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Extracting amplitudes for single and double ionization from a time-dependent wave packet

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A method is described for extracting double ionization amplitudes from a quantum wave packet for an atom after a short radiation pulse, but while the electrons are still interacting. The procedure involves the use of exterior complex scaling to effectively propagate the field-free solution to infinite times, and allows the use of existing integral formulas for double ionization amplitudes for two electron atoms and molecules.

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I. INTRODUCTION

Experimental studies of electron dynamics with short radiation pulses, and in particular studies making use of newly developed attosecond sources [1], are stimulating the development of accurate *ab initio* theoretical methods with which to interpret them and explore the effects of electron correlation on these time scales. Multiple ionization of atoms and molecules by one or more photons is a central focus for many of these studies.

In the case of experiments with either continuous XUV sources or very long pulses, there is now an array of methods capable of accurately solving at least the one-photon double ionization problem accurately from first principles for either atoms [2–9] or for two-electron molecules [10–14]. Because the boundary conditions for three-body Coulomb breakup are mathematically difficult and numerically problematic, a key issue for all of these methods is the extraction of the amplitudes and cross sections for double ionization from a solution of the Schrödinger equation, and these references contain extensive discussions of this point. However, recently Foumouo *et al.* [15] have raised this question anew in the context of solutions of the time-dependent Schrödinger equation for either single or double ionization of an atom by a short radiation pulse.

It is that question that we seek to address in this study. We propose a procedure for extracting the amplitudes for ejecting electrons of particular energies and directions from a quantum wave packet at the end of a short pulse (or series thereof), while the electrons are still interacting with the target nucleus and each other. Since the final state for double ionization, in the case of a two-electron atom for example, is the three-body Coulomb breakup wave function, the idea of projecting the solutions of the time-independent Schrödinger equation on the wave packet to construct the physical amplitudes for ejection is completely impractical. Nonetheless projection on approximate final states, namely, a product of independent Coulomb functions for each of the outgoing electrons, has yielded practical results [5].

The basic problem remains open, however, as Foumouo *et al.* [15] point out when they observe that the results of such approximate projection schemes, while frequently successful if applied long enough after the radiation pulse is over, yield different results in the Schrödinger and interaction pictures. In the molecular case, the problem is still more complicated, because even the noninteracting approximation to the final state is then not a product of known one-electron Coulomb functions, and would instead be a product of one-electron molecular continuum functions.

In previous work in which the method of exterior complex scaling (ECS) was used to impose the correct boundary conditions on the solution of the time-independent Schrödinger equation, we have developed a method for extracting the amplitudes for double ejection of electrons from both atoms [2,3] and molecules [10,12–14]. We propose here the extension of that formalism to the time-dependent case. We show that using the same underlying methods in which ECS has previously been implemented, such as the discrete variable method (DVR) or B-splines, to numerically propagate solutions of the time-dependent Schrödinger equation allows us to apply the complete methodology of ECS amplitude
analysis.

In Sec. II we develop the theory for this new approach to extracting double ionization information from a wave packet while the electrons are still interacting. We begin with a description of the idea for single ionization, where it reduces to an already well-understood procedure. Then, using the same logic, but making use of recent formal results of Kadyrov *et al.* [16] on the asymptotic form of the three-body Coulomb wave function, we show how to extend those ideas to the case of double ionization. In Sec. III we describe a simple application to a one-electron test case with which we can demonstrate that this approach is valid for multiphoton ionization, and also derive a formula with which the two-photon ionization cross section can be extracted for all the energies within the bandwidth of a pulse in the weak field limit. Then in Sec. IV we very briefly describe the numerical methods we use here, and in Sec. V present some numerical results of simple tests of these ideas.

II. EXTRACTION OF IONIZATION AMPLITUDES FROM A WAVE PACKET AFTER A RADIATION PULSE

Our goal is to extract unambiguously the energy and angular dependence of the electrons ejected from an atom or molecule by a radiation pulse. Of course, this question has meaning only if we analyze the wave packet after the pulse is over. The full Hamiltonian is the sum of the time-independent Hamiltonian H of the target atom or molecule, and the perturbation $U(t)$ due to the radiation field,

$$\mathcal{H}(t) = H + U(t), \tag{1}$$

where the perturbation is

$$U(t) = \begin{cases} f(r,t) & \text{for } 0 \leq t \leq t_{\text{final}} \\ 0 & \text{for } t > t_{\text{final}}, \end{cases} \tag{2}$$

and r denotes all the electronic coordinates. Our point of departure is a numerical representation of the wave function $\Psi(t)$ that evolves from the time $t=0$, at which the perturbation is turned on and is a solution of the time-dependent Schrödinger equation as follows:

$$i\frac{\partial}{\partial t}\Psi(t) = \mathcal{H}(t)\Psi(t). \tag{3}$$

The central idea of our approach, as we will show in the following subsection, is that *if* we solve the time-independent-driven Schrödinger equation whose right hand side is the ionizing wave packet $\Psi(t_{\text{final}})$ at the end of the pulse,

$$(E - H)\Psi_{\text{sc}} = \Psi(t_{\text{final}}), \tag{4}$$

with pure outgoing boundary conditions, *then* all the single and double ionization information about a two-electron system can be extracted from Ψ_{sc}. With the particular form assumed for the Hamiltonian in Eqs. (1) and (2), the definition of Ψ_{sc} and Eq. (4) follow directly from the time-dependent Schrödinger equation, as we show in the Appendix.

Although essentially any numerical representation can be used for the time integration needed to solve Eq. (3), a grid method using exterior complex scaling [2] gives a particularly convenient representation of Eq. (4), because it allows the automatic imposition of pure outgoing boundary conditions no matter how many electrons are leaving the ionized target.

In this work we employ the combined finite element method (FEM) and discrete variable representation (DVR) [17], which we have previously used in atomic [2] and molecular [12,13] double ionization calculations. We have also shown, in a different context, how to carry out time propagation under ECS using FEM-DVR methods [18–20]. In the FEM-DVR approach we can easily complex scale the coordinates at some large radius R_0 beyond which the packet $\Psi(t_{\text{final}})$ has no appreciable extension, according to the ECS transformation

$$r \to \begin{cases} r & \text{for } r \leq R_0 \\ R_0 + (r - R_0)e^{i\eta} & \text{for } r > R_0. \end{cases} \tag{5}$$

Then Eq. (4) becomes a set of linear equations, whose solution is effectively the propagation of the wave packet from $t=t_{\text{final}}$ to infinity.

We have shown previously that there are convenient integral formulas for the single and double ionization amplitudes [2,3] that involve only Ψ_{sc} and known one-electron functions. We will specialize our treatment in this section to atomic targets, although the generalization of the final working equations to the case of diatomic molecules with fixed nuclei is straightforward.

A. One-electron target

Before addressing the two-electron case, it is instructive to see how the amplitude for ejection can be constructed in the case of a one-electron target using these ideas. For a one-electron target, the atomic Hamiltonian for atomic number Z (in atomic units, $\hbar = m_e = e = 1$) is

$$H = T - Z/r_1, \tag{6}$$

where T is the kinetic energy operator.

