Wannier threshold law for two electron escape in the presence of an external electric field

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(received ; accepted )

PACS. 34.80.Dp – Atomic excitation and ionization by electron impact.
PACS. 32.60.+i – Zeeman and Stark effects.

Abstract. – We consider double ionization of atoms or ions by electron impact in the presence of a static electric field. As in Wannier’s analysis of the analogous situation without external field the dynamics near threshold is dominated by a saddle. With a field the saddle lies in a subspace of symmetrically escaping electrons. Near threshold the classical cross section scales with excess energy $E$ like $\sigma \sim E^\alpha$, where the exponent $\alpha$ can be determined from the stability of the saddle and does not depend on the field strength. For example, if the remaining ion has charge $Z = 2$, the exponent is 1.292, significantly different from the 1.056 without the field.

The threshold behavior of double electron escape from an atom or ion was first tackled by Wannier in a famous paper in 1953 [1, 2, 3]. On the basis of the classical dynamics of two electrons in an atom he concluded that on account of the electron repulsion the two escaping electrons are correlated and that the cross section increases with excess energy $E$ like $\sigma(E) \propto E^\alpha$, with a non-integer exponent $\alpha$ that depends on the charge of the remaining ion. Since the original paper many fine details of the process have been elucidated in both theory and experiment (for recent reviews see [4, 5, 6]).

Electron–electron correlations are also important in the time-dependent process of double ionization in strong laser pulses. Measurements of the ion and electron momenta show that in non-sequential double ionization the escaping electrons prefer symmetry related motions [7, 8, 9]. The processes that are important for this double ionization are a matter of debate, but when discussed within the rescattering model [10, 11] similarities to the Wannier problem show up [12, 13, 14]. In the rescattering model one electron is temporarily ionized by tunneling, but driven back to the atom when the field changes the phase. During this rescattering event a highly excited two electron complex close to the nucleus is formed which then decays towards double ionization. For the field strengths where the characteristics of correlated electron escape are observed it seems crucial that the external field does not vanish when the decay takes place; otherwise the electrons do not have enough energy for double ionization [12, 13].

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In our previous presentations of the process in a time-dependent field we argued that the electron motion is fast compared to the field oscillations so that an adiabatic analysis can be applied. But it is possible to discuss the process also in the presence of a static field, where no adiabatic assumption is needed, and to push the analogy to the Wannier problem further by deriving the threshold laws for non-sequential double ionization in the presence of a static field. This is our aim here.

Wannier's analysis divides into two parts: the identification of the configuration that leads to double ionization at the threshold and the determination of the threshold law from the stability exponents of the fixed point. In Wannier's case the threshold configuration had two electrons escaping symmetrically on opposite sides of the nucleus, thus minimizing electron repulsion. The presence of the field introduces a preference for motion in the direction of the field gradient. At the threshold for the process the energy is equally distributed between the two electrons. Furthermore, the distance of the electrons to the nucleus should be the same for otherwise any difference would be amplified by electron repulsion and the electrons would not escape simultaneously. Therefore, in the presence of an electric field the configuration that corresponds to Wannier is one where the electrons escape along trajectories which are reflection symmetric with respect to the field axis [12, 13].

Due to the rotational symmetry around the field axis the component of angular momentum along the field axis is conserved and for the configuration with lowest threshold this component vanishes. We can therefore analyze the process in a subspace of zero angular momentum with symmetrically placed electrons. In this subspace we introduce cylindrical coordinates with $z_1 = z_2 = z$ the distance along the field direction and $\rho_1 = \rho_2 = r$ the transverse distance.

