Time-dependent formation of the profile of the He $2s2p\ ^1P^o$ state excited by a short laser pulse

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We produce quantitatively accurate data for the energy- and time-dependent formation of the profile of the differential ionization probability of the He $1s^2\ ^1S$ ground state from the coherent excitation and decay of the doubly excited He $2s2p\ ^1P^o$ resonance state induced by a pulse of duration of 450 a.u. and field strength in the range $F=0.4\times10^{-3}$ a.u. to $F=0.4\times10^{-1}$ a.u. Two general methods were applied. One is analytic, using Fano's configuration interaction in the continuum in the framework of first order time-dependent perturbation theory. The other is numerical, using the state-specific expansion approach for the nonperturbative solution of the time-dependent Schrödinger equation. Electronic structures and electron correlation are incorporated via the use of state-specific wave functions for the initial state, the resonance state, and the continuum of scattering states. The results from the two methods are in perfect agreement, with a small discrepancy starting at $F=0.4\times10^{-1}$ a.u. The weak field analytic formulas show explicitly the dependence of the profile formation on the pulse characteristics. In the limit of large times, the system becomes stationary and the computed resonance state profile yields the Fano asymmetry parameter of $q=-2.8$, with energy $E_r=60.20$ eV and width $\Gamma=0.038$ eV. These values agree with previously published ones obtained from time-independent calculations and from photoabsorption measurements of the type initiated by Madden and Codling in 1963.

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I. INTRODUCTION

As a consequence of continuing developments in the science and technology of techniques that produce and control electromagnetic pulses with frequencies that are found in a broad part of the spectrum, from the ir to the xuv and soft x rays, it is possible to have *hyperfast* pump-probe time delay (PPTD) spectroscopic techniques capable of time resolving the dynamics of various atomic and molecular systems involving excited states. By hyperfast we mean times in the range of a few femtoseconds down to the attosecond regime. These are necessary for the possible recording of time-resolved processes caused by the "motion" of electrons in certain categories of situations in atoms and molecules (see below).

Such prospects evidently imply the preparedness of theoretical analysis and methods for interpretation and prediction based on reliable quantum mechanical computations that start from first principles of atomic and molecular structure and produce reliable data quantitatively.

In this context, and in view of the announced observation of trains [1] and of single [1] attosecond (as) pulses (1 a.u. of time$=2.42\times10^{-17}$ s$=24.2$ as), a few years ago [2,3], we investigated, via the *ab initio* solution of the time-dependent Schrödinger equation (TDSE), cases in which the interplay between electronic structure and electron dynamics can be such as to allow, in principle, the recognition of processes whose time evolution takes place within the as scale. Indeed, it was found that it might be possible via hyperfast PPTD schemes to observe effects that result from the quantum mechanical motion of strongly correlating pairs of electrons. The investigations focused on the time resolution of processes induced at the pump step, since, apart from the fundamental interest in understanding computationally such quantum dynamics from first principles, it is crucial to acquire quantitatively data on the efficiency of preparing such highly excited electronic states by short pulses.

Specifically, in [2,3] we studied from first principles the time-resolved coherent excitation and decay of He $^1P^o$ nonstationary states above 60 eV, labeled by doubly excited configurations that were excited simultaneously with two short femtosecond pulses. These configurations and their simultaneous excitation secure the conditions for the anticipated appearance of quantum beats (see below).

The results indicated that, in a representation of superposition of configurations (SOC), the dynamics of strongly correlating electrons is the cause of hyperfast processes that can, in principle, be time-resolved in PPTD schemes in the as scale, with the final state being in the discrete or in the continuous spectrum. Three of these processes are: (i) The state-specific *electron correlation beats* (ECBs) that carry the information not only of the energy difference between the localized states over which the system oscillates due to its own Hamiltonian, but also of their wave function characteristics, such as amplitudes of oscillation and mixing coefficients of configurations, and good quantum numbers of zero order labels; (ii) the intraatomic (or intramolecular) spatial motion of pairs of electrons recognized through the time-dependent geometries of their probability densities; and (iii) the time-resolved decay due to autoionization of the doubly excited (or inner-hole) states to the available open channels. It was pointed out [2] that analogous time-resolved effects of motions of electron pairs in doubly excited Rydberg configu-

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rations have been observed at longer time scales, e.g., [4,5].

In this paper, we study yet another aspect of possible processes occurring in hyperfast PPTD schemes in real systems, formally as well as numerically. The quantity of interest is the differential ionization probability of polyelectronic atoms in the neighborhood of a resonance state. This quantity is given by

$$P(E,t) = |\langle \textit{scattering state}|\Psi(t)\rangle|^2. \quad (1)$$

The time-dependent $|\Psi(t)\rangle$ contains the information for the coherent excitation by a short pulse of the system, from an initial discrete state to the energy region of a resonance state.

The calculation of $P(E,t)$ was considered recently by Wickenhauser *et al.* [6] as part of an intriguing proposal on the feasibility of hyperfast measurements of "*time resolved Fano resonances*." They discussed a PPTD scheme involving a model inner-hole spectrum with input parameters from the Lanthanide group. As is known, creation of one or more holes in inner subshells of large atoms results in states with strong *hole-filling* pair correlations that cause autoionization into multichannel continua with very small decay lifetimes—normally of the order of $10^{-14}-5\times10^{-15}$ s.

For the pump part, which is the object of our investigations in this and in our previous work [2,3], Wickenhauser *et al.* solved a related time-dependent model of an isolated resonance in the framework of first order time-dependent perturbation theory (FOTDPT) and of Fano's theory of the phenomenology of the photoabsorption profile [7]. By projecting their FOTDPT solution on the unperturbed (by the localized wave function of the resonance state) scattering wave function, which we symbolize by $|u_E\rangle$, they computed the differential ionization probability $P(E,t)$ of Eq. (1). In such a time-dependent framework, $|u_E\rangle$ represents a nonstationary state, in analogy with the bound nonstationary states of [2,3] which exhibit the ECBs. Wickenhauser *et al.* [6] stated that, "*in the limit where the influence of the probe laser pulse can be neglected*, $\lim_{t\to\infty}P(E,t)$ *converges to the time-integral emission spectrum of a Fano resonance*." Their result on $P(E,t)$ for a Gaussian pulse envelope is given in their Fig. 2 and depicts the formation of an asymmetric resonance profile as a function of time.

