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Shaping long-lived electron wavepackets for customizable optical spectra: supplementary material

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This document provides supplementary information to "Shaping long-lived electron wavepackets for customizable optical spectra," https://doi.org/10.1364/OPTICA.6.001089. It is organized as follows. In section 1 we discuss the solutions of the Schrödinger equation that yield the Whittaker wavepackets and show that they are physical wavepackets. In section 2 we describe the dynamics of the Whittaker wavepackets and their underlying mathematical properties. In section 3 we discuss the time-dependent spontaneous emission formalism. In section 4 we explain our numerical experiments.

1. DERIVATION AND PROPERTIES OF WHITTAKER WAVEPACKETS

In this section we will motivate the origin of the Whittaker constructions. There are two steps in our construction: to solve the Schrödinger equation for the extended eigenstates and then to construct the wavepackets from superpositions of these states.

We look for spherically symmetric extended states, i.e. $l = 0$ and from separation of variables, the angular part is the spherical harmonic $Y_{00}(\theta, \phi) = (1/2)\pi^{-1/2}$. For the radial part f_{El}, the Schrödinger equation takes the following form

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \left(V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right)\cdot(rf_{El}) = E\cdot(rf_{El}). \quad \text{(S1)}$$

Equation Eq. (S1) yields both bound eigenstate solutions (for $E < 0$) and extended eigenstate solutions (for $E > 0$). Given the mass of the electron m_e and the electric constant ϵ_0 we use the Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r$. It is useful to write $u(r) = rf_{Elm}$ and define the dimensionless parameter $x = r/(a_0/2)$, where a_0 is the Bohr radius. Likewise, let $\kappa = ka_0$ be the dimensionless parameter from momentum k. Substituting the parameters into equation Eq. (S1) we obtain the following differential equation for u

$$\left(\frac{\partial^2}{\partial x^2} + \frac{1}{x} + \kappa^2\right)u = 0. \quad \text{(S2)}$$

The crux of our analysis is understanding the solutions to equation Eq. (S2). Luckily, we can reduce it to a known differential equation after some algebraic manipulations. Namely, let $W = u$, $z' = 2ikx$, $k' = -i/2\kappa$ and $m' = 1/2$. Then Eq. (S2) is equivalent to the following

$$W'' + \left(-\frac{1}{4} + \frac{k'}{z'} + \frac{\frac{1}{4} - m'^2}{z'^2}\right)W = 0,$$

which is known as a version of the *Whittaker differential equation* [1]. A basis for the solutions is the following expression

$$u_\kappa(x) = \frac{2i\kappa x e^{-i\kappa x}}{\Gamma\left(1 - \frac{i}{2\kappa}\right)\Gamma\left(1 + \frac{i}{2\kappa}\right)}\int_0^1 e^{2i\kappa x s} s^{\frac{i}{2\kappa}}(1-s)^{-\frac{i}{2\kappa}}\,\mathrm{d}s, \quad \text{(S3)}$$

and its conjugate $\overline{u}_\kappa(x)$ [2]. We need to divide by x to obtain f_{Elm}, which yields the equation in the main text for the Whittaker modes

$$w_\kappa(x,0) = \frac{4i\kappa^2 e^{-i\kappa x}}{\pi\,\mathrm{csch}\,(\pi/2\kappa)}\int_0^1 e^{2i\kappa x s}\left(\frac{s}{1-s}\right)^{\frac{i}{2\kappa}}\mathrm{d}s, \quad \text{(S4)}$$

where $w_k(x,0) \equiv f_{Elm}(x)$, as desired and $w_\kappa(x,t) = w_\kappa(x,0)\exp\left(-i\omega t\kappa^2\right)$ where the time evolution frequency is given by $\omega = 2e^2/a_0\hbar \approx 82\ \mathrm{fs}^{-1}$. From Eq. (S4) we obtained the

Whittaker wavepackets in

$$\Psi_{E,\Delta E}(\mathbf{r},t) = \mathcal{N}\int_{-\infty}^{\infty} e^{-(\kappa-\mu)^2/2\sigma^2} w_\kappa(x,t)\mathrm{d}\kappa, \tag{S5}$$

where $\mathcal{N}$ is a normalization constant, μ and σ are the mean and spread (standard deviation) of momentum. In SI units the energy E is parameterized as $E(\kappa) = (2e^2/4\pi\epsilon_0 a_0)\kappa^2$ via the dimensionless κ. We denote $E = E(\mu)$ and ΔE for the spread (standard deviation). □

We claim that the wave function Eq. (S5) is square-integrable and therefore its probability density can have a physical meaning. We prove this via the following result.

