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Error of finite basis expansions in time-dependent calculations of atom-laser interaction

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We propose a method to quantitatively estimate the error made with a finite basis expansion in time-dependent calculations. This method is applied to the hydrogen atom in intense laser fields and used to compare different basis sets with each other. We also show how to construct a Gaussian basis set suitable for the description of ionization dynamics in intense laser fields.

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I. INTRODUCTION

The experimental and theoretical investigation of the interaction mechanisms of atoms, molecules and clusters with intense laser fields represents one of the most challenging problems of the present research. In strong dependence on the laser parameters, very different phenomena can be observed, e.g., high harmonic generation [1–3], above threshold ionization [4–6], or stabilization against ionization [6–9] in atoms. In molecules, due to the additional nuclear degrees of freedom (DOF), further mechanisms do occur, such as molecular stabilization against dissociation [10–12], bond softening [13–17], above threshold dissociation [17–19], or charge resonance enhanced ionization [17,20–22], to name but a few effects.

The theoretical understanding of these mechanisms requires, in principle, the solution of the time-dependent Schrödinger equation (TDSE) for all electrons and all nuclear DOF. However, only for the smallest systems, laser aligned H_2^+ [23], atomic hydrogen [24,25] and atomic helium [26,27] numerical solutions of the TDSE exist. In all other systems approximations are necessary, with promising approaches being, e.g., time-dependent Hartree-Fock (TDHF) or time-dependent density functional theory (TDDFT) in basis expansion (see, e.g., Ref. [28]). The different approaches have one common problem, namely the choice of a "good" basis set.

In this paper we focus on this problem. The standard method is to increase the basis size until the results can be called converged (see, e.g., Ref. [25]). However, this is not a satisfactory solution as one does *in general* not know what kind of basis functions must be added and when the solution is converged.

Shortly after the development of quantum mechanics the situation was even worse. At that time only very small basis sets could be used and the aim was to find an approximation for the lower bound of the calculated ground-state energy (Refs. [29–32], and references therein). These studies were continued and extended two decades later (Refs. [33–39], and references therein) even with the aim to derive error bounds for general expectation values (Refs. [40,41], and references therein). The method of Bazley and Fox [40,42] is nowadays standard in quantum chemistry (see, e.g., Ref. [43], p. 94).

The evaluation of the error made with a finite basis expansion in time-dependent scattering calculations was discussed also (Refs. [44–48], and references therein) and used, e.g., to calculate errors of transition amplitudes for the charge transfer in $H+H^+$ collisions [49,50]. Further works used this as a basis to develop a formalism for obtaining optimal translation factors (see, e.g., Refs. [51,52]).

One of the most sophisticated formalisms is the so-called basis generator method (BGM) [53] which is numerically very demanding. The time-dependent basis functions are generated by multiplying the functions of the initial basis with powers of all occurring potentials. Therefore, all matrix elements have to be calculated numerically. Up to now, it has mainly been applied to ion-atom collisions excluding dynamical electron-electron interactions [54–57].

The aim of this paper is to present a formalism to obtain a quantitative measure for the accuracy of a basis expansion in time-dependent calculations and to test different possible basis expansions for the description of ionization dynamics with this measure. The basic quantity Δ is introduced and its properties are discussed in Sec. II. An estimate that allows one to quantitavely compare the results of time-dependent calculations using different basis sets is introduced in Sec. III. The calculation of the occurring matrix elements is sketched in Sec. IV for atomic hydrogen. The hydrogen atom is the optimal test system since the choice of the basis set is the only approximation that has to be made. Furthermore, reference calculations [24,25] exist. In Sec. V the results are shown and discussed also in comparison to the calculations of Hansen *et al.* [25].

II. THE BASIC QUANTITY Δ

In this section we introduce the basis quantity Δ which has been used to obtain estimates for the accuracy of time-independent as well as time-dependent calculations.

A. Time-dependent Schrödinger equation

We are interested in the modeling of processes such as the interaction of atoms or atomic many-body systems with ions or intense laser fields. In the nonrelativistic regime these processes can be described with the TDSE or with many elec-

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*Electronic address: Mathias.Uhlmann@gmx.de tron approximations such as TDDFT. A standard way for solving these equations is the usage of a finite basis set. In the following we define the basic quantity to evaluate the error of a basis expansion when the Schrödinger equation is solved. The extension to TDDFT [28], applicable for the description of many electron systems, is straightforward and only mentioned briefly.

