Time-development of many-body wave functions

Dynamics arise when...

...the initial state is not stationary

- *-Breakup of molecule; dissociative wave packet*
- *-Coherent state of the harmonic oscillator*

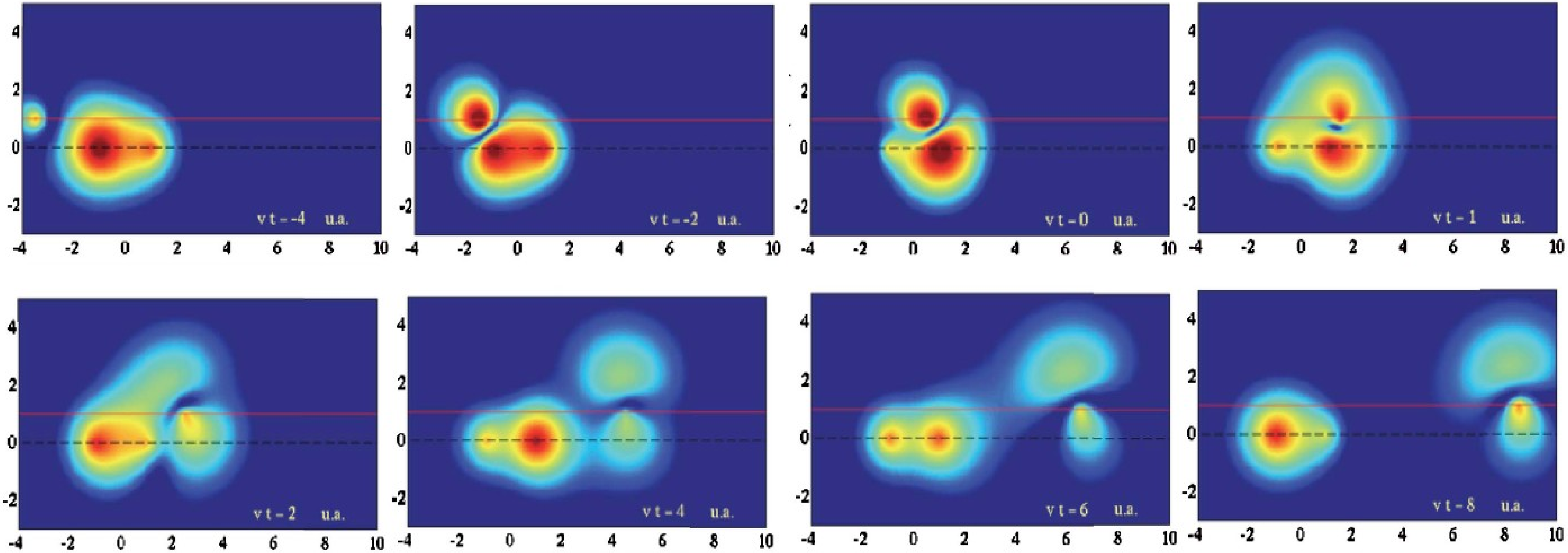
Dynamics arise when...

...the system is exposed to some external (semi-classical) influence

Dynamics arise when...

...the system is exposed to some external (semi-classical) influence

-Collision, projectile follows classical trajectory

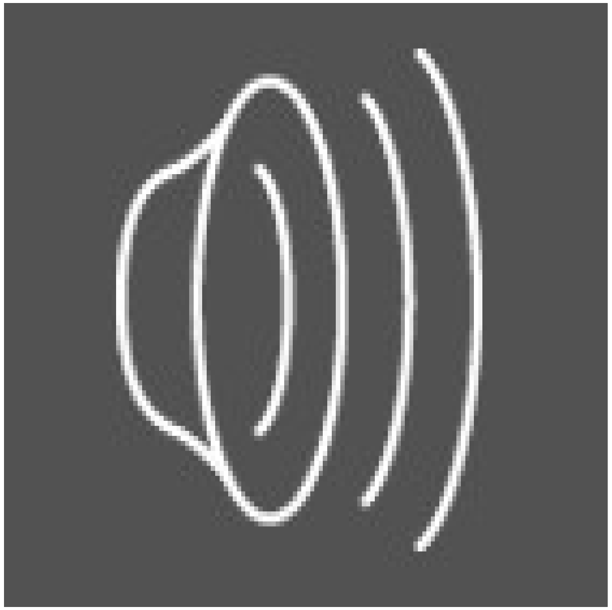


J. Caillat, I. Sunvor et al., *Phys. Rev. A* **73**, 014701 (2006)

Dynamics arise when...

...the system is exposed to some external (semi-classical) influence

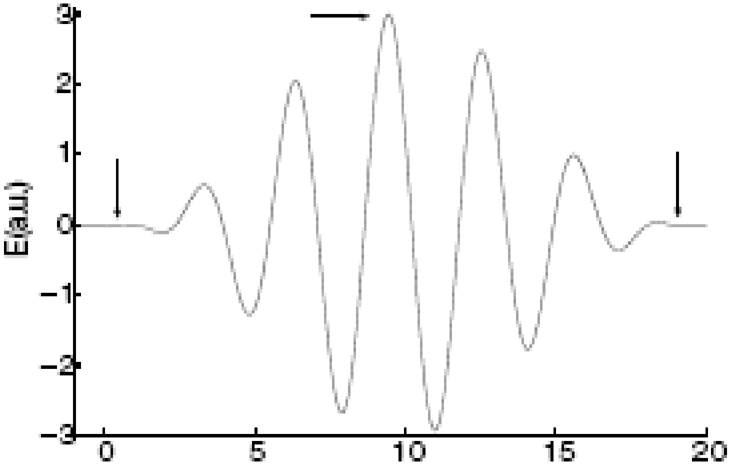
-System exposed to strong external electromagnetic field