For any time $t > t_{\text{final}}$ when the perturbation $U(t)$ is zero, the wave function can be formally expanded in eigenstates of H as

$$\Psi(\mathbf{r},t) = \int d\mathbf{k}_1^3 C(\mathbf{k})\psi_{\mathbf{k}}^{-}(\mathbf{r})e^{-(ik^2/2)(t-t_{\text{final}})} + \psi_{\text{bound}}(\mathbf{r}, t - t_{\text{final}}), \tag{7}$$

where $\psi_{\mathbf{k}}^{-}$ is a momentum-normalized continuum solution of the Schrödinger equation $H\psi_{\mathbf{k}}^{-} = (k^2/2)\psi_{\mathbf{k}}^{-}$, with incoming wave boundary conditions, and $\psi_{\text{bound}}(\mathbf{r},t)$ contains the contributions of all the bound states of the target. We use $\psi_{\mathbf{k}}^{-}(\mathbf{r})$ and not $\psi_{\mathbf{k}}^{+}(\mathbf{r})$ in this expansion, because this is formally a "half collision problem," and we want the coefficients $C(\mathbf{k})$ to have the physical meaning of ionization amplitudes. A key point is that the functions $\psi_{\mathbf{k}}^{-}(\mathbf{r})$ are orthogonal to those with different values of $\mathbf{k}$, and to all the bound states contributing to ψ_{bound}.

Our problem is to extract the coefficient $C(\mathbf{k})$ in Eq. (7) [which is the amplitude that an electron has been ejected into continuum state $\psi_{\mathbf{k}}^{-}(\mathbf{r})$] from a numerical representation of the wave packet $\Psi(\mathbf{r}, t_{\text{final}})$ at the end of the pulse. To do so, we solve the driven equation

$$(E - H)\Psi_{\text{sc}}(\mathbf{r}) = \Psi(\mathbf{r}, t_{\text{final}}), \tag{8}$$

using ECS to enforce pure outgoing boundary conditions on $\Psi_{\text{sc}}(\mathbf{r})$ and extract $C(\mathbf{k})$ from its asymptotic behavior.

Equation (8) can be formally solved as

$$\Psi_{\text{sc}}(\mathbf{r}) = \frac{1}{(E-H)}\Psi(\mathbf{r}', t_{\text{final}}) = G^{+}(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}', t_{\text{final}}). \tag{9}$$

Since the wave packet $\Psi(\mathbf{r}', t_{\text{final}})$ is square integrable, the large r behavior of $\Psi_{\text{sc}}(\mathbf{r})$ can be deduced using the asymptotic form of the full Green's function for the target (the Coulomb Green's function in this case), which is [21]

$$G_c^{+}(\mathbf{r},\mathbf{r}') \underset{r\to\infty}{\sim} -\sqrt{2\pi}\frac{e^{i[kr+(Z/k)\ln 2kr]}}{r}\langle\psi_{\mathbf{k}}^{-}|\mathbf{r}'\rangle, \tag{10}$$

with $\mathbf{k} = \hat{\mathbf{r}}\sqrt{2E} = k\hat{\mathbf{r}}$. With this relation, we can operate with the Green's function on the expansion of $\Psi(\mathbf{r}, t_{\text{final}})$ in Eq. (7), and using the orthogonality of the solutions of the Schrödinger equation, we immediately deduce the asymptotic form of Ψ_{sc},

$$\Psi_{\mathrm{sc}}(\mathbf{r}) = G_c^{+}\Psi(\mathbf{r},t_{\mathrm{final}}) \underset{r\to\infty}{\sim} -\sqrt{2\pi}C(k\hat{\mathbf{r}})\frac{e^{i[kr+(Z/k)\ln 2kr]}}{r}, \tag{11}$$

and see that indeed the amplitude associated with the pure outgoing wave function, Ψ_{sc}, is a constant times $C(\mathbf{k})$.

We can also express this amplitude as a surface integral using Green's theorem, as we have done previously in two-electron problems [2],

$$\begin{aligned} C(\mathbf{k}) &= \langle \psi_{\mathbf{k}}^{-}|E - T - V_1|\Psi_{\mathrm{sc}}\rangle \\ &= \frac{1}{2}\int (\psi_{\mathbf{k}}^{-*}(\mathbf{r})\,\nabla\,\Psi_{\mathrm{sc}}(\mathbf{r}) - \Psi_{\mathrm{sc}}(\mathbf{r})\,\nabla\,\psi_{\mathbf{k}}^{-*}(\mathbf{r}))\cdot dS, \end{aligned} \tag{12}$$

where $V_1 = -Z/r$.

So we see that solving a driven equation for Ψ_{sc} and performing the surface integral in Eq. (12) produces the complete amplitude for photoejection. For a one-electron target this formalism is obviously not necessary, because the first line of Eq. (12) is equal to $\langle \psi_{\mathbf{k}}^{-}|\Psi(t_{\mathrm{final}})\rangle$, and since we already know the wave functions $\psi_{\mathbf{k}}^{-}$ we could simply project with them on the wave packet at the end of the pulse. However, for a two-electron target that is *not* the case since we do not know the correlated two-electron final states analytically. Nonetheless, the same logic produces a practical method to calculate the complete energetic and angular dependence of double ionization.

B. Two-electron target

For a two-electron target the Hamiltonian is

$$H = T_1 + T_2 - Z/r_1 - Z/r_2 + 1/r_{12}, \tag{13}$$

and we begin again by formally expanding the wave packet after the pulse is over ($t \geqslant t_{\mathrm{final}}$) in its eigenstates,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = \int d^3k_1 \int d^3k_2 C(\mathbf{k}_1,\mathbf{k}_2)\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}(\mathbf{r}_1,\mathbf{r}_2)e^{-i(k_1^2+k_2^2)/2(t-t_{\mathrm{final}})} + \psi_{\mathrm{single\ ion}}(\mathbf{r}_1,\mathbf{r}_2,t-t_{\mathrm{final}}) + \psi_{\mathrm{bound}}(\mathbf{r}_1,\mathbf{r}_2,t-t_{\mathrm{final}}). \tag{14}$$

The function $\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}(\mathbf{r}_1,\mathbf{r}_2)$ is a solution of the Schrödinger equation

$$H\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}(\mathbf{r}_1,\mathbf{r}_2) = \frac{k_1^2+k_2^2}{2}\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}(\mathbf{r}_1,\mathbf{r}_2), \tag{15}$$

whose initial channel has both electrons in the continuum, and the states contributing to $\psi_{\mathrm{single\ ion}}(\mathbf{r}_1,\mathbf{r}_2,t)$ and $\psi_{\mathrm{bound}}(\mathbf{r}_1,\mathbf{r}_2,t)$ are also eigenstates of H. The amplitude for double ionization, with outgoing momenta for the two electrons $\mathbf{k}_1$ and $\mathbf{k}_2$, is $C(\mathbf{k}_1,\mathbf{k}_2)$, and that is the quantity we seek to calculate. The remaining two terms in Eq. (14) contain the contributions of target eigenstates with either one or no electrons in the continuum.