We start with the TDSE

$$i\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle \tag{1}$$

which has to be solved. The Hamiltonian

$$\hat{H} = -\frac{\nabla^2}{2} + V \tag{2}$$

consists of the kinetic energy and an external potential V (atomic units are used throughout this paper). A finite basis expansion serves to find an approximate solution

$$|\Psi'\rangle = \sum_{\alpha=1}^{N_b} a_\alpha |\phi_\alpha\rangle \tag{3}$$

to the exact solution $|\Psi\rangle$. N_b is the number of used basis functions. In general, the time-independent basis functions $|\phi_\alpha\rangle$ are not eigenfunctions to $\hat{H}$. The basis is assumed to be orthonormal, i.e., $\langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha\beta}$. This assumption does not restrict the general applicability since every basis set can be diagonalized. Putting the basis expansion (3) into the TDSE (1) results in

$$i\frac{d}{dt}\sum_{\alpha=1}^{N_b} a_\alpha|\phi_\alpha\rangle = \hat{H}\sum_{\alpha=1}^{N_b} a_\alpha|\phi_\alpha\rangle. \tag{4}$$

By multiplying Eq. (4) with $\langle\phi_\beta|$ we find

$$i\frac{d}{dt}a_\beta = \sum_{\alpha=1}^{N_b} H_{\beta\alpha}a_\alpha, \tag{5}$$

where $H_{\alpha\beta}$ is the Hamilton matrix

$$H_{\alpha\beta} = \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle. \tag{6}$$

Equation (5) is the TDSE in basis expansion. Now a condition for the case that the solution of Eq. (5) is also a solution of Eq. (1) is derived. Equation (5) is multiplied with $|\phi_\beta\rangle$ and one obtains

$$i\frac{d}{dt}\sum_{\beta=1}^{N_b} a_\beta|\phi_\beta\rangle = \sum_{\alpha\beta}^{N_b} |\phi_\beta\rangle H_{\beta\alpha}a_\alpha. \tag{7}$$

Equation (7) is satisfied by solutions of Eq. (5). With Eqs. (3) and (6) and

$$\hat{P} = \sum_{\beta=1}^{N_b} |\phi_\beta\rangle\langle\phi_\beta| \tag{8}$$

this can be written as

$$i\frac{\partial}{\partial t}|\Psi'\rangle = \hat{P}\hat{H}|\Psi'\rangle. \tag{9}$$

Equation (9), which is satisfied by the same solutions as Eq. (5) [and in this sense identical to Eq. (5)], expresses the approximation of Eqs. (5)–(9) in an instructive way. The use of a finite basis set is identical to restricting the Hamiltonian $\hat{H}$ to the part of the Hilbert space spanned by the finite basis set, i.e., to using the projected Hamiltonian $\hat{P}\hat{H}$ instead of $\hat{H}$. Therefore, solutions of Eq. (5) represent solutions of Eq. (1) if

$$\hat{H}|\Psi'\rangle = \hat{P}\hat{H}|\Psi'\rangle. \tag{10}$$

This is satisfied, e.g., for the case of a complete basis set, $\hat{P}=1$. However, Eq. (10) can also be satisfied if incomplete basis sets are used (e.g., a basis that contains only eigenfunctions to $\hat{H}$). In general, Eq. (10) is not satisfied and solutions of Eq. (5) do not represent solutions of Eq. (1). Using $\hat{P}|\Psi'\rangle = |\Psi'\rangle$ and the abbreviation

$$\hat{X} = \hat{P}\hat{H}\hat{P} - \hat{H}, \tag{11}$$

Eq. (10) is equivalent to $\hat{X}|\Psi'\rangle = 0$. Therefore, we define the measure Δ

$$\begin{aligned}\Delta(t) &= |\hat{X}(t)|\Psi'(t)\rangle|^2 \\ &= \langle\Psi'(t)|\hat{X}^2(t)|\Psi'(t)\rangle \\ &= \langle\Psi'(t)|\hat{H}^2 - \hat{H}\hat{P}\hat{H}|\Psi'(t)\rangle.\end{aligned} \tag{12}$$

The quantity Δ has been used in time-independent calculations for a long time to obtain lower bounds for obtained expectation values (Refs. [29–33,35–39], and references therein). Δ integrated over time, i.e., $\int_{-\infty}^{\infty}\Delta(t)dt$, has been used in time-dependent scattering calculations to compute errors of transition amplitudes (Refs. [44–46,50], and references therein) or to obtain optimal translations factors (see, e.g., Refs. [51,52]).

The use of $\Delta(t)$ as a direct measure of the quality of time-dependent calculations is discussed in Sec. V. There, it is also shown that *in general* it is not possible to use Δ integrated over time (used, e.g., in Refs. [45,46,50–52]) to estimate the error made with a finite basis expansion.

The properties of Δ are addressed in the remainder of this section. An estimate for the time-dependent case is proposed in Sec. III. Please note, that parts of the discussion, in particular in the time-independent case, were already given elsewhere (Refs. [29–39,45–48], and references therein) and are included for completeness, here too.

In Ref. [28] the operator $\hat{X}$ has been given for the case of implicitly time-dependent basis functions and TDDFT. For this case the measure Δ can be defined with Eq. (12) using the operator $\hat{X}$ from Ref. [28].