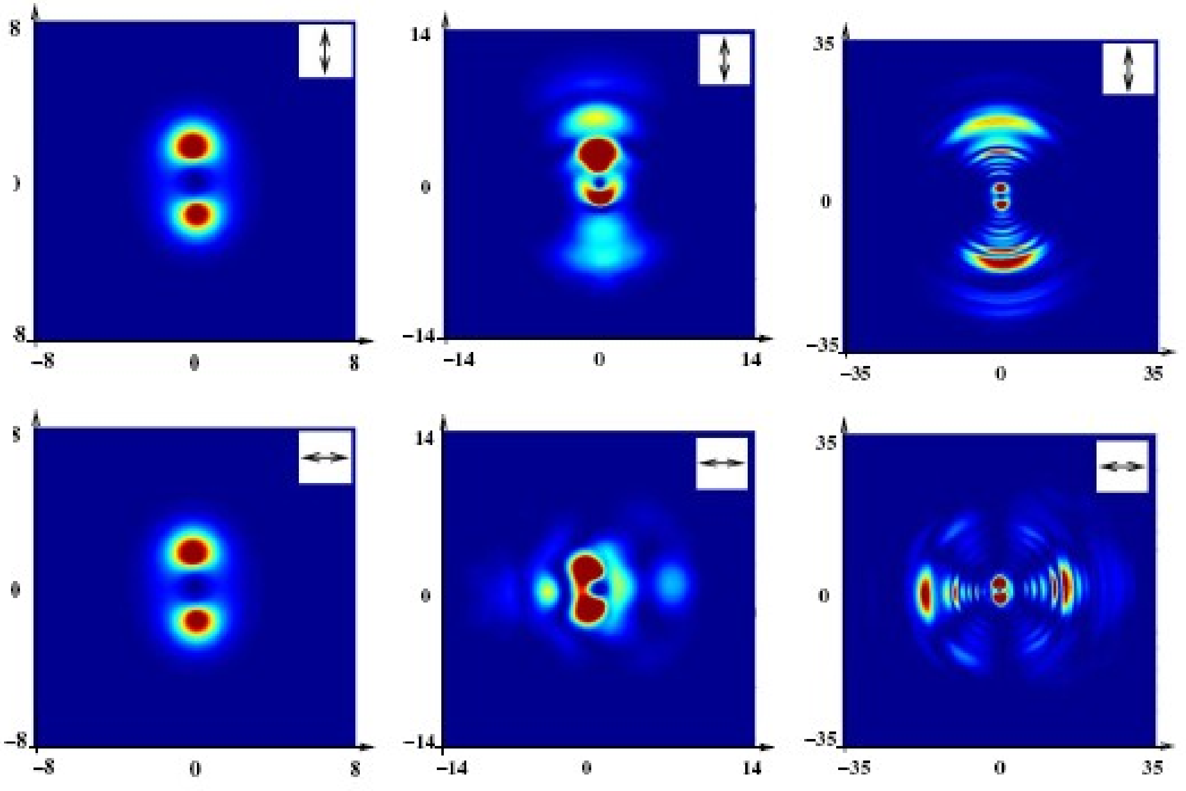


Dynamics arise when...

...the system is exposed to some external (semi-classical) influence

-System exposed to strong external electromagnetic field





Origin/ motivation for the time dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi$$

- Schrödinger: Free particle solutions of form $\exp\left(i(\boldsymbol{p}\cdot\boldsymbol{r} - Et)/\hbar\right)$

$$E\psi = H_0\psi \quad \longrightarrow \quad i\hbar\frac{\partial}{\partial t}\Psi = H_0\Psi$$

Postulate: $i\hbar\frac{\partial}{\partial t}\Psi = \left(H_0 + H'(t)\right)\Psi$

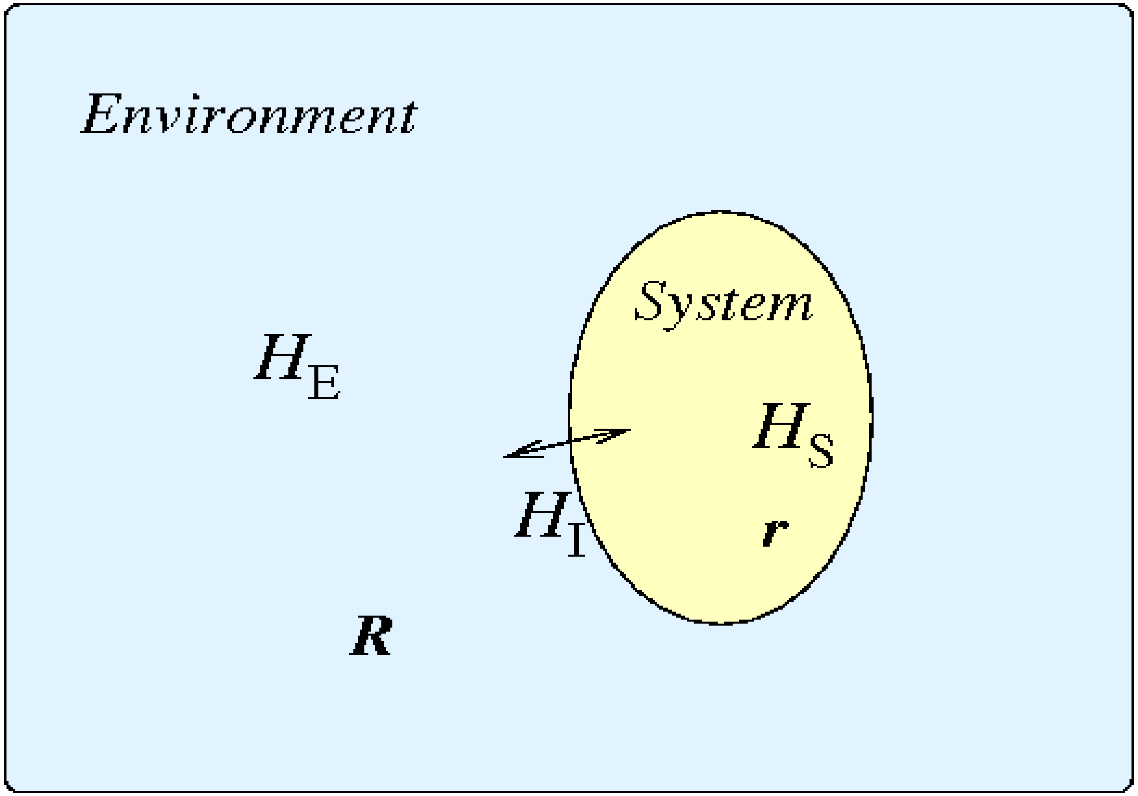
- Different argument:

$\boldsymbol{p}$ relates to $\boldsymbol{r}$ as $\boldsymbol{p} = -i\hbar\nabla$

hence H should relate to t as $H = -i\hbar\frac{\partial}{\partial t}$

Briggs and Rost, *Eur. Phys. J. D* **10**, 311 (2000):

-Claim that the time dependent Schrödinger equation can derived *from the time independent one.*