The incoming function $\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}(\mathbf{r}_1,\mathbf{r}_2)$ must be specified by its leading term in the region where all three particles are well separated. That asymptotic form was originally given by Redmond [22], and is (with momentum normalization)

$$\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-(0)}(\mathbf{r}_1,\mathbf{r}_2) = (2\pi)^{-3}e^{i\mathbf{k}_1\cdot\mathbf{r}_1+i\mathbf{k}_2\cdot\mathbf{r}_2+i\gamma}, \tag{16}$$

where

$$\begin{aligned} \gamma = {} & \frac{Z}{k_1}\ln(k_1r_1+\mathbf{k}_1\cdot\mathbf{r}_1) + \frac{Z}{k_2}\ln(k_2r_2+\mathbf{k}_2\cdot\mathbf{r}_2) \\ & - \frac{1}{2k_{12}}\ln(k_{12}r_{12}+\mathbf{k}_{12}\cdot\mathbf{r}_{12}), \end{aligned} \tag{17}$$

with $\mathbf{k}_{12} = (\mathbf{k}_1-\mathbf{k}_2)/2$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$.

Now, as we did in the case of one-electron, we can write the driven Schrödinger equation with the wave packet at $t = t_{\mathrm{final}}$, when the pulse is over, as the driving term

$$(E-H)\Psi_{\mathrm{sc}}(\mathbf{r}_1,\mathbf{r}_2) = \Psi(\mathbf{r}_1,\mathbf{r}_2,t_{\mathrm{final}}), \tag{18}$$

and use ECS to solve it with pure outgoing boundary conditions. Since $\Psi(\mathbf{r}_1,\mathbf{r}_2,t_{\mathrm{final}})$ is a square-integrable function we need to construct the solution of this equation on a large enough grid to both enclose this right hand side and reach the asymptotic region. Here, as in the one-electron case, the asymptotic form of $\Psi_{\mathrm{sc}} = G^{+}\Psi(\mathbf{r}_1,\mathbf{r}_2,t_{\mathrm{final}})$ contains the amplitudes $C(\mathbf{k}_1,\mathbf{k}_2)$ that we seek to construct. However, to prove that fact explicitly we require the asymptotic form of the Green's function for this equation.

Following the groundbreaking work of Alt and Mukhamedzhanov [23] on the asymptotic form of the Coulomb three-body wave function, Kadyrov *et al.* [16] have explicitly given the asymptotic form of the full Coulomb three-body Green's function for general charges and masses. We require it in the region where all three particles are well separated (denoted as region Ω_0 in their work), and specializing the result of Ref. [16] to the present case we find the required asymptotic form to be

$$\begin{aligned} G(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1'\mathbf{r}_2') \equiv (K^2/2 - H + i\epsilon)^{-1} & \xrightarrow[\rho\to\infty]{} \sqrt{2\pi i}\left(\frac{K^3}{\rho^5}\right)^{1/2} \\ & \times e^{iK\rho+\zeta\ln 2K\rho+i\sigma_0}\langle\psi_{\mathbf{k}_1,\mathbf{k}_2}^{-}|\mathbf{r}_1'\mathbf{r}_2'\rangle, \end{aligned} \tag{19}$$

where the total energy is $K^2/2 = k_1^2/2 + k_2^2/2$, and the other quantities are defined by

$$\alpha = \tan^{-1} r_2/r_1, \tag{20}$$

$$\mathbf{k}_1 = K\hat{\mathbf{r}}_1 \cos\alpha, \tag{21}$$

$$\mathbf{k}_2 = K\hat{\mathbf{r}}_2 \sin\alpha, \tag{22}$$

$$\begin{aligned}\zeta &= \frac{1}{K}\left(\frac{Z}{\cos\alpha} + \frac{Z}{\sin\alpha} + \frac{1}{\sqrt{1-\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_1 \sin 2\alpha}}\right)\\ &= \frac{Z}{k_1} + \frac{Z}{k_2} - \frac{1}{|\mathbf{k}_1 - \mathbf{k}_2|},\end{aligned} \tag{23}$$

$$\begin{aligned}\sigma_0 = \frac{1}{K}\Bigg(&\frac{Z\ln\cos^2\alpha}{\sin\alpha} + \frac{Z\ln\sin^2\alpha}{\sin\alpha}\\ &- \frac{\ln[(1-\sin 2\alpha\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)/2]}{(1-\sin 2\alpha\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)^{1/2}}\Bigg).\end{aligned} \tag{24}$$

Applying the Green's function in Eq. (19) to the expansion in Eq. (14), and using the orthogonality of the solutions of Eq. (15), we can immediately write the asymptotic form of Ψ_{sc} (in Ω_0),

$$\Psi_{\mathrm{sc}} \underset{\substack{\rho\to\infty\\ \text{in } \Omega_0}}{\longrightarrow} \sqrt{2\pi i}\left(\frac{K^3}{\rho^5}\right)^{1/2} e^{iK\rho + \zeta \ln 2K\rho + i\sigma_0} C(\mathbf{k}_1,\mathbf{k}_2), \tag{25}$$

and we see that its amplitude is indeed proportional to $C(\mathbf{k}_1,\mathbf{k}_2)$ appearing in Eq. (14). This asymptotic form was previously derived by Kadyrov *et al.* [24] in the context of electron-impact ionization with a different amplitude appearing in place of $C(\mathbf{k}_1,\mathbf{k}_2)$.

Having shown that the asymptotic behavior of the solution of Eq. (18) in fact contains the amplitude for double ionization, we are now presented with a practical problem: Given the solution of Eq. (18) on a region bounded by R_0 in Eq. (18), how do we extract $C(\mathbf{k}_1,\mathbf{k}_2)$ from it, and also disentangle double ionization from the single ionization contributions we see in Eq. (14)?

Fortunately we can appeal to a well-tested formalism that involves a surface integral and two "testing functions" that evaluate the amplitude for double ionization from Ψ_{sc}. This formalism does not follow immediately from Eqs. (18)–(25), but instead relies on a stationary phase argument with Eq. (25) as a starting point [25,26]. We have shown previously [2], in the contexts of both double photoionization and electron-impact ionization, that we can extract the amplitude, *up to an overall volume-dependent phase* χ [26] from a function with this asymptotic form using an integral form involving a pair of testing functions $\psi^-_{\mathbf{k}}(\mathbf{r})$ that are momentum-normalized, one-electron Coulomb functions with nuclear charge Z. Applying that relation here we find immediately that $C(\mathbf{k}_1,\mathbf{k}_2)$ is given by

$$e^{i\sigma_0} C(\mathbf{k}_1,\mathbf{k}_2) = e^{i\chi}\langle \psi^-_{\mathbf{k}_1}(\mathbf{r}_1)\psi^-_{\mathbf{k}_2}(\mathbf{r}_2)|E - T - V_1|\Psi_{\mathrm{sc}}(\mathbf{r}_1,\mathbf{r}_2)\rangle, \tag{26}$$

where $V_1 = -Z/r_1 - Z/r_2$ and the integration over $\mathbf{r}_1$ and $\mathbf{r}_2$ is over a finite volume large enough for the asymptotic form in Eq. (25) to hold exactly. From the formal theory of ionization as developed by Peterkop [27] and by Rudge and co-workers [25], one knows that the phase χ diverges on an *infinite* volume, unless the effective charge Z is chosen to satisfy a certain kinematic condition. On a finite volume, there are of course no problems with divergent phase factors, but as we have shown previously, there can be serious numerical problems if the charge Z is not chosen properly. In the case of double ionization of helium, for example, it is critical that the functions $\psi^-_{\mathbf{k}}(\mathbf{r})$ correspond to $Z=2$, because it is the resulting orthogonality of these testing functions to the bound states of He$^+$ that eliminates the contribution of the single ionization channels [2].