A solution of the TDSE in basis expansion (5) solves the exact TDSE (1) if and only if $\Delta(t)=0$ for all times t. This statement has to be proved. To do this, we start with Eq. (9)

$$i\frac{d}{dt}|\Psi'\rangle = \hat{H}'|\Psi'\rangle \tag{13}$$

which is equivalent to Eq. (5). Since $\hat{H}'|\Psi'\rangle=\hat{H}|\Psi'\rangle$ if and only if $\Delta(t)=0$ we find that Eq. (13) is equivalent to

$$i\frac{d}{dt}|\Psi'\rangle = \hat{H}|\Psi'\rangle \tag{14}$$

if and only if $\Delta(t)=0$. This is the usual TDSE. Therefore, $|\Psi(t)\rangle=|\Psi'(t)\rangle$ for all times t if and only if

$$\Delta(t) = \langle\Psi'(t)|[\hat{H}'(t)-\hat{H}(t)]^2|\Psi'(t)\rangle = 0 \tag{15}$$

for all times t and

$$|\Psi(t_{\text{initial}})\rangle = |\Psi'(t_{\text{initial}})\rangle. \tag{16}$$

In basis expansion (3) the quantity Δ is

$$\Delta(t) = \sum_{\alpha\beta}^{N_b} a_\alpha^* H^2_{\alpha\beta} a_\beta - \sum_{\alpha\beta\gamma}^{N_b} a_\alpha^* H_{\alpha\gamma} H_{\gamma\beta} a_\beta \tag{17}$$

with the abbreviation

$$H^2_{\alpha\beta} = \langle\phi_\alpha|\hat{H}^2|\phi_\beta\rangle. \tag{18}$$

The challenging part of the numerical evaluation of Eq. (12) is the calculation of $H^2_{\alpha\beta}$ which will be discussed in Sec. IV.

B. Time-independent Schrödinger equation (TISE)

Before a time-dependent calculation is done a good description of the initial state has to be found. Therefore, the properties of the measure Δ are discussed also for the time-independent case. The TISE in basis expansion is

$$\sum_{\beta=1}^{N_b} H_{\alpha\beta} a_\beta = E' a_\alpha. \tag{19}$$

Solutions of Eq. (19) solve the TISE

$$\hat{H}|\Psi'\rangle = E|\Psi'\rangle \tag{20}$$

if and only if

$$\Delta[\Psi'] = 0. \tag{21}$$

The first part of the proof is (20)→(21). For this we let $\hat{P}$ act on Eq. (20) and use $\hat{P}|\Psi'\rangle=|\Psi'\rangle$:

$$\hat{P}\hat{H}\hat{P}|\Psi'\rangle = E|\Psi'\rangle. \tag{22}$$

With Eq. (20) we obtain

$$\hat{P}\hat{H}\hat{P}|\Psi'\rangle = \hat{H}|\Psi'\rangle. \tag{23}$$

This yields Eq. (21) immediately. To show (21) → (20) we start with $\Delta[\Psi']=0$ which is equivalent to Eq. (23). Using Eqs. (3), (6), and (8) we obtain

$$\hat{P}\hat{H}\hat{P}|\Psi'\rangle = \sum_{\alpha\beta} |\phi_\alpha\rangle H_{\alpha\beta} a_\beta. \tag{24}$$

With Eqs. (23) and (19) this is Eq. (20) with $E'=E$:

$$\hat{H}|\Psi'\rangle = \sum_\alpha |\phi_\alpha\rangle a_\alpha E' = E'|\Psi'\rangle. \tag{25}$$

Thus, we have shown (20)↔(21) under the condition (19).

In real calculations the eigenstate $|\Psi'\rangle$ to $\hat{H}'$ is only close to the corresponding eigenstate to $\hat{H}$. Now we want to give an upper limit for the deviations of $|\Psi'\rangle$ and E' from the exact solutions $|\phi_0\rangle$ and E_0. In general, $|\phi_0\rangle$ is *not* the ground state. Using Eqs. (3), (6), and (8) the TISE in basis expansion (19) can be written as

$$\hat{H}'|\Psi'\rangle = E'|\Psi'\rangle \tag{26}$$

with

$$\hat{H}' = \hat{P}\hat{H}\hat{P}. \tag{27}$$

The measure Δ for the error of $|\Psi'\rangle$ is

$$\Delta = \langle\Psi'|(\hat{H}'-\hat{H})^2|\Psi'\rangle = \langle\Psi'|(E'-\hat{H})^2|\Psi'\rangle. \tag{28}$$

$|\Psi'\rangle$ can now be written as a linear combination of the eigenstates $|\phi_k\rangle$ to $\hat{H}$,

$$|\Psi'\rangle = \sum_{k=0}^{\infty} c_k|\phi_k\rangle. \tag{29}$$

The states $|\phi_k\rangle$ have been sorted in such a way that

$$|E'-E_0| \leqslant |E'-E_1| \leqslant |E'-E_2| \leqslant \cdots , \tag{30}$$

where E_k is the eigenenergy of $|\phi_k\rangle$ to $\hat{H}$

$$\hat{H}|\phi_k\rangle = E_k|\phi_k\rangle. \tag{31}$$

The state $|\phi_0\rangle$ is the eigenstate to $\hat{H}$ that is approximated with $|\Psi'\rangle$. In general, $|\phi_0\rangle$ is not the ground state and E_0 is not the ground-state energy. Δ (28) is then

$$\Delta = \sum_{k=0}^{\infty} |c_k|^2 (E'-E_k)^2. \tag{32}$$

The right-hand side can be estimated as

$$\sum_{k=0}^{\infty} |c_k|^2(E'-E_k)^2 \geqslant \sum_{k=0}^{\infty} |c_k|^2(E'-E_0)^2 = (E'-E_0)^2. \tag{33}$$