Theorem 1. *The Whittaker wavepacket $\Psi_{E,\Delta E}$, defined in* Eq. (S5)*, is square-integrable, hence its probability density has a physical meaning.*

Proof. Let $\Psi \equiv \Psi_{E,\Delta E}$ for convenience. It suffices to show that $\int_0^\infty |\Psi|^2 x^2 \mathrm{d}x$ is finite. We care only for the large x behavior since the integral for small x gives a finite contribution. Ignoring constant factors, for large x we can use the approximation

$$x\Psi \sim \int_0^{3\sigma} \mathrm{d}\kappa \exp\left(-\frac{(\kappa-\mu)^2}{2\sigma^2}\right)\exp(-i\kappa x)\exp(i(1/2\kappa)\ln(x)).$$

Using the fact that $(e^{-i\kappa x})' = -ixe^{-i\kappa x}$ we can apply integration by parts to multiply the integral by a factor of $1/x$ and get additional contributions from constants. Ignoring the constants, we apply integration by parts again to obtain another factor of $1/x$. In conclusion, we obtain the following

$$x|\Psi| < \frac{\text{const}}{x} + \frac{\text{const}\ln x}{x} + \frac{\text{const}(\ln x)^2}{x^2}. \tag{S6}$$

When we square the RHS of equation Eq. (S6), the results is a function in x that decays sufficiently fast, i.e. when we integrate that function from zero to infinity we get a finite number. Hence, $\int_0^\infty |\Psi|^2 x^2 \mathrm{d}x$ is bounded from above by a finite number, so the wavepacket is square-integrable, as desired. □

2. DYNAMICS OF THE WHITTAKER WAVEPACKETS

In this section we introduce two important arguments: we describe the nature of the equations for the spatial spread Δr and the diffraction lifetime Δt; we argue for a property that signifies the quasi-shape-invariant stability of the wavepackets Eq. (S5).

First, we can develop simple analytic tools to get an understanding of the evolution in time of the Whittaker superpositions. Then we can conjecture a functional form for Δr and Δt that would yield formulas

$$\Delta r \approx \frac{2.471\ a_0}{\sqrt{(\Delta E)/\mathrm{eV}}}. \tag{S7}$$

and

$$\Delta t \approx \frac{0.136\ \mathrm{eV}\cdot\mathrm{fs}}{\sqrt{(\Delta E)E}}. \tag{S8}$$

after fitting to our simulations.

Theorem 2. *The Whittaker wavepacket* Eq. (S5) *can be approximated as a Gaussian function in position space with mean μ_x and standard deviation σ_x satisfying*

$$\mu_x(t) = 2\mu\omega t \quad \textit{and} \quad \sigma_x^2(t) = \frac{1}{\sigma^2} + 4\sigma^2\omega^2 t^2. \tag{S9}$$

Moreover, a natural functional anzats for the spatial spread Δr Eq. (S7) *and the diffraction lifetime Δt* Eq. (S8) *is given as follows*

$$\Delta r = \frac{\text{const}}{\sqrt{\Delta E}} \quad \textit{and} \quad \Delta t = \frac{\text{const}}{\sqrt{(\Delta E)E}}. \tag{S10}$$

Proof. After a large x approximation, the integrand in Eq. (S5) looks as follows:

$$\exp\left(-\frac{(\kappa-\mu)^2}{2\sigma^2}\right)\frac{u_\kappa(x)}{x}\exp\left(-i\omega t\kappa^2\right).$$

