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Ionization of Atoms and Molecules by Short Strong Laser Pulses

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Abstract

We consider a molecule (including a many electron atom or an ion as particular cases) under the influence of a short, strong laser pulse within the theoretical context of a Stark Hamiltonian. We prove an upper bound on the ionization probability involving the electric field only through the pulse duration τ and its total energy. In particular for fixed energy this bound tends to zero with $\tau \rightarrow 0$. This result extends a previous result for Rydberg atoms obtained by the authors.

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1 Introduction

The ionization of Rydberg atoms with ultrashort laser pulses (i.e. the duration of the pulse is of the order or shorter than the corresponding classical Kepler period of the electron in the atom) has received increasing experimental (Jones *et al* 1993, 1995, Tielking *et al* 1995) and theoretical (Reinhold and Burgdörfer 1993, Reinhold *et al* 1993a,b, 1994, Enss *et al* 1994, Schwieters and Delos 1995a,b, Bugacov *et al* 1995a,b) interest. Recently the authors rigorously proved an upper bound for the ionization probability of Rydberg atoms under the influence of ultrashort laser pulses (Kostykin and Schrader 1995). The aim of the present paper is to extend our previous result to arbitrary molecules (atoms and ions as particular cases).

We use the Stark Hamiltonian as a basis of our theoretical discussion. This means that we describe the laser pulse by a classical time-dependent electric field $E(t)$. In particular we neglect possible effects due to the presence of a magnetic field and due to the spin of the nuclei. Also we neglect relativistic effects which would make a quantum field theoretic discussion necessary. Therefore our results should be mostly applicable to bound states of low-electrons atoms and molecules.

We assume $E(t)$ to be continuous and supported on the interval $[0, \tau]$ such that τ is the pulse duration. Our bound on the ionization probability will be given in terms of the norm

$$\|E\| = \left(\int_0^\tau E^2(t) dt \right)^{1/2} \quad (1)$$

and τ . Note that $\|E\|^2$ essentially measures the total energy carried by the pulse $E(t)$. Our main result is stated below as a theorem. In particular, it shows suppression of ionization for pulses with decreasing τ and bounded $\|E\|$. Its proof is based on the Kramers-Henneberger relation (Kramers 1956, Henneberger 1968) in its general form (Cycon *et al* 1987). We note that earlier the Kramers-Henneberger relation was utilized by Korotyaev (1980) for an analysis of three-particle quantum systems in a periodic electric field.

It is important to realize that the limit $\tau \rightarrow 0$ does not correspond to the high frequency limit $\omega \rightarrow \infty$ for photoionization for which the cross section is known to fall off. These limits are different in both the perturbative and in the strong field regimes. As $\tau \rightarrow 0$ the spectral distribution $D(\omega)$ of the pulse becomes, indeed, very broad with $\omega_{max} \approx 2\pi\tau$. The ionization probability is, however, determined by the low frequency components of this distribution. An illustrative example is provided by the δ -shaped pulse $\delta(t)$

(see Enss *et al* 1994) with pulse length zero. Its spectrum is constant. Even though $\omega_{max} \rightarrow \infty$ in this case, the ionization cross section remains finite for $\tau \rightarrow 0$.

It is instructive to compare our method with arguments involving generalized time-energy uncertainty relations as given by Pfeifer (1993) and Pfeifer and Fröhlich (1994). We compare both results in the last part of the present work.

