PHYSICAL REVIEW A **76**, 033403 (2007)

# Dressed-state strong-field approximation for laser-induced molecular ionization

W. Becker,[1] J. Chen,[2] S. G. Chen,[2] and D. B. Milošević[3,1]
[1]*Max-Born-Institut, Max-Born-Strasse 2a, 12489 Berlin, Germany*
[2]*Institute of Applied Physics and Computational Mathematics, P. O. Box 8009(28), 100088 Beijing, People's Republic of China*
[3]*Faculty of Science, University of Sarajevo, Zmaja od Bosne 35, 71000 Sarajevo, Bosnia and Herzegovina*

(Received 21 December 2006; published 5 September 2007)

In the customary formulation of the strong-field approximation (SFA) for laser-induced ionization, the initial bound state is taken as field-free. In the formulation of a length-gauge SFA for ionization of a molecule described by a two-center binding potential with sufficiently large internuclear separation, we argue that the initial state has to be dressed in order to account for the different scalar potentials at the various centers. We propose a "dressed-state" SFA to this end.

DOI: 10.1103/PhysRevA.76.033403 PACS number(s): 33.80.Rv, 42.50.Hz, 32.80.Rm

## I. INTRODUCTION

The strong-field approximation (SFA) is the workhorse of laser-atom physics [1,2]. While the exact dynamics of a bound electron in the presence of a laser field are extremely complicated, the SFA yields simple expressions for the transition amplitudes of laser-induced processes. In particular, it affords the amplitude for laser-induced ionization into a continuum state with asymptotic momentum $\mathbf{p}$. It allows for straightforward computation, especially in the tunneling limit. It is three dimensional, and it can be applied for any laser field and arbitrary polarization, including few-cycle pulses [3]. In the tunneling limit, the amplitude can be evaluated by the method of steepest descent. In this case, when it makes sense to envisage the electron tunneling out at some specific time, the SFA also yields a great deal of physical insight into the tunneling process. While the *total* ionization rate calculated by integrating over the spectrum is not always reliable [4,5], the angle-resolved energy spectrum normally is, except for very low energies [6]. In its standard forms, the SFA accounts only for "direct electrons," which after ionization leave the ion without any recollision. The SFA can readily be generalized to allow rescattering [7,8], and the corresponding expressions work extremely well in comparison with an exact numerical solution of the time-dependent Schrödinger equation [9].

The shortcomings of the SFA are well known. Most are connected with the presence of the Coulomb potential. So the SFA does not account for the effects of excited bound states, nor does it contain the consequences of the final-state interaction of the freed electron with its parent ion except, in its generalized form, for one "hard" interaction upon a recollision [7,8]. Obviously, the SFA is particularly well suited for the description of laser detachment of an electron off a negative ion, owing to the lack of excited bound states and the absence of the Coulomb interaction between the detached electron and the neutral atom [10,11]. A notorious problem of the SFA is its gauge dependence. This has received some attention lately, and several recent papers have concluded that the length gauge is better suited than the velocity gauge for the atomic SFA [12–15].

Recently, interest has focused on laser ionization of molecules [16]. *Ab initio* numerical simulations are significantly more complicated than in the atomic case [17], and the need to deal with the relative orientation of the molecule with respect to the laser field generates additional complexity. In this situation, a benchmark formula that admits quick computation and provides physical insight is even more desirable than for atomic ionization. A generalization of the atomic SFA would serve this purpose well [18,19]. However, the problem of which gauge to apply has so far not led to any consensus [20–22]. This is compounded by the fact that the predictions of the two gauges commonly used—the length and velocity gauges—diverge much more than for the case of atoms [23].

There is another limitation of the various forms of the SFA, which is sometimes not realized but crucial for the case of a molecule. Derivations of the SFA that start from the $S$ matrix in its time-reversed form invariably imply an initial state that is unperturbed by the laser field; cf, e.g., Ref. [24]. While this form is exact, the approximations that are subsequently made prevent certain features of the full problem from being represented in the SFA [25]. These are features that are associated with the effect of the laser on the initial state preceding ionization, such as the ac Stark shift or laser depletion of the ground state. If one intends to include such effects into the SFA amplitude, one has to derive a modified SFA, or one may attempt to introduce them by hand into the standard expression by using a laser-dressed ground state [25].

The purpose of this paper is to propose a SFA for ionization of a molecule with large internuclear separation. We will do so simply by enforcing that ionization be translation invariant, that is, independent of the position of the atom. The meaning of "large" will become clear from the derivation. Essentially, it means that the separation should be at least comparable with if not larger than the range of the atomic orbitals. This is satisfied, for example, for the rare-gas molecules. While this falls short of a general formulation of a molecular SFA, it still is an important special case, which has received a good deal of attention lately [21]. It is conceivable that the proposed SFA will work well for arbitrary internuclear separations, but we cannot prove this by simple consistency checks.

In the second section, we study the translation invariance of the length-gauge time-dependent Schrödinger equation for a binding potential that is displaced from the origin. In the third section, we introduce a version of the SFA that obeys translation invariance for an arbitrarily positioned binding potential and let this guide us to the formulation of the "dressed-state SFA" in length gauge for a diatomic molecule with sufficiently large internuclear separation. We provide additional support for this formulation by considering the saddle-point evaluation of the ionization amplitude, which yields unphysical results if the ground state is not dressed. In Sec. IV, we support the dressed-state SFA with a more formal derivation. We start from the fact that for large internuclear distance the ground state is almost degenerate with the lowest excited state, which has the opposite symmetry. The laser field couples to this two-level system. If we modify the SFA to allow for this coupling, we retrieve the dressed-state SFA. Section V presents our conclusions.