We can pull the $1/x$ term out of the integration since it does not affect the spread nor the lifetime. Suppose we make a large x approximation and thus replace the exact Whittaker solution $u_\kappa(x)$ in $\Psi_{E,\Delta E}$ with its plane wave approximation $\exp(-i\kappa t)$. Without loss of generality we are left to consider the following integral

$$\Psi_{\text{approx.}} = \int_{-\infty}^{\infty} \mathrm{d}\kappa \exp\left(-\frac{(\kappa-\mu)^2}{2\sigma^2}\right) e^{-i\kappa x} e^{-i\omega t\kappa^2}. \tag{S11}$$

Now, having the approximation Eq. (S11) we can produce an analytic estimate for Δx (and thus for Δr). Equation Eq. (S11) combines the exponential with the κ^2 dependence to obtain $\exp(-a\kappa^2 + b\mu + \text{const})$, where for convenience we denote $a = (1/2\sigma^2 + i\omega t)$ and $b = \kappa/\sigma^2$. Performing a Fourier transform from momentum space to position space and ignoring the constants in the exponential (as they only change the amplitude and not the mean and the spread of the Gaussian), we obtain the following Gaussian in x:

$$\Psi_{\text{approx.}} \sim \exp\left(\frac{(b-ix)^2}{4a}\right) \sim \exp\left(-\frac{(x-2\mu\omega t)^2}{2\left(\frac{1}{\sigma^2}+4\sigma^2\omega^2 t^2\right)}\right).$$

In the last line we substituted for a, b and c and ignored the phase factors and the constants that do not affect the evolution of the probability density $x^2|\Psi|^2$. From the last equation we extract the μ_x and σ_x of the Gaussian in position space to obtain the statement Eq. (S9). To conclude the theorem, observe from Eq. (S11) that $\Delta x = \sigma_x(0) = 1/\sigma$. Converting to r from the unitless x, and a conversion to units of energy yields the anzats. Furthermore, a stationary phase argument yields $\Delta x \sim 2\mu\omega\Delta t$. Hence, $\Delta t \propto 1/\mu\sigma$, which concludes the proof. □

Theorem 2 is the theoretical foundation for obtaining equations Eq. (S7) and Eq. (S8), which govern the dynamics of the Whittaker wavepackets. In section 4 we describe the procedure of fitting the constants in the anzats Eq. (S10).

Now, we claim that the mathematical properties of the Whittaker wavepackets of angular momentum zero can be used to explain their quasi-shape-invariance. As we show below, the Whittaker wave functions Eq. (S4) are purely imaginary. This property results in the Whittaker wavepacket at time zero Eq. (S5) $\Psi(r,0)$ also being purely imaginary. Thus, the nodes of the probability density $r^2|\Psi(r,0)|^2$ are the double roots of the zeros of the real wave function $\operatorname{Im}\Psi(r,0)$. Those zeros of the imaginary part of $\Psi(r,0)$ are closely related to the zeros of the Whittaker functions. In S1 we show that the zeros of the extended states are closely spaced near the origin as we vary κ slowly. Therefore, in between the regions of vanishing (circled on figure S1), $\operatorname{Im}\Psi(r,0)$ would take alternating signs. Hence, by the Intermediate Value Theorem, for small distance r, the wavepacket is forced to have a node near the nodes of each of the extended states.

Therefore, it suffices to show that the functions Eq. (S3) are purely imaginary. It is convenient to plug the exponential $e^{-i\kappa x}$ from the numerator in Eq. (S3) into the integral and consider the following resulting expression

$$\int_0^1 e^{i\kappa x(2s-1)} s^{\frac{i}{2\kappa}}(1-s)^{-\frac{i}{2\kappa}}\mathrm{d}s. \tag{S12}$$

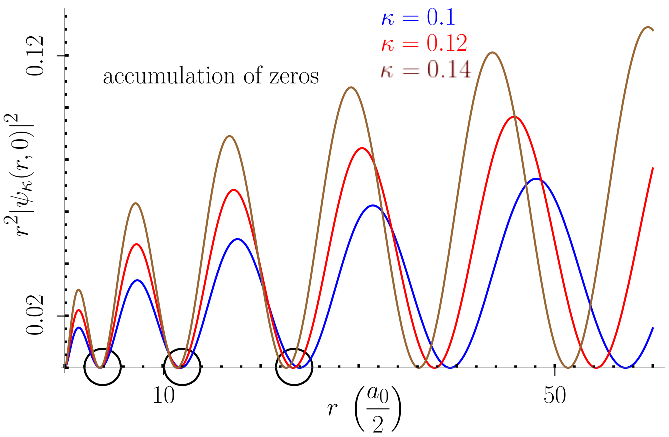

Fig. S1. The zeros of the Whittaker modes generate the nodes of the Whittaker wavepackets at time $t = 0$. The zeros of these functions are close to each other for small r and deviate from each other as r becomes larger.