The volume-dependent phase χ can be calculated if necessary at considerable additional effort [2,26], but since the ejection probabilities depend only on $|C(\mathbf{k}_1,\mathbf{k}_2)|^2$, the overall phase is irrelevant for our purposes. The matrix element in Eq. (26) can be written in a more convenient form for calculation as a surface integral, and that is our working equation for the calculation of the amplitudes:

$$\begin{aligned}&\langle \psi^-_{\mathbf{k}_1}(\mathbf{r}_1)\psi^-_{\mathbf{k}_2}(\mathbf{r}_2)|E - T - V_1|\Psi_{\mathrm{sc}}(\mathbf{r}_1,\mathbf{r}_2)\rangle\\ &\quad= \frac{1}{2}\int [\psi^{-*}_{\mathbf{k}_1}(\mathbf{r}_1)\psi^{-*}_{\mathbf{k}_2}(\mathbf{r}_2)\,\boldsymbol{\nabla}\,\Psi_{\mathrm{sc}}(\mathbf{r}_1,\mathbf{r}_2)\\ &\qquad- \Psi_{\mathrm{sc}}(\mathbf{r}_1,\mathbf{r}_2)\,\boldsymbol{\nabla}\,\psi^{-*}_{\mathbf{k}_1}(\mathbf{r}_1)\psi^{-*}_{\mathbf{k}_2}(\mathbf{r}_2)]\cdot d\mathbf{S},\end{aligned} \tag{27}$$

where $\boldsymbol{\nabla}$ is the six-dimensional gradient operator, $\boldsymbol{\nabla} = (\nabla_1, \nabla_2)$. Equation (27) is an identity which follows from the fact that the product $\psi^-_{\mathbf{k}_1}(\mathbf{r}_1)\psi^-_{\mathbf{k}_2}(\mathbf{r}_2)$ is an eigenfunction of $T + V_1$, and the application of Gauss' theorem. It is important to note that in this equation the functions $\psi^-_{\mathbf{k}_1}(\mathbf{r}_1)$ and $\psi^-_{\mathbf{k}_2}(\mathbf{r}_2)$ do *not* describe the final state of the system, but are merely the testing functions which extract the necessary amplitude from Ψ_{sc}.

So the overall procedure we propose for calculating the energy and angle dependence of double photoejection by a short radiation pulse is as follows:

(1) Propagate the solution of the time-dependent Schrödinger using the FEM-DVR approach until t_{final} when the pulse is over.

(2) Solve driven equation, Eq. (18) using ECS.

(3) Extract the amplitude using Eq. (27) and calculate the ejection probability $|C(\mathbf{k}_1,\mathbf{k}_2)|^2$.

A final comment about the application of these ideas to two-electron molecules is in order. The amplitude formula in Eq. (27) has been extended to that case and applied to double photoionization of the H_2 molecule [10,12–14]. The essence of that idea is to replace the testing functions $\psi^-_{\mathbf{k}_i}$ with H_2^+ continuum wave functions. Although that replacement entails numerical solution of the time-independent Schrödinger equation for electron scattering from H_2^{2+}, it provides a powerful and practical approach to the molecular double ionization problem as the most recent comparisons with experiment demonstrate [13,14]. For short enough pulses for which the fixed nuclei approximation is valid, the extension of the results of this section to that molecular case can be made in exactly the same way.

III. EXAMPLE: ONE- AND TWO-PHOTON IONIZATION OF ATOMIC HYDROGEN

Using a one-electron test case, we can explore some of the numerical aspects of the general method we propose here for attacking the multiphoton double and single ionization problem in two-electron atoms. While these methods are applicable at any intensity of the applied field, we will focus in Sec. V on low intensity fields where results obtained with the present formalism can be compared with well-known results for one- and two-photon ionization cross sections of the hydrogen atom obtained in the perturbative limit.

The time-dependent Schrödinger equation (TDSE) for this one-electron system is

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = [H(\mathbf{r}) + U(\mathbf{r},t)]\Psi(\mathbf{r},t), \tag{28}$$

where $H(\mathbf{r})$ is the atomic Hamiltonian,

$$H(\mathbf{r}) = -\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{\hat{\mathbf{L}}^2}{2r^2} - \frac{1}{r}, \tag{29}$$

and $\hat{\mathbf{L}}$ is the angular momentum operator. In the dipole approximation, the laser-atom interaction $U(\mathbf{r},t)$ in the velocity gauge is given in terms of the electron's momentum operator $\mathbf{p}$ and the vector potential $\mathbf{A}$ by $U(\mathbf{r},t)=(e/mc)\mathbf{A}(t)\cdot\mathbf{p}$. In the length gauge it is $U(\mathbf{r},t)=e\mathbf{E}(t)\cdot\mathbf{r}$, with the corresponding electromagnetic field $\mathbf{E}(t)$ defined as $\mathbf{E}(t)=-(1/c)\partial\mathbf{A}(t)/\partial t$.

For a photon energy ω and a total pulse duration T, $\mathbf{A}(t)$ may be written

$$\mathbf{A}(t) = \begin{cases} A_0 F_\omega(t)\boldsymbol{\epsilon} & t \in [0,T] \\ 0, & \text{elsewhere}, \end{cases} \tag{30}$$

where $\boldsymbol{\epsilon}$ is the polarization vector. For the time and frequency dependence of the pulse $F_\omega(t)$, in these examples we choose a sine squared envelope,

$$F_\omega(t) = \sin^2\left(\frac{\pi}{T}t\right)\sin(\omega t). \tag{31}$$

The initial state $\Psi(\mathbf{r},0)$ is the ground state of the hydrogen atom Ψ_0.

A. Amplitudes for one-photon single ionization for energies within the pulse bandwidth

In general the amplitude for ionization extracted via Eq. (12) or Eq. (27) will depend on the parameters of the radiation pulse that produced the wave packet being analyzed. However, in the case that the intensities involved allow the accurate description of the process using time-dependent perturbation theory (TDPT), we can use these methods to extract the amplitudes over the range of energies within the bandwidth of the pulse.

The textbook expression in first order TDPT for the transition amplitude $C^{(1)}(\mathbf{k})$, between an initial state of energy $E_i=\hbar\omega_i$ and a continuum final state of energy $E_k=\hbar\omega_k$, caused by a pulse of duration T characterized as in Eqs. (30) and (31) is

$$C^{(1)}(\mathbf{k}) = \frac{-ieA_0}{\hbar mc}\langle\psi_{\mathbf{k}}^{-}|\boldsymbol{\epsilon}\cdot\mathbf{p}|\psi_i\rangle\tilde{F}^{(1)}(\omega,\omega_{ki},T), \tag{32}$$

where

$$\tilde{F}^{(1)}(\omega,\omega_{ki},T) = \int_0^T e^{i(\omega_k-\omega_i)t}F_\omega(t)dt \tag{33}$$

and $\langle\psi_{\mathbf{k}}^{-}|\boldsymbol{\epsilon}\cdot\mathbf{p}|\psi_i\rangle$ is the dipole matrix element connecting the initial and continuum states for a particular wave vector $\mathbf{k}$. We can evaluate the energy-dependent factor $\tilde{F}^{(1)}(\omega,\omega_{ki},T)$ explicitly in this case and thereby find the connection, over the bandwidth of energies where $\tilde{F}^{(1)}(\omega,\omega_{ki},T)$ is appreciably nonzero, between the amplitude $C(\mathbf{k})$ we extract after the pulse for a particular $\mathbf{k}$ and the dipole matrix element.

