Degenerate Wannier Theory for Multiple Ionization

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It is shown that the cross section for multiple breakup of a system into charged fragments near the threshold energy $\epsilon = 0$ follows a power law modified by logarithmic correction terms if the system possesses degenerate normal mode frequencies about the fixed point of the equilibrium configuration. For more than two identical particles, e.g., a multielectron atom, this will be the generic case since the equilibrium configuration is highly symmetric. The modified threshold law is derived using consistently the properties of the classical monodromy matrix about the fixed point to formulate the threshold cross section. [S0031-9007(98)06296-6]

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The interest in threshold ionization of atoms dates back to the classical paper by Wannier in 1953 [1]. Subsequent semiclassical treatments revealed the same result in a quantum mechanical environment, namely, that the cross section for electron impact ionization of an atom near threshold $\epsilon = 0$ follows a power law, $\sigma(\epsilon) \propto \epsilon^m$, where m is a function of the nuclear charge of the atom and $\epsilon = E/I$ is the excess energy E scaled by the ionization potential I [2]. Experimental confirmations of this prediction followed in 1968 with a hydrogen target [3] and in 1974 [4] with a helium target. Later, the power law was also confirmed in double photoionization [5].

Recent interest in the threshold ionization process has been fueled by Feagin's extension of the Wannier theory to the next order [6] and by the so called "hidden crossing theory" of ionization which leads to similar results [7]. Furthermore, the analytical Wannier law was finally numerically confirmed, classically [8] as well as quantum mechanically [9].

One may ask if anything fundamentally different happens if the threshold fragmentation leads to more than two electrons in the continuum. Such an experiment is feasible and has actually been realized by measuring triple photoionization of oxygen and neon [10]. A power law for the cross section was found whose exponent m is in agreement with the one calculated by Klar and Schlecht [11] and by Grujic [12]. However, the experimental cross section shows a bend in the slope already at a low excess energy of about 5% of the triple ionization energy which prompted a speculation about two different Wannier exponents coming into play [13]. In the present Letter we show that, indeed, two exponents corresponding to two unstable normal modes about the equilibrium configuration exist. However, they are *equal* and this fact requires the formulation of a degenerate threshold theory with the result that the threshold law for triple ionization is modified by a logarithmic term,

$$\sigma(\epsilon) \propto \epsilon^m/(\ln \epsilon)^2. \qquad (1)$$

Since multiple threshold ionization with $N - 1$ free electrons proceeds from an equilibrium configuration of these $N - 1$ electrons, the degenerate case is the generic one. Only in the most studied case of two electrons does the existence of a single unstable normal mode prevent degeneracy.

The degeneracy and the existence of normal modes with the same frequency is evident if one looks at the simplest case of three electrons which form, in the equilibrium configuration, an equilateral triangle with the nucleus in the middle. Complete ionization near threshold occurs if the system approaches this triangular shape while all electrons recede from each other. A failure to reach the equilibrium shape at infinite separation will lead to double or single ionization. This failure is determined by the excitation of unstable normal modes about the equilibrium configuration. A given electron has two topologically different but otherwise identical possibilities to depart from its equilibrium position (see Fig. 1). The two possibilities define two unstable normal modes which can be mapped onto each other by interchanging the label of two of the electrons. This is the origin of the degeneracy. It always occurs if at least three of the fragments are identical.

To cast this intuitive picture into a mathematical formalism we will analyze the problem in terms of a classical

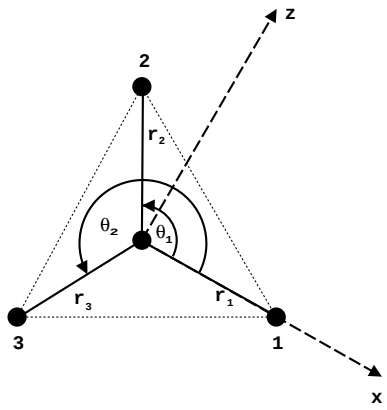

FIG. 1. The equilibrium position for a three electron atom. The coordinates and angles are indicated.