![Potential energy in the symmetric subspace](image-url)
The electrons are on opposite sides of the core with respect to the field axis, so that \( \varphi_1 = \phi \) and \( \varphi_2 = \phi + \pi \). The momenta are \( p_{z1} = p_{z2} = p_z/2 \), \( p_{\rho 1} = p_{\rho 2} = p_\rho/2 \) (the factor 2 in the momenta is related to the proper canonical transformation and restriction of the dynamics to the symmetry subspace [13]) and \( p_{\varphi 1} = p_{\varphi 2} = 0 \). With these coordinates for the symmetric subspace the Hamiltonian becomes, in atomic units,

\[
H = \frac{p_r^2 + p_z^2}{4} - \frac{2Z}{\sqrt{r^2 + z^2}} + \frac{1}{2r} - 2Fz, \tag{1}
\]

where \( F \) is electric field strength and \( Z \) the charge of the ion after removal of the two electrons [12, 13]. Equipotential curves for \( Z = 2 \) are shown in Fig. 1. Clearly noticeable is the saddle at

\[
r_s = \frac{(2a - 1)^{1/4}}{2\sqrt{|F|}}, \quad |z_s| = \frac{(2a - 1)^{3/4}}{2\sqrt{|F|}}, \tag{2}
\]

of energy \( V_s = -2(2a - 1)^{3/4}\sqrt{|F|} \), where

\[
a = (2Z^2)^{1/3}. \tag{3}
\]

The ratio \( r_s/|z_s| \) depends on the charge of the nucleus but not on the field strength. Thus, when the field strength varies the saddle moves along a line that forms a fixed angle with the field axis, as indicated in Fig. 1.

The potential shows that in the symmetric subspace double ionization requires crossing of the saddle. In the full phase space this saddle acquires an additional unstable eigenvalue, so that the symmetric subspace is an unstable subset of the full phase space. Nevertheless, it controls double ionization events since trajectories leading to non-sequential double ionization must pass close to the saddle in the symmetric subspace: the instability of the subspace is connected with an increasing asymmetry in position, momentum and energy between the two electrons. Near the threshold for double ionization this results in trajectories being pushed towards single rather than double ionization.

The stability analysis of the saddle in full configuration space gives one neutral direction, connected with an overall separable rotation around the field axis, three stable directions and two unstable ones: one unstable direction is the ‘reaction coordinate’ [15, 16] across the saddle, clearly visible in the potential in Fig. 1, and the other corresponds to motion away from this subspace. In the vicinity of the saddle the potential can be expanded to second order in the deviations from the saddle and the Hamiltonian can thus be approximated as

\[
H \approx V_s + \frac{p_x^2}{2} - \frac{\mu^2 x^2}{2} + \frac{p_y^2}{2} - \frac{\nu^2 y^2}{2} + \sum_{i=1}^{3} \left( \frac{p_{u_i}^2}{2} + \frac{\omega_i^2 u_i^2}{2} \right), \tag{4}
\]

where \( x \) denotes the reaction coordinate in the symmetric subspace, \( y \) the unstable mode away from the subspace and \( u_i \) are the stable modes with frequencies \( \omega_i \). For the case of zero total angular momentum projection on the field axis we consider here there is no contribution to (4) from the neutral mode. For later reference we note the eigenvalues of the two unstable directions: for the reaction coordinate it is

\[
\mu^2 = \frac{\sqrt{50a - 49 + 12/a} - \sqrt{2a - 1}}{(2a - 1)^{5/4}} F^{3/2}, \tag{5}
\]

and for the motion away from the symmetric subspace it is

\[
\nu^2 = \frac{\sqrt{32a - 28 + 6/a} + 2\sqrt{2a - 1}}{(2a - 1)^{5/4}} F^{3/2}. \tag{6}
\]
The escape from the subspace \( y \) is such that \( \rho_1 = r_s + c_r y \) and \( z_1 = z_s + c_z y \) increase but \( \rho_2 = r_s - c_r y \) and \( z_2 = z_s - c_z y \) decrease. The constants \( c_r \) and \( c_z \) have the same sign and determine the direction of the unstable mode in the configuration space (see [13] for further details).

For the energy equal to the saddle energy only a trajectory living in the symmetric subspace can lead to simultaneous double escape. This reduces the dimensionality of the process below that of the energy shell and consequently the cross section vanishes. For higher energy some deviations from the symmetric configuration are allowed, bringing the subset to non-zero measure on the energy shell. The energy dependence of the cross section near threshold is determined by a competition between the two unstable modes [17]. This is in close correspondence to the motion on the Wannier ridge where only trajectories sufficiently close to the symmetric configuration can leave the Coulomb zone and ionize [1].