In Eq. (33) the inequality (30) and $\Sigma_{k=0}^{\infty}|c_k|^2=1$ have been used. Thus, we find

$$\Delta \geqslant (E'-E_0)^2. \tag{34}$$

Another estimate can be derived from Eq. (32). Now, the first term of the sum in Eq. (32) is omitted in the first step and the E_k with $k\geqslant 1$ are replaced by E_1 in the second step:

$$\Delta = \sum_{k=0}^{\infty} |c_k|^2 (E' - E_k)^2 \geqslant \sum_{k=1}^{\infty} |c_k|^2 (E' - E_k)^2$$
$$\geqslant \sum_{k=1}^{\infty} |c_k|^2 (E' - E_1)^2. \tag{35}$$

The overlap of $|\Psi'\rangle$ with the eigenstate $|\phi_0\rangle$ is

$$P_0 = |\langle \phi_0 | \Psi' \rangle|^2 = |c_0|^2 = 1 - \sum_{k=1}^{\infty} |c_k|^2. \tag{36}$$

Therefore we find that

$$\Delta \geqslant (1 - P_0)\, \delta E^2, \tag{37}$$

where $\delta E = E' - E_1$. From this the population of the eigenstate to $\hat{H}$ can be estimated when the eigenstate in basis expansion has been determined,

$$P_0 \geqslant 1 - \frac{\Delta}{\delta E^2}. \tag{38}$$

The level distance δE is not known exactly but can usually be approximated using the results of the basis calculation. Equations (34) and (38) provide an estimate of the accuracy of the basis expansion *without* any knowledge of the correct solution. These equations prove that Δ can be used as a direct measure for the quality of time-independent calculations. If the aim is to calculate lower boundaries for the calculated energies (or expectation values) better estimates are available (Ref. [29–42], and references therein).

III. THE ESTIMATE *Y*

Storm and Rapp [50] and Riera [51] had used the integrated quantity Δ, i.e., $\int_{-\infty}^{\infty} \Delta(t) dt$, as a measure for the quality of their time-dependent calculations which is, *in general*, problematic as will be shown in Sec. V B. Here we present a new estimate of the error made in time-dependent cases. We start with

$$y(t) = 1 - |\langle \Psi(t) | \Psi'(t) \rangle|. \tag{39}$$

This quantity is 0 for the exact solution and 1 if $|\Psi\rangle$ and $|\Psi'\rangle$ are orthogonal. The time derivative of y can be estimated as

$$\frac{d}{dt} y = - \frac{d}{dt} |\langle \Psi | \Psi' \rangle| \leqslant \left| \frac{d}{dt} |\langle \Psi | \Psi' \rangle| \right| \leqslant \left| \frac{d}{dt} \langle \Psi | \Psi' \rangle \right|. \tag{40}$$

By substituting the time-derivatives with the Schrödinger equations (1) and (9) we obtain

$$\frac{d}{dt} y \leqslant |\langle \Psi | \hat{H}' - \hat{H} | \Psi' \rangle|. \tag{41}$$

We define

$$\hat{P}' = |\Psi'\rangle\langle\Psi'|. \tag{42}$$

In the next step, we employ the fact that

$$\langle \Psi | \hat{P}' (\hat{H}' - \hat{H}) | \Psi' \rangle = \langle \Psi | \Psi' \rangle \langle \Psi' | (\hat{H}' - \hat{H}) | \Psi' \rangle$$
$$= \langle \Psi | \Psi' \rangle \langle \Psi' | \hat{P} (\hat{H}' - \hat{H}) \hat{P} | \Psi' \rangle$$
$$= \langle \Psi | \Psi' \rangle \langle \Psi' | (\hat{H}' - \hat{P}\hat{H}\hat{P}) | \Psi' \rangle = 0. \tag{43}$$

In Eq. (43) the identity $\hat{P}|\Psi'\rangle = |\Psi'\rangle$ has been used. We substitute with Eq. (43)

$$|\langle \Psi | \hat{H}' - \hat{H} | \Psi' \rangle| = |\langle \Psi | (1 - \hat{P}')(\hat{H}' - \hat{H}) | \Psi' \rangle| \tag{44}$$

in Eq. (41). Using Schwartz's inequality we obtain

$$\frac{d}{dt} y \leqslant |(1 - \hat{P}')|\Psi\rangle| |(\hat{H}' - \hat{H})|\Psi'\rangle|. \tag{45}$$