In the present contribution to the nascent field of theoretical-computational hyperfast time-resolved spectroscopy of multiply excited (inner-hole) states, the focus is again on the quantitative determination of the time resolution of the preparation and decay of superpositions of nonstationary states, considering as the test case the coherent excitation and decay dynamics of the well-defined prototypical He $2s2p\ ^1P^o$ resonance state [7,8]. We recall that for this state, the combination of Fano's theory of line profiles [7] with the experimental results of Madden and Codling [8] (use of synchrotron radiation), yielded $E_r=60.133\pm0.015$ eV, $\Gamma=0.038\pm0.004$ eV, and $q=-2.80\pm0.25$. (The value 60.133 eV corresponds to the position of the resonance and not to the absorption maximum, which is at 60.123 eV.) Additional such measurements have since been reported by other workers [9]. The more recent experimental values, by Domke *et al.* [9], are thought of as being the most accurate ($E_r=60.147\pm0.001$ eV, $\Gamma=0.037\pm0.001$ eV, and $q=-2.75\pm0.01$).

In Sec. II we summarize the essential contents of the paper. In Sec. III we explain briefly the form and theoretical background of the state-specific wave functions that are used as input in our calculations. In Sec. IV we present our numerical nonperturbative calculation and its results, and in Sec. V we present an analytical treatment in conjunction with FOTDPT. Section VI presents additional aspects of the results of the calculations, and we conclude in Sec. VII.

II. CONTENT OF THE PRESENT WORK

The analysis and computations reported here are concerned with the *ab initio* calculation of $P(E,t)$ numerically as well as analytically, for the case of the He $2s2p\ ^1P^o$ resonance. The physical processes involved in the problem are

$$\mathrm{He}\Psi_g(1s^2\ ^1S) \xrightarrow[\textit{electric dipole coupling}]{\textit{laser pulse}} \mathrm{He}^+(1s) + (\varepsilon p)\ \textit{in the vicinity of}\ \Psi_0(2s2p\ ^1P^o),$$

$$\mathrm{He}\Psi_0(2s2p\ ^1P^o) \xrightarrow[\textit{Coulomb interaction}]{\textit{autoionization}} \mathrm{He}^+(1s) + (\varepsilon p).$$

At $t=0$, the atom is in the ground state, $\Psi_g(1s^2\ ^1S)$. $\Psi_0(2s2p\ ^1P^o)$ is the square-integrable wave function representing the localized part of the resonance. Autoionization is taking place during and after the atom-laser pulse interaction—at least until decay is over.

The next three sections discuss the theory and computation of accurate time-resolved results on $P(E,t)$. These account for the details of electronic structure via the use of state specific wave functions and for the characteristics of the pulse. Although no experiment exists for direct comparison with the behavior of $P(E,t)$ during and immediately after the application of the atom-laser pulse interaction, such a comparison is possible for long times, in terms of the energy, the width, and the Fano parameter q, already cited in Sec. I. The agreement is excellent. Thus, this work constitutes an example where these observables for the He $2s2p\ ^1P^o$ resonance state are obtained from the *ab initio* solution of the TDSE. Finally, independent information is obtained from the time-resolved exponential decay [2,3,10], which gives a lifetime of 17 fs, i.e., 703 atomic units of time corresponding to a Lorentzian width of 0.039 eV, in agreement with experiment.

The study was carried out along two axes, where two different approaches to the calculation of $\Psi(t)$ and of $P(E,t)$ were followed. One approach is analytic, via which explicit formulas involving matrix elements are obtained in FOTDPT based on the application of the Fano formalism of configuration interaction in the continuum (CIC) for the scattering state. It is discussed in Sec. V. The analytic formulas are generally valid for weak field situations. They add insight into the physics of the time-resolved profile of the resonance state during the excitation and the mixing of bound and scattering components.

The other approach is the numerical state-specific expansion approach (SSEA) for the nonperturbative solution of the TDSE [11]. Its present implementation is described in Sec. IV. The comparison of the results from two types of computation of $\Psi(t)$ can be used for delineating the boundary of validity of the FOTDPT for each system (atom plus field) of interest.

The calculations of the time-dependent wave functions of Secs. IV and V solve the TDSE for the coherent excitation and decay of He $2s2p\ ^1P^o$, which is resonantly excited from the ground state by a linearly polarized laser pulse of $\sin^2$ shape, of duration 450 a.u. (11 femtoseconds) and of field strength ranging from $F=0.4\times10^{-3}$ a.u. to $F=0.4\times10^{-1}$ a.u.

Numerical comparison of the two approaches shows perfect agreement for weak fields and the beginning of some discrepancy at $F=0.4\times10^{-1}$ a.u. (Sec. VI).

We stress that the structure of both approaches is perfectly suitable for permitting the treatment of time-dependent systems where the initial state is excited. For example, such is the case of excitation from the He $1s2s\ ^1S$ state which was considered in [2]. In other words, the computational methodology which is followed here is practical not only for two-electron systems or for closed-subshell initial states such as the ground states of the noble gases and of many molecules, but for any type of polyelectronic system and initial state, since it is based on the use of polyelectronic electronic structure methods for ground or excited states, as explained below. In this context, since high frequency excitation of neutral atoms inevitably involves resonance states labeled by multiply excited (inner-hole) configurations, Sec. III comments on the justification of the treatment of such states in terms of state-specific wave functions.

Finally, we note that for the execution of this work, of interest and concern to us was the choice of the scattering state that ought to be included in Eq. (1). Is it the unperturbed background continuum (symbolized here by $|u_E\rangle$), or is it the perturbed continuum (symbolized here by $|U_E\rangle$), where the effects of the resonance are incorporated? As is discussed at the end of Sec. V, for the calculation of $P(E,t)$ it does not make a difference. This permits the reduction of the size of the calculation of $P(E,t)$ in terms of the full $\Psi(t)$ of Sec. IV, where the final calculations were run with $|u_E\rangle$. However, a difference might exist in the case where the amplitude of the probe interaction is added, since then, phases may play a role.