All trajectories leading to the simultaneous escape of the electrons have to pass near the saddle. Thus, to estimate the cross section close to the threshold we may employ the Hamiltonian of the system in the harmonic approximation, Eq. (4). The cross section can be calculated from the phase space flux [1, 16] associated with the trajectories that lead to double ionization. With \( P \) the projector onto these trajectories, the microcanonical phase space flux \( j_\sigma \) at energy \( E \) that crosses the saddle can be calculated at the surface \( x_0 = 0 \) with the phase space velocity projected onto the normal of that surface,

\[
j_\sigma = \int p_{x_0} \rho \delta(x_0) \delta(E - H) P \, dp_{x_0} \, dx_0 \, dp_{y_0} \, dy_0 \prod_{i=1}^{3} dp_{u_{i0}} \, du_{i0}
\]

\[
= \int \rho \, P \, dp_{y_0} \, dy_0 \prod_{i=1}^{3} dp_{u_{i0}} \, du_{i0},
\]

where \( \rho = \rho(p_{x_0}, x_0, p_{y_0}, y_0, p_{w_{i0}}, w_{i0}) \) is the initial phase space density.

We are interested in the dependence of the cross section on the energy \( \varepsilon = E - V_s \) above the saddle. The integration limits of the stable degrees of freedom are arbitrary but finite, so that they cannot go to infinity, as required for the escape from the reaction zone towards ionization [1]. The stable directions thus do not contribute to the energy dependence, just as in Wanniers example [1, 18, 17]. Thus the only degree of freedom with a critical energy dependence in (7) is the unstable mode associated with \( y_0 \) and \( p_{y_0} \). Assuming the initial phase space distribution to be approximately uniform and energy independent [1] we get \( j_\sigma(E) \propto \int P \, dp_{y_0} \, dy_0 \).

Taking the initial reaction coordinate on one side of the saddle, e.g. \( x_0 < 0 \) with \( p_{x_0} > 0 \), the initial conditions of the unstable mode must be chosen so that after crossing the saddle both electrons escape. Since \( x \) and \( y \) are center of mass and relative coordinates, respectively, double escape requires that both \( x + y \) and \( x - y \) simultaneously go to infinity. Thus, the projection operator \( P \) selects those orbits that at some distance \( x \) after crossing the saddle satisfy

\[
|y| < |x|.
\]

From this it follows that initially only a small amount of energy \( \varepsilon = E - V_s \) can be put in the \( y \) mode because the Lyapunov exponent for the desymmetrization is larger than that for motion along the reaction coordinate, \( \nu > \mu \). Hence for small \( \varepsilon \), the initial momentum \( p_{x_0} \) can be approximated as

\[
p_{x_0} = \sqrt{2\varepsilon + \mu^2 x_0^2 - p_{y_0}^2 + \nu^2 y_0^2} \approx \mu |x_0| + \frac{\varepsilon}{\mu |x_0|}.
\]
Expressing $y$ in terms of the initial conditions gives, for large time,

$$y \approx \frac{1}{2} \left( y_0 + \frac{p_{y0}}{\nu} \right) \left( \frac{2\nu}{x_0 + \frac{p_{x0}}{\mu}} \right)^{\nu/\mu}$$  \hspace{1cm} (10)

Substituting (10) and (9) into (8) then results in

$$|y_0 + \frac{p_{y0}}{\nu}| < \text{const} \cdot e^{\nu/\mu},$$  \hspace{1cm} (11)

which is precisely the restriction we need. Changing to canonical variables $y' = y + \frac{p_y}{\nu}$ and $p_{y'} = p_y/2 - \nu y/2$, one finds that $p_{y'}(t) = p_{y'0} \exp(-\nu t)$ while $y'(t) = y'_0 \exp(\nu t)$. The inequality (11) is thus the restriction on the unstable direction in the phase space. The initial condition along the stable direction, $p_{y'0}$, can be arbitrary – it is, of course, finite due to the requirement that ionizing trajectories must emerge from the reaction zone [1]. The cross section $\sigma(E)$ is proportional to the flux $j$, so that we find for the threshold behaviour the law