## II. DISPLACED BINDING POTENTIAL AND TWO-CENTER POTENTIAL

Let us start by considering a potential that is centered about some point $\mathbf{a}$ away from the origin,

$$V_{\mathbf{a}}(\mathbf{r}) = V_{\mathbf{0}}(\mathbf{r}-\mathbf{a}), \tag{1}$$

where $V_{\mathbf{0}}(\mathbf{r})$ is concentrated about the origin. Usually, we have $\mathbf{a}=\mathbf{0}$. This is the situation that naturally arises in a neutral atom where the vector $\mathbf{r}$ points from the ionic charge to the atomic electron. There is nothing, however, that would forbid considering a displaced potential with $\mathbf{a}\neq\mathbf{0}$. In the presence of a laser field and in the electric-field gauge, the corresponding Schrödinger equation

$$\left(i\partial_t - \frac{\hat{\mathbf{p}}^2}{2m} - V_{\mathbf{a}}(\mathbf{r}) + e\mathbf{r}\cdot\mathbf{E}(t)\right)\psi_{\mathbf{a}}(\mathbf{r},t) = 0 \tag{2}$$

is solved by

$$\psi_{\mathbf{a}}(\mathbf{r},t) = \exp[-ie\mathbf{a}\cdot\mathbf{A}(t)]\psi_{\mathbf{0}}(\mathbf{r}-\mathbf{a},t) \tag{3}$$

provided $\psi_{\mathbf{0}}(\mathbf{r},t)$ solves the Schrödinger equation (2) with $\mathbf{a}=\mathbf{0}$. Here, $\mathbf{A}(t)$ is any vector potential such that $\mathbf{E}(t)=-d\mathbf{A}(t)/dt$.

Next, let us consider the Schrödinger equation

$$D\Psi_{\mathbf{a}}(\mathbf{r},t) \equiv \left(i\partial_t - \frac{\hat{\mathbf{p}}^2}{2m} - W_{\mathbf{a}}(\mathbf{r}) + e\mathbf{r}\cdot\mathbf{E}(t)\right)\Psi_{\mathbf{a}}(\mathbf{r},t) = 0 \tag{4}$$

with the two-center potential

$$W_{\mathbf{a}}(\mathbf{r}) = V_{\mathbf{a}}(\mathbf{r}) + V_{-\mathbf{a}}(\mathbf{r}) = V_{\mathbf{0}}(\mathbf{r}-\mathbf{a}) + V_{\mathbf{0}}(\mathbf{r}+\mathbf{a}). \tag{5}$$

This potential may describe a molecular ion such as $H_2^+$, in which case $V_{\mathbf{0}}(\mathbf{r})$ would be a Coulomb potential [26], but also a neutral molecule or a negative molecular ion such as $H_2^-$. In the latter cases, one might approximate $V_{\mathbf{0}}(\mathbf{r})$ by a zero-range potential [27]. We make the ansatz

$$\Psi_{\mathbf{a}}(\mathbf{r},t) = N_{\mathbf{a}}^{-1}[\psi_{\mathbf{a}}(\mathbf{r},t) + \psi_{-\mathbf{a}}(\mathbf{r},t)] \tag{6}$$

and normalize the orbitals to unity, $\int d^3\mathbf{r}\,\psi_{\mathbf{a}}^*(\mathbf{r},t)\psi_{\mathbf{a}}(\mathbf{r},t) = \int d^3\mathbf{r}\,\psi_{-\mathbf{a}}^*(\mathbf{r},t)\psi_{-\mathbf{a}}(\mathbf{r},t)=1$, while their overlap is $\int d^3\mathbf{r}\,\psi_{-\mathbf{a}}^*(\mathbf{r},t)\psi_{\mathbf{a}}(\mathbf{r},t)\equiv S_{\mathbf{a}}$. This determines the normalization factor as

$$N_{\mathbf{a}} = \sqrt{2(1+\mathrm{Re}S_{\mathbf{a}})}. \tag{7}$$

The ansatz (6) yields

$$D\Psi_{\mathbf{a}}(\mathbf{r},t) = -N_{\mathbf{a}}^{-1}[V_{-\mathbf{a}}(\mathbf{r})\psi_{\mathbf{a}}(\mathbf{r},t) + V_{\mathbf{a}}(\mathbf{r})\psi_{-\mathbf{a}}(\mathbf{r},t)]. \tag{8}$$

If the two centers are sufficiently far apart, the right-hand side is small, and the ansatz (6) solves the Schrödinger equation (4) reasonably well. Note that the right-hand side of Eq. (8) may be small while the overlap $S_{\mathbf{a}}$ is still significantly different from zero. In view of the translation property (3), our ansatz reads

$$\Psi_{\mathbf{a}}(\mathbf{r},t) = N_{\mathbf{a}}^{-1}[e^{-ie\mathbf{a}\cdot\mathbf{A}(t)}\psi_{\mathbf{0}}(\mathbf{r}-\mathbf{a},t) + e^{ie\mathbf{a}\cdot\mathbf{A}(t)}\psi_{\mathbf{0}}(\mathbf{r}+\mathbf{a},t)]. \tag{9}$$

Reasonable and manageable approximations to the bound-state wave functions (3) and (9) are obtained if the wave function $\psi_{\mathbf{0}}(\mathbf{r},t)$, which solves the Schrödinger equation in the presence of the field, is replaced by $\psi_{\mathbf{0}}^{(0)}(\mathbf{r},t)$ in the absence of the field, while the field-dependent exponentials are kept.