Using

$$\langle \Psi | (1 - \hat{P}') | \Psi \rangle = 1 - |\langle \Psi | \Psi' \rangle|^2 = 2y - y^2 \tag{46}$$

and

$$|(\hat{H}' - \hat{H})|\Psi'\rangle| = \sqrt{\Delta} \tag{47}$$

we get

$$\frac{d}{dt} y(t) \leqslant \sqrt{2y(t) - y(t)^2} \sqrt{\Delta(t)}. \tag{48}$$

For the upper bound Y [$Y(t) \geqslant y(t)$ for all times t] the differential equation

$$\frac{d}{dt} Y(t) = \sqrt{2Y(t) - Y(t)^2} \sqrt{\Delta(t)} \tag{49}$$

results. For a given $\Delta(t)$ Eq. (49) can be solved easily by numerical propagation [65]. The final basic estimate $Y(t)$ is an upper limit to the accuracy of the time-dependent wave function at time t. This can be used to prove the correctness of a particular solution when $Y(t)$ is small. The opposite is of course not true, i.e., a large Y is not sufficient to conclude bad accuracy. Note, in contrast to $y(t)$ (39), the estimate $Y(t)$ can become larger than one ($Y \leqslant 2$). In addition, in contrast to the measure $\Delta(t)$ (12), the estimate $Y(t)$ is always monotonic increasing which has advantages in the analysis of the calculated data (see Sec. V).

Thus, $Y(t)$ is a measure for the accuracy of a time-dependent calculation. It can be used to judge the quality of time-dependent calculations as well as to compare different basis sets. This is demonstrated in Sec. V.

IV. CALCULATION OF THE MATRIX ELEMENTS

The calculation of the matrix elements is sketched for the hydrogen atom in a laser field. The Hamiltonian of the considered system is

$$\hat{H} = \hat{T} + \hat{V} + \hat{L} \tag{50}$$

with $\hat{T} = -\nabla^2/2$, $\hat{V} = -1/r$ and the dipole interaction

$$\hat{L} = E(t)\hat{z}. \tag{51}$$

The square of the Hamiltonian is then

$$\hat{H}^2 = \hat{T}^2 + \hat{V}^2 + \hat{T}\hat{V} + \hat{V}\hat{T} + \hat{L}^2 + \hat{T}\hat{L} + \hat{L}\hat{T} + \hat{V}\hat{L} + \hat{L}\hat{V}. \tag{52}$$

To be able to calculate the matrix elements analytically we use Gaussians as basis functions

$$\phi_\alpha(\vec{r}) = N_\alpha e^{-(\vec{r}-\vec{R}_{A_\alpha})^2/\sigma_\alpha^2} z^l, \tag{53}$$

with $l \geqslant 0$, N_α the norm constant, and $\vec{R}_{A_\alpha}$ the position of the center of the Gaussian. Matrix elements between the basis functions with $l > 0$ were calculated iteratively from the matrix elements of the s-type Gaussians [58], i.e., those with $l=0$. For the iteration of $H^2_{\alpha\beta}$ to $l > 0$ it is convenient to expand the Coulomb potential with Gaussian functions

$$V(r) = \sum_\beta c_\beta e^{-r^2/\sigma_\beta^2}. \tag{54}$$

The evaluation of all matrix elements containing the Coulomb potential of the nucleus is thus simplified dramatically without an appreciable loss of accuracy. Furthermore, the $\hat{V}^2$ matrix elements are reduced to four-center overlaps which can be calculated analytically for the general case of four different centers. The expansion of the Coulomb potential is used throughout the paper instead of the Coulomb potential itself, i.e., also in the calculation of the Hamilton matrix (6).

V. APPLICATION TO THE HYDROGEN ATOM

A. The ground state

As a first test, results of the calculation of the hydrogen ground state are presented. It was shown in Sec. II B that the quantity Δ of a state is only zero when the state is an eigenstate. Furthermore, it was shown that Δ is a measure for the accuracy of the calculated eigenstate in basis expansion [60–66].

In the following the ground state of the hydrogen atom is determined from a basis of s-type Gaussians. The usual approach to the construction of a new basis set is to start with an even tempered basis, i.e., the exponents form a geometric series

$$\sigma_i = \sigma_1 f^{i-1} \quad (1 \leqslant i \leqslant N). \tag{55}$$

Within this ansatz three parameters occur, N the number of basis functions, σ_1 the smallest width used and f the factor determining the spacing between the σ_i. It is convenient to specify a width $\sigma_{\max}$ which is a lower bound for the largest occurring σ instead of N, which is then determined in such a way that $\sigma_N \geqslant \sigma_{\max}$. To obtain an accurate eigenstate it is necessary to vary all three parameters. Here, only the effect of the variation of f is shown (Fig. 1). The energy and the measure Δ of the ground state are plotted. The error of the ground-state energy as well as Δ decrease with decreasing f, as expected. However, the quality of the solution can be judged with the measure Δ even when the energy is not converged and the exact ground state is not known: Equations (34) and (38) allow one to estimate the overlap with the correct ground state as well as to give a lower bound for the energy of the ground state. To obtain a ground-state description which is at least 99% correct, i.e., $P_0 > 0.99$ [see Eq. (38)], it is sufficient to use a basis set for which the measure Δ of the ground state is 1.4×10^{-3} a.u. This corresponds to a factor $f=2$. Furthermore, the influence of the *expansion* of the Coulomb potential can be seen in Fig. 1: The final difference of the ground-state energy to the real hydrogen ground state is 7×10^{-6} a.u.