fixed point and its instabilities. From the symmetry of the equilibrium position it is convenient to work in hyperspherical coordinates where the hyperradius $r = (r_1^2 + r_2^2 + r_3^2)^{1/2}$ measures the overall volume of the system. All other coordinates are described by angles. Overall rotation of the system is irrelevant for the threshold ionization, and for the ionization probability it is sufficient to consider total angular momentum $L = 0$ [11]. Hence, we may restrict our analysis to the planar configuration of Fig. 1 which is parametrized by two angles θ_1 and θ_2. Two hyperangles describe the relative distances of the electrons from the nucleus, $\tan\alpha_2 = (r_1^2 + r_2^2)^{1/2}/r_3$ and $\tan\alpha_1 = r_1/r_2$. For $\alpha_i \in (0, \pi/2)$ after the interaction, all the electrons are free since a bound state of one of the electrons corresponds to α_1 or $\alpha_2 = 0$ or $\pi/2$ for $r \to \infty$. In these coordinates we can formulate a relatively simple expression for the total (classical) ionization cross section, even for N particles. Without exactly specifying the angles we use the convention of a vector $\vec{\omega} = (\alpha_1, \ldots, \alpha_{N-2}, \theta_1, \theta_2, \ldots)$, where the α_i are hyperangles describing ratios of distances while the θ_i are geometrical angles. The probability in the $L = 0$ partial wave to ionize $N - 2$ electrons by electron impact, leading to fragmentation into $N - 1$ electrons and the ion, can be written as an integral over initial phase space projected onto the fragmented final states:

$$P_N = \prod_{i=1}^{3N-6} \left(1/2\pi \int d\eta_i^- \right) K_N(\vec{\eta}^-) . \qquad (2)$$

The η_i^- are angles conjugated to the classical actions of the $N - 2$ bound electrons before the ionization. The respective actions are fixed which can be thought of as a consequence of the specified initial state. The projector onto N-fold fragmentation is given by

$$K_N(\vec{\eta}^-) = \lim_{\substack{\delta \to 0 \\ t \to \infty}} \prod_{i=1}^{N-2} \times \left(\frac{2}{\pi} \int_{\delta}^{\frac{\pi}{2}-\delta} d\alpha_i \delta(\alpha_i(t, \vec{\eta}^-) - \alpha_i) \right) . \qquad (3)$$

Exclusion of the limits ($\delta = 0$) ensures that no bound states occur.

The mechanism of threshold ionization of an atom proceeds via a fixed point of the Hamiltonian as shown for the first time by Wannier [1]. Again, this has a simple physical reason: All electrons must come apart; i.e., the radial kinetic energy is positive. However, very close to threshold $\epsilon = 0$ the little excess energy available must be used for the radial momentum such that all particles come apart. Hence, all other velocities but the radial one are zero. This implies that the corresponding angles do not change which defines the mathematical situation of a fixed point. We can extend the fixed point condition to the radial coordinate as well if we use energy scaled distances $\tilde{r} = \epsilon r$. We will work with the regularized Hamiltonian (see, e.g., [14])

$$H = up^2/8 + uD/2 + C(\vec{\omega})u - u^3 = 0 , \qquad (4)$$

where p is the momentum conjugated to $u = \sqrt{r}$ and $D = \sum_{i \le j} l_{ij}(\vec{\omega}) P_i P_j / u^2$ is the kinetic energy from the internal angular momentum of the N particles, containing all the momenta P_i conjugated to the angles ω_i. Finally, $C(\vec{\omega}) = V(\vec{\omega}, u^2)u^2$ is the angular dependent "charge" of the multielectron Coulomb potential V. The form Eq. (4) of the Hamiltonian involves already a modified time variable τ related to t by $dt = u^3 d\tau$. Nevertheless, at $u = 0$, some of the equations of motion can become singular. This can be avoided by a (noncanonical) transformation of the momenta P_i to $p_i = P_i/u$. Accordingly, Hamilton's equations for the angular coordinates are modified to

$$\dot{\omega}_i \equiv \frac{d\omega_i}{d\tau} = \frac{1}{2} \frac{\partial D(\vec{\omega}, \vec{p})}{\partial p_i} , \qquad (5)$$

$$\dot{p}_i \equiv \frac{dp_i}{d\tau} = -\frac{\partial C(\vec{\omega})}{\partial \omega_i} - \frac{1}{2} \frac{\partial D(\vec{\omega}, \vec{p})}{\partial \omega_i} - p_i p/4 . \qquad (6)$$