2 Ionization of Molecules

Let the molecule (atom or ion as particular cases) consists of N nuclei with charges eQ_i ($1 \leq i \leq N$, $Q_i > 0$ integer) and masses $M_i > 0$, and N' electrons with charges $-e$ and whose mass is denoted by m . In particular, for electrically neutral system $N' = \sum_{i=1}^N Q_i$. Let $\mathbf{x} = (x_1, \dots, x_N) \in \mathbf{R}^{3N}$ be the coordinates of the nuclei and $\mathbf{x}' = (x'_1, \dots, x'_{N'}) \in \mathbf{R}^{3N'}$ those of the electrons. In units where $\hbar = e = 1$ the Stark Hamiltonian is given by

$$H(t) = H_0 + V + ZE(t), \tag{2}$$

where

$$Z = -\sum_{j=1}^{N'} z'_j + \sum_{i=1}^N z_i Q_i. \quad (3)$$

Here z'_j and z_i are the third components of x'_j and x_i respectively. Also,

$$H_0 = -\sum_{i=1}^N \frac{1}{2M_i} \Delta_i - \frac{1}{2m} \sum_{j=1}^{N'} \Delta'_j, \quad (4)$$

where Δ_i (Δ'_j) is the Laplacian with respect to the variable x_i (x'_j). The potential V is supposed to be Coulombic, i.e. of the form

$$\begin{aligned} V(\mathbf{x}, \mathbf{x}') = & \sum_{i < i', 1 \leq i \leq N, 1 \leq i' \leq N'} \frac{Q_i Q_{i'}}{|x_i - x_{i'}|} \\ & - \sum_{1 \leq i \leq N, 1 \leq j \leq N'} \frac{Q_i}{|x_i - x'_j|} + \sum_{j < j', 1 \leq j \leq N, 1 \leq j' \leq N'} \frac{1}{|x'_j - x'_{j'}|}. \end{aligned} \quad (5)$$

Other forms of the potential may also be considered (see e.g. Kostykin and Schrader 1995). Also we set

$$H = H_0 + V. \quad (6)$$

With $M = mN' + \sum_{i=1}^N M_i$ being the total mass of the molecule, the coordinate of the center of mass is given by

$$R = \frac{1}{M} \left(\sum_{i=1}^N M_i x_i + m \sum_{j=1}^{N'} x'_j \right) \in \mathbf{R}^3. \quad (7)$$

Then

$$H_{0,cm} = H_0 + \frac{1}{2M} \Delta_R \quad (8)$$

is the kinetic energy operator in the center of mass frame. Here we have denoted by Δ_R the Laplace operator with respect to the center of mass coordinate R . We set

$$H_{cm} = H + \frac{1}{2M} \Delta_R = H_{0,cm} + V, \quad (9)$$

and

$$H_{cm}(t) = H(t) + \frac{1}{2M} \Delta_R - R_z Q E(t),$$

with R_z being the z -component of R given by (7) and

$$Q = \sum_{i=1}^N Q_i - N'$$

is the total electric charge of the molecule.

These operators are supposed to act in the Hilbert space $\mathcal{H} \subset L^2(\mathbf{R}^{3(N+N')})$ of all square integrable functions $\Psi(\mathbf{x}, \mathbf{x}')$ which are antisymmetric in the electron variables $(x'_1, \dots, x'_{N'})$. Let $\mathcal{H}_{cm} \subset L^2(\mathbf{R}^{3(N+N'-1)})$ be the Hilbert space of square integrable functions in relative coordinates, antisymmetric with respect to permutations of the electrons ($j \leftrightarrow j'$). Our discussion below would also apply to a situation where some of the nuclei had to be treated

as identical particles (bosons or fermions). In what follows we will often identify operators B_{cm} acting in $\mathcal{H}_{cm}$ with the operators $B_{cm} \otimes I$ acting in $\mathcal{H} = \mathcal{H}_{cm} \otimes L^2(\mathbf{R}^3)$. The tensor product $\mathcal{H} = \mathcal{H}_{cm} \otimes L^2(\mathbf{R}^3)$ (Reed and Simon, 1978) generates the natural decomposition of the following operators in $\mathcal{H}$:

$$\begin{aligned} H_0 &= H_{0,cm} \otimes I + I \otimes \left(-\frac{1}{2M} \Delta_R \right), \\ H &= H_{cm} \otimes I + I \otimes \left(-\frac{1}{2M} \Delta_R \right), \\ H(t) &= H_{cm}(t) \otimes I + I \otimes \left(-\frac{1}{2M} \Delta_R + R_z Q E(t) \right). \end{aligned}$$

