Ionization of Rydberg atoms by an electric-field kick

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We provide a rigorous lower bound for the ionization probability of a Rydberg atom under the perturbation by a time-dependent electric field in the form of an ultrashort pulse idealized as a Dirac δ function. This estimate is of the form $1 - O(F_0^{-4})$ for large values of the electric field F_0. For the hydrogen atom we also prove the scaling behavior $F_0 \sim n^{-1}$, predicted recently by Reinhold *et al.* [Phys. Rev. Lett. **70**, 4026 (1993); J. Phys. B **26**, L659 (1993)], for the electric field required to ionize a given percentage of states with principal quantum number n.

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Recently the ionization of Rydberg states of an atom with "half-cycle" laser pulses (i.e., the duration of the pulse is of the order or shorter than the classical orbital period of the electron in the atom) has been studied experimentally [1]. In this case the atom may be considered to be subject to a strong homogeneous electric field confined to a very short time interval. This suggests looking at the time-dependent Stark effect in the idealized case where the time dependence is given by the Dirac δ function. Therefore we will call it the Stark kick. The Stark kick was also used in [2] as a model of ionization in fast ion-atom collisions.

More precisely we analyze the quantum Hamiltonian of the form

$$H(t) = H_0 + V + F_0\, z\, \delta(t) = H + F_0\, z\, \delta(t),\ F_0 > 0, \quad (1)$$

with $H_0 = -\Delta$ being the operator of the kinetic energy on the Hilbert space $L^2(\mathbf{R}^3)$. Thus we work in dimensionless units where $e = \hbar = 2m = 1$. The potential V is supposed to be Kato small (see, e.g., Ref. [3]), i.e., there are $a < 1$ and $b < \infty$ such that for all Ψ in the domain $\mathcal{D}(H_0)$ of H_0

$$\|V\,\Psi\| \le a\|H_0\,\Psi\| + b\|\Psi\|. \quad (2)$$

In particular, the potentials of atoms or molecules arising from Coulomb pair potentials belong to this wide class.

Although analytic expressions for the ionization probabilities under the Stark kick are known [2,4], they are too cumbersome to provide reliable qualitative information about the dependence of these probabilities on the field strength F_0. One aim of the present paper is to prove rigorously a simple and efficient lower bound for the ionization probability in the case of large and of small F_0. In fact, we show below (Theorem 1) that the ionization probability goes like $1 - O(F_0^{-4})$ for large F_0. Furthermore, if we specialize to the Coulomb potential $V = -1/|\mathbf{x}|$, then we obtain a rigorous scaling estimate of F_0 for the ionization of the state Ψ_{nlm} of the form $F_0 \sim n^{-1}$ when $n \to \infty$ (Theorem 2), in agreement with the prediction given by Reinhold *et al.* [5] for ultrashort laser pulses. Similar results are obtained for Rydberg atoms under reasonable assumptions on the potential (Corollary).

We now turn to the precise formulation and its proof. Let $U(t,t')$ describe the unitary time evolution for a suitable time dependent Hamiltonian $H(t)$, i.e., $U(t,t')$ satisfies

$$i\partial_t\, U(t,t') = H(t)\, U(t,t'),$$
$$U(t,t')\, U(t',t'') = U(t,t''),$$
$$U(t,t) = I.$$

For the case that $H(t)$ is of the form (1), it is clear that $U(t,t') = \exp\{-i(t-t')H\}$ for $tt' > 0$. By approximation with smooth $H(t)$ and by the Trotter product formula (see, e.g., Ref. [3]) one also obtains

$$U(t,t') = \exp\{-itH\}\, U(F_0)\, \exp\{it'H\} \quad \text{for } t' < 0 < t. \quad (3)$$

Here $U(F_0)$ is the unitary operator given as multiplication operator in the configuration space representation, i.e., $[U(F_0)\,\Psi](\mathbf{x}) = \exp -iF_0 z\, \Psi(\mathbf{x})$. Note that in the momentum space representation $U(F_0)$ is just the translation by $F_0\,\mathbf{e}_z$, i.e., $[U(F_0)\,\hat{\Psi}](\mathbf{p}) = \hat{\Psi}(\mathbf{p} + F_0\,\mathbf{e}_z)$, where $\mathbf{e}_z$ is the unit vector in the z direction and $\hat{\Psi}$ is the Fourier transform of Ψ. Thus the Stark kick causes a shift in momentum which implies high kinetic energy for large F_0. From this follows that the total energy becomes far separated from all eigenvalues of H.