$$\sigma(E) \propto j \propto \int P \, dy'_0 \propto (E - V_s)^\alpha,$$

with the exponent $\alpha$ given by

$$\alpha^2 = \frac{\nu^2}{\mu^2} = \frac{\sqrt{32a - 28 + 6/a + 2\sqrt{2a - 1}}}{\sqrt{50a - 49 + 12/a - \sqrt{2a - 1}}},$$  \hspace{1cm} (13)

where $a$ is defined in Eq. (3). In Fig. 2 we show $\alpha$ as a function of the nuclear charge together with the Wannier exponent; the values are also listed in Table I. For increasing charge $Z$ the exponent $\alpha$ decreases and approaches the limiting value $\sqrt{3/2} \approx 1.225$.

The exponent $\alpha$ does not depend on the field amplitude but only on the charge of the nucleus. This raises the question how the classical Wannier theory can be recovered for vanishing field strength $F$. The answer can be given easily by appealing to Wannier’s analysis: he introduced a Coulomb dominated zone inside which potential energy exceeds kinetic energy. The outer boundary of this zone is then energy dependent and increases without bound as the total energy approaches zero. As long as the saddle induced by the field is inside this radius we expect the exponent given above (13), but if it is outside we expect the classical Wannier exponent. In the limit of vanishing field strength but for fixed excess energy the saddle moves outside the Coulomb zone and the classical exponents are restored. This transition might be accessible experimentally.

The classical Wannier theory for double ionization without external field gives the same threshold law as do semiclassical and quantum calculations [2, 3, 6]. This may be traced to the fact that a remarkable scaling law relates the limits of energy approaching threshold and of Planck’s constant becoming small [1, 6]. In the present case the saddle is at a finite distance and can be overcome by tunneling. This will modify the threshold law very close to the classical saddle, in an energy interval of about $\hbar\mu$, with $\mu$ the frequency for motion along the reaction coordinate (eq. (5)). In the semiclassical limit and for weak fields this can be made arbitrarily small, so that the algebraic behaviour should become accessible.

The most direct experimental study of the proposed threshold behavior would be double-photoionization [4, 5] in the presence of an external field. The photon resolution of 0.1 eV achieved in recent experiments [19] should enable detection of deviations from Wannier theory e.g. in double-photoionization of He atoms in a static field of 30 kV/cm, where the saddle energy is $-0.3$ eV.

Pulsed lasers provide stronger fields but add a time-dependence. However, the laser field can be considered as stationary if the time needed to cross the barrier is a small fraction of
the field cycle, only. Double ionization could be triggered by a crossed electron beam. The energy of the saddle and of the electronic beam change with the field phase but both are well defined. The field intensity can then be adjusted so that the excess energy reaches the energy of the saddle only at specific moments in time. Such an experiment would also provide a very interesting direct test for the rescattering model for double ionization in strong fields [10, 11].

Finally we should mention that the correlated escape used to derive the threshold law is not the only pathway to double ionization. Trajectory studies [12, 13] show that initial conditions started near the saddle that do not lead to immediate double ionization can lead to sequential ionization in that one electron escapes immediately but the other escapes after a return to the nucleus. However, in such a sequential escape the momenta of the second electron are not correlated to the ones of the first electron and this can perhaps be used to distinguish correlated from sequential escape [13].

To conclude we have presented the analysis of the threshold law for the double ionization in electron impact in the presence of a static electric field. Simultaneous ionization of the electrons then proceeds via a correlated crossing of the saddle induced by the external field. The cross section behavior close to the threshold is algebraic in excess energy with an exponent determined from the ratio of the positive Lyapunov exponents of the unstable modes of the saddle. We hope that the generalization of the Wannier theory to the case with an additional external field presented here will stimulate experimental and further theoretical investigations.

Financial support by the Alexander von Humboldt Foundation is gratefully acknowledged. The work is also a part of KBN project No. 5 P03B 088 21 (K.S.).

REFERENCES

Table I. – Threshold exponent $\alpha$, Eq. (13), and Wannier exponent for different charge of the remaining ion.

<table>
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