Using the rotating wave approximation to evaluate $\tilde{F}^{(1)}$ $\times(\omega,\omega_{ki},T)$, gives

$$\tilde{F}^{(1)}_{\mathrm{RW}}(\omega,\omega_{ki},T) = \frac{e^{-i\omega T}(e^{i(\omega-\omega_{ki})T}-1)\pi^2}{[T^2(\omega-\omega_{ki})^2-4\pi^2](\omega-\omega_{ki})}, \tag{34}$$

and the modulus squared of this amplitude has a frequently quoted [15] form that is useful when computing the single ionization cross section,

$$|\tilde{F}^{(1)}_{\mathrm{RW}}(\omega,\omega_{ki},T)|^2 = \frac{4\pi^4\sin^2[(\omega-\omega_{ki})T/2]}{[T^2(\omega-\omega_{ki})^2-4\pi^2]^2(\omega-\omega_{ki})^2}. \tag{35}$$

Note that $|\tilde{F}^{(1)}_{\mathrm{RW}}(\omega,\omega_{ki},T)|^2$ tends to $(3\pi T/16)\delta(\omega-\omega_{ki})$ for long pulse durations.

The cross section for one-photon single ionization in the velocity gauge is

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2\alpha k}{m\hbar\omega_{ki}}|\langle\psi_{\mathbf{k}}^{-}|\boldsymbol{\epsilon}\cdot\mathbf{p}|\psi_i\rangle|^2, \tag{36}$$

where $\hbar\omega_{ki}$ is the energy difference between the initial and the final states, and $\psi_{\mathbf{k}}^{-}$ is momentum normalized. Using Eq. (32) we can easily relate the differential cross section to $C^{(1)}(\mathbf{k})$ to obtain

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 ke^2 m}{\hbar\omega_{ki}\alpha}\frac{|C^{(1)}(\mathbf{k})|^2}{|A_0|^2|\tilde{F}^{(1)}_{\mathrm{RW}}(\omega,\omega_{ki},T)|^2}. \tag{37}$$

So the factorability of the expression in first order TDPT for the transition probability allows us to extract the differential single ionization cross section from a single pulse within its bandwidth, defined as the range of photon frequencies for which $\tilde{F}^{(1)}_{\mathrm{RW}}(\omega,\omega_{ki},T)$ is appreciably nonzero. This is a well-known result. However, we show next that, more significantly, we can effectively do the same thing for two-photon processes where the TDPT expressions are *not* factorable.

B. Amplitudes for two-photon single ionization for energies within the pulse bandwidth

For a two-photon transition between an initial state of energy $E_i=\hbar\omega_i$ and a continuum final state of energy

$E_k=\hbar\omega_k$, we begin with the second order TDPT expression for the transition amplitude as follows:

$$C^{(2)}(\mathbf{k}) = \left(\frac{-i}{\hbar}\right)^2 \sum_m U_{\mathbf{k}m} U_{mi} F^{(2)}(E_k,E_m,E_i,\omega,T), \tag{38}$$

where the dipole matrix elements $U_{\mathbf{k}m}$ and U_{mi} are

$$U_{\mathbf{k}m} = \frac{e}{mc} A_0 \langle \psi_{\mathbf{k}}^- | \boldsymbol{\epsilon}\cdot\mathbf{p} | \psi_m \rangle,$$

$$U_{mi} = \frac{e}{mc} A_0 \langle \psi_m | \boldsymbol{\epsilon}\cdot\mathbf{p} | \psi_i \rangle, \tag{39}$$

the summation over m denotes a sum and integral over all the eigenstates of the target and the coefficient $F^{(2)}(E_k,E_m,E_i,\omega,T)$ is given, in the rotating wave approximation, by

$$F^{(2)}(E_k,E_m,E_i,\omega,T) = \frac{1}{2}\int_0^T dt'\, e^{i(\omega_{km}-\omega)t'} \sin^2(t'\pi/T) \times \frac{1}{2}\int_0^{t'} dt''\, e^{i(\omega_{mi}-\omega)t''} \sin^2(t''\pi/T). \tag{40}$$

$F^{(2)}(E_k,E_m,E_i,\omega,T)$ can be evaluated analytically to give an algebraically complicated result.

To connect $C^{(2)}(\mathbf{k})$ with the familiar expression for the two-photon cross section obtained in the time-independent theory, we define the reduced coefficient or "shape function" $\tilde{F}^{(2)}(E_k,E_m,E_i,\omega,T)$ as follows:

$$\tilde{F}^{(2)}(E_k,E_m,E_i,\omega,T) = (E_i + \hbar\omega_{ki}^{(2)} - E_m) F^{(2)}(E_k,E_m,E_i,\omega,T), \tag{41}$$

where $\hbar\omega_{ki}^{(2)}=(E_k-E_i)/2$, is a half of the difference between the initial and the final state energies (i.e., the photon energy for an infinitely long pulse duration). It turns out that if the photon frequency ω is not too close to being in resonance with a transition to one of the intermediate states m, then the shape function $\tilde{F}^{(2)}$ is well approximated by an expression that does not depend on the energies of the intermediate states in the sum in Eq. (38) and which becomes exact in the long T limit as follows:

$$\tilde{F}^{(2)}(E_k,E_m,E_i,\omega,T) \approx \tilde{\mathfrak{F}}(E_{\mathbf{k}},E_i,\omega,T), \tag{42}$$

with

$$\tilde{\mathfrak{F}}(E_{\mathbf{k}},E_i,\omega,T) = \frac{6e^{-iT(E_i-E_k+2\omega)}(-1+e^{iT(E_i-E_k+2\omega)})\pi^4}{(E_i-E_k+2\omega)[T^4(E_i-E_k+2\omega)^4 - 20\pi^2T^2(E_i-E_k+2\omega)^2 + 64\pi^4]}. \tag{43}$$

So $\tilde{\mathfrak{F}}(E_{\mathbf{k}},E_i,\omega,T)$ factors out of the sum in Eq. (38) in this approximation. We note in passing that $|\tilde{\mathfrak{F}}(E_{\mathbf{k}},E_i,\omega,T)|^2$ tends to $(70\pi T/64^2)\delta(\omega_i-\omega_k+2\omega)$ for large T.