In analogy with the scattering theory for time-independent Hamiltonians, we may define the scattering

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matrix between the time evolutions with and without a Stark kick as the weak limit

$$S = \operatorname*{lim_w}_{\substack{t \to \infty \\ t' \to -\infty}} \exp\{itH\} U(t,t') \exp\{-it'H\},$$

which by (3) for the present situation takes the simple form $S = U(F_0)$. For any normalized bound state Ψ we define its ionization probability $I(\Psi, F_0)$ as

$$I(\Psi, F_0) = \|(1-P)\, S\, \Psi\|^2 = 1 - \|P\, U(F_0)\, \Psi\|^2,$$

where P is the orthogonal projection onto the subspace spanned by the eigenvectors of H. Hamiltonians with Kato bounded potentials (2) are bounded below and if the (pair) potentials decay suitably at infinity, then there are no positive eigenvalues. It has been shown [6,7] for a large class of potentials including atomic and molecular ones that the eigenvalues are contained in $[\inf \sigma(H), 0]$, where $\sigma(H)$ denotes the spectrum of H. Thus we may assume the even weaker hypothesis that all eigenvalues belong to a bounded interval, i.e.,

$$\|PH\| < \infty. \tag{4}$$

Thus any bound state $\Psi = P\Psi$ lies in the domain $\mathcal{D}(H)$ of H, which equals the domain $\mathcal{D}(H_0)$ of H_0 for Kato potentials. Then we write

$$\begin{aligned} P\, U(F_0)\, \Psi = P\,(H+i)\,(H+i)^{-1}\,(H_0+1)\, U(F_0) \\ \times U(F_0)^{-1}\,(H_0+1)^{-1} \\ \times U(F_0)\,(H_0+1)^{-1}\,(H_0+1)\,\Psi. \end{aligned}$$

Furthermore, for Kato potentials $(H+i)^{-1}(H_0+1)$ is bounded and thus with (4)

$$\|P\,(H+i)\,(H+i)^{-1}\,(H_0+1)\| = c_1 < \infty.$$

The operator $\mathcal{R}(F_0) = U(F_0)^{-1}\,(H_0+1)^{-1}\,U(F_0)$ in the momentum-space representation is just the multiplication operator

$$\mathcal{R}(F_0)(\mathbf{p}) = [(p_z - F_0)^2 + p_x^2 + p_y^2 + 1]^{-1}.$$

Hence we have

$$\|P\, U(F_0)\, \Psi\| \le c_1 \sup_{\mathbf{p}}\{\mathcal{R}(F_0)(\mathbf{p})\; (\mathbf{p}^2+1)^{-1}\} \|(H_0+1)\,\Psi\|,$$

where c_1 is independent of F_0 and Ψ. Now an easy estimate shows that

$$\sup_{\mathbf{p}}\{\mathcal{R}(F_0)(\mathbf{p})\; (\mathbf{p}^2+1)^{-1}\} \le \frac{1}{F_0^2}\ .$$

We have proved the following.

Theorem 1. For any Kato potential V which satisfies (4) and for any normalized bound state $\Psi = P\Psi$ the ionization probability $I(\Psi, F_0)$ can be estimated

$$I(\Psi, F_0) \ge 1 - \frac{c_1^2}{F_0^4}\|(H_0+1)\,\Psi\|^2\ . \tag{5}$$

Here c_1 depends on V only.

For some exactly solvable Hamiltonians, such as e.g., a δ potential with one bound state, the decrease $\sim F_0^{-4}$ of the second term in (5) exactly reproduces the asymptotics of $I(\Psi, F_0)$ when $F_0 \to \infty$. This observation indicates that the estimate (5) should be optimal.