Wave function:

$$\Phi = \chi(\{\boldsymbol{R}\}) \times \psi(\{\boldsymbol{r}\}, \{\boldsymbol{R}\})$$

Asymmetry condition:

$$E_E \gg E_S$$

$\{\boldsymbol{R}\}$ reduced to classical variables;

$$\hat{R}_i \rightarrow R_i(t)$$

$$\left(H_E(\boldsymbol{R}) + H_S(\boldsymbol{r}) + H_I(\boldsymbol{R}, \boldsymbol{r})\right)\Phi = E\,\Phi \;\; \rightarrow$$

$$\left(H_S(\boldsymbol{r}) + H_I(\boldsymbol{r}, t)\right)\psi(\boldsymbol{r}, t) = i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r}, t)$$

Methods

Wave packet propagation on a grid

-Finite difference (Crank-Nicolson method)

-Split operator techniques

Expansion in both space and time dependent basis functions

-Adiabatic basis

-Floquet theory

-Analytic methods

Expansion in spatially dependent basis functions:

$$\Psi(t,\{\mathbf{r}\})=\sum_n c_n(t)\phi_n(\{\mathbf{r}\})$$

Obtain time dependent expansion coefficients by solving first order ODE

$$\dot{\mathbf{c}}=-\frac{i}{\hbar}\tilde{H}\mathbf{c},\quad \tilde{H}_{i,j}=\langle\phi_i|H|\phi_j\rangle$$

The propagator:

$$\Psi(t+\Delta t)=U(t+\Delta t,t)\Psi(t)$$

The propagator:

$$\Psi(t+\Delta t)=U(t+\Delta t,t)\Psi(t)$$

Time independent: $U(t,0)=e^{-iH_0 t/\hbar}$

Ground state: $t\rightarrow\tau=-it$

$$U\rightarrow e^{-H_0\tau/\hbar}$$

$$\Psi(t=0)=\sum_n c_n\phi_n\rightarrow\sum_n c_n e^{-\varepsilon_n\tau/\hbar}\phi_n\approx c_0 e^{-\varepsilon_0\tau/\hbar}\phi_0$$

Energy:

$$\varepsilon_0\approx-\frac{\hbar}{2\Delta\tau}\ln\frac{\langle\Psi(\tau+\Delta\tau)|\Psi(\tau+\Delta\tau)\rangle}{\langle\Psi(\tau)|\Psi(\tau)\rangle}$$

The propagator:

$$\Psi(t+\Delta t) = U(t+\Delta t, t)\Psi(t)$$

Time independent: $U(t,0) = e^{-iH_0 t/\hbar}$

Spectrum: $\Psi(t=0) = \sum_n c_n \phi_n, \quad \Psi(t) = \sum_n c_n e^{-i\varepsilon_n t/\hbar} \phi_n$

$$F\left\{ \left\langle \Psi(t=0) \middle| \Psi(t) \right\rangle \right\} = \sum_n k_n \delta(\omega - \varepsilon_n/\hbar)$$

The propagator:

$$\Psi(t+\Delta t)=U(t+\Delta t,t)\Psi(t)$$

$$U(t+\Delta t,t)=T\exp\left(-i\int_t^{t+\Delta t}H(t')\,dt'/\hbar\right)=$$

$$1-\frac{i}{\hbar}\int_t^{t+\Delta t}dt_1 H(t_1)+\left(-\frac{i}{\hbar}\right)^2\int_t^{t+\Delta t}dt_1\int_t^{t_1}dt_2 H(t_1)H(t_2)+\left(-\frac{i}{\hbar}\right)^3\int_t^{t+\Delta t}dt_1\int_t^{t_1}dt_2\int_t^{t_2}dt_3 H(t_1)H(t_2)H(t_3)+\ldots=$$

$$\exp\left(-i\int_t^{t+\Delta t}H(t')\,dt'/\hbar\right)+O(\Delta t^3)=$$

$$\exp\left(-iH(t)\Delta t/\hbar\right)+O(\Delta t^2)$$

The propagator:

$$\Psi(t+\Delta t) = U(t+\Delta t, t)\Psi(t)$$

$$U(t+\Delta t, t) = T\exp\left(-i\int_t^{t+\Delta t} H(t')\,dt'/\hbar\right) =$$

$$1 - \frac{i}{\hbar}\int_t^{t+\Delta t} dt_1 H(t_1) + \left(-\frac{i}{\hbar}\right)^2 \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 H(t_1) H(t_2) + \left(-\frac{i}{\hbar}\right)^3 \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \int_t^{t_2} dt_3 H(t_1) H(t_2) H(t_3) + \ldots =$$

$$\exp\left(-i\int_t^{t+\Delta t} H(t')\,dt'/\hbar\right) + O(\Delta t^3) =$$

$$\exp\left(-iH(t)\Delta t/\hbar\right) + O(\Delta t^2)$$

S. Blanes, P. C. Moan, *Phys. Lett. A* **265**, 35 (2000):

$$U(t+\Delta t, t) = e^{H^{(1)}} e^{H^{(0)}} e^{-H^{(1)}} + O(\Delta t^5)$$

$$H^{(0)} = -\frac{i}{\hbar}\int_t^{t+\Delta t} H(t')\,dt', \quad H^{(0)} = -\frac{i}{\hbar\Delta t}\int_t^{t+\Delta t} \left[t' - (t+\Delta t/2)\right] H(t')\,dt'$$

Example:

Split operator method on a spherical grid

$$\Psi(r_i,\Omega_{(j)},t_k)=\sum_{l,m}\frac{f_{l,m}(r_i,t_k)}{r_i}Y_{l,m}(\Omega_{(j)})$$

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\underbrace{\frac{\hat{L}^2}{2mr^2}+V(r)}_{V_S}+W(\boldsymbol{r},t)$$

$$\boxed{e^{(A+B)\Delta t}=e^{A\Delta t/2}e^{B\Delta t}e^{A\Delta t/2}+O(\Delta t^3)}$$

$$U\approx e^{-iT\Delta t/2\hbar}e^{-iV_S\Delta t/2\hbar}e^{-iW\Delta t/\hbar}e^{-iV_S\Delta t/2\hbar}e^{-iT\Delta t/2\hbar}$$

Example:

Split operator method on a spherical grid

$$\Psi(r_i,\Omega_{(j)},t_k)=\sum_{l,m}\frac{f_{l,m}(r_i,t_k)}{r_i}Y_{l,m}(\Omega_{(j)})$$