The trick we present here is a change of variables of the following form

$$s = 1 - s'. \tag{S13}$$

Going through the algebra and relabeling s' back to s, we obtain that expression Eq. (S12) is equivalent to the following

$$\int_0^1 e^{i\kappa x(1-2s)} s^{-\frac{i}{2\kappa}} (1-s)^{\frac{i}{2\kappa}} \mathrm{d}s. \tag{S14}$$

The symmetry of Eq. (S12) is key to the proof that follows.

Theorem 3. *The functions $w_\kappa(x,0)$ are purely imaginary.*

Proof. In equation Eq. (S3) we plug the exponential from the numerator to factor out expression Eq. (S12). We are left with $2i\kappa x$ in the numerator, which is purely imaginary. The denominator is $\Gamma\left(1-\frac{i}{2\kappa}\right)\Gamma\left(1+\frac{i}{2\kappa}\right)$. By conjugating the Gamma function we see that this product is real. Hence, it suffices to show that expression Eq. (S12) is real. We conjugate it and obtain equation Eq. (S14). The same equation came from the *change-of-variables* trick Eq. (S13), which means that the integral equals its conjugate, hence it is real, as desired. □

3. RADIATIVE DECAY FORMALISM

The goal of this section is to derive a general framework of our spontaneous emission calculations for wavepackets that are not necessarily eigenstates of the Hamiltonian. As a direct consequence, we can determine the transition rates from the Whittaker wavepackets Eq. (S5) to the bound states of the hydrogen atom. Our approach is based on computing the matrix elements of the S-matrix [3]. The S-matrix is given through the matrix elements of the time-ordered unitary evolution operator as follows

$$S_{\mathrm{fi}} = \langle \mathrm{f}|\, T \exp\left[-\frac{i}{\hbar}\int_0^t \hat{H}_{\mathrm{int}} \mathrm{d}t'\right] |\mathrm{i}\rangle\,,$$

for an initial state $|i\rangle$ and a final state $|f\rangle$, where the interaction Hamiltonian is given by

$$\hat{H}_{\mathrm{int}} = \int \mathrm{d}^3\mathbf{x}\,\psi^* \hat{H}_{\mathrm{para}}(\mathbf{x},t)[\psi] = -\frac{i\hbar e}{m_e}\int \mathrm{d}^3\mathbf{x}\,\psi^* \hat{\mathbf{A}}(\mathbf{x},t)\cdot\boldsymbol{\nabla}\psi.$$

Then the infinitesimal probability of transition from $|i\rangle$ to $|f\rangle$ is given by the following equation

$$\mathrm{d}P_{\mathrm{fi}}(\mathbf{k},\lambda) = \frac{V\mathrm{d}^3\mathbf{k}}{(2\pi)^3}|S_{\mathrm{fi}}(\mathbf{k},\lambda)|^2, \tag{S15}$$

where V is a finite volume needed for defining our measure. We would like to integrate (and sum) over all possible transition $|\mathrm{i}\rangle \to |\mathrm{f}\rangle$ involving the emission of a photon $\gamma(\mathbf{k},\lambda)$. In the Heisenberg picture, the vector potential looks as follows

$$\hat{\mathbf{A}}(\mathbf{x},t) = \sum_{\mathbf{k},\lambda=1,2}\sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}\left(e^{i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}a_{\mathbf{k}\lambda}\hat{\boldsymbol{\varepsilon}}_{\mathbf{k}\lambda} + e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega_k t)}a^\dagger_{\mathbf{k}\lambda}\hat{\boldsymbol{\varepsilon}}^*_{\mathbf{k}\lambda}\right),$$