Although the physical interpretation of the ionization is for bound states Ψ only, we have actually proved $\|P\, U(F_0)\, \Psi\| \to 0$ as $F_0 \to \infty$ for any $\Psi \in \mathcal{D}(H)$ and any P with $\|PH\| < \infty$. For the strong limit therefore one has

$$\operatorname*{lim_s}_{F_0 \to \infty} \; P\, U(F_0) = 0.$$

Furthermore, Theorem 1 remains valid if we replace P by the projection onto a subspace where H is bounded from above, say by E_0. Then (5), with the constant c_1 now depending on E_0 and V, gives the ionization probability with the outgoing electron having energy larger than E_0.

Let now $V = -1/|\mathbf{x}|$. We will choose $\Psi = \Psi_{nlm}$, i.e., Ψ is a normalized eigenstate of H with eigenvalue $E_n = -1/4n^2$. Here n is the principal quantum number, l the total angular momentum, and m the magnetic quantum number. We are interested in the scaling relation between F_0 and n (for arbitrary l and m) for ionization of the state Ψ_{nlm} with given probability I_0. We will use the virial theorem (see, e.g., Refs. [7,8]), which reads here for normalized eigenvectors

$$\langle \Psi_{nlm} | H_0 | \Psi_{nlm} \rangle = -E_n = 1/4n^2. \tag{6}$$

Let for the moment $c > 0$ be arbitrary. Then

$$\begin{aligned} P\, U(F_0)\, \Psi_{nlm} &= P\,(H-c)^{-1}\, U(F_0) \\ &\quad \times U(F_0)^{-1}\,(H-c)\, U(F_0)\, \Psi_{nlm} \\ &= P\,(H-c)^{-1}\, U(F_0)\,[H(F_0) - c]\,\Psi_{nlm}, \end{aligned}$$

where $H(F_0) = H + 2p_z F_0 + F_0^2$. Thus with $PH \le 0$

$$\|P\, U(F_0)\, \Psi_{nlm}\| \le \frac{1}{c}\|(E_n + F_0^2 - c + 2p_z F_0)\,\Psi_{nlm}\|.$$

Now choose $c = E_n + F_0^2$. In particular this means that we restrict ourselves to those values of the field which satisfy $F_0^2 > -E_n$. In the context of classical mechanics this means that the field is strong enough to ionize the particle with energy E_n. Then

$$\begin{aligned} \|P\, U(F_0)\, \Psi_{nlm}\| &\le \frac{2F_0}{c}\|p_z\, \Psi_{nlm}\| \\ &= \frac{2F_0}{c}\langle \Psi_{nlm} | p_z^2 | \Psi_{nlm} \rangle^{1/2} \\ &\le \frac{2F_0}{c}\langle \Psi_{nlm} | H_0 | \Psi_{nlm} \rangle^{1/2} \\ &= \frac{2F_0}{c}(-E_n)^{1/2}. \end{aligned} \tag{7}$$

Choose $F_0 = \kappa\sqrt{-E_n}$, $\kappa > 1$ such that $c = E_n + F_0^2 = (\kappa^2 - 1)(-E_n)$. Then $\|P\, U(F_0)\, \Psi_{nlm}\| \le 2\kappa/(\kappa^2 - 1)$.

This can be made arbitrarily small for κ sufficiently large. We have proved the first part of the following.

Theorem 2. Let $H = H_0 - 1/|\mathbf{x}|$. For any given $0 < I_0 < 1$ there is a sufficiently large $\kappa(I_0)$ such that $I[\Psi_{nlm}, F_0 = \kappa(I_0)\sqrt{-E_n}] \geq I_0$ for all n, l, m. Conversely, for any $\epsilon > 0$ there is sufficiently small $\kappa(\epsilon) > 0$ such that $I[\Psi_{nlm}, F_0 = \kappa(\epsilon)\sqrt{-E_n}] \leq \epsilon$ for all n, l, m. In particular, for a prescribed ionization probability I_0, one has the scaling law $F_0 \sim n^{-1}$ for large n.