It is well known (see e.g. Reed and Simon 1975) that H , $H(t)$, H_{cm} , and $H_{cm}(t)$ define self-adjoint operators. By definition a bound state in the present context is an eigenstate of H_{cm} with eigenvalue $\lambda < 0$. Let P be the orthogonal projector on the subspace of $\mathcal{H}_{cm}$ spanned by the bound state eigenfunctions. If S denotes the scattering operator for the pair $(H(t), H)$, then its restriction S_{cm} to $\mathcal{H}_{cm}$ is the scattering operator for the pair $(H_{cm}(t), H_{cm})$ (see below). The ionization probability for a normalized bound state $\Psi \in \mathcal{H}_{cm}$ is defined as

$$I(\Psi) = \|(1 - P)S_{cm}\Psi\|^2 = 1 - \|PS_{cm}\Psi\|^2.$$

The main result of the present paper is given by:

Theorem: The ionization probability $I(\Psi)$ for the Stark Hamiltonian (2) satisfies an upper bound of the form

$$I(\Psi) \leq \left[(C\tau + 4\tau^{3/2}\|E\|) \cdot \|(H_{0,cm} + 1)\Psi\| + \tau^{1/2}\|E\| \cdot \|(Z - QR_z)\Psi\| \right]^2, \quad (10)$$

where Z is given by (3) and the constant C only depends on the charges and masses of the particles involved.

Note that since $Z - QR_z$ can be represented as a linear combination of relative coordinates, the finiteness of $\|(Z - QR_z)\Psi\|$ for bound states Ψ is guaranteed by the O'Connor-Combes-Thomas theorem (Reed and Simon 1979).

We turn to a proof of the theorem which is an adoption of the arguments used by Kostykin and Schrader (1995). Let $U(t, t')$ describe the unitary time evolution for the Hamiltonian $H(t)$, i.e. $U(t, t')$ satisfies

$$i\partial_t U(t, t') = H(t)U(t, t'), \quad U(t, t')U(t', t'') = U(t, t''), \quad U(t, t) = 1. \quad (11)$$

The existence of $U(t, t')$ can be established by the arguments similar to

(Kostykin and Schrader 1995). Since $\text{supp} E(\cdot) \in [0, \tau]$, we obviously have

$$U(t, t') = \exp\{-i(t - \tau)H\}U(\tau, 0)\exp\{it'H\} \quad (12)$$

for $t > \tau_0$, $t' < 0$. In analogy with the scattering theory for time independent Hamiltonians, one may define the scattering matrix between the time evolutions with $H(t)$ and H as the weak limit

$$S = \text{w-lim}_{t \rightarrow \infty, t' \rightarrow -\infty} \exp\{itH\}U(t, t')\exp\{-it'H\}$$

which by (12) for the present situation takes the form

$$S = \exp\{i\tau H\}U(\tau, 0). \quad (13)$$

In particular S is unitary.

Let $U_{cm}(t, t')$ be the analogous time evolution operator for $H_{cm}(t)$. Since

$$A(t) = -\frac{1}{2M}\Delta_R + R_z Q E(t)$$

commutes with $H_{cm}(t)$ it is easy to see that

$$U(t, t') = U_{cm}(t, t') \otimes W(t, t'), \quad (14)$$

where $W(t, t')$ is the evolution operator for $A(t)$. Therefore we have

$$S_{cm} = \exp\{i\tau H_{cm}\}U_{cm}(\tau, 0). \quad (15)$$

and

$$S = S_{cm} \otimes \exp \left\{ -\frac{i\tau}{2M} \Delta_R \right\} W(\tau, 0). \quad (16)$$

Note that the second factor describes the S -matrix for the center of mass motion which is nontrivial if $Q \neq 0$.