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\underbrace{\frac{\hat{L}^2}{2mr^2}+V(r)}_{V_s}+W(\boldsymbol{r},t)$$

$$U\approx e^{-iT\Delta t/2\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iW\Delta t/\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iT\Delta t/2\hbar}$$

Diagonal in “momentum space”; FFT -> propagate -> IFFT

Example:

Split operator method on a spherical grid

$$\Psi(r_i,\Omega_{(j)},t_k)=\sum_{l,m}\frac{f_{l,m}(r_i,t_k)}{r_i}Y_{l,m}(\Omega_{(j)})$$

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\underbrace{\frac{\hat{L}^2}{2mr^2}+V(r)}_{V_s}+W(\boldsymbol{r},t)$$

$$U\approx e^{-iT\Delta t/2\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iW\Delta t/\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iT\Delta t/2\hbar}$$

$Y_{l,m}(\Omega)$ eigenstates to $\hat{L}^2$

Example:

Split operator method on a spherical grid

$$\Psi(r_i,\Omega_{(j)},t_k)=\sum_{l,m}\frac{f_{l,m}(r_i,t_k)}{r_i}Y_{l,m}(\Omega_{(j)})$$

$$H=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+\underbrace{\frac{\hat{L}^2}{2mr^2}+V(r)}_{V_s}+W(\boldsymbol{r},t)$$

$$U\approx e^{-iT\Delta t/2\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iW\Delta t/\hbar}e^{-iV_s\Delta t/2\hbar}e^{-iT\Delta t/2\hbar}$$

Construct full wave function, propagate, project back

The adiabatic basis

Instantaneous eigenstate to the time-dependent Hamiltonian:

$$H(t)\chi_n(t)=\varepsilon_n(t)\chi_n(t)$$

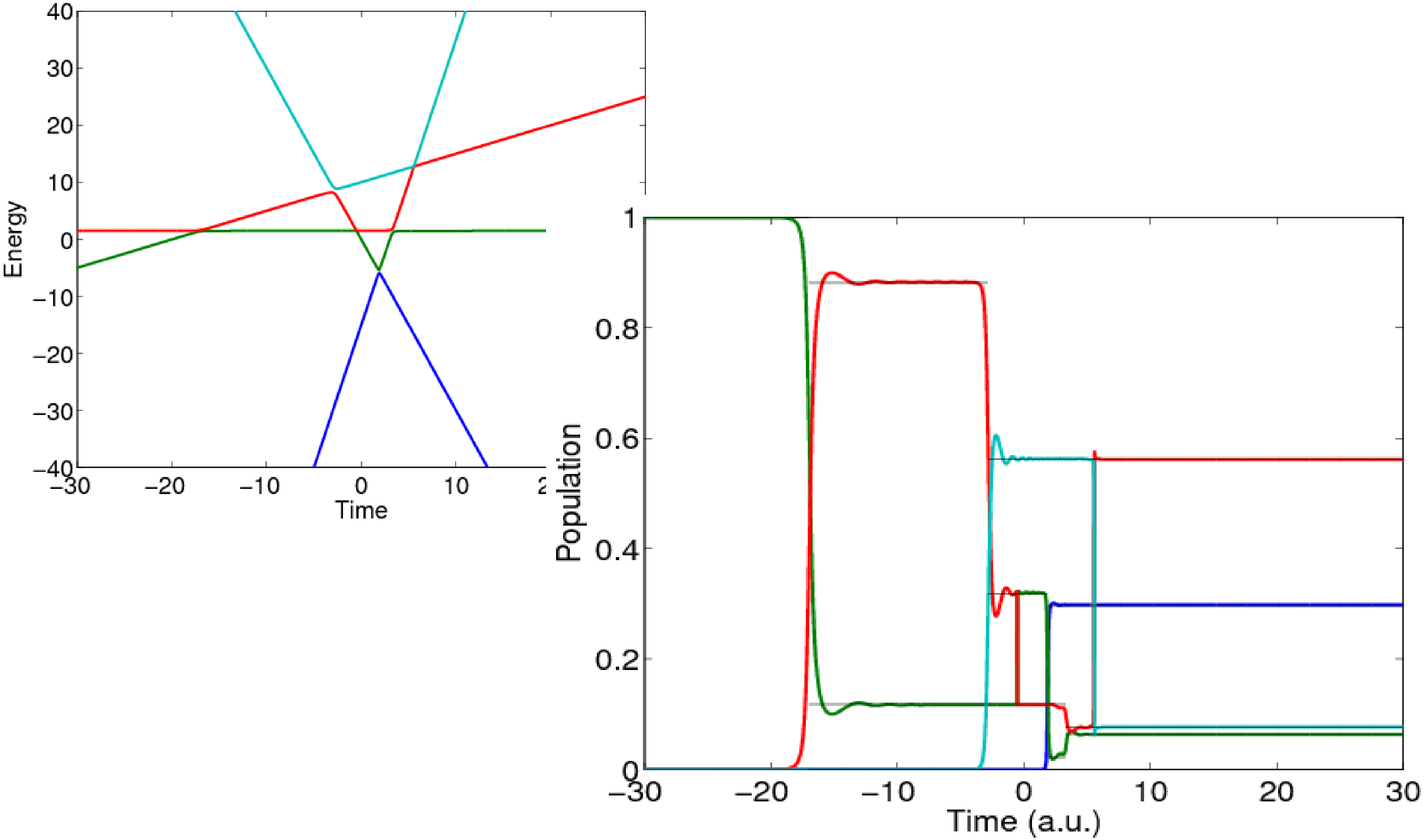
Propagator diagonal:

$$U(t+\Delta t,t)\approx e^{-iH(t)\Delta t/\hbar}=\sum_n e^{-i\varepsilon_n(t)\Delta t/\hbar}|\chi_n(t)> \ <\chi_n(t)|$$

With $\Psi(t)=\sum_n a_n(t)e^{-i\int_0^t \varepsilon_n(t')\,dt'/\hbar}\chi_n(t)$

$$\boxed{\dot{a}_k=\sum_{j,j\neq k}\frac{\langle\chi_k|\dot{H}|\chi_j\rangle}{\varepsilon_k-\varepsilon_j}e^{i\int_0^t \Delta\varepsilon_{kj}(t')\,dt'/\hbar}a_j}$$