## III. DRESSED-STATE STRONG-FIELD APPROXIMATION IN LENGTH GAUGE

### A. Displaced one-center potential

The SFA matrix element for ionization of an electron bound by the potential $V(\mathbf{r})$ into a state with asymptotic momentum $\mathbf{p}$ can be written in one of the two equivalent forms (see, e.g., Ref. [2])

$$M_{\mathbf{p}} = -i\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^*V(\mathbf{r})\psi_0^{(0)}(\mathbf{r},t) \tag{10a}$$

$$= -i\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^*H_I(\mathbf{r},t)\psi_0^{(0)}(\mathbf{r},t), \tag{10b}$$

where $H_I(\mathbf{r},t)=-e\mathbf{r}\cdot\mathbf{E}(t)$ represents the electron-field interaction operator in length gauge,

$$\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t) = (2\pi)^{-3/2}\exp\{i[\mathbf{p}-e\mathbf{A}(t)]\cdot\mathbf{r}\} \times \exp\left(-\frac{i}{2m}\int_{-\infty}^{t} d\tau[\mathbf{p}-e\mathbf{A}(\tau)]^2\right) \tag{11}$$

the Volkov wave function in length gauge, and $\psi_0^{(0)}(\mathbf{r},t)$ the (field-free) atomic ground state. The superscript (0) refers to the absence of the laser field, and the subscript 0 to the ground state. For the displaced potential (1), the form (10a) reads

$$M_{\mathbf{ap}} = -i\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^*V_{\mathbf{a}}(\mathbf{r})\psi_{\mathbf{a}0}(\mathbf{r},t). \tag{12}$$

By the usual framework of the SFA, the wave function $\psi_{\mathbf{a}0}(\mathbf{r},t)$ should have a superscript (0), to denote the field-free ground state of the displaced binding potential in the absence of the field. This will be discussed below.

Clearly, the ionization probability must not depend on the position of the atom, so the only possible dependence of $M_{\mathbf{ap}}$ on $\mathbf{a}$ should be via a phase factor, which will cancel from the probability. Upon the translation $\mathbf{r}\to\mathbf{r}+\mathbf{a}$, the matrix element (12) reads

$$\begin{aligned} M_{\mathbf{ap}} &= -i\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r}+\mathbf{a},t)^* V_{\mathbf{0}}(\mathbf{r})\psi_{\mathbf{a}0}(\mathbf{r}+\mathbf{a},t) \\ &= -ie^{-i\mathbf{p}\cdot\mathbf{a}}\int d^3\mathbf{r}\,dt\,e^{ie\mathbf{a}\cdot\mathbf{A}(t)} \\ &\quad\times \psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^* V_{\mathbf{0}}(\mathbf{r})\psi_{\mathbf{a}0}(\mathbf{r}+\mathbf{a},t). \end{aligned} \tag{13}$$

Since, by the principles of the SFA, the shifted ground-state wave function $\psi_{\mathbf{a}0}(\mathbf{r}+\mathbf{a},t)$ is to be independent of the field, it cannot cancel the phase $\exp[ie\mathbf{a}\cdot\mathbf{A}(t)]$ in the integrand. Hence, translation invariance of the ionization probability will be violated. However, if (and only if) we take

$$\psi_{\mathbf{a}0}(\mathbf{r},t) = \exp[-ie\mathbf{a}\cdot\mathbf{A}(t)]\psi_{\mathbf{00}}^{(0)}(\mathbf{r}-\mathbf{a},t) \tag{14}$$

as suggested by Eq. (3), then indeed we have

$$M_{\mathbf{ap}} = \exp(-i\mathbf{a}\cdot\mathbf{p})M_{\mathbf{0p}}. \tag{15}$$

The effect of the phase $\exp[-ie\mathbf{a}\cdot\mathbf{A}(t)]$ in Eq. (14) is to cancel the opposite phase that results from the Volkov wave function. The latter reflects the scalar potential $\Phi_{\mathbf{a}}(t)=-e\mathbf{a}\cdot\mathbf{E}(t)$ at the position of the atom, which leads to $\int^t d\tau\,\Phi_{\mathbf{a}}(\tau)=e\mathbf{a}\cdot\mathbf{A}(t)$. If the initial state is not dressed according to Eq. (14), the scalar potential is taken into account in the final state but not in the initial state, which will cause artifacts.

However, derivations of the SFA hold that the initial state must be an eigenstate of the operator $H_0=\hat{\mathbf{p}}^2/(2m)+V(\mathbf{r})$. This means that it *must not be dressed* explicitly by the external field [24]. (There is a recent derivation of a modified SFA that does yield a dressed initial state [25].) Is it legitimate, then, to introduce it by hand as we did in Eq. (14)? The answer is that the assumptions made in the above-mentioned derivations of the SFA preclude any dressing of the initial state, in the same way as they do not allow for the ac Stark shift or depletion of the ground state. Dressing the ground state by hand constitutes an *ad hoc* attempt to heal this shortcoming. Whether or not this is a good approximation can, ultimately, only be decided by comparison with an exact solution of the time-dependent Schrödinger equation (TDSE). However, this statement holds for any approximation method, including the usual SFA.

