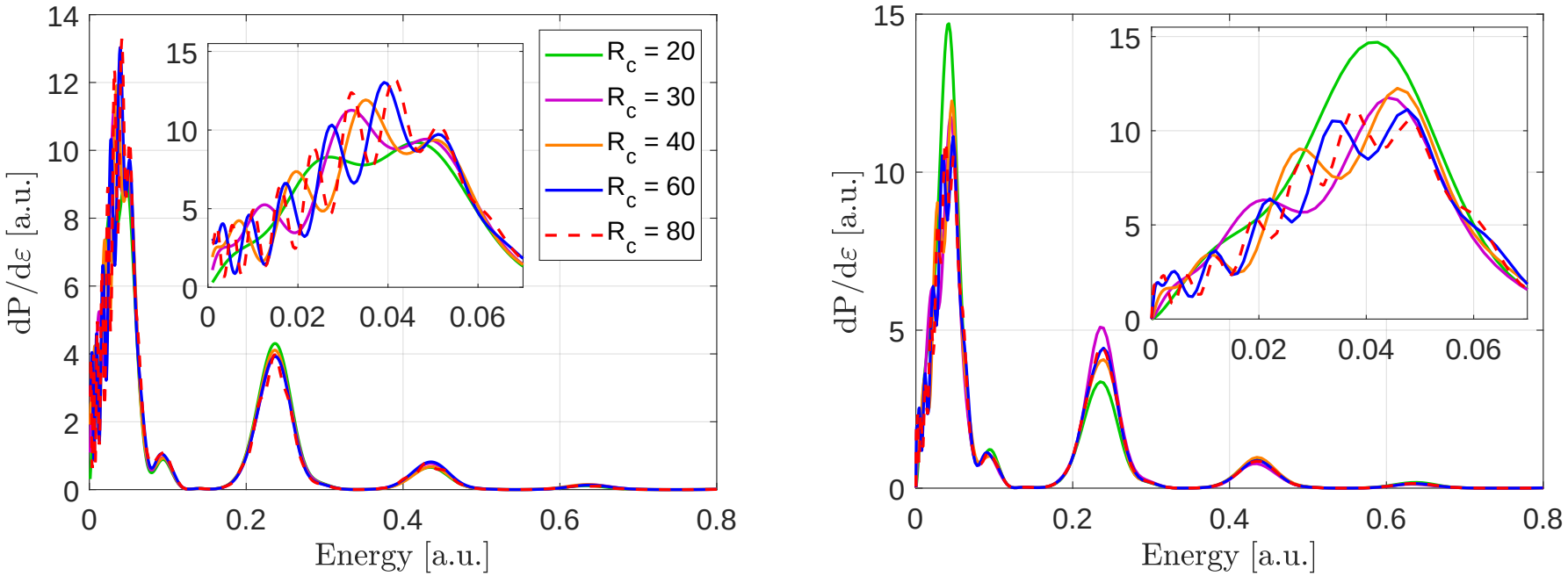

Figure: Energy probability distribution ($\frac{\partial P}{\partial \Omega}$), with different values for CAP onset, for Mask and tSURFF methods.