where there is a photon with momentum $\mathbf{k}$ and polarization λ, and the a-operator, with its conjugate $a^\dagger$, are respectively the annihilation and creation operators for the same photon. The photon has a frequency ω_k and a polarized direction $\hat{\varepsilon}_{\mathbf{k}\lambda}$. We are interested in the coupling of the atom to the EM field, so we concentrate on the paramagnetic term of the total Hamiltonian, which is given as follows

$$\hat{H}_{\mathrm{para}}(\mathbf{x},t) = \frac{e}{m_e}\hat{\mathbf{A}}(\mathbf{x},t)\cdot\hat{\mathbf{p}},$$

where m_e is the mass of the electron. Suppose we look at the spontaneous emission from the initial state $|\mathrm{i}\rangle$ to the final state $|\mathrm{f}\rangle$ by emitting a photon.

Next we simplify the S-matrix. For $\langle \mathbf{x}|f\rangle(t) = \Psi_{\mathrm{fin.}}(\mathbf{x},t)$ and $\langle \mathbf{x}|i\rangle(t) = \Psi_{\mathrm{in.}}(\mathbf{x},t)$, up to first order, we obtain the following

$$S_{\mathrm{fi}}(\mathbf{k},\lambda) = -\frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0\omega_k V}}\int_0^t \mathrm{d}t' e^{i\omega_k t'}\hat{\varepsilon}_{\mathbf{k}\lambda}\cdot \int \mathrm{d}^3\mathbf{x}\Psi_{\mathrm{fin.}}(\mathbf{x},t')^* \exp(-i\mathbf{k}\cdot\mathbf{x})\boldsymbol{\nabla}\Psi_{\mathrm{in.}}(\mathbf{x},t').$$

The last equation yields the following expansion of $|S_{\mathrm{fi}}(\mathbf{k},\lambda)|^2$ as an Einstein summation

$$\frac{e^2\hbar}{2m_e\epsilon_0\omega_k V}\int_0^t \mathrm{d}t'\int_0^t \mathrm{d}t'' e^{i\omega_k(t'-t'')}\cdot \int \mathrm{d}^3\mathbf{x}\mathrm{d}^3\mathbf{y}\,\varepsilon^i_{\mathbf{k}\lambda}\varepsilon^j_{\mathbf{k}\lambda}\Psi^*_{\mathrm{fin.}}(\mathbf{x},t')\Psi_{\mathrm{fin.}}(\mathbf{y},t'')\exp(i\mathbf{k}\cdot(\mathbf{y}-\mathbf{x}))\cdot \frac{\partial\Psi_{\mathrm{in.}}(\mathbf{x},t')}{\partial x_i}\frac{\partial\Psi^*_{\mathrm{in.}}(\mathbf{y},t'')}{\partial y_j}. \tag{S16}$$

Now, we rely on the following chain of basic derivations

$$\hat{k} = \frac{\mathbf{k}}{|\mathbf{k}|}; \qquad \text{(normalization)}$$

$$\hat{\varepsilon}_{\mathbf{k}\lambda_1}\otimes\hat{\varepsilon}_{\mathbf{k}\lambda_1} + \hat{\varepsilon}_{\mathbf{k}\lambda_2}\otimes\hat{\varepsilon}_{\mathbf{k}\lambda_2} + \hat{k}\otimes\hat{k} = \mathbf{1}_3; \qquad \text{(orthogonality)}$$

$$\sum_\lambda \varepsilon^i_{\mathbf{k}\lambda}\varepsilon^j_{\mathbf{k}\lambda} + \hat{k}_i\hat{k}_j = \delta_{ij}; \qquad \text{(component-wise orthogonality)}$$

$$\sum_\lambda \varepsilon^i_{\mathbf{k}\lambda}\varepsilon^j_{\mathbf{k}\lambda} = \delta_{ij} - \frac{\hat{k}_i\hat{k}_j}{|\mathbf{k}|^2}; \qquad \text{(rewriting)}$$

$$v_i = \int \mathrm{d}^3\mathbf{x}\exp(-i\mathbf{k}\cdot\mathbf{x})\Psi^*_{\mathrm{fin.}}(\mathbf{x},t')\frac{\partial\Psi_{\mathrm{in.}}(\mathbf{x},t')}{\partial x_i}; \qquad \text{(extracted from Eq. (S16))}$$