The Landau-Zener model



The continuum

On a grid

Absorbing boundary
-Imaginary potential

$$H \rightarrow H + i f(r_{max} - r)$$

-Exterior complex scaling

$$r \rightarrow \left\{ \begin{matrix} r, & r < R \\ R + (r - R) e^{i\theta}, & r \geq R \end{matrix} \right\}$$

Spectral decomposition

Discretize by imposing confining outer potiential, “box”
(or vice verca)

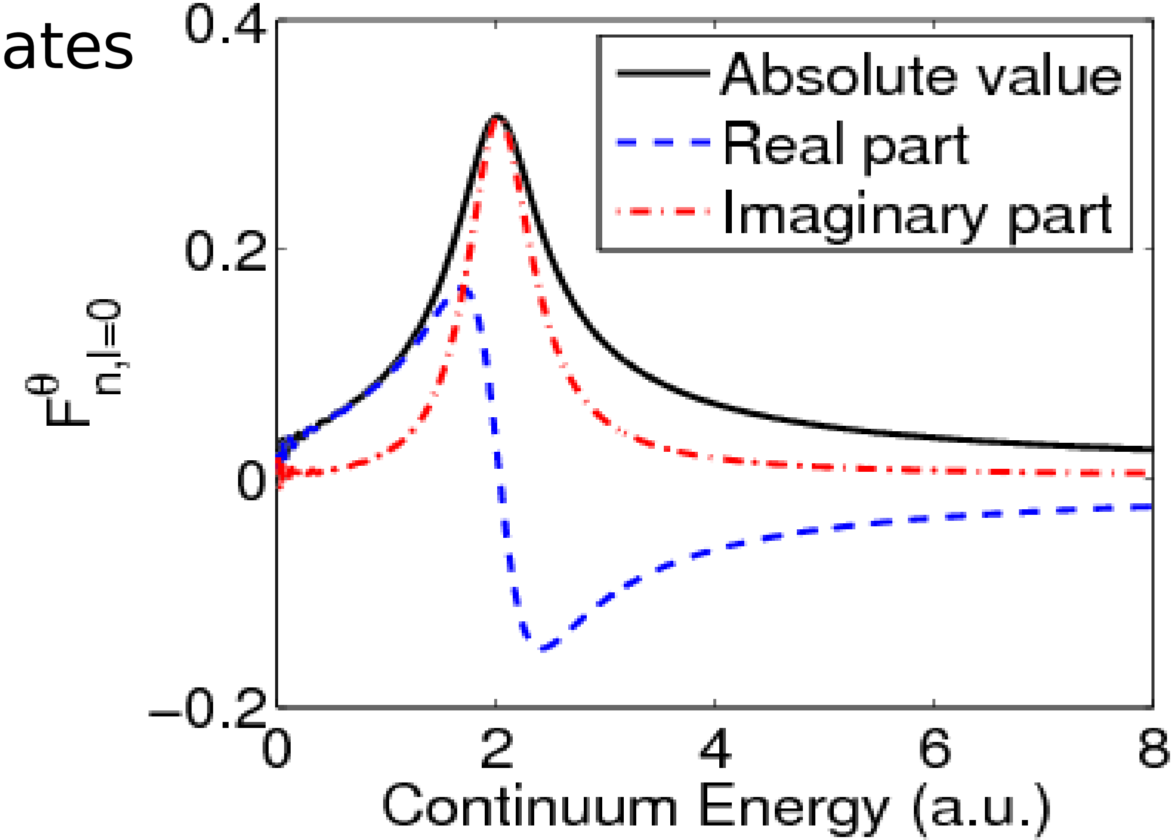
Large extension of WF =>
need big box =>
many continuum states in basis

Uniform complex scaling

$$r \rightarrow r e^{i\theta}, \quad \theta \in [0, 45^\circ]$$

$$E_n \rightarrow \sim E_n \cos(2\theta) - i E_n \sin(2\theta)$$

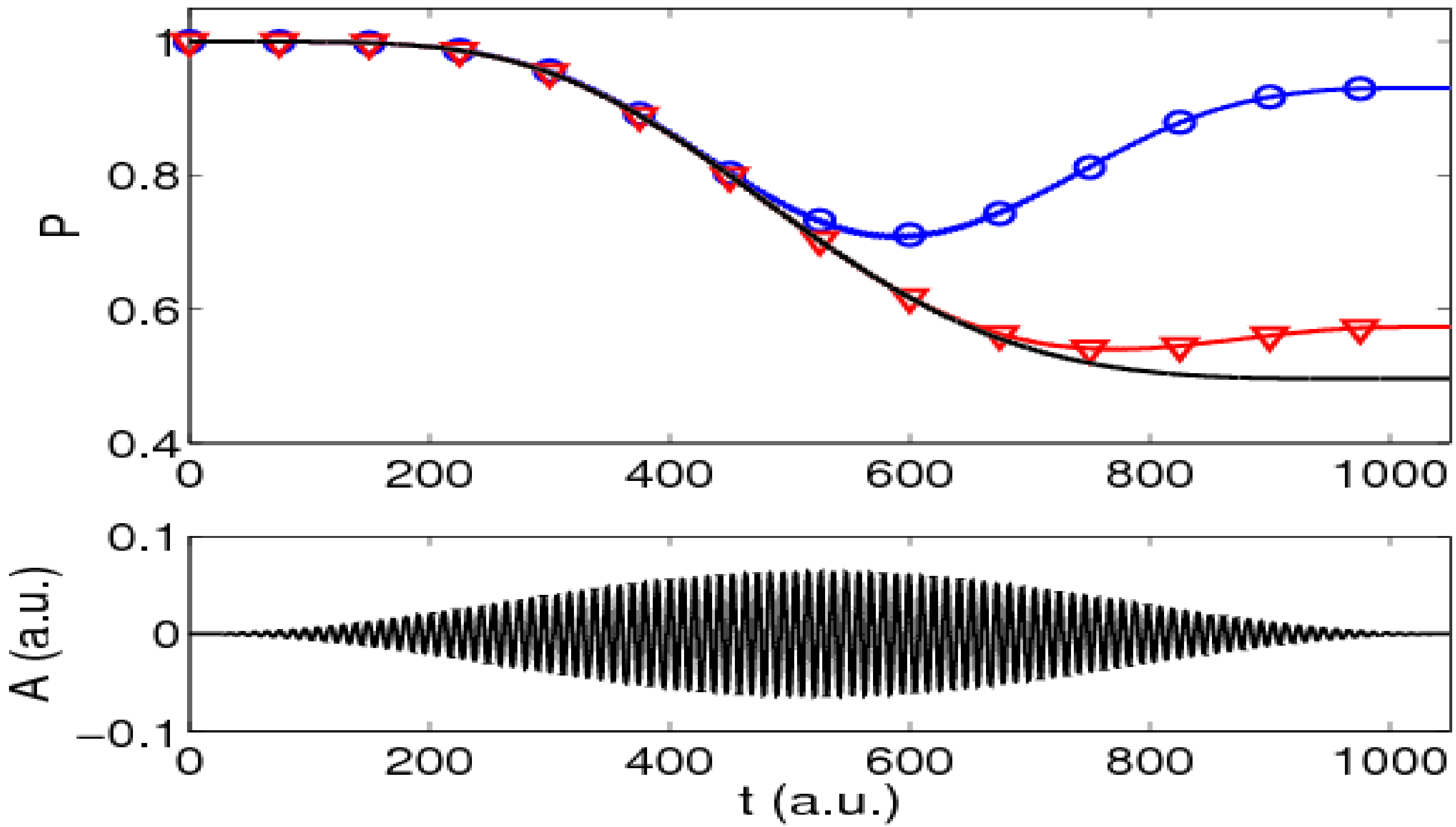
Increased energy-width
of pseudo-continuum states