In summary, the herein reported results were obtained from *ab initio* calculations of the following quantities:

$$P(E,t)=|\langle u_E|\Psi(t)\rangle|^2 \quad \text{(Sec. IV)}, \tag{2a}$$

$$\bar{P}(E,t)=|\langle U_E|\Psi(t)\rangle|^2 \quad \text{(Sec. V)}. \tag{2b}$$

III. JUSTIFICATION OF THE WAVE FUNCTIONS THAT ARE COMPUTED AND USED IN THE APPROACHES OF SECS. IV AND V

The most difficult part of the *ab initio* calculation of $P(E,t)$ for an arbitrary polyelectronic system is obtaining the solution of the TDSE, $|\Psi(t)\rangle$, for a total Hamiltonian that includes the time-dependent atom-field interaction. This is a time-dependent many-electron problem (TDMEP) whose solution to all orders of perturbation theory requires the application of a method that pays attention to electronic structure and handles complexity with efficacy and accuracy.

A theoretical analysis and computational methodology for the practical nonperturbative solution of the TDMEP in atoms and small molecules was presented in [11,12], with applications to processes such as probabilities of multiphoton ionization and dissociation, of photoassociation, high order harmonic generation, etc.

The methodology in [11,12], which is called the SSEA for reasons that are explained briefly below, computes nonperturbatively $|\Psi(t)\rangle$ by implementing the basic quantum mechanical rule of expansion over a complete set of stationary wave functions with time-dependent coefficients. In practice, this implies that the wave functions which are employed must be optimized solutions of the time-independent Schrödinger equation for each state that is deemed relevant to the time-dependent process under consideration and contributes in a significant way to $|\Psi(t)\rangle$. This basic requirement of quantum physics is taken into account in the SSEA [11,12], which, in the case of electronic transitions, yields a wave function, $\Psi_{SSEA}(t)$, as a superposition of state-specific bound and energy-normalized scattering wave functions that are computed according to the state-specific theory (SST) and methods that have been described in detail and applied in previous publications, e.g., [2,3,10,11,13–18].

The methods that are implemented in the framework of the SST are systematic in the computation of wave functions of both the discrete and the continuous spectrum, including cases of heavy valence-Rydberg-scattering state mixing in which the wave functions are corrected for the quantum defect and the phase shift [17].

What is significant for practical applications is that the form of the bound wave functions for discrete states or for the localized component of resonance states is the same. It is given as a superposition of configurations, consisting of a state-specific zero order multiconfigurational (in general) wave function, ψ^0_{MCHF}, computed in the Hartree-Fock (HF) or multiconfigurational Hartree-Fock (MCHF) approximation, and a remaining correlation part. Thus, for each localized state $|n\rangle$, the normalized square integrable wave function form is ([18] and references therein)

$$|\psi_{SST}\rangle_n = a_0^{(n)}|\psi^0_{\mathrm{MCHF}}\rangle^{(n)} + \sum_k a_k^{(n)}\varphi_k^{(n)}, \tag{3}$$

where the $\varphi_k^{(n)}$ are symmetry-adapted configurations containing occupied (MCHF) and optimized virtual orbitals. It should be emphasized that, depending on the problem, the size of each of the two terms on the right-hand side of (3) varies in practice.

In this context, since for high-energy excitation sources the states of interest are mostly in the continuous spectrum, we briefly comment on the theory and computation of multiply excited (inner-hole) resonance states, such as the He $2s2p\ ^1P^o$, since the many-body treatment for these states re-

quires, in principle, special justification and consideration of complex cases of zero order wave functions and of electron correlation [13–18]. This is so because, contrary to the easily handled by many-body methods closed-subshell ordinary discrete states, the polyelectronic resonance states have special characteristics, such as:

(1) They are embedded in the multichannel (in general) scattering continuum of the same symmetry, and, therefore, they belong to the continuous energy spectrum.
(2) They are most often labeled in zero order by open subshell configurations, where orbitals and electron correlations are term-dependent. Both the localized and the corresponding scattering function spaces ought to reflect this fact.
(3) They may be subject to serious near-degeneracies with other real or virtual resonances, in which case the single configuration label is inadequate.
(4) They have an infinity of lower states of the same symmetry, a problem that has to be understood and solved in the framework of electronic structure.

In view of the above, and of related serious difficulties in dealing practically with the many-electron computation from a scattering point of view (e.g., search for poles of the S matrix), a decaying state approach was introduced and justified in [13] (see also [10,15,18]). Among other things, it was argued that, for the many-electron problem, and in order to handle the large variety of electronic structures that can represent wave packets that are created and then decay into the continuous spectrum, the emphasis must be on the zero order and correlation function spaces describing the localized component of the resonance. A practical and theory-based way of doing so is to adjust state-specific many-electron methods that focus on a zero order solution that is obtained from the solution of the self-consistent field equations (as is done for ground states), rather than, say, to apply scattering type expansions or to use common basis sets for the discrete and the continuous spectrum on which the total Hamiltonian is diagonalized.

The above requirement necessitates the solution of appropriate state-specific HF or MCHF equations and the subsequent appropriate optimization of the function spaces representing the remaining electron correlations. The efficacy and physical economy of this approach for multiply excited and for inner-hole resonance states has been demonstrated in a series of publications since the 1970s, where the use of state-specific analytic HF [13] zero order wave functions and, later, of state-specific numerical HF and MCHF zero order wave functions, e.g., [15,16], were combined with formalisms of many-electron calculations and of resonance states that are practical and applicable to all types of nonstationary excited states, e.g., [2,10,13–18].

As regards the scattering part of the full resonance wave function, in the framework of the proposals in [13,15,17], it is assumed that for practical purposes the asymptotically correct basis set of scattering wave functions may be chosen from symmetry adapted products of a core bound wave function and the state-specific scattering orbitals in the potential of the main component of the core (e.g., frozen core HF scattering orbitals). Such bases are suitable for the development and implementation of K matrix, CIC type calculations for the continuous spectrum of polyelectronic atoms [17].