A different argument in support of the ansatz (14) can be built on a saddle-point evaluation of the temporal integral in Eq. (13). For a large displacement $\mathbf{a}$, we must include exponentials of the kind $\pm ie\mathbf{a}\cdot\mathbf{A}(t)$ into the total phase of the integrand when we determine the saddle points [21]. Without the exponential in Eq. (14), the saddle-point condition that renders the exponential of the integrand of Eq. (13) stationary is

$$\frac{1}{2m}[\mathbf{p}-e\mathbf{A}(t)]^2 - e\mathbf{a}\cdot\mathbf{E}(t) + I_p = 0, \tag{16}$$

where $I_p>0$ is the ionization potential of the ground state. Let us consider, for the moment, a monochromatic linearly polarized field with the vector potential $\mathbf{A}(t)=\hat{\mathbf{e}}_x A_0\cos\omega t$. Without the term $-e\mathbf{a}\cdot\mathbf{E}(t)$, for given $\mathbf{p}$ the saddle-point equation (16) has two solutions $t_{1,2}(\mathbf{p})$ per cycle of the field in the upper half complex $t$ plane. The imaginary parts $\mathrm{Im}\,t_{1,2}(\mathbf{p})$ of these two solutions are equal, reflecting the fact that the direction of the electric field at the time of ionization has no effect on the ionization probability. Let us now keep the term $-e\mathbf{a}\cdot\mathbf{E}(t)$ in Eq. (16). It has opposite signs at the two times $t_1$ and $t_2$: $E_x(\mathrm{Re}\,t_1)=-E_x(\mathrm{Re}\,t_2)$. In consequence, one of the two solutions now will be real—the one for which $-e\mathbf{a}\cdot\mathbf{E}(t)<0$—while the other one will exhibit a much increased imaginary part. Ionization will be well over the barrier for the first solution, while strongly inhibited for the second. This makes no physical sense and is due to the fact that we did not consider the scalar potential at the position of the atom in a consistent fashion: it is taken into account by the Volkov solution but not by the initial state. To include it consistently, we have to dress the initial state by adopting the wave function (14). This will cancel the term $-e\mathbf{a}\cdot\mathbf{E}(t)$ in the saddle-point equation (16). In consequence, ionization will be independent of the position of the atom, as it should be.

The preceding arguments should have made it clear that we have to choose the ansatz (14) for the initial-state wave function, so that the phase $\exp[ie\mathbf{a}\cdot\mathbf{A}(t)]$ in the matrix element (13) is canceled. We shall refer to this procedure as the "dressed-state SFA" (DSSFA) in length gauge. Of course, for an atom located at the origin, it is identical with the usual length gauge.

There is no problem with translation invariance in the velocity gauge. The velocity-gauge Volkov wave function differs from the length-gauge form (11) by the absence of the exponential $\exp[-ie\mathbf{A}(t)\cdot\mathbf{r}]$. There is no need to dress the initial state, because in the velocity gauge there is no scalar potential. Equation (12) with $\psi_{\mathbf{a}0}(\mathbf{r},t)=\psi_{\mathbf{00}}^{(0)}(\mathbf{r},t)$ immediately leads to an amplitude that satisfies Eq. (15). Both the length-gauge DSSFA and the usual velocity-gauge SFA lead to the form

$$M_{\mathbf{ap}} = -ie^{-i\mathbf{p}\cdot\mathbf{a}}\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^* V_{\mathbf{0}}(\mathbf{r})\psi_{\mathbf{00}}^{(0)}(\mathbf{r},t), \tag{17}$$

with the Volkov function in the corresponding gauge.

It should be noted that, with the dressed initial-state wave function (14), the two forms (10a) and (10b) are no longer equivalent. The equivalence was a consequence of the initial state $|\psi_0^{(0)}(t)\rangle$ being an eigenstate of $H_0$, which is not the case for the state (14). At the same time, the nonequivalence of Eqs. (10a) and (10b) is also due to the lack of orthogonality between the Volkov state and the bound state. If this were enforced, the operator $H_I(\mathbf{r},t)$ in Eq. (10b) could be augmented by terms $\pm e\mathbf{a}\cdot\mathbf{E}(\tau)$, which would restore the equivalence of the two forms. We will return to this point at the end of Sec. IV.

### B. Two-center potential

After these preparations, we calculate the SFA matrix element

$$M_{\mathbf{a},-\mathbf{a},\mathbf{p}} = -i\int d^3\mathbf{r}\,dt\,\psi_{\mathbf{p}}^{(\mathrm{Vv})}(\mathbf{r},t)^{*}W_{\mathbf{a}}(\mathbf{r})\Psi_{\mathbf{a}0\pm}(\mathbf{r},t) \tag{18}$$

for ionization of an electron bound by the two-center potential (5). The ground state may be symmetric or antisymmetric, and according to Eqs. (9) and (14) we describe it by the wave function

$$\Psi_{\mathbf{a}0\pm}(\mathbf{r},t) = N_{\mathbf{a}}^{-1}[e^{-ie\mathbf{a}\cdot\mathbf{A}(t)}\psi_{\mathbf{00}}^{(0)}(\mathbf{r}-\mathbf{a},t) \pm e^{ie\mathbf{a}\cdot\mathbf{A}(t)}\psi_{\mathbf{00}}^{(0)}(\mathbf{r}+\mathbf{a},t)] \tag{19}$$

in the length-gauge DSSFA, or by the same wave function but without the exponentials in the usual length-gauge SFA. Note that the two field-free wave functions $\psi_{\mathbf{00}}^{(0)}(\mathbf{r}\pm\mathbf{a},t)$ are multiplied by different phases, which reflect the different scalar potentials at $\mathbf{r}=\pm\mathbf{a}$. Let us neglect, for the time being, the cross terms, which contain $\psi_{\mathbf{00}}^{(0)}(\mathbf{r}\pm\mathbf{a},t)V_{\mathbf{0}}(\mathbf{r}\mp\mathbf{a})$. In length-gauge DSSFA, we then obtain