It remains to prove the second part of the theorem. For arbitrary $d > 0$ we can write

$$(1-P)\,U(F_0)\,\Psi_{nlm} = (1-P)\,(H+d)^{-1}\,U(F_0)\,U(F_0)^{-1}\,(H+d)\,U(F_0)\,\Psi_{nlm}$$
$$= (1-P)\,(H+d)^{-1}\,U(F_0)\,[H(F_0)+d]\,\Psi_{nlm}.$$

Thus with $(1-P)H \geq 0$

$$\|(1-P)\,U(F_0)\,\Psi_{nlm}\| \leq \frac{1}{d}\|(E_n + F_0^2 + d + 2p_z F_0)\,\Psi_{nlm}\|.$$

We choose $d = -F_0^2 - E_n$ such that $F_0^2 < -E_n$, i.e., we now restrict ourselves to fields below the classical ionization threshold. Then in analogy with (7) we obtain

$$\|(1-P)\,U(F_0)\,\Psi_{nlm}\| \leq \frac{2F_0}{d}(-E_n)^{1/2}.$$

With $F_0 = \kappa\sqrt{-E_n}$, $0 < \kappa < 1$ we get $d = -E_n(1-\kappa^2)$. Then $\|(1-P)\,U(F_0)\,\Psi_{nlm}\| \leq 2\kappa/(1-\kappa^2)$, which can be made arbitrarily close to zero by making κ sufficiently small. This completes the proof of the theorem.

For Rydberg atoms the effective potential of the outer electron has a dominant Coulomb tail with corrections of faster decay

$$V(\mathbf{x}) = -\frac{q}{|\mathbf{x}|} + \tilde{V}(\mathbf{x}), \quad |\mathbf{x}||\tilde{V}(\mathbf{x})| \to 0 \quad \text{as } |\mathbf{x}| \to \infty,\ q > 0. \tag{8}$$

Now the virial theorem (see, e.g., Ref. [7]) reads that for any eigenfunction Ψ_j, $j = 0, 1, \ldots$,

$$2\langle\Psi_j|H_0|\Psi_j\rangle = 2\langle\Psi_j|(E-V)|\Psi_j\rangle = \langle\Psi_j|\mathbf{x}\cdot\nabla V(\mathbf{x})|\Psi_j\rangle. \tag{9}$$

The expression on the right-hand side is

$$\mathbf{x}\cdot\nabla V(\mathbf{x}) = \frac{q}{|\mathbf{x}|} + \mathbf{x}\cdot\nabla\tilde{V}(\mathbf{x}) = -\rho V(\mathbf{x}) + W_\rho(\mathbf{x}),$$

where for some parameter $\rho > 1$

$$W_\rho(\mathbf{x}) := (1-\rho)\frac{q}{|\mathbf{x}|} + \rho\tilde{V}(\mathbf{x}) + \mathbf{x}\cdot\nabla\tilde{V}(\mathbf{x}). \tag{10}$$

If $\mathbf{x}\cdot\nabla\tilde{V}(\mathbf{x})$ decays faster than $|\mathbf{x}|^{-1}$, as well, then $W_\rho(\mathbf{x}) \leq 0$ for $|\mathbf{x}|$ larger than some $R(\rho)$. Since highly excited states are localized far out it is natural to assume for eigenvectors Ψ_j with $H\Psi_j = E_j\Psi_j$ that

$$\langle\Psi_j|W_\rho|\Psi_j\rangle \leq 0 \tag{11}$$

for j larger than some $j_\rho \geq 0$. Then from the virial theorem (9) we get instead of (6) the inequality

$$\langle\Psi_j|H_0|\Psi_j\rangle = \frac{\rho}{2-\rho}(-E_j) + \frac{1}{2-\rho}\langle\Psi_j|W_\rho|\Psi_j\rangle \leq \frac{\rho}{2-\rho}(-E_j).$$

The estimate (7) now changes to

$$\|PU(F_0)\Psi_j\| \leq \frac{F_0}{c}\frac{2\rho}{2-\rho}(-E_j)^{1/2}$$

and the conclusions of Theorem 2 remain true.

Corollary. Let $H = H_0 + V$ satisfy (8), (10), and (11) for some $1 < \rho < 2$. For any given $0 < I_0 < 1$ there are sufficiently large $\kappa(I_0)$ and j_ρ such that $I[\Psi_j, F_0 = \kappa(I_0)\sqrt{-E_j}] \geq I_0$ for all $j \geq j_\rho$. Conversely, for any $\epsilon > 0$ there is a sufficiently small $\kappa(\epsilon) > 0$ such that $I[\Psi_j, F_0 = \kappa(\epsilon)\sqrt{-E_j}] < \epsilon$ for all $j \geq j_\rho$.

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