Uniform complex scaling

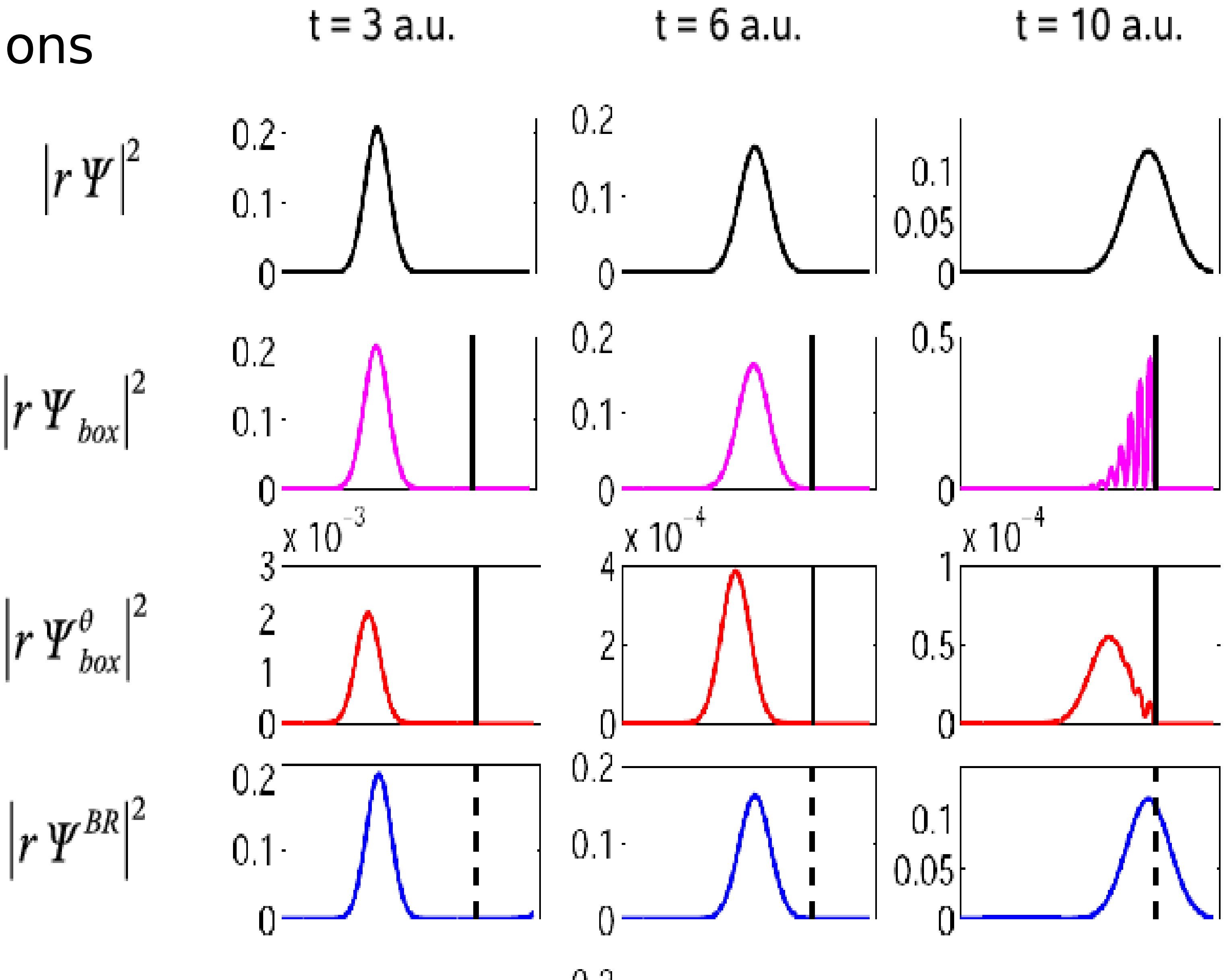
$$r \rightarrow r e^{i\theta}, \quad \theta \in [0, 45^{\circ}]$$

Converged results with fewer continuum states in basis



Uniform complex scaling

Avoid reflections



$\Psi^{BR} = \Psi^{\theta}_{box}(\boldsymbol{r}\, e^{-i\theta})$

What are *really* the differences between (effective) one particle dynamics and multi particle dynamics?