$$M_{\mathbf{a},-\mathbf{a},\mathbf{p}} = N_{\mathbf{a}}^{-1}(e^{-i\mathbf{p}\cdot\mathbf{a}} \pm e^{i\mathbf{p}\cdot\mathbf{a}})M_{\mathbf{0p}}, \tag{20}$$

expressing the interference of electrons emitted by one or the other center, which may be constructive or destructive according to the symmetry of the ground-state wave function (19). For an antisymmetric ground state, emission of low-energy electrons along the nuclear symmetry axis is suppressed, as is predicted by the usual velocity-gauge SFA [18]. Averaging the square of the matrix element (20) over all directions of $\mathbf{a}$ yields (note that the normalization factor $N_{\mathbf{a}}$ does not depend on the direction of $\mathbf{a}$)

$$\int \frac{d\Omega_{\mathbf{a}}}{4\pi}|M_{\mathbf{a},-\mathbf{a},\mathbf{p}}|^2 = N_{\mathbf{a}}^{-2}\left(1 \pm \frac{\sin(2pa)}{2pa}\right)|M_{\mathbf{0p}}|^2, \tag{21}$$

provided the ground-state orbital $\psi_{\mathbf{00}}^{(0)}$ is an $s$ orbital. For other orbitals, no simple factorization like Eq. (21) is possible. Hence, for low electron momenta and/or small internuclear separations, the symmetry of the ground-state wave functions has a large effect on the orientation-averaged ionization yield.

For the standard length gauge, the integrand of Eq. (18) contains the time-dependent exponentials $\exp[\pm ie\mathbf{a}\cdot\mathbf{A}(t)]$, which preclude the simple form (20). These exponentials will again give rise to the unphysical saddle-point equation (16).

The cross terms, which contain the terms $\psi_{\mathbf{00}}^{(0)}(\mathbf{r}\pm\mathbf{a},t)V_{\mathbf{0}}(\mathbf{r}\mp\mathbf{a})$, generally will decrease with increasing $|\mathbf{a}|$, as the overlap between the potential $V_{\mathbf{0}}(\mathbf{r})$ and its shifted ground-state wave function approaches zero. In length-gauge DSSFA, now the cross terms give rise to the unphysical saddle-point equation (16). For small $|\mathbf{a}|$, the consequences are hard to estimate, but for large $|\mathbf{a}|$, the cross terms will tend to zero, and the emission of the two centers will be (up to a small reduction due to the nonzero overlap $S_{\mathbf{a}}$) the coherent superposition of the emission of two atoms placed at a distance $2\mathbf{a}$, as one would expect.

Problems in diatomic molecules arising from the presence or absence of terms like $\pm e\mathbf{a}\cdot\mathbf{E}(t)$ in the total phase have also been investigated in Ref. [21] and led the authors to rule out the standard length-gauge SFA for the case of high-order harmonic generation, since it predicts the cutoffs in wrong positions. Their case is more complicated than ours since it involves rescattering.

## IV. THE DRESSED INITIAL STATE RECONSIDERED

In the preceding section, we justified taking the dressed initial state (19) in the molecular SFA matrix element (18) by the need to maintain translation invariance for ionization of a one-center binding potential. Here, we will present a different argument that will lead again to the dressed-state wave function (19). For simplicity, consider the case when the molecular orbitals have positive parity. For large internuclear separation $2\mathbf{a}$, the energy separation $\Delta E$ between the field-free molecular ground state

$$\Psi_{\mathbf{a}0+}^{(0)}(\mathbf{r},t) = N_{\mathbf{a}}^{-1}e^{iI_pt}[\psi_{\mathbf{00}}^{(0)}(\mathbf{r}-\mathbf{a}) + \psi_{\mathbf{00}}^{(0)}(\mathbf{r}+\mathbf{a})] \equiv e^{iI_pt}\psi_{+}(\mathbf{r}) \tag{22}$$

and the field-free excited state

$$\begin{aligned}\Psi_{\mathbf{a}0-}^{(0)}(\mathbf{r},t) &= N_{\mathbf{a}}^{-1}e^{i(I_p-\Delta E)t}[\psi_{\mathbf{00}}^{(0)}(\mathbf{r}-\mathbf{a}) - \psi_{\mathbf{00}}^{(0)}(\mathbf{r}+\mathbf{a})]\\ &\equiv e^{i(I_p-\Delta E)t}\psi_{-}(\mathbf{r})\end{aligned} \tag{23}$$

becomes smaller and smaller until the two states are practically degenerate: $\Delta E\to 0$ for large $|\mathbf{a}|$. These two states are strongly coupled even by a weak external field. However, the presence of the excited state (23) is not accounted for by the SFA in its standard form with the field-free ground state. In order to mend this deficiency, we proceed similarly to Ref. [28].

The exact matrix element for ionization from the molecular ground state $|0(t')\rangle$ at an early time $t'$ before the arrival of the laser pulse to a continuum state $|\mathbf{p}(t)\rangle$ at some time $t$ when the pulse has passed is given by

$$M_{\mathbf{p}}(t,t') = \langle \mathbf{p}(t)|U(t,t')|0(t')\rangle, \tag{24}$$

where $U(t,t')$ denotes the exact time-evolution operator of the full Hamiltonian $H=T+W_{\mathbf{a}}+H_I(t)\equiv H_0+H_I(t)$. We decompose the total state space into the space $\mathcal{H}_b$ of the two low-lying bound states (22) and (23) and the state $\mathcal{H}_c$ of the remaining states, which comprise the higher excited bound states and the continuum; see Ref. [25] for a similar procedure. We denote the corresponding projectors by $P_b$ and $P_c=1-P_b$, respectively. For the matrix element (24) we need the part $P_cU(t,t')P_b\equiv U_{cb}(t,t')$ of the time-evolution operator, which leads from one of the bound states into the continuum.