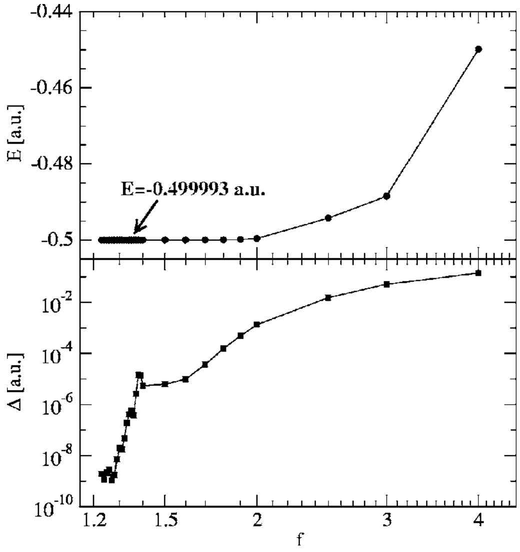

FIG. 1. Energy (top) and the measure Δ (bottom) as a function of the factor f for $\sigma_1 = 10^{-5}$ a.u. and $\sigma_{\max} = 50$ a.u.

In the following the hydrogen basis will be built using the parameters $\sigma_1 = 10^{-5}$ a.u., $\sigma_{\max} = 50$ a.u., and $f=1.5$. A contracted basis set that consists of atomic eigenfunctions which in turn are represented by Gaussians is used.

B. Intense laser field

The hydrogen atom is now considered in a laser field of the form

$$E(t) = E_0 f(t) \sin(\omega t + \varphi), \tag{56}$$

where the shape function $f(t)$ is given by

$$f(t) = \begin{cases} \sin^2\left(\dfrac{\pi}{2T} t\right) & \text{for } 0 < t < 2T, \\ 0 & \text{otherwise} \end{cases} \tag{57}$$

and T is the duration of the laser pulse, ω the frequency, φ the phase, and E_0 the amplitude.

The hydrogen atom is exposed to a $2T=4.8$ fs laser pulse with a wavelength of 253 nm and an intensity of 1.0×10^{14} W/cm^2. In Fig. 2, the energy $E = \langle \Psi | -\nabla^2/2 + V | \Psi \rangle$, the part of the electronic density in states with positive energy, the measure $\Delta(t)$ and the estimate $Y(t)$ [see Eq. (49)] are shown as a function of time for different basis sets.

Three basis sets have been used. The first basis consists only of the 1s functions. 2s and 2p_z have been added for the second basis. The third and largest basis set contains all eigenfunctions (resulting from the chosen primary basis) up to an energy of 1 a.u. ($\approx$27.21 eV). It is clear, that the use of

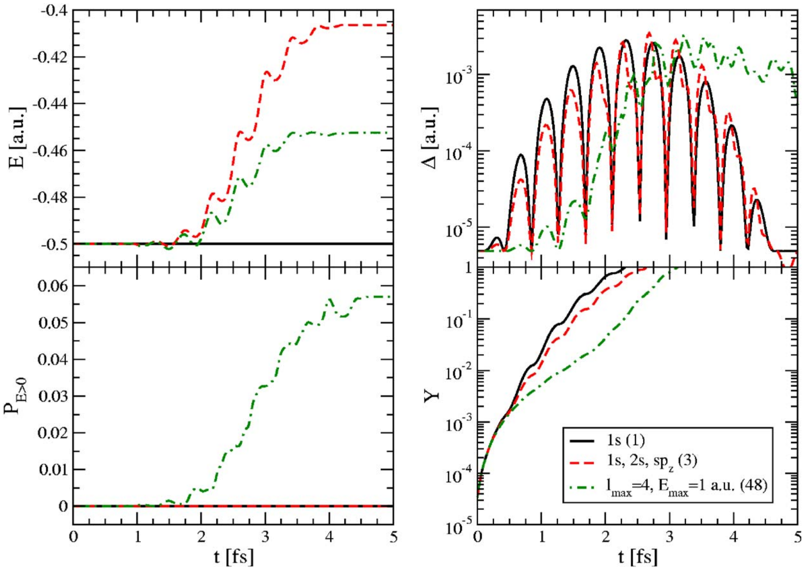

FIG. 2. (Color online.) Energy (top left), occupation of states with positive energy (bottom left), the measure $\Delta(t)$ (top right) and the estimate $Y(t)$ (bottom right) as a function of time for a 2.4 fs laser pulse with a frequency of 0.18 a.u. (~253 nm) and an intensity of 1×10^{14} W/cm^2. The numbers in brackets in the legend indicate the corresponding basis size.

the third basis set leads to the best description of the ongoing dynamics and the use of the first basis serves as a limiting case.