Comparison with Mask and tSURFF

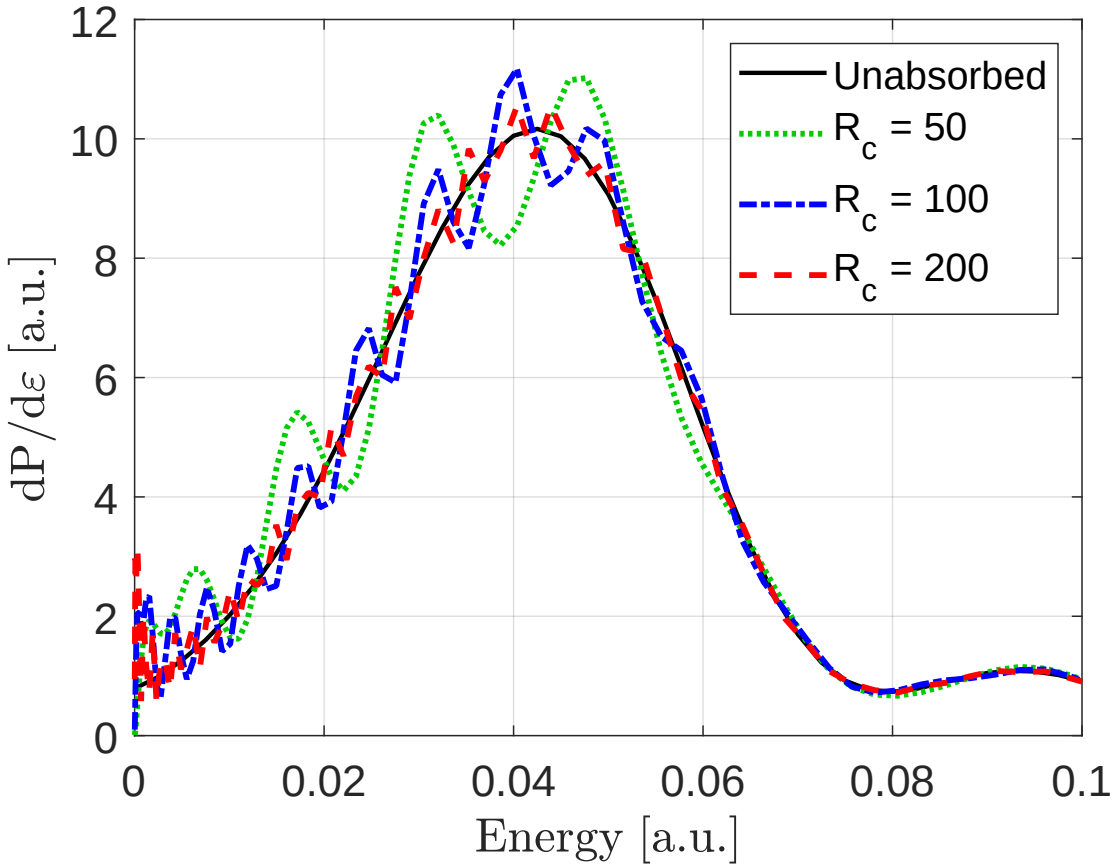

Figure: First peak of energy probability distribution ($\frac{\partial P}{\partial \Omega}$), with different values for CAP onset, for tSURFF.

Doubly Differential Distribution ($\frac{\partial^2 P}{\partial \varepsilon \partial \Omega_k}$)

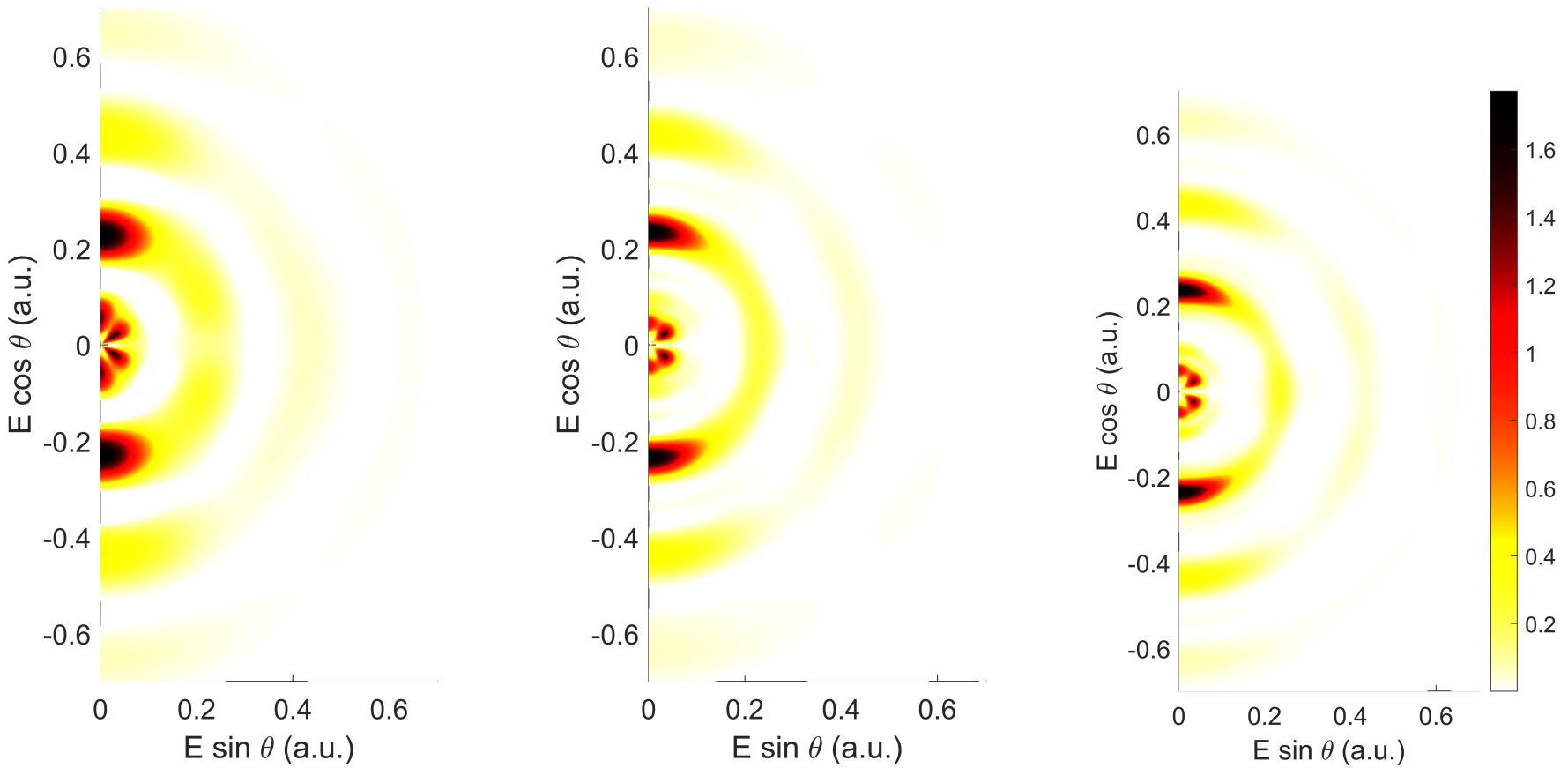

Figure: Doubly differential probability distribution ($\frac{\partial^2 P}{\partial \varepsilon \partial \Omega_k}$), with various CAP onset

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Conclusions and Outlook

- PESCADO works well for the given case
- Outlook
  - After the pulse $H(t > T) = H_0$
    - Skip to $\Psi(t = \infty)$
  - Multi-particle systems
  - Optimise a shaped pulse