In order to construct $U_{cb}$ we start from the symbolic solution for the exact time-evolution operator $U(t,t')$,

$$U(t,t') = e^{-itH_0}T\exp\left(-i\int_{t'}^{t}d\tau\,\hat{H}_I(\tau)\right)e^{it'H_0} \tag{25}$$

with

$$\hat{H}_I(t) = e^{itH_0} H_I(t) e^{-itH_0} \tag{26}$$

and $T$ the time-ordering operator. We note that the field-free Hamiltonian $H_0$ transforms states only within the spaces $\mathcal{H}_b$ and $\mathcal{H}_c$. With the notation $P_i A P_j \equiv A_{ij}$ $(i,j=b,c)$ for any operator $A$, we have

$$H_0 = H_{0cc} + H_{0bb}, \quad H_{0bc} = H_{0cb} = 0. \tag{27}$$

Transitions from $\mathcal{H}_b$ to $\mathcal{H}_c$ or vice versa are accomplished by the interaction operator

$$H_I(t) = H_{Ibb}(t) + H_{Icc}(t) + H_{Ibc}(t) + H_{Icb}(t). \tag{28}$$

Owing to the time-ordering prescription in Eq. (25), we can freely commute operators, so that

$$\begin{aligned} U_{cb}(t,t') = e^{-itH_{0cc}} T \Biggl\{ & \left[ T \exp\left( -i \int_{t'}^{t} d\tau \, \hat{H}_{Icc}(\tau) \right) \right] \\ & \times \left[ T \exp\left( -i \int_{t'}^{t} d\tau [\hat{H}_{Icb}(\tau) + \hat{H}_{Ibc}(\tau)] \right) \right] \\ & \times \left[ T \exp\left( -i \int_{t'}^{t} d\tau \, \hat{H}_{Ibb}(\tau) \right) \right] \Biggr\} e^{it' H_{0bb}}. \end{aligned} \tag{29}$$

Next, we keep only terms such that the electron makes the transition from the bound-state space $\mathcal{H}_b$ to the continuum space $\mathcal{H}_c$ at one particular time $\tau$ which, intuitively, corresponds to the instant of ionization. Formally, this comes about by expanding the exponential $\exp\{-i\int_{t'}^{t} d\tau [\hat{H}_{Icb}(\tau) + \hat{H}_{Ibc}(\tau)]\}$ to first order. We neglect terms where the electron temporarily returns to the bound-state space after this first ionization. The result is

$$\begin{aligned} U_{cb}(t,t') = -ie^{-itH_{0cc}} \int_{t'}^{t} d\tau & \left[ T \exp\left( -i \int_{\tau}^{t} d\tau' \hat{H}_{Icc}(\tau') \right) \right] \\ & \times \hat{H}_{Icb}(\tau) \left[ T \exp\left( -i \int_{t'}^{\tau} d\tau'' \hat{H}_{Ibb}(\tau'') \right) \right] e^{it' H_{0bb}} \end{aligned} \tag{30}$$

or

$$U_{cb}(t,t') = -i \int_{t'}^{t} d\tau \tilde{U}_{cc}(t,\tau) P_c H_I(\tau) P_b \tilde{U}_{bb}(\tau,t'), \tag{31}$$

where $\tilde{U}_{bb}(t,t')$ and $\tilde{U}_{cc}(t,t')$ are the exact time-evolution operators restricted to the subspaces $\mathcal{H}_b$ and $\mathcal{H}_c$, respectively, as written down explicitly in Eq. (30).

The initial ground state has the wave function (22). In the limit where $t \to \infty$ and $t' \to -\infty$, the lowest-order term (31) yields

$$M_{\mathbf{p}} = -i \lim_{t\to\infty} \int_{-\infty}^{t} d\tau \langle \mathbf{p}(t) | \tilde{U}_{cc}(t,\tau) P_c H_I(\tau) P_b | 0(\tau) \rangle, \tag{32}$$

where $|0(\tau)\rangle = \lim_{t'\to-\infty} \tilde{U}_{bb}(\tau,t')|0(t')\rangle$ is the state that has developed out of the initial field-free ground state under the action of $H_I$, but restricted to the subspace $\mathcal{H}_b$, that is to say, without "ionization." This state has the wave function

$$\Psi_{\mathbf{a}0}(\mathbf{r},t) = a_+(t) \Psi^{(0)}_{\mathbf{a}0+}(\mathbf{r},t) + a_-(t) \Psi^{(0)}_{\mathbf{a}0-}(\mathbf{r},t), \tag{33}$$

which is determined by the solution of the time-dependent Schrödinger equation restricted to the space of the two bound states. Actually, this is the Jaynes-Cummings model, and its general solution is well known; see, e.g., Ref. [29]. The amplitudes $a_+(t)$ and $a_-(t)$ obey the equations

$$\begin{aligned} i\dot{a}_+(t) &= \mathbf{E}(t) \cdot \mathbf{d}_{+-} a_-(t), \\ i\dot{a}_-(t) &= \mathbf{E}(t) \cdot \mathbf{d}_{-+} a_+(t), \end{aligned} \tag{34}$$

with

$$\mathbf{d}_{\pm\pm} = -\int d^3\mathbf{r} \, \psi_\pm(\mathbf{r})^* e\mathbf{r} \psi_\pm(\mathbf{r}) \tag{35}$$

and the wave functions (22) and (23). For parity eigenstates, we have $\mathbf{d}_{++} = \mathbf{d}_{--} = \mathbf{0}$. Here, we will be satisfied with the degenerate case, as discussed above. Then, in the limit of large $|\mathbf{a}|$, we have $\mathbf{d}_{+-} = \mathbf{d}^*_{-+} = -e\mathbf{a}$. The solution is

$$a_\pm(t) \sim \exp[-ie\mathbf{a} \cdot \mathbf{A}(t)] \pm \exp[ie\mathbf{a} \cdot \mathbf{A}(t)]. \tag{36}$$