$$v^*_j = \int \mathrm{d}^3\mathbf{y}\exp(-i\mathbf{k}\cdot\mathbf{y})\Psi_{\mathrm{fin.}}(\mathbf{y},t')\frac{\partial\Psi^*_{\mathrm{in.}}(\mathbf{y},t')}{\partial y_j}; \qquad \text{(extracted from Eq. (S16))}$$

$$v_i(\delta_{ij} - \hat{k}_i \cdot \hat{k}_j)v_j^* = |\mathbf{v}|^2 - |\mathbf{v} \cdot \hat{k}|^2 = |\mathbf{v} \times \hat{k}|^2. \quad \text{(combining)}$$

Finally, to sum over the polarizations Eq. (S15), we need the last step from the chain of the derivations to obtain

$$\sum_\lambda |S_{\text{fi}}(\mathbf{k},\lambda)|^2 = \frac{e^2\hbar}{2m_e^2\epsilon_0\omega_k V}\left| \int_0^t \mathrm{d}t' \int \mathrm{d}^3\mathbf{x} e^{i\omega_k t'} \Psi^*_{\text{fin.}}(\mathbf{x},t') \cdot e^{-i\mathbf{k}\cdot\mathbf{x}} \left(\hat{k} \times \boldsymbol{\nabla}\Psi_{\text{in.}}(\mathbf{x},t')\right) \right|^2. \quad \text{(S17)}$$

Equation Eq. (S17) is the most general formula in our analysis. From now on we assume that $\Psi_{\text{in.}}$ is the Whittaker wavepacket Eq. (S5) and that $\Psi_{\text{fin.}}$ is the standard bound state $\psi^*_{nlm}(\mathbf{x})e^{-i\omega_n t'}$. Thus, in our case, $|i\rangle$ is given by Eq. (S5), which means that the initial state is spherically symmetric, hence the quantum number l is zero and thus has no angular dependence. Applying those remarks to Eq. (S17) we directly get

$$\sum_\lambda |S_{\text{fi}}(\mathbf{k},\lambda)|^2 = \frac{e^2\hbar}{2m_e^2\epsilon_0\omega_k V}\left| \int_0^t \mathrm{d}t' \int \mathrm{d}^3\mathbf{x} e^{i(\omega_k+\omega_n)t'} \psi^*_{nlm}(\mathbf{x}) \cdot e^{-i\mathbf{k}\cdot\mathbf{x}} \hat{k} \times \boldsymbol{\nabla}\Psi_{E,\Delta E}(\mathbf{x},t') \right|^2.$$

To further simplify this formula we express both the position $\mathbf{x}$ and momentum $\mathbf{k}$ vectors in spherical coordinates: (r,θ_x,ϕ_x) and (k,θ_k,ϕ_k). We use the formula for wavepackets Eq. (S5) and the decomposition of the bound state into a radial part and a spherical harmonic respectively: $\psi_{nlm} = R_{nl}Y_{lm}$ (with standard notation for the quantum numbers). The azimuth dependence for $\mathbf{k}$ is trivially 2π. Then after simplifying, and integrating Eq. (S15) over $\mathbf{k}$ and using the conventions from the previous paragraph, the formula for the Whittaker's probability of decay becomes as follows

$$P(t) = \frac{e^2\hbar}{16m_e^2\epsilon_0 c\pi^3 a_0^4} \int_0^\infty k\mathrm{d}k \int_0^{2\pi} \mathrm{d}\phi_k \int_0^\pi \sin\theta_k \mathrm{d}\theta_k \cdot \left| \int \mathrm{d}\phi_x \sin\theta_x \mathrm{d}\theta_x (\hat{k}\times\hat{x}) Y^*_{lm}(\theta_k,\phi_k) e^{-i\mathbf{k}\cdot\mathbf{x}} \right|^2 \left| \int_{-\infty}^\infty \mathrm{d}z e^{-(z-\mu)^2/2\sigma^2} \cdot \left[\int_0^\infty r^2 \mathrm{d}r R^*_{nl}(r) \frac{\partial w_z(r/a_0,0)}{\partial r}\right] \frac{e^{(\omega_k+\omega_n-\omega z^2)t} - i}{\omega_k+\omega_n-\omega z^2} \right|^2, \quad \text{(S18)}$$