IV. THE CALCULATION OF $P(E,t)$ FROM THE STATE SPECIFIC EXPANSION APPROACH (SSEA) TO THE NONPERTURBATIVE SOLUTION OF THE TDSE

As already stated in Sec. III, the form of the SSEA solution of the TDSE for electronic processes is [11]

$$\Psi_{SSEA}(t) = \sum_n a_n(t)\Phi_n + \int dE a_E(t)\Phi_E, \tag{4}$$

where Φ_n are state-specific bound wave functions and Φ_E are state- and energy-specific scattering wave functions with Dirac function normalization. It is the nature of each problem of interest that defines the Hamiltonian and the values of the coefficients at the initial time $t=0$, together with the type and number of the wave functions in (4).

As regards the present problem, for linear polarization and the electric dipole approximation, the time-dependent Hamiltonian is

$$H(t) = H^A + V(\omega,t), \tag{5a}$$

H^A is the free-atom Hamiltonian and

$$V(\omega,t) = zFg(t)\sin(\omega t). \tag{5b}$$

$g(t)$ is the temporal shape of the pulse. Here it was taken as a $\sin^2\Omega t$ function. F is the field strength and ω is the frequency.

The form of the $\Psi_{SSEA}(t)$ was

$$\Psi_{SSEA}(t) = c_g(t)\Psi_g(1s^2\,{}^1S) + c_0(t)\Psi_0(2s2p\,{}^1P^o) + \int_0 dE c_E(t)u(E), \tag{6}$$

where $u(E)$ is the energy-normalized scattering wave function for the ionized state, $\mathrm{He}|1sEp\rangle\,{}^1P^0$, at each value of the energy, E, that is used in the computation of the coupling matrix elements [19]. A computationally convenient practice in the framework of the SST is for the scattering orbitals to be computed in the single or multiconfigurational frozen core of the ion, accounting for the exchange integrals. In the present case, the situation is very simple, since the core is the He^+ $1s$ orbital.

As before [2,3], the bound wave functions were computed, according to theory (e.g., 13, 15, 18), as small MCHF expansions, using the code published by Froese-Fischer [20]. Such expansions not only are accurate for such purposes, but also provide a clear understanding of the magnitude of various configurational contributions. For the $\Psi g(1s^2\,{}^1S)$ state, the numerical MCHF wave function consists of the configurations $1s^2$, $2s^2$, $2p^2$, $3s^2$, $3p^2$, $3d^2$ and its energy is -2.901840 a.u., when the accurate value is -2.903724 a.u. For the $\Psi_0(2s2p\,{}^1P^o)$ wave function, the calculated MCHF wave function is

$$\Psi_0(2s2p\ ^1P^o) = 0.948\phi_1(2s2p) - 0.308\phi_2(2p3d) - 0.074\phi_3(3s3p) \quad (7)$$

whose energy is −0.6906 a.u., i.e., 60.21 eV above the ground state, only 0.06 eV above the experimental value [9]. Using these bound and scattering HF wave functions and the "golden rule" expression for autoionization, the width comes out to be 0.038 eV, in agreement with experiment.

Substitution of (6) into the TDSE ($\hbar=1$),

$$i\frac{\partial\Psi_{SSEA}(t)}{\partial t} = [H^A + V(\omega,t)]\Psi_{SSEA}(t), \quad (8)$$

transforms it into a system of equations having the form of coupled integrodifferential equations with time-dependent coefficients ($c_{initial} \equiv c_g$):

$$i\frac{dc_g}{dt} = E_g c_g + V_{g0}(\omega,t)c_0 + \int dE V_{gE}(\omega,t)c_E, \quad (9a)$$

$$i\frac{dc_0}{dt} = V_{0g}(\omega,t)c_g + E_0 c_0 + \int dE H^A_{0E} c_E, \quad (9b)$$

$$i\frac{dc_E}{dt} = V_{Eg}(\omega,t)c_g + H^A_{E0}c_0 + Ec_E. \quad (9c)$$

The initial condition at $t=0$ is $V(\omega,0)=0$ and $c_g(0)=1$. As soon as $t>0$, all configurations are mixed via the $H(t)$. The matrix elements, $V_{g0}(\omega,t)$, $V_{gE}(\omega,t)$, H^A_{0E}, etc. are computed numerically [11]. The coupling matrix elements resulting from the integral over the continuum are constructed as accurately as is necessary, by extending the energy range and by increasing the density of energy points via direct computation and interpolation [11,19]. Finally, the propagation of $\Psi_{SSEA}(t)$ in time, i.e., the calculation of the time-dependent coefficients, is done by the Taylor-series expansion method described in [11].

The final results were obtained from the solution of Eqs. (9) with 4845 terms, for a range of energy from 0 to 2.0 a.u.

Figure 1 depicts the calculated $P(E,t)$. Slices of this surface are presented in Figs. 2 and 3, after the discussion of the analytic theory and its results in Sec. V.

Here we note that, for both numerical and analytic calculations, the limit $\lim_{t\to\infty}P(E,t)$ produces a Fano profile with $q=-2.8$, in agreement with experiment [7–9]. The cross section to the unperturbed continuum at the resonance energy is calculated to be 1.21×10^{-18} cm^2. Based on the experimental data [8], Fano and Cooper [7] deduced a value of $1.4\pm0.2\times10^{-18}$ cm^2 for this quantity.

V. ANALYTIC CALCULATION OF $\bar{P}(E,t)$ AT THE LEVEL OF FIRST ORDER TIME-DEPENDENT PERTURBATION THEORY (FOTDPT): APPLICATION TO THE He $2s2p\ ^1P^0$ RESONANCE

We assume that the excitation of an isolated resonance state is effected by a pulse of a weak electromagnetic field. Therefore, the conditions of FOTDPT apply, i.e., the time-dependent coefficient of the initial state is close to unity.