Next we invoke the unitary Kramers-Henneberger transformation (Kramers 1956, Henneberger 1968, Cycon *et al* 1987) given as

$$T(t) = \exp\{-ia(t)\Omega\} \exp\{-ib(t)Z\} \exp\{-ic(t)P_z\}, \quad t > 0, \quad (17)$$

where the $E(\cdot)$ - dependent quantities $a(t)$, $b(t)$ and $c(t)$ are given by

$$b(t) = \int_0^t E(s) ds, \quad (18)$$

$$c(t) = -2 \int_0^t b(s) ds, \quad (19)$$

$$a(t) = \int_0^t b(s)^2 ds. \quad (20)$$

Note that $a(t)$, $b(t)$, and $c(t)$ are continuously differentiable in t . The multiplication operator Z is defined above by (3) and P_z can be expressed through the canonically conjugated momenta $p'_{zj} = -i\partial/\partial z'_j$ and $p_{zi} = -i\partial/\partial z_i$,

$$P_z = \sum_{j=1}^{N'} \frac{p'_{zj}}{m_j} - \sum_{i=1}^N \frac{Q_i}{M_i} p_{zi}.$$

The number Ω is given by

$$\Omega = \sum_{j=1}^{N'} \frac{1}{m_j} + \sum_{i=1}^N \frac{Q_i^2}{M_i}.$$

Direct calculations show that the operator (17) can be represented in the form

$$T(t) = T_{cm}(t) \otimes W(t, 0) \exp \left\{ \frac{it}{2M} \Delta_R \right\},$$

where

$$T_{cm}(t) = T(t)W(t, 0)^{-1} \exp \left\{ - \frac{it}{2M} \Delta_R \right\}.$$

In a next step we introduce the time-dependent vectors $\mathbf{x}(t) = (x_1(t), \dots, x_N(t))$ and $\mathbf{x}'(t) = (x'_1(t), \dots, x'_{N'}(t))$ with

$$x_i(t) = x_i + Q_i c(t) e_z, \quad 1 \leq i \leq N, \quad (21)$$

and

$$x'_j(t) = x'_j - c(t) e_z, \quad 1 \leq j \leq N', \quad (22)$$

where e_z is the unit vector in the z -direction. Let $V(t)$ be the multiplication operator on $\mathcal{H}$ given as

$$V(t)(\mathbf{x}, \mathbf{x}') = V(\mathbf{x}(t), \mathbf{x}'(t)). \quad (23)$$

This defines a time dependent Hamiltonian in $\mathcal{H}$

$$H_1(t) = H_0 + V(t). \quad (24)$$

In analogy with (11) let $U_1(t, t')$ denote the resulting unitary time evolution. By means of direct inspection one can see that formally the generalized

Kramers-Henneberger relation

$$U(t, t') = T(t)U_1(t, t')T(t')^{-1} \quad (25)$$

holds for any t . The necessary domain consideration for the one particle Hamiltonian can be found in (Kostykin and Schrader 1995).

In particular the S-matrix now takes the form

$$S = \exp\{i\tau H\}T(\tau)U_1(\tau, 0). \quad (26)$$

Alternatively, let $U_{1,cm}(t, t')$ describe the unitary time evolution defined by

$$H_{1,cm}(t) = H_1(t) + \frac{1}{2M}\Delta_R, \quad (27)$$

so that

$$H_1(t) = H_{1,cm}(t) \otimes I + I \otimes \left(-\frac{1}{2M}\Delta_R\right).$$

Note that since $V(t)$ defines an operator in $\mathcal{H}_{cm}$, $H_{1,cm}(t)$ also defines an operator in $\mathcal{H}_{cm}$. Since $V(t)$ commutes with Δ_R one also has

$$U_{1,cm}(t, t') = U_1(t, t') \exp\left\{-\frac{i(t-t')}{2M}\Delta_R\right\} = \exp\left\{-\frac{i(t-t')}{2M}\Delta_R\right\}U_1(t, t'). \quad (28)$$

As a consequence of (16) and (26) we get

$$S_{cm} = \exp\{i\tau H_{cm}\}T_{cm}(\tau)U_{1,cm}(\tau, 0).$$

The proof of (10) now uses the same arguments as those used by Kostykin and Schrader (1995) by noting that in the norm sense

$$\|V(t)(H_{0,cm} + 1)^{-1}\| \leq C,$$

and

$$\|P_z \Psi\| \leq C \|(H_{0,cm} + 1)\Psi\|$$

for a suitable constant C depending on the charges and masses of the particles.