where $\mathbf{k}\cdot\mathbf{x} = kr(\sin\theta_x\sin\theta_k\cos(\phi_x-\phi_k) + \cos\theta_x\cos\theta_k)$ and in the standard basis $\hat{k}\times\hat{x} = (\sin\phi_k\sin\theta_k\cos\theta_x - \sin\phi_x\sin\theta_x\cos\theta_k, \cos\phi_x\sin\theta_x\cos\theta_k - \sin\phi_k\sin\theta_k\cos\theta_x, \sin\theta_x\sin\theta_k\sin(\phi_x-\phi_k))$.

4. NUMERICAL EXPERIMENTS

Our numerical experiments are synthesized in modules in the software *Mathematica*, available at [4]. In this section we discuss methods for calculating the parameters Δr Eq. (S7), Δt Eq. (S8) and the average rate $\tilde{\Gamma} = P(2(\Delta t))/2(\Delta t)$.

- Diffraction lifetime Δt: to compute the lifetime we need to evaluate the overlap function and then fit into the anzats given by Theorem 2. By definition we need to integrate for r in the range $(0,\infty)$. In practice, this integration can be done efficiently by observing that the overlap $\mathbb{O}(t)$ is well-approximated by a Gaussian form. Moreover, by a numerical experiment we find that the shape of the decay does not change significantly if we only evaluate the integral up to some finite number. Therefore, we chose $(0,5a_0)$ as the range of integration. The procedure yields the constant of proportionality in Eq. (S8). The uncertainty coming from our fits is less than 5% and hence it does not affect the claims of the paper.

- Spatial spread Δr: to compute Δr we observe that the upper envelope of the wavepackets at time zero is converging to the right half of a Gaussian as ΔE tends to zero. Hence, we extract the envelope numerically and then we fit a Gaussian for the data points.

- Average rate of decay $\tilde{\Gamma}$: to compute τ we first evaluate the integral Eq. (S18). Our computations allow us to plot $P(t)$ as a function of time. In order to simplify our calculations we assume the dipole approximation. Note that this approximation is accurate for transition energies in the visible spectrum, but becomes less accurate for transition energies in the soft and hard X-rays. Moreover, the approximation is useful for better understanding the results because it enables a selection rule for the quantum number l of the bound state ψ_{nlm}: $l=1$ since $\Psi_{E,\Delta E}$ is spherically symmetric and hence $m=-1,0,1$ (the probability of decay is independent of the selected m). Another interesting feature for the plot of $P(t)$ (shown in figure S2) is that there is a steady state for the probability, i.e. after a certain point in time, the rate of decay becomes zero. We can explain this phenomenon from a physical point of view: we know that the Whittaker wavepackets spreads with time. Hence, after some time the electron will be far away from the hydrogen atom range, so its overlap with the bound states vanishes. Figure S2 also shows the decay probability for a range of energies and their energy spreads up to a transition energy at the soft X-ray spectrum. The plots start with a quadratic behavior and then switch to a linear regime before they reach their steady state. Note that this behavior of probability resembles the one for transitions between bound states.

REFERENCES

1. NIST, "Digital Library of Mathematical Functions," (2019). https://dlmf.nist.gov/13.14.
2. E. T. Whittaker and G. N. Watson, *A Course in Modern Analysis, 4th ed.* (Cambridge University Press, 1995). P. 340.
3. M. Peskin and D. Schroeder, *An Introduction to Quantum Field Theory* (Westview Press, 1995).
4. R. Dangovski, "Simulations for "Shaping Long-lived Electron Wavepackets for Customizable Optical Spectra"," (2019). Available at https://drive.google.com/drive/folders/0B4FK9pSy4zn4NG8wZ1BOME0tb2c.