In this first case, $1s$ only, the energy and $P_{E>0}$ are constant because no excitation is possible. The measure $\Delta(t)$ has a small but finite value at the beginning and at the end of the laser pulse which represents the error of the ground state. During the laser pulse, $\Delta(t)$ grows almost by a factor of 1000 because excitation is not possible. Accordingly, the estimate $Y(t)$ swiftly rises towards unity and the calculated approximate solution is only close to the exact solution for times $t<1$ fs.

In the second case, $1s$, $2s$, and $2p_z$, the measure $\Delta(t)$ stays smaller than in the first case at the beginning of the laser pulse due to the better representation of the initial excitation. However, for later times it is again as high as with the first basis set because further excitation would occur and more states are needed to describe the ongoing dynamics correctly. Correspondingly, the rise of the estimate $Y(t)$ is delayed in comparison to the $1s$-only basis.

In the last case, the largest basis set, the measure $\Delta(t)$ stays nearly at its initial value during the first period of the laser. Afterwards it rises but remains smaller than that of the two smaller basis sets up to 3 fs. However, the measure $\Delta(t)$ is around 3 orders of magnitude larger after the laser pulse as compared to that of the other two cases. The reason for this is the bad description of ionized states which cannot be represented exactly using a local basis. This also leads to a fast increase of Y after around 2 fs. Up to that time, the calculation using this large LCAO basis set is close to the exact solution as the overlap between the exact solution and the calculated approximated solution is larger than 0.96 [see Eqs. (49) and (39)].

It is obvious, that the use of the integration of $\Delta(t)$ over time, i.e., $\int_{t_0}^{t_{\max}}\Delta(t)dt$, as a measure for the quality of the calculation (as, e.g., done in Refs. [49–51]) would lead to the conclusion that the largest of the three basis sets produces the least reliable results. This conclusion is simply wrong since the largest basis set contains the basis functions used in each of the smaller ones. Therefore, it is *in general* not possible to use $\Delta(t)$ integrated over time as a measure for the quality of the calculation.

On the other side, the estimate $Y(t)$ does allow one to compare different basis sets and judge which produces more reliable results. As seen in Fig. 2, $Y(t)$ is smallest for the largest basis set at any time [in accordance with intuition and in striking contrast to the behavior of $\Delta(t)$]. The advantage of $Y(t)$ is that this quantity can easily be used as a measure for the quality of the results at a given time t. In contrast, it is not possible to use the measure $\Delta(t)$ at a certain time t to judge the quality of the used basis [cf. the oscillating values of $\Delta(t)$ in Fig. 2].

In Fig. 3, the calculation with the largest LCAO basis from above is compared to that of a qualitatively different type of basis expansion. In this expansion a small LCAO basis ($1s$, $2s$, and $2p_z$) is extended with s-type Gaussian functions laid out chainlike along the laser polarization axis [59]. These functions are defined by the width σ of each Gaussian, the distance d between neighboring Gaussians with the same σ and the number of Gaussians n. The parameters of this basis are given in Table I. These additional basis functions are referred to as "chains" in the following. Both basis sets have nearly the same size $N_b=48$ and $N_b=40$, respectively. Their geometric properties, however, are qualitatively different.

The resulting total energies E are almost identical in both calculations (see Fig. 3). However, the total populations in states with positive energy $P_{E>0}$, i.e., the ionization probabilities, differ slightly for times later than 3.5 fs. In that case, both quantities $\Delta(t)$ and $Y(t)$ indicate that the chain like basis will lead to more reliable results.

However, in contrast to the oscillating behavior of $\Delta(t)$ in Fig. 3, the monotonic and nearly equal estimates $Y(t)$ for both basis sets at small times ($t\leqslant1.5$ fs) allow one to predict equal results for both basis sets for short or weak laser pulses, i.e., for small ionization probabilities. For longer pulses the chainlike basis is expected to provide better results. In addition, a small value of $Y(t)\ll1$ guarantees a rela-