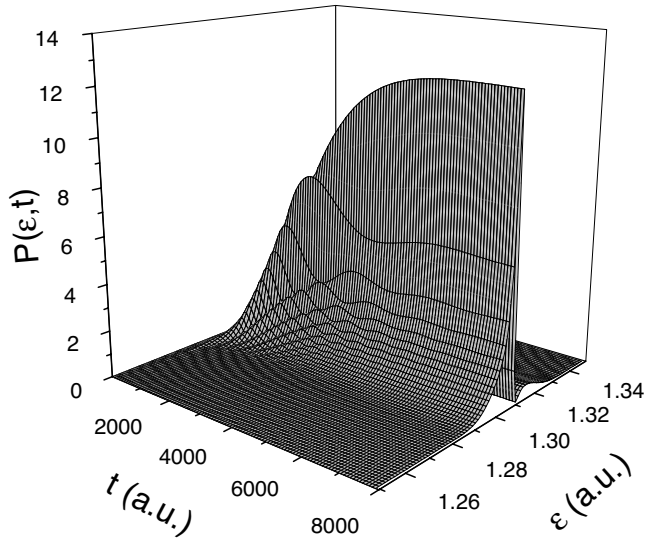

FIG. 1. The differential ionization probability, $P(\varepsilon,t)$, computed by the SSEA in this work, for the excitation of the He $2s2p\ ^1P^o$ resonance state. ε is the energy above the ionization threshold. The scattering wave function represents a nonstationary state, whose projection on the solution of the TDSE reveals the time-resolved excitation profile, with its characteristic asymmetric profile [see Eq. (32)]. The laser pulse has a $\sin^2$ envelope and duration of 450 a.u. ($\approx$11 fs). At the frequency of the excitation energy it contains 158 cycles. This profile is the same for field strengths in the range $F=0.4\times10^{-3}$ a.u. to $F=0.4\times10^{-1}$ a.u., apart from the modulating factor $G(E,t)$, given by Eqs. (23) and (34), which depends linearly on field strength F.

In what follows we draw from the CIC formalism of Fano [7]. We proceed by replacing (6) by an expansion over eigenfunctions. To achieve this we first diagonalize the atomic

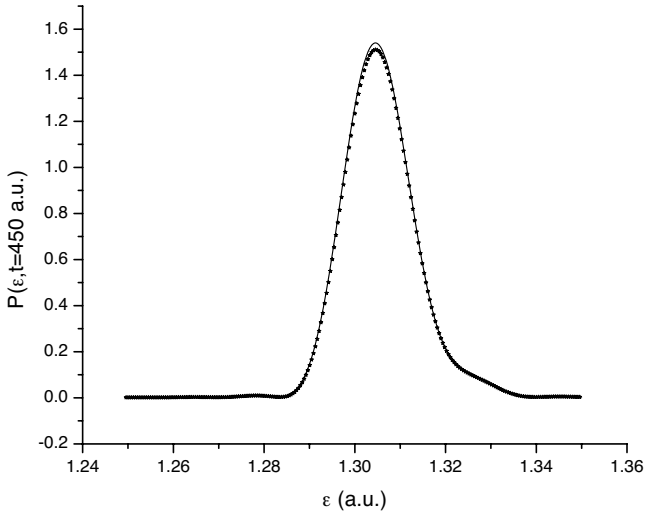

FIG. 2. Comparison between the SSEA and the analytic results, for field strength $F=0.4\times10^{-1}$ a.u. at the end of the duration of the pulse ($t=450$ a.u.). There is a minute discrepancy at the maximum, suggesting the beginning of the deviation of the FOTDPT [Eq. (32)] (solid line), from the nonperturbative approach.