We can now connect the amplitude $C^{(2)}(\mathbf{k})$ we extract from the wave packet using Eq. (12) with differential cross section (units of cm^4 sec) for two-photon ionization. The differential cross section for two-photon ionization is defined as the transition rate from Fermi's golden rule divided by the square of the photon flux [28], giving in the velocity gauge,

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^3\hbar k\alpha^2}{\bar{\omega}_{ki}^2 m^3} |\langle \psi_{\mathbf{k}}^- | \boldsymbol{\epsilon}\cdot\mathbf{p}(E_i + \hbar\bar{\omega}_{ki}^2 - H)^{-1}\boldsymbol{\epsilon}\cdot\mathbf{p}|\psi_i\rangle|^2, \tag{44}$$

where $\bar{\omega}_{ki}\equiv(\omega_k-\omega_i)/2$, and where the length gauge expression is given by replacing $\mathbf{p}$ by $\mathbf{r}$ in this expression and multiplying by $(\bar{\omega}_{ki}m)^4$. Using the combination of Eqs. (38), (39), (41), and (42), we can relate this cross section to the amplitude extracted from the packet via Eq. (12) at the end of the pulse,

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^3\hbar k\alpha^2}{\bar{\omega}_{ki}^2 m^3} \frac{|C^{(2)}(\mathbf{k})|^2}{\left(\frac{e^2|A_0|^2}{m^2c^2\hbar^2}\right)^2 |\tilde{\mathfrak{F}}(E_{\mathbf{k}},E_i,\omega,T)|^2}, \tag{45}$$

and a similar expression can be derived in the length gauge. We mention in passing that, when comparing with the results of Karule [29,30] below, we follow her definition of a proportional quantity called the "ionization rate" in that work,

$$\frac{Q^{(2)}}{I} = \frac{2\pi^2\alpha k a_0^2}{I_0\bar{\omega}_{ki}^3} |\langle \psi_{\mathbf{k}}^- | \boldsymbol{\epsilon}\cdot\mathbf{p}(E_i + \hbar\bar{\omega}_{ki} - H)^{-1}\boldsymbol{\epsilon}\cdot\mathbf{p}|\psi_i\rangle|^2, \tag{46}$$

where I_0 is the atomic unit of intensity $I_0=ce^2/[(4\pi)^2\epsilon_0 a_0^4]$ $=7.0189\times10^{16}$ W/cm^2.

To our knowledge Eqs. (43) and (45), which allow us to extract the two-photon ionization cross section within the bandwidth of a pulse, provided the energies are not close to a resonance feature, have not appeared previously in the literature. Similar expressions making use of Eq. (43) can be derived for two-photon double ionization and may be useful in extracting cross sections from large-scale converged calculations on two-electron systems where each solution of the TDSE is expensive to compute.

IV. TIME PROPAGATION USING THE FEM-DVR APPROACH

In the FEM-DVR method the wave function is expanded in a product basis of the FEM-DVR radial basis functions and spherical harmonics as follows:

$$\Psi(\mathbf{r},t)=\sum_{i,l} a_{i,l}(t)\chi_i(r)Y_{l,0}(\theta,\phi), \tag{47}$$

where for linear polarization in this example we need include only $m=0$ contributions, and the wave function is a function of only r and θ. The vector of coefficients $a_{i,l}(t)$ is the representation of the wave function that we must propagate in time.

The FEM-DVR radial basis functions $\chi_i(r)$ have been discussed at length elsewhere [2,17], and on the DVR grid each is nonzero only at a single point r_i. Like all discrete variable representations, this one, based on finite elements and Gauss-Lobatto quadrature, has the key property that the matrix elements of any local function of the electronic coordinates are diagonal in the radial basis, when evaluated using the underlying Gauss quadrature rule. For example, when evaluated by Gauss quadrature, the laser-atom interaction has the matrix elements

$$\langle\chi_i Y_{l,0}|U(\mathbf{r},t)|\chi_j Y_{l',0}\rangle = U_{l,l'}(r_i,t)\delta_{i,j}, \tag{48}$$

where r_i is the DVR radial grid point at which $\chi_i(r)$ is nonzero. This follows from the fact that the DVR basis functions have the property

$$\chi_i(r_j)=\frac{\delta_{i,j}}{\sqrt{w_i}}, \tag{49}$$

where w_i is a quadrature weight. The matrix elements are of course not diagonal in the angular momenta. In the two-electron problem the convenient numerical properties of this basis have been exploited in time-independent double ionization and electron-impact ionization calculations.

We use the split operator approach, writing the propagator for a time step Δt as

$$e^{-i(H+U_t)\Delta t}=e^{-iH\Delta t/2}e^{-iU_t\Delta t}e^{-iH\Delta t/2}. \tag{50}$$

Since the atomic Hamiltonian is block diagonal in the angular momentum indices, we can write the exponential of its matrix representation in the FEM-DVR basis as

$$e^{-iH\Delta t}=\prod_{l=0}^{l=l_{\max}} e^{-iH^l\Delta t}. \tag{51}$$

Each of the exponential matrix operators in this product can be constructed using the Cranck-Nicholson propagator,

$$e^{-iH^l\Delta t/2}=\left(1+iH^l\frac{\Delta t}{4}\right)^{-1}\left(1-iH^l\frac{\Delta t}{4}\right). \tag{52}$$

However, since these operators depend on Δt, but not t, their construction by solution of linear equations need be done only once. These simplifications carry over to the two-electron case if we choose H to consist of only the kinetic energy and nuclear attraction potential.

The fact that matrix representation of U_t in Eq. (48) is not diagonal in l complicates the construction of the remaining factor, $\exp(-iU_t\Delta t)$, of the propagator in Eq. (50). As the number of angular momenta in the basis increases, exponentiating the matrix of U_t becomes increasingly time consuming.

At each time step we must apply this exponential operator to the function $\Psi(\mathbf{r},t)$ to produce the intermediate result $\Psi'(\mathbf{r},t)$,

$$\Psi'(\mathbf{r},t)=e^{-iU_t\Delta t}\Psi(\mathbf{r},t). \tag{53}$$

The function Ψ is expanded as in Eq. (47), and we require the expansion of Ψ' in the same basis, for which the coefficients are

$$a'_{i,l}(t)=\langle\chi_i Y_{l,0}|e^{-iU_t\Delta t}|\Psi(\mathbf{r},t)\rangle. \tag{54}$$

To avoid exponentiating the matrix representation of the operator U_t obtained through Eq. (48) at each time step, we follow the ideas of Chu and co-workers [31,32] and construct a diagonal representation of U_t in coordinate space by discretizing both the radial and angular variables. If we restrict ourselves to the length gauge, we can write the exponential explicitly as a function of coordinates

$$e^{-iU_t\Delta t}=e^{-ieE(t)r\cos(\theta)\Delta t}. \tag{55}$$

Substituting the expansion of Ψ in Eq. (47) into Eq. (54), we can simply quadrature this integral using the properties of the DVR in the radial variables, and a Gaussian quadrature in the angular variables. The result shows the simplification intrinsic to the DVR, which keeps the operation diagonal in the DVR index i,

$$a'_{i,l}(t)=\sum_{l'} M(r_i)_{l,l'}\Psi_{i,l'}(t), \tag{56}$$

with

$$M(r_i)_{l,l'}=\sum_q w_q Y^*_{l,0}(\theta_q)e^{-ieE(t)r_i\cos(\theta_q)\Delta t}Y_{l',0}(\theta_q). \tag{57}$$

In an efficient numerical implementation, the sums and multiplications in Eqs. (56) and (57) are carried out in a stepwise manner with the sum over l' first and the sum over q, second. For the sizes of the time steps in this work, ten point Gauss Legendre quadrature in $\cos(\theta)$ suffices to converge this integral. More interestingly, this algorithm is also effective in the two-electron problem when we include the electron repulsion $1/r_{12}$ in U_t, because while $1/r_{12}$ is not diagonal in angular momentum indices, its FEM-DVR representation is still diagonal in the radial coordinates [2]. Although this procedure can only be implemented in the length gauge, it strongly reduces the computational effort for time propagation in both the one- and two-electron cases.