For $t \to -\infty$, when the field is absent, this leads to the ground state (22). Hence, the solution satisfies the desired initial condition. With the field on, it yields

$$\Psi_{\mathbf{a}0}(\mathbf{r},t) = e^{iI_p t} N_{\mathbf{a}}^{-1} [e^{-ie\mathbf{a}\cdot\mathbf{A}(t)} \psi^{(0)}_{\mathbf{00}}(\mathbf{r}-\mathbf{a}) + e^{ie\mathbf{a}\cdot\mathbf{A}(t)} \psi^{(0)}_{\mathbf{00}}(\mathbf{r}+\mathbf{a})], \tag{37}$$

which agrees with the ansatz (19).

We now have

$$M_{\mathbf{p}} = -i \lim_{t\to\infty} \int_{-\infty}^{t} d\tau \langle \mathbf{p}(t) | \tilde{U}_{cc}(t,\tau) P_c H_I(\tau) P_b | \Psi_{\mathbf{a}0}(\tau) \rangle. \tag{38}$$

The SFA neglects the binding potential after the electron has been promoted into the continuum. This leads to the amplitude

$$M_{\mathbf{p}} = -i \int_{-\infty}^{\infty} d\tau \langle \psi^{(\mathrm{Vv})}_{\mathbf{p}}(\tau) | P_c H_I(\tau) | \Psi_{\mathbf{a}0}(\tau) \rangle \tag{39}$$

with the Volkov state (11). Owing to the presence of the projectors, we may replace in the amplitude (39)

$$\begin{aligned} & P_c H_I(\tau) | \Psi_{\mathbf{a}0}(\tau) \rangle \\ & \quad \to P_c e^{iI_p t} N_{\mathbf{a}}^{-1} \{ e^{-ie\mathbf{a}\cdot\mathbf{A}(\tau)} [-e(\mathbf{r}-\mathbf{a}) \cdot \mathbf{E}(\tau)] \\ & \qquad \times \psi^{(0)}_{\mathbf{00}}(\mathbf{r}-\mathbf{a}) + e^{ie\mathbf{a}\cdot\mathbf{A}(\tau)} [-e(\mathbf{r}+\mathbf{a}) \cdot \mathbf{E}(\tau)] \\ & \qquad \times \psi^{(0)}_{\mathbf{00}}(\mathbf{r}+\mathbf{a}) \}. \end{aligned} \tag{40}$$

Shifting the origins of the spatial integrations leads to

$$M_{\mathbf{p}} = -i \int_{-\infty}^{\infty} d\tau \langle \psi^{(\mathrm{Vv})}_{\mathbf{p}}(\tau) | P_c H_I(\tau) | \psi_{\mathbf{0}0}(t) \rangle N_{\mathbf{a}}^{-1} (e^{-i\mathbf{p}\cdot\mathbf{a}} + e^{i\mathbf{p}\cdot\mathbf{a}}). \tag{41}$$

Here, we may again replace $H_I(\tau)$ by $V_0(\mathbf{r})$. Hence, this result agrees with Eq. (20) if we now drop the projector $P_c$.

We should add a word of caution. In the derivation above, we have several times exploited the orthogonality between the field-free continuum states and the bound states. However, the SFA, by introducing the Volkov states, violates this orthogonality. This is not a problem as long as we keep the projector $P_c$. Depending upon at which stage of the derivation the projector is dropped, different final results may be obtained. Therefore, more important than its derivation is that the final result incorporate the desired physics and pass consistency checks.

In velocity gauge, the coupling between the states (22) and (23) is accomplished by the matrix elements of $\hat{\mathbf{p}}=-i\boldsymbol{\nabla}$. Since $\hat{\mathbf{p}}=im[H_0,\mathbf{r}]$, all those matrix elements vanish in the limit of degenerate states. Hence, there is no coupling, the initial state does not have to be dressed, and the velocity-gauge SFA with the field-free ground state is all right from this point of view. Above, we arrived at the same conclusion starting from the fact that the scalar potential is zero in velocity gauge.

## V. CONCLUSIONS

For large internuclear separation, the standard length-gauge SFA no longer provides a satisfactory approximation. In contrast, the length-gauge dressed-state SFA passes all consistency checks that we investigated above, but so does the standard velocity-gauge SFA. However, we know from studies of the detachment of negative ions that the standard velocity gauge fails for odd-parity ground states, in that it predicts the interference minima and maxima in the wrong positions [14]. Similar contradictions to the solution of the TDSE can be expected here, as soon as the building-block field-free atomic orbitals $\psi_{00}^{(0)}(\mathbf{r},t)$ have odd parity. Hence, only the length-gauge DSSFA is compatible with all requirements that we are aware of. This conclusion is supported if the internuclear separation is large enough for the cross terms between the potential of one center and the wave function concentrated about the other center to be negligible. This case covers, for example, rare-gas molecules at equilibrium internuclear distance and molecular ions such as $H_2^+$ near the turning points of higher vibrational states. For the case of small and intermediate internuclear separation $2\mathbf{a}$, we cannot draw any conclusion. We expect the length-gauge DSSFA also to be applicable for more complicated molecules (multicenter problems) provided all centers are well separated.