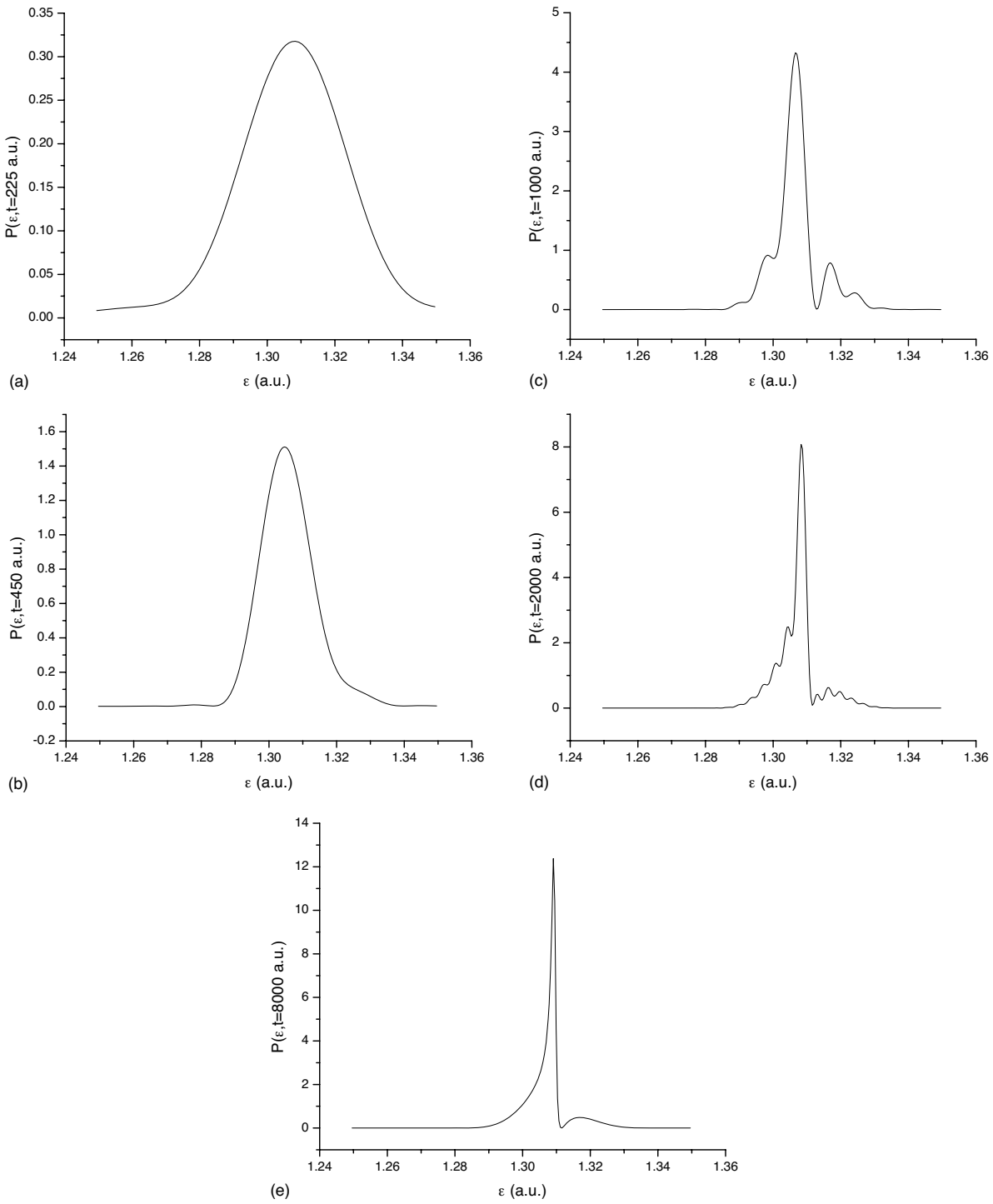

FIG. 3. (a) Time-resolved formation of the asymmetric profile of the differential ionization probability of the He $2s2p\ ^1P^o$ resonance state for excitation from the ground state with a pulse whose characteristics are given in the caption of Fig. 1 and in the text. For $t=225$ a.u. (b) As in (a), for $t=450$ a.u. (c) As in (a), for $t=1000$ a.u. (d) As in (a), for $t=2000$ a.u. (e) As in (a), for $t=8000$ a.u.

Hamiltonian in the basis Ψ_o, u_E, obtaining the eigenfunction of the stationary state at E

$$\psi_E = a\Psi_0 + U_E \equiv a\Psi_0 + \int dE' b_{E'} u_{E'}. \tag{10}$$

The coefficients α and b were obtained by Fano by solving the system of equations

$$E_0 a + \int dE' H^A_{0E'} b_{E'} = Ea, \tag{11a}$$

$$H^A_{0E'} a + E' b_{E'} = E b_{E'}. \tag{11b}$$

The solution is

$$b_{E'}(E) = \left[\frac{1}{E - E'} + \frac{E - E_0 - \Delta(E)}{|H^A_{0E}|^2} \delta(E - E') \right] H^A_{0E'} a(E), \tag{12}$$

$$a(E) = \left[\frac{|H^A_{0E}|^2}{(E - E_0 - \Delta(E))^2 + (\pi |H^A_{0E}|^2)^2} \right]^{1/2}. \tag{13}$$

Equation (13) results from the energy normalization of the eigenfunction (10).

The energy shift function, $\Delta(E)$, is given by the principal value integral

$$\Delta(E) = \mathrm{P} \int dE' \frac{|H^A_{0E'}|^2}{E - E'}. \tag{14}$$

Multiplying Eq. (9c) by b_E, integrating over E, and adding Eq. (9b) multiplied by α, we obtain

$$i \frac{dh_E(t)}{dt} = W_{E'g} c_g(t) + E h_E(t), \tag{15}$$

where we have defined

$$h_E(t) = a c_0(t) + \int dE' b_{E'} c_{E'}(t), \tag{16a}$$

$$W_{Eg} = a V_{0g} + \int dE' b_{E'} V_{E'g}. \tag{16b}$$

The following expressions for $c_0(t)$ and $c_E(t)$ in terms of $h(t)$ are obtained from (16a) through the use of the orthogonality relations between the α and b coefficients derived in the Appendix

$$c_0(t) = \int dE a h_E(t), \tag{17a}$$

$$c_{E'}(t) = \int dE b_{E'} h_E(t). \tag{17b}$$

They can be used to transform (6) into an expansion over eigenfunctions

$$\Psi(t) = c_g(t) \Psi_g + \int dE h_E(t) \psi_E \tag{18}$$

while Eq. (9a) is written as

$$i \frac{dc_g}{dt} = E_g c_g + \int dE W_{gE} h_E. \tag{19}$$

Equations (19) and (15) constitute the system of equations satisfied by the coefficients of the expansion (18). This system can now be solved perturbatively in the standard way, by putting $h_E = \bar{h}_E e^{-iEt}$, $c_g = \bar{c}_g e^{-iE_g t}$, and then $\bar{c}_g \approx 1$.

The quantity of interest is the probability amplitude $A_E(t)$ for the system to be in the ionized continuum. Using Eq. (10) we have

$$A_E(t) \equiv \langle \psi_E | \Psi(t) \rangle - a \langle \Psi_0 | \Psi(t) \rangle = h_E(t) - a \int dE' h_{E'}(t) a = \int dE' b_{E'} c_{E'}(t). \tag{20}$$

Evaluation of $A_E(t)$ requires the calculation of a principal value integral of the form

$$\mathrm{P} \int dE' H^A_{0E'} \frac{1}{E - E'} c_{E'}(t),$$

which is similar to the energy shift integral Eq. (14). This has to be added to the on-the-energy-shell contribution provided by the δ function of Eq. (12).