V. NUMERICAL RESULTS

To demonstrate the basic idea of extracting amplitudes for ionization from a time-dependent description using Eqs. (8)

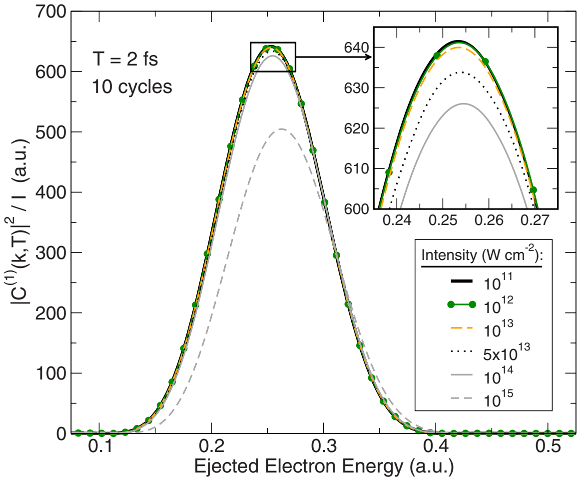

FIG. 1. (Color online) Square of the transition amplitudes over the intensity as a function of the ejected energy for different intensity values, in the region in which one-photon ionization dominates. The central frequency of the pulse is 0.76 a.u. (20.68 eV).

and (12) for a one-electron case, we have calculated the one- and two-photon ionization cross sections of the hydrogen atom using short XUV pulses in order to compare with the known cross sections in the perturbative limit.

To choose the intensities for these test calculations, we first check that the square of the transition amplitude at the end of the pulse evaluated using Eq. (12) is proportional to I^N (with N being the number of absorbed photons).

For example, Fig. 1 shows $|C^{(1)}(k)|^2/I$ for one-photon absorption, using pulses of 2 fs and ten cycles (ω=0.76 a.u.) at different intensities. Above I=10^{13} W/cm^2, nonlinear processes appear, and we therefore employ a laser intensity of I=10^{12} W/cm^2, so as to produce a relatively high ionization rate but still in the perturbative limit.

Figure 1 illustrates that the electron energy distributions for one-photon absorption reflect the energy profile of the pulse (with width $\Delta\omega$=$4\pi/T$, for a sine squared time envelope [33]), as given by the shape function defined by Eq. (35). We can extract the cross sections on this energy interval, and each TDSE calculation for a given pulse frequency (for a given number of cycles) allows us to reproduce cross sections for the photon energies contained in this bandwidth.

In Fig. 2 we compare one-photon ionization cross sections for a hydrogen atom as a function of photon energy obtained by applying perturbation theory and by extracting them from the time propagated wave packet.

The time propagation has been carried out with a time step Δt=0.1 a.u. (1 a.u.=2.418 88 $\times$ 10^{-17} s), for a total pulse duration of 2 fs, I=10^{12} W cm^{-2}, and different pulse frequencies (corresponding to different numbers of cycles). The radial part of the wave function is represented in a DVR basis set with R_0=150 a.u. and the spherical harmonics expansion includes a maximum value of angular momentum l_{max}=1 (only s and p partial waves are included). Length and velocity gauge results are indistinguishable on this scale, and the time-dependent results agree perfectly with those of perturbation theory, even using such a relatively short pulse.

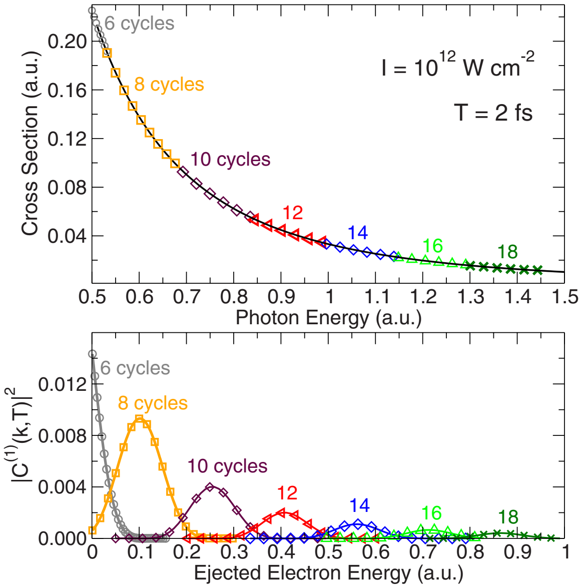

FIG. 2. (Color online) Upper panel: one-photon ionization cross sections for atomic hydrogen as a function of photon energy. Black full line: perturbation theory results. TDSE results are obtained for I=10^{12} W cm^{-2}, T=2 fs, and different number of cycles, represented with different symbols and colors. Lower panel: the squared moduli of the amplitudes corresponding to the cross sections in the upper panel.

The lower panel of Fig. 2 shows the corresponding electron energy distributions, including those whose central frequencies correspond to photon energies close to the ionization threshold. For instance, a 2 fs pulse of six cycles is centered at a photon energy (0.456 a.u.) below the ionization limit, but the energy bandwidth is wide enough to populate the ionization continuum and allow us to extract the perturbation theory limit cross sections for ionization.

For the more interesting case of extracting the cross section over the bandwidth of the pulse for a two-photon ionization process, more partial waves are included (convergence is achieved for a maximum value of angular momentum l_{max}=3 at these intensities), and the density of the DVR functions is increased.

In Fig. 3 we show the partial two-photon ionization cross sections (s and d contributions) for above-threshold ionization (ATI) photon energies >0.5 a.u., where the time-dependent propagation has been computed with a time step Δt=0.0138 a.u., for a total pulse duration of 4 fs and I =10^{12} W cm^{-2}.

There is essentially perfect agreement with perturbation theory results [29,34–37], demonstrating that we are able to reproduce the long time limit in the ATI region with a relatively short pulse. This result verifies that using the analytic expression Eq. (43) for the energy profile function in the two-photon case is a reliable approximation as long as no sharp resonant contributions lie within its bandwidth.