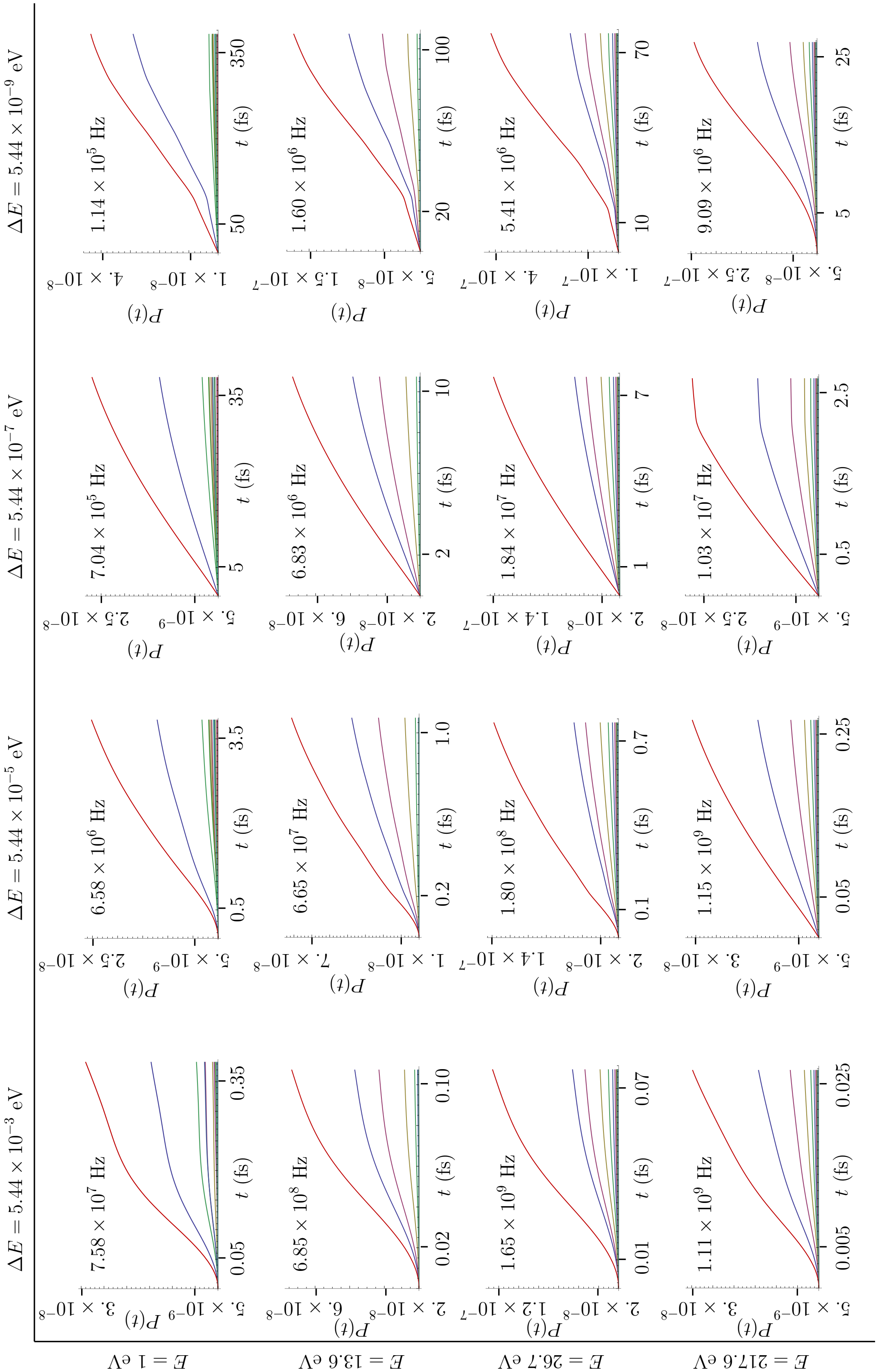

Fig. S2. The spontaneous emission dynamics of our wavepacket to bound states, marking the average transition rates. The transition dynamics is obtained based on the radiate decay formalism Eq. (S15), exhibiting a monotonous patterns in the case of varying ΔE. The dipole approximation is used to simplify the calculation (the formalism can be applied more generally as discussed in section 3).