We now proceed to the first order perturbation solution of the system of Eqs. (15) and (19). We define the matrix elements

$$d_{g0}(E) = \langle \Psi_g | z | \Psi_0 \rangle, \quad d_{gE} = \langle \Psi_g | z | u_E \rangle. \tag{21}$$

In terms of these, we have

$$h_E(t) = e^{-iEt} G(E,t) D_{gE}, \tag{22}$$

where

$$G(E,t) = -iF \int_0^t dt' e^{-i(E_i - E)t'} g(t') \sin \omega t' \tag{23}$$

with $g(t)$ being the temporal pulse shape appearing in the expression (5b) and

$$D_{gE} = a \left[d_{g0}(E) + \mathrm{P} \int dE' d_{gE'} \frac{1}{E - E'} H^A_{E'0} + \frac{E - E_0 - \Delta(E)}{H^A_{0E}} d_{gE} \right]. \tag{24}$$

Now we invoke the expression for the parameter q given by Fano [7]

$$q = \frac{d_{g0}(E) + \mathrm{P} \int dE' d_{gE'} \frac{1}{E - E'} H^A_{E'0}}{\pi H^A_{E0} d_{gE}} \tag{25}$$

in order to express the ratio of the transition probability amplitude D_{gE} to the analogous quantity referring to the unperturbed continuum, d_{gE}, as follows:

$$h_E(t) = a e^{-iEt} G(E,t) \pi H^A_{E0} d_{gE} \left[q + \frac{E - E_0 - \Delta}{\Gamma} \right], \tag{26}$$

where

$$\Gamma = \pi |H^A_{0E}|^2 \tag{27}$$

is the half width of the autoionizing state.

If the quantities q, Δ, and Γ are sufficiently constant in the energy range of a few widths around the shifted energy $E_0 + \Delta$, from (13) one obtains the known result of the Lorentzian distribution

$$a^2(E) = \frac{1}{\pi} \frac{\Gamma}{(E - E_0 - \Delta)^2 + \Gamma^2}, \tag{28}$$

with energy poles at z_0 and z_0^*, where

$$z_0 = E_0 + \Delta - i\Gamma. \tag{29}$$

These poles appear in the expression for the amplitude below. Application of the second term of (20), with $h_E(t)$ given by Eq. (26), produces the expression

$$A_E(t) = C_E e^{-iEt} G(E,t)\left[q + \frac{E - E_0 - \Delta}{\Gamma}\right] + C_E \frac{q-i}{2\pi i}\int dE' \frac{e^{-iE't}}{E' - z_0} G(E',t) + C_E \frac{q+i}{2\pi i}\int dE' \frac{e^{-iE't}}{E' - z_0^*} G(E',t), \tag{30}$$

where

$$C_E = \frac{\Gamma d}{\sqrt{(E - E_0 - \Delta)^2 + \Gamma^2}}. \tag{31}$$

The integrals of Eq. (30) are easily calculated via contour integration assuming the energy range to extend from $-\infty$ to ∞. Thus, by closing the contour in the lower half plane we obtain the main result of this section, namely

$$A_E(t) = C_E e^{-iEt} G(E,t)\left[q + \frac{E - E_0 - \Delta}{\Gamma}\right] - C_E \frac{q-i}{2\pi i} e^{-iz_0 t} G(z_0,t), \tag{32}$$

where the exact form of the function G, which is given by Eq. (23), depends on the shape of the pulse $g(t)$.

A simple case for G is obtained when $g(t)$ has the form

$$g(t) = \begin{cases} \sin^2 \dfrac{2\pi t}{T} & t < T/2 \\ 0 & t > T/2 \end{cases}. \tag{33}$$

Specifically, putting $\Omega = \frac{2\pi}{T}$, where $\Omega \ll \omega$, and assuming the rotating wave approximation, the function G is given by

$$G(E,t) = -\frac{F}{8i}\left\{\frac{e^{i(E-E_g-\omega+2\Omega)t} - 1}{E - E_g - \omega + 2\Omega + i\varepsilon} + \frac{e^{i(E-E_g-\omega-2\Omega)t} - 1}{E - E_g - \omega - 2\Omega + i\varepsilon} - 2\frac{e^{i(E-E_g-\omega)t} - 1}{E - E_g - \omega + i\varepsilon}\right\} \tag{34a}$$

for $t \leqslant T/2$, while

$$G(E,t) = G(E,T/2), \text{ i.e. independent of t, for } t \geqslant T/2. \tag{34b}$$

By combining Eqs. (32) and (34) we obtain an analytic expression for the quantity of interest

$$\bar{P}(E,t) \equiv |A_E(t)|^2. \tag{35}$$

In the limit $t \to \infty$, the last term of (32) goes to zero. The first term is the Fano profile, modulated by the pulse factor $G(E,t)$.

The above formalism can be extended to take into account the presence of N ionization channels. To this purpose, it is advantageous to draw from already developed time-independent CIC approaches [7,21,17]. In the case where the direct interchannel coupling can be neglected, the channels are coupled through their interaction with the autoionizing state Ψ_0. There are N matrix elements H^A_{0jE}, $j=1,N$ and the resulting diagonalization of the system of $N+1$ equations analogous to Eqs. (11) gives rise to N independent linear combinations $\psi^{(k)}$ each expressed through its own set of coefficients $a^{(k)}, b_j^{(k)}$. As Fano has shown [7], a choice can be made so that the autoionizing state is contained in only one of these combinations, say $\psi^{(1)}$, the rest $N-1$ acting as a structureless background. In this choice $a^{(k)}=0$ for $k>1$ and the coefficients $b_j^{(k)}, k>1$ are proportional to delta functions of the energy [21]. The characteristic resonant behavior is contained in the coefficients $a^{(1)}$ and $b_j^{(1)}$ of $\psi^{(1)}$ which are rapidly varied as a function of energy in the vicinity of the autoionizing state. They are given by expressions similar to (12) and (13) where the squares of the matrix elements $|H^A_{0E}|^2$, contained within the brackets, are being replaced by $\Sigma_i |H^A_{0iE}|^2$. The same holds for the energy shift $\Delta(E)$, Eq. (14), and the width $\Gamma(E)$, Eq. (27). In the case where interchannel coupling cannot be neglected, this approach is not applicable straightforwardly, due to the presence of the off-the-energy-shell K matrices that account for all the important couplings to all orders ([17] and references therein).