However, in the two-photon resonant region where bound states are populated by one-photon absorption ($0.25 < \omega < 0.5$ a.u.), longer pulses are required to reproduce the long time limit. In Fig. 4 we see that with a pulse duration of 4 fs,

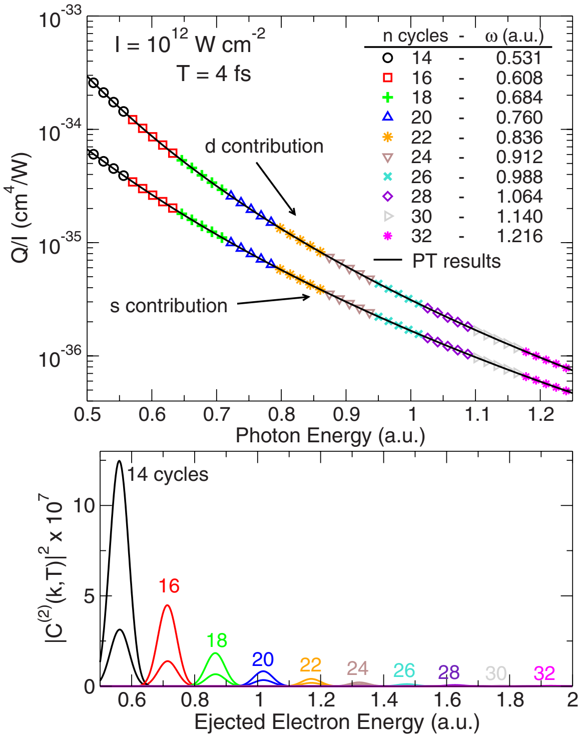

FIG. 3. (Color online) Two-photon ATI cross sections (s and d contributions) as a function of the photon energy. Black full lines: perturbation theory results. TDSE results are calculated for $T=4$ fs and $I=10^{12}$ W cm^{-2}, at different pulse frequencies (different symbols and colors). $R_0=314$ a.u. and 573 DVR functions.

the ATI region is properly described, but the sharp features appearing when one-photon absorption is resonant with an intermediate bound state in perturbation theory are smoothed out because of the finite energy bandwidth in the pulse. The inset in Fig. 4 shows that at longer pulse durations those sharp features can be better distinguished as we approach the long time limit, but still with pulses of less than 20 fs.

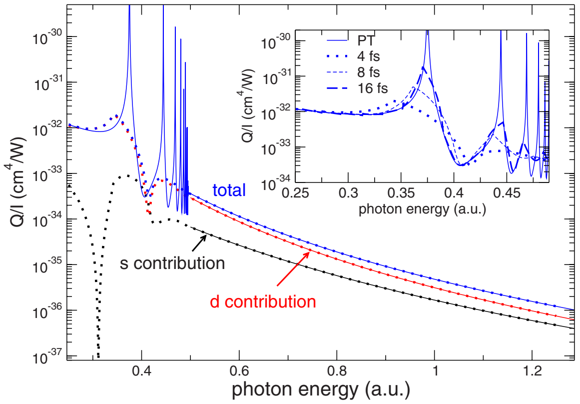

FIG. 4. (Color online) Total (and s and p contribution) two-photon ionization cross sections. Thin lines: perturbation theory results. Dots: TDSE results for 4 fs and $I=10^{12}$ W cm^{-2}. Inner picture: Total cross sections for different pulse durations and $I=10^{12}$ W cm^{-2}.

VI. CONCLUSIONS

The development of a new generation of intense, ultrashort, pulsed x-ray light sources is stimulating the development of accurate, nonperturbative theoretical methods for studying the quantum dynamics of strongly correlated atomic and molecular targets driven by short-wavelength electromagnetic fields. For simple atoms and molecules, attacking such problems by direct numerical solution of the time-dependent Schrödinger equation on modern supercomputers has become feasible. With this approach, however, a central question, which has yet to be fully resolved, is how best to extract quantitative scattering information from a propagated wave packet. In particular, there are evidently open questions about using projection schemes which involve approximate, uncorrelated final states, while projection onto exact time-independent scattering states is not really feasible in the case of multiple electron ejection.

The approach we have described here builds on the progress made over the past few years in using exterior complex scaling to solve the time-independent Schrödinger equation for Coulomb breakup problems while avoiding the detailed specification of asymptotic boundary conditions. We have shown that it is possible to use the time-propagated wave packet that is the solution of the time-dependent Schrödinger equation at the end of a short radiation pulse as the driving term for a driven time-independent equation that can be solved under ECS. The scattered wave function so obtained can be used to compute amplitudes that give the complete angle- and energy-dependent ejection probabilities for the photoelectrons.

We have illustrated these ideas with calculations of the one- and two-photon ionization cross sections for atomic hydrogen and shown how, with weak fields and relatively short pulses, a single time-propagated packet can be used to extract cross sections over all energies within the bandwidth of the pulse.

We have also outlined how the method can be used to study targets with two active electrons. In this context, it is interesting to compare our approach with the one recently described by Foumouo *et al.* [15]. The latter authors compute the probabilities for single-continuum ionization by projecting the wave packet onto accurate multichannel scattering wave functions. Probabilities for double ionization are then correctly obtained by subtracting the single ionization probabilities from the total ionization probability. In our approach, the double ionization amplitudes are obtained directly from the solution of a driven equation. In addition to providing double ionization probabilities, the approach we have outlined also allows for the computation of energy-sharing and angular ionization probabilities. Application of the methods outlined here to two-electron targets is currently underway.

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APPENDIX: DERIVATION OF THE DRIVEN SCHRÖDINGER EQUATION

We consider an atom (molecule) in a stationary eigenstate that is subjected to a time-dependent pulse initiated at $t=0$. The wave function evolves under the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(t)=\mathcal{H}(t)\Psi(t). \tag{A1}$$

At $t=t_{\mathrm{final}}$, the pulse ends and the wave function continues to evolve under the time-independent atomic (molecular) Hamiltonian H of Eq. (1). The time dependence of $\Psi(t)$ for $t>t_{\mathrm{final}}$ is then given explicitly as

$$\Psi(t)=e^{-iH(t-t_{\mathrm{final}})}\Psi(t_{\mathrm{final}}) \quad t>t_{\mathrm{final}}. \tag{A2}$$

We now take the Fourier transform (from t_{final} to infinity) of both sides of Eq. (A2), at the same time defining the scattered wave Ψ_{sc} as

$$\begin{aligned}\Psi_{sc}&\equiv -ie^{-iEt_{\mathrm{final}}}\int_{t_{\mathrm{final}}}^{\infty}dte^{i(E+i\epsilon)t}\Psi(t)\\ &=-ie^{-iEt_{\mathrm{final}}}\int_{t_{\mathrm{final}}}^{\infty}dte^{i(E+i\epsilon)t}e^{-iH(t-t_{\mathrm{final}})}\Psi(t_{\mathrm{final}}).\end{aligned} \tag{A3}$$

Making the change of variable $t\rightarrow t-t_{\mathrm{final}}$, we obtain

$$\begin{aligned}\Psi_{sc}&=-i\int_{0}^{\infty}dte^{i(E+i\epsilon-H)t}\Psi(t_{\mathrm{final}})\\ &=\frac{1}{(E+i\epsilon-H)}\Psi(t_{\mathrm{final}})=G^{+}\Psi(t_{\mathrm{final}}),\end{aligned} \tag{A4}$$

or, equivalently,

$$(E-H)\Psi_{sc}=\Psi(t_{\mathrm{final}}). \tag{A5}$$

The rest of the logic leading to the working equations for the amplitudes follows from expanding $\Psi(t_{\mathrm{final}})$ in terms of the eigenstates of H and proceeding as in Secs. II A and II B.

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