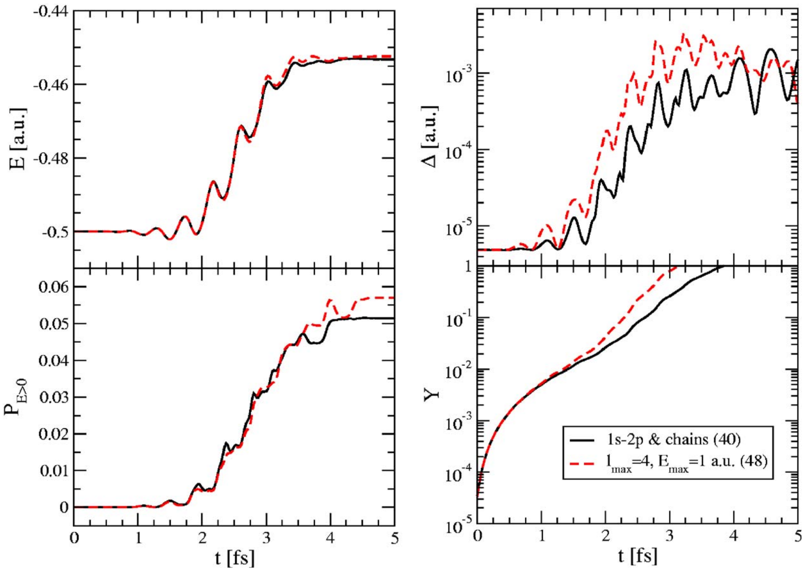

FIG. 3. (Color online.) Energy (top left), occupation of states with positive energy (bottom left), the measure Δ (top right) and the estimate Y (bottom right) as a function of time for a 2.4 fs laser pulse with a frequency of 0.18 a.u. (~253 nm) and an intensity of 1×10^{14} W/cm^2. The numbers in parentheses in the legend indicate the corresponding basis size.

tively high accuracy of the results and, thus, allows one to reduce drastically the basis size in actual calculations. To demonstrate both aspects we compare the results of our calculations with the high precision data of Hansen *et al.* [25]. In these calculations [25] nearly 3000 basis functions were used which is about two orders of magnitude larger as compared to our sizes (48, respectively, 40 basis functions). In Fig. 4, the calculated populations of states with positive energy (i.e., the ionization probabilities) are plotted as functions of the laser duration T for two frequencies (ω=0.55 and 0.18 a.u.) and two intensities ($I=3.8\times10^{15}$ and 8.78×10^{13} W/cm^2). Evidently, as long as the laser pulses are quite short and/or the intensity is low the agreement between our results obtained with *both* basis sets and those of Hansen *et al.* is good. Good agreement is found also for ω=0.18 a.u. (λ=253 nm) for long pulse lengths when the chain basis is used, as expected from the discussion above. The differences between our calculations and that of Hansen *et al.* [25] for the large frequency ω=0.55 a.u. at high intensities are due to the fact that our relatively small basis does not contain enough energetically high lying states.

VI. CONCLUSIONS

We have proposed a method to evaluate the error made with a finite basis expansion in time-dependent calculations. To this end we have defined the estimate Y (49). The method was applied to the hydrogen atom in intense laser fields and it was shown that it can be used to compare different basis sets without knowing the converged result. Furthermore, we have shown that *in general* it is not possible to use Δ integrated over time as an estimate.

The method was also used to find relatively small basis sets suitable for the description of ionization dynamics for

TABLE I. The parameters (σ of the, respectively, chain, distance between neighboring functions of the same chain, and number of Gaussians used in that chain) of the five chains of s-type Gaussians laid out along the laser polarization axis are shown. All chains were positioned to have the hydrogen atom in the center.

σ [a.u.]	d [a.u.]	n
3.57	2.47	9
4.58	3.41	9
5.25	3.76	7
6.31	4.40	7
7.70	8.32	5

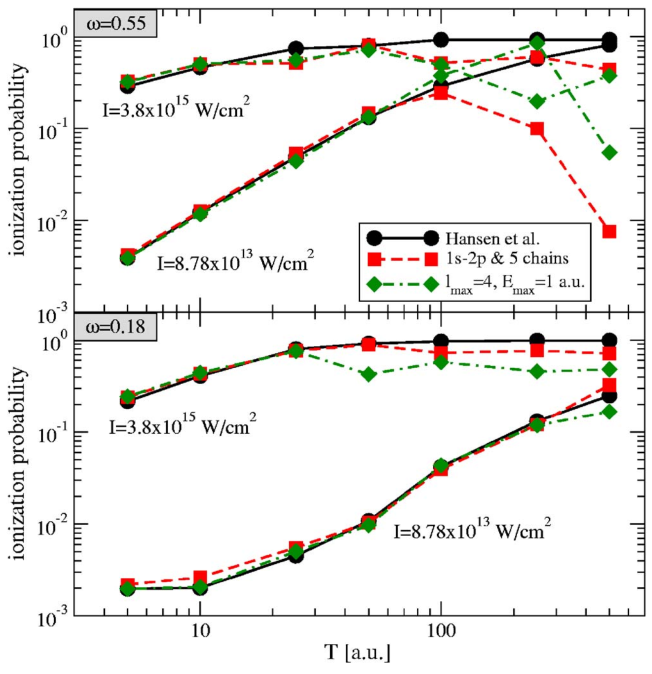

FIG. 4. (Color online.) Ionization probability as a function of laser duration T for ω=0.55 a.u. (top) and ω=0.18 a.u. (bottom) and two laser intensities [8.78×10^{13} W/cm^2 (lower curves) and 3.8×10^{15} W/cm^2 (upper curves)]. For comparison the results of Hansen *et al.* [25] have been included. The basis sets of our calculations are the same as in Fig. 3.

which in addition *all* matrix elements can be calculated analytically. It could be shown that the usage of so-called chains (of Gaussians) [59] is an alternative to the usage of basis functions of high dimension and with high angular momenta. Yet, it is still necessary to introduce absorbing boundary conditions to extend the description to arbitrarily long times. This will be done in a subsequent work.

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