3 The Ultrashort Pulse Limit $\tau \rightarrow 0$

To discuss the ultrashort pulse limit $\tau \rightarrow 0$ we consider as an example the Rydberg atom (see Kostykin and Schrader 1995). We recall that the corresponding upper bound on the ionization probability of the bound state Ψ reads

$$\begin{aligned} I(\Psi) &\leq \left\{ C|\tau| \|(H_{0,cm} + 1)\Psi\| + \|z\Psi\| \left| \int_0^\tau E(t)dt \right| \right. \\ &\quad \left. + 2 \left| \int_0^\tau (\tau - t)E(t)dt \right| \|p_z \Psi\| \right\}^2 \\ &\leq \left[(C\tau + 4\tau^{3/2}\|E\|) \|(H_{0,cm} + 1)\Psi\| + \tau^{1/2}\|E\| \|z\Psi\| \right]^2, \end{aligned} \quad (29)$$

with $H_{0,cm} = -\Delta$. The physical meaning of this bound can be easily illustrated in the ultrashort pulse limit $\tau \rightarrow 0$ (Burgdörfer 1994). In this limit the first inequality in Eq.(29) becomes to leading order in τ ,

$$I(\Psi) \leq \|z\Psi\|^2 \left(\int_0^\tau |E(t)| dt \right)^2. \quad (30)$$

The implication of Eq.(30) is that the total electromagnetic energy delivered by the pulse to the atom during the period τ provides an upper bound for the ionization probability. The latter can be easily illustrated using perturbation theory but, due to correspondence identities, it holds also in the strong field limit. Indeed, first order perturbation theory gives

$$I(\Psi) = \left| \int_0^\tau E(t) dt \right|^2 \sum_{n_c} |(n_c, z\Psi)|^2, \quad (31)$$

where n_c stand for complete set of positive energy states. The first factor corresponds to the energy transfer ΔE_0 of the pulse to a free electron

$$\Delta E_0 = \Delta p^2 = \left| \int_0^\tau E(t) dt \right|^2.$$

The second factor describes the strength of the dipole coupling to the continuum. It is bounded by

$$\sum_{n_c} |(n_c, z\Psi)|^2 \leq \|z\Psi\|^2.$$

Thus we obtain precisely the bound (30).

A bound similar to (29) was given by Pfeifer and Fröhlich. It based on a generalized time-energy uncertainty relation (Pfeifer 1993, Pfeifer and Fröhlich 1994). They showed that the survival probability $|(\Psi, \Psi_\tau)|$ of the bound state Ψ , where $\Psi_\tau = U(\tau, 0)\Psi$, can be estimated from below as

$$|(\Psi, \Psi_\tau)| \geq \cos \left\{ \int_0^\tau \Delta(t) dt \right\}, \quad (32)$$

where in the present context

$$\Delta(t) = a_\Psi |E(t)|, \quad a_\Psi = \left| \|z\Psi\|^2 - (\Psi, z\Psi)^2 \right|^{1/2}.$$

In the ultrashort pulse limit $\tau \rightarrow 0$ the estimate (32) leads to the following bound for the ionization probability

$$I(\Psi) \leq 1 - |(\Psi, \Psi_\tau)|^2 \leq a_\Psi^2 \left(\int_0^\tau |E(t)| dt \right)^2.$$

For potentials, which are invariant with respect to the reflection $z \rightarrow -z$, we have $(\Psi, z\Psi) = 0$. In this case the last estimate coincides precisely with (30).

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