We close by commenting on the formulas (1, 2) where, in the place of the scattering state, the use of the unperturbed ($|u_E\rangle$) as well as of the perturbed ($|U_E\rangle$) continuum state has been made. The former involves the distribution $|c_E|^2$, while the latter involves $|\int dE' b_{E'}(E) c_{E'}|^2$, thereby accounting for the time delay due to the presence of the localized component of the resonance. In the Appendix, it is shown why the ionization probability, $P(t)=\int dE P(E,t)$, is independent of whether $|u_E\rangle$ or $|U_E\rangle$ is used. This is due to the fact that the two amplitudes differ by a factor $\exp\left[i\tan^{-1}\left(\frac{\Gamma}{E-E_0-\Delta}\right)\right]$ which is the phase shift of the perturbed scattering state. Thus, although the amplitudes are different, the calculated probability is the same.

However, we point out that in a PPTD scheme, where amplitudes including the second pulse (probe) are added coherently, the difference between the unperturbed background scattering wave function and the perturbed one should in principle, depending on the final states, affect the final results.

VI. RESULTS

The essential results are included in Fig. 1. Additional information is contained in Figs. 2 and 3.

The numerical results from the application of the analytic theory and use of the state-specific wave functions agree with those of the SSEA. i.e., $P(E,t)=\bar{P}(E,t)$ [see Eqs. (2)]. Only when the field strength becomes $F=0.4\times10^{-1}$ a.u. does a minute discrepancy start. This is shown in Fig. 2, where the comparison is made at $t=450$ a.u., i.e., at the end of the pulse.

In Figs. 3(a)–3(e) we have plotted the time-resolved formation of the profile of the diffential ionization probability, $P(E,t)$, for different times, $t=225$ a.u., 450 a.u., 1000 a.u., 2000 a.u., and 8000 a.u. For very short times [Figs. 3(a) and 3(b)], a rather symmetric form is obtained. For longer times [Figs. 3(c) and 3(d)], asymmetry starts appearing. The small oscillations are due to interference of the two terms of Eq. (32).

Finally, for long times, [Fig. 3(e)], the system becomes stationary and so the final asymmetric form of the profile for the photoexcitation of the He $2s2p\ ^1P^o$ resonance is obtained, described by the first term of Eq. (32). When the function $G(E,t)$ is set equal to one, the profile corresponds to $q=-2.8$, in agreement with the experimental value [7–9].

VII. CONCLUSION

The theme of the present paper combines the theory and *ab initio* computation of resonance states labeled by multiply excited or inner-hole excited configurations with the exploration of the possibility of creating nonstationary states in the continuous spectrum of an atom or molecule whose fingerprints can, in principle, be time-resolved in hyperfast pump-probe delay schemes. There are two principal prerequisites for doing so. First, one must be able to prepare appropriate nonstationary states whose time evolution is resolvable experimentally and computationally. Second, as regards theory, one must be able to compute and apply $\Psi(t)$, namely the time-dependent solution of the TDSE, where the total Hamiltonian contains the time-dependent perturbation due to the atom (molecule)-field interaction.

Depending on the mode of excitation and the characteristics of the laser pulse(s) with respect to the atomic spectrum, the preparation of excited states in the continuous spectrum via hyperfast excitations may involve either an isolated state (as in the present study), or a superposition of states (as in [2,3], or if a single pulse is broad and the quasi-discrete excited states are close in energy).

The problem that was tackled in this work is the *ab initio* calculation of the coherent excitation and decay of the doubly excited He $2s2p\ ^1P^o$ resonance state, and in particular the demonstration of its time-resolved formation of its asymmetric profile, as revealed quantitatively via the computation of the differential ionization probability, $P(E,t)$—see Figs. 1–3.

Here, the calculation of $\Psi(t)$ was carried out from first principles with very good accuracy, as indicated by the agreement of the experimental energy, width, and the Fano profile parameter, q, [7–9] with the values obtained from our computations in the limit of times that are much longer than the pulse duration (450 a.u.). Two approaches were implemented. One is the numerical solution of the TDSE to all orders of perturbation theory by the SSEA (Sec. IV), and the other is the weak field analytic solution in the context of FOTDPT, introduced here (Sec. V). For this system, it appears that the limit where FOTDPT starts losing accuracy for the problem at hand is for field strengths of about $F=0.4\times10^{-1}$ a.u. (Fig. 2).

It should be noted that our analytic theory shows explicitly the energy- and time-dependent modulation of the Fano profile due to the effect of the excitation pulse [function $G(E,t)$ of Eq. (32)].

Finally, we mention that the treatments of this paper have been implemented for the *ab initio* determination of the time-dependent coherent excitation and decay of inner-hole states in larger atoms, where the added complexity includes the problem of accounting for two-electron continua [22].

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APPENDIX

On resonance, the stationary scattering state fulfills the orthonormality relation

$$\langle\psi_E|\psi_{\bar{E}}\rangle = a(E)a(\bar{E}) + \int dE' b_{E'}(E)b_{E'}(\bar{E}) = \delta(E-\bar{E}), \tag{A1}$$

where the energy dependence of the α and b coefficients is stated explicitly.

By multiplying Eq. (A1) with $a(E)$, integrating over E, and making use of the normalization of the Lorentzian distribution, i.e., $\int dE a^2(E)=1$, one obtains

$$\int dE a(E)b_{E'}(E) = 0. \tag{A2}$$

Alternatively, multiplying Eq. (A1) by $b_{E''}(E)$, integrating over E, and making use of (A2), one obtains

$$\int dE b_{E'}(E)b_{E''}(E) = \delta(E'-E''). \tag{A3}$$

Thus, the orthonormality relation between wave functions has been transformed into orthonormality relations between coefficients.

From (A3), the following result is valid for a given distribution $|c_{E'}|^2$ [e.g., see Eq. (20) and (35)]

$$\begin{aligned} P(t) &= \int dE\bar{P}(E,t) = \int dE\left|\int c_{E'}b_{E'}(E)dE'\right|^2 \\ &= \int dE \int dE' c_{E'}b_{E'}(E) \int dE'' c_{E''}b_{E''}(E) \\ &= \int dE' \int dE'' c_{E'}c_{E''} \int dE b_{E'}(E)b_{E''}(E) \\ &= \int dE' \int dE'' c_{E'}c_{E''}\delta(E-E') = \int dE'|c_{E'}|^2. \end{aligned} \tag{A4}$$

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