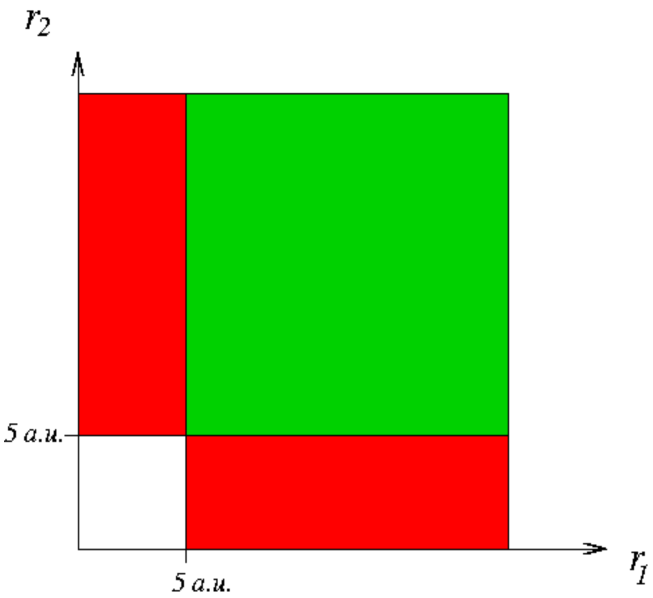
Increased complexity
- *-Need larger basis sets*
- *-Electron-electron correlation*
- *-Make sure to fulfill the Pauli principle*

For unbound systems:

Multiple continua
- *-May be hard to distinguish*

Multiply excited states
- *-”Bound states” embedded in continuum*

Example: Ionization of He



J. Parker, K. Taylor et al., *J. Phys. B* **29**, L33 (1996):

$$P_{SI} \approx 2\int_{5\,a.u.}^{\infty} d^3 r_1 \int_0^{5\,a.u.} d^3 r_2 \; |\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, T_{final})|^2$$

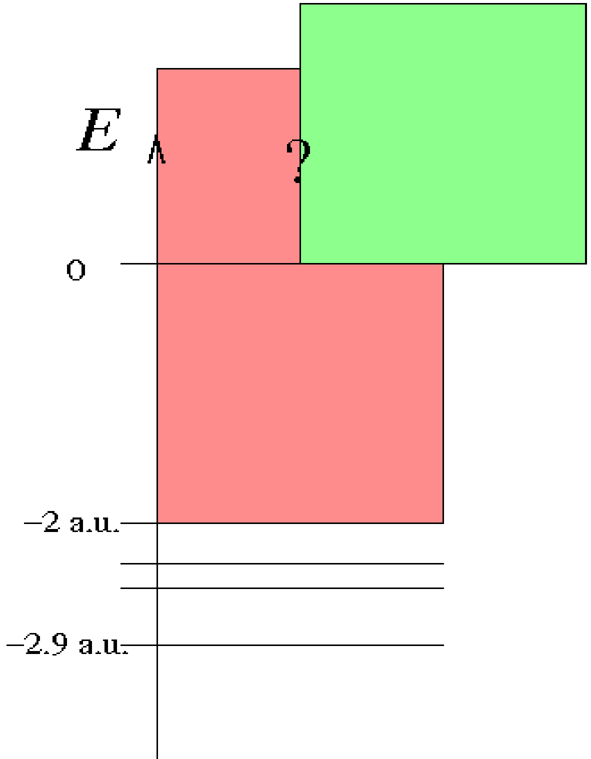
$$P_{DI} \approx \int_{5\,a.u.}^{\infty} d^3 r_1 \int_{5\,a.u.}^{\infty} d^3 r_2 \; |\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, T_{final})|^2$$

Spectral

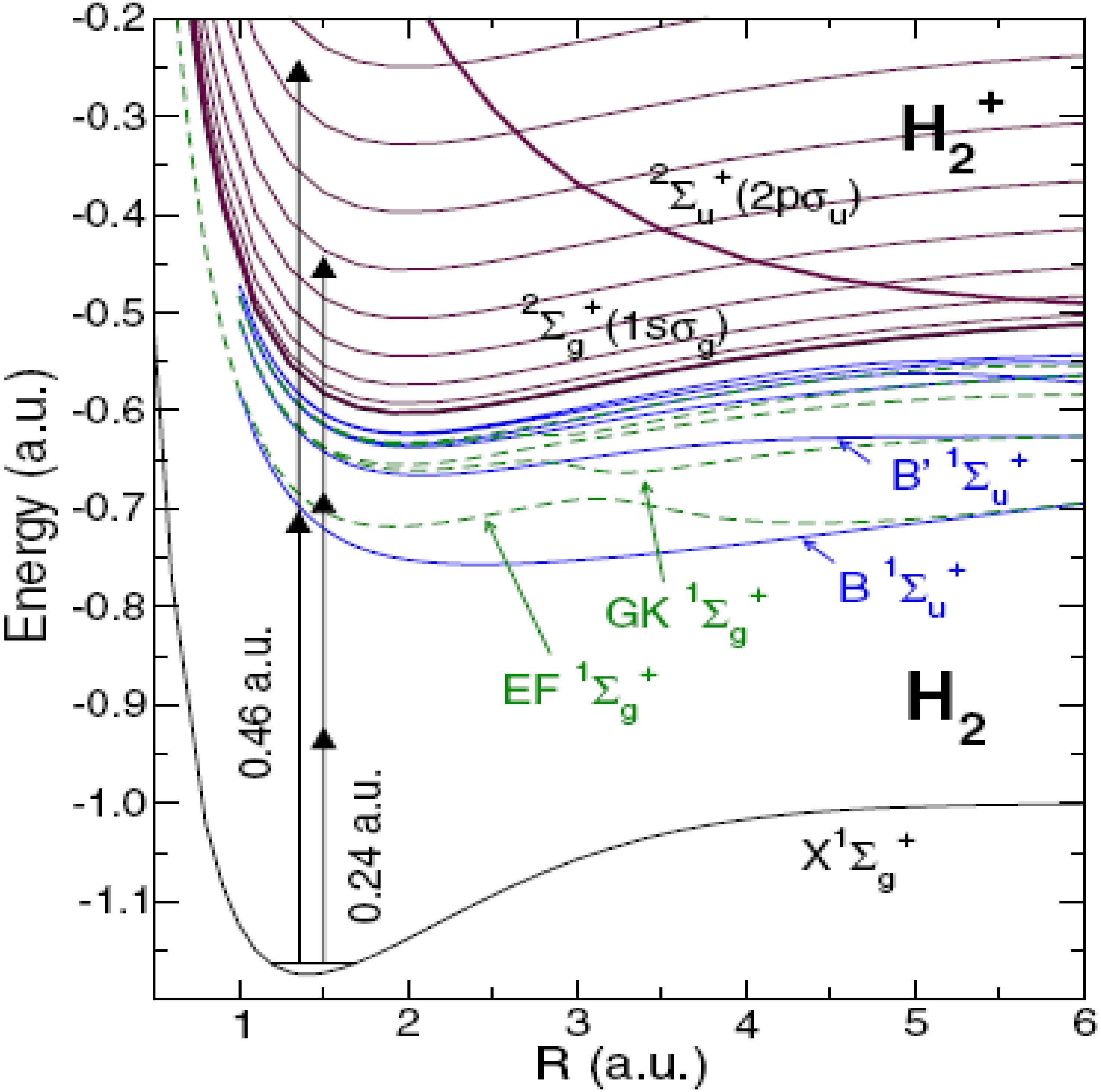
Eigenstate of H_0 with $E_n>0$ – Doubly or singly ionized?