## ACKNOWLEDGMENTS

We enjoyed discussions with S. P. Goreslavski, M. Yu. Ivanov, M. Klaiber, and H. Rottke. We gratefully appreciate the hospitality of the Kavli Institute for Theoretical Physics. This research was supported in part by the National Science Foundation under Grant No. PHY99-07949, by the VolkswagenStiftung, by the Ministry of Education and Science, Canton Sarajevo, by the Federal Ministry of Education and Science, Bosnia and Herzegovina, and by the National Natural Science Foundation of China under Grant No. 10574019 and 973 Research Project No. 2006CB806000.

---

[1] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1945 (1964) [Sov. Phys. JETP **20**, 1307 (1965)]; F. H. M. Faisal, J. Phys. B **6**, L89 (1973); H. R. Reiss, Phys. Rev. A **22**, 1786 (1980).
[2] For a review, see, e.g., W. Becker, F. Grasbon, R. Kopold, D. B. Milošević, G. G. Paulus, and H. Walther, Adv. At., Mol., Opt. Phys. **48**, 35 (2002).
[3] For a review, see, e.g., D. B. Milošević, G. G. Paulus, D. Bauer, and W. Becker, J. Phys. B **39**, R203 (2006).
[4] A. Becker, L. Plaja, P. Moreno, M. Nurhuda, and F. H. M. Faisal, Phys. Rev. A **64**, 023408 (2001).
[5] Y. V. Vanne and A. Saenz, Phys. Rev. A **75**, 063403 (2007).
[6] M. Wickenhauser, X. M. Tong, D. G. Arbó, J. Burgdörfer, and C. D. Lin, Phys. Rev. A **74**, 041402(R) (2006).
[7] A. Lohr, M. Kleber, R. Kopold, and W. Becker, Phys. Rev. A **55**, R4003 (1997).
[8] D. B. Milošević and F. Ehlotzky, Phys. Rev. A **58**, 3124 (1998).
[9] D. B. Milošević, D. Bauer, and W. Becker, J. Mod. Opt. **53**, 125 (2006); D. Bauer, D. B. Milošević, and W. Becker, *ibid.* **53**, 135 (2006).
[10] G. F. Gribakin and M. Yu. Kuchiev, Phys. Rev. A **55**, 3760 (1997).
[11] D. B. Milošević, A. Gazibegović-Busuladžić, and W. Becker, Phys. Rev. A **68**, 050702(R) (2003); A. Gazibegović-Busuladžić, D. B. Milošević, and W. Becker, *ibid.* **70**, 053403 (2004).
[12] M. V. Frolov, N. L. Manakov, E. A. Pronin, and A. F. Starace, Phys. Rev. Lett. **91**, 053003 (2003).
[13] S. Beiser, M. Klaiber, and I. Yu. Kiyan, Phys. Rev. A **70**, 011402(R) (2004).
[14] D. Bauer, D. B. Milošević, and W. Becker, Phys. Rev. A **72**, 023415 (2005).
[15] M. Klaiber, K. Z. Hatsagortsyan, and C. H. Keitel, Phys. Rev. A **73**, 053411 (2006).
[16] For reviews, see A. D. Bandrauk, *Molecules in Laser Fields* (Dekker, New York, 1994); J. H. Posthumus, Rep. Prog. Phys. **67**, 623 (2004); H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2005).
[17] H. Z. Lu and A. D. Bandrauk, J. Chem. Phys. **115**, 1670 (2001); B. Pons, Phys. Rev. A **67**, 040702(R) (2003); Y. V. Vanne and A. Saenz, J. Phys. B **37**, 4101 (2004); X. Chu and S.-I Chu, Phys. Rev. A **70**, 061402(R) (2004); D. Dundas and J. M. Rost, *ibid.* **71**, 013421 (2005); G. Lagmago Kamta and A. D. Bandrauk, *ibid.* **71**, 053407 (2005).
[18] J. Muth-Böhm, A. Becker, and F. H. M. Faisal, Phys. Rev. Lett. **85**, 2280 (2000).
[19] Z. X. Zhao, X. M. Tong, and C. D. Lin, Phys. Rev. A **67**, 043404 (2003); K. Mishima, K. Nagaya, M. Hayashi, and S. H. Lin, *ibid.* **70**, 063414 (2004).
[20] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. Lett. **95**, 073004 (2005); V. I. Usachenko and S.-I Chu, Phys. Rev. A **71**, 063410 (2005); V. I. Usachenko, P. E. Pyak, and S.-I Chu,

Laser Phys. **16**, 1326 (2006).
[21] C. C. Chirilă and M. Lein, Phys. Rev. A **73**, 023410 (2006).
[22] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A **73**, 047401 (2006); **73**, 059903(E) (2006); V. I. Usachenko, *ibid.* **73**, 047402 (2006).
[23] D. B. Milošević, Phys. Rev. A **74**, 063404 (2006).
[24] H. R. Reiss, Prog. Quantum Electron. **16**, 1 (1992).
[25] O. Smirnova, M. Spanner, and M. Ivanov, J. Phys. B **39**, S307 (2006).
[26] M. Lein, N. Hay, R. Velotta, J. P. Marangos, and P. L. Knight, Phys. Rev. Lett. **88**, 183903 (2002).
[27] R. Kopold, W. Becker, and M. Kleber, Phys. Rev. A **58**, 4022 (1998).
[28] Y. Chen, J. Chen, and J. Liu, Phys. Rev. A **74**, 063405 (2006).
[29] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Dover, New York, 1987).