Impose asymptotic behaviour on basis states;

$$\phi_n(\boldsymbol{r}_1, \boldsymbol{r}_2) \underset{r_2\to\infty}{\to} \psi_m^{Bound}(\boldsymbol{r}_1)\,\psi_n^{Continuum}(\boldsymbol{r}_2)$$



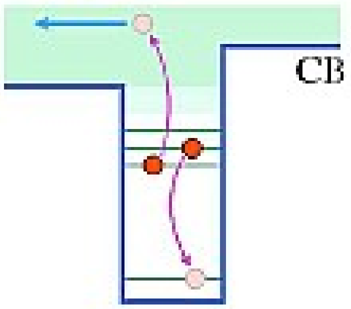
Another example: H_2 in the Born-Oppenheimer approximation

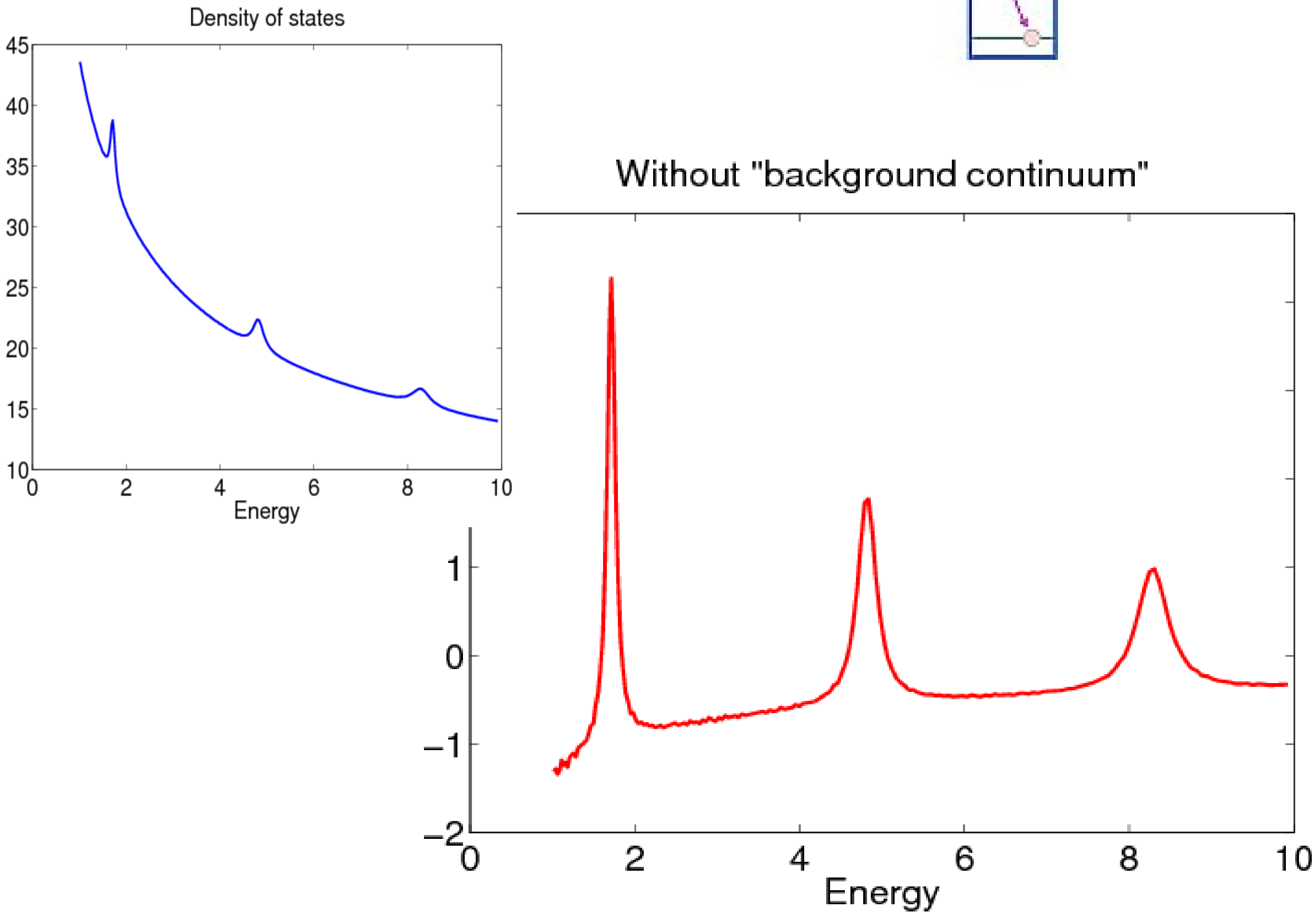


A. Palacios et al., *Phys. Rev. Lett.* **96**, 143001 (2006)

Resonances

T. Gebhard et al., *Appl. Phys. Lett.* **93**, 052103 (2008)





Exponential decay?

Resonances typically found by complex scaling,

$$H^{\theta}\psi^{\theta}_{res}=(\varepsilon_{pos}-i\Gamma/2)\psi^{\theta}_{res}$$

Amplitude in time:

$$\left|\exp[-i(\varepsilon_{pos}-i\Gamma/2)t/\hbar]\right|^{2}=\exp(-\Gamma t/\hbar)$$

Problem for two-particle wave functions:

The entire wave function disappears, not just the ionized part

Exponential decay?

Sakurai, *“Modern Quantum Mechanics”*:

Exponential decay corresponds to Breit-Wigner shaped distribution in energy;

$$\left|\left\langle \varepsilon \middle| \psi_{res} \right\rangle\right|^2 = \frac{\Gamma/(2\pi)}{(\varepsilon-\varepsilon_{res})^2+(\Gamma/2)^2}$$

Prohibited by the fact that there is a lower bound in energy – the ground state energy,

$$\left|\left\langle \varepsilon \middle| \psi_{res} \right\rangle\right|^2 = 0 \ \ for \ \ \varepsilon < \varepsilon_0$$

Claim: “The decay must be slower than exponential for long times”