The condition for the fixed point is that all time derivatives of the components of the phase space vector $\vec{x} = (p, p_1, \ldots, u, \omega_1, \ldots)$ vanish, $\dot{x}_i = 0$. This condition leads, for the Hamiltonian Eq. (4), to the fixed point $u^* = p_i^* = 0$ and the ω_i^* are the solutions to $\partial C/\partial \omega_i = 0$. From energy conservation we obtain $p^* = [-8C(\vec{\omega}^*)]^{1/2}$. All momenta but the radial one vanish in accordance with our argument that no kinetic energy should be wasted in the process of threshold fragmentation. However, why does $u^* = 0$ correspond to a fragmentation process? At the fixed point itself, and this means at $\epsilon = 0$, the electrons will not come apart. We need small deviations δu etc. about the fixed point to describe the behavior for small excess energies ϵ. After the fragmentation the hyperradius must tend to infinity. In scaled coordinates this can be achieved by a finite but arbitrary δu which corresponds to an unscaled $\sqrt{r} = \delta u \epsilon^{-1/2} \to \infty$ for $\epsilon \to 0$.

If fragmentation has occurred the particles must have had some interaction in order to exchange energy between the projectile (or the photon) and the bound particles at an earlier time $\tau^- = 0$. Nonvanishing interaction requires some finite hyperradius r_0 at this time. In scaled coordinates this distance will tend to zero with $\tilde{r}_0 = \epsilon r_0 \to 0$. Hence, the fact that an interaction between the particles takes place forces the system at threshold to a vanishing scaled radial extension $u^* = 0$. As the energy rises the system will depart from $u^* = 0$ and we can write for a small departure

$$\delta u^- = \sqrt{\epsilon}\, u_0 , \qquad (7)$$

where u_0 is an arbitrary constant and $\delta u^- = \delta u(\tau^-)$. These considerations show that we may use the linearized equations of motion about the fixed point to fragment the system near threshold with

$$\delta u / \delta u^- \propto \epsilon^{-1/2} . \qquad (8)$$

The linearized equations of motion define a matrix equation $\delta\dot{x}_i = \sum_j M_{ij}\delta x_j$ with elements $M_{ij} = \delta\dot{x}_i/\delta x_j$. Note that the stability or monodromy matrix $\mathcal{M}$ is not of the standard form and also not symplectic due to the noncanonical transformations. Nevertheless, the linear system can be solved at the fixed point by standard eigenvalue techniques. We obtain a set of eigenvalues λ_i and eigenvectors $\delta\gamma_i$ whose time evolution is given by

$$\delta\gamma_i(\tau) = \exp(\lambda_i\tau)\delta\gamma_i^- . \tag{9}$$

Because of the structure of $\mathcal{M}^*$ the radial motion is orthogonal to the angular dynamics and $\delta u(\tau)$ is simply given by

$$\delta u(\tau) = \exp(p^*\tau/4)\delta u^- . \tag{10}$$

We can now turn to an approximate evaluation of the ionization probability Eq. (2) near the fixed point. First, we note that for large times t we may replace t with τ in Eq. (3). Second, we change $N-2$ of the integration variables η_j^- to $\alpha_i(\tau)$ such that the corresponding Jacobi matrix J with elements $J_{ij} = \partial\alpha_i(\tau)/\partial\eta_j^-$ is nonsingular. Now the δ functions can be trivially fulfilled, and we have to evaluate the Jacobi determinant. For the linearized dynamics about the fixed point this can be done explicitly by using the time dependence Eq. (9) of the normal modes. For large times τ the mode with the largest eigenvalue (Liapunov exponent) λ_1 dominates (we assume a numbering $\lambda_1 > \lambda_2 > \cdots$) and the elements for the Jacobi matrix acquire the simple form

$$J_{ij}(\tau) = \exp(\lambda_1\tau)J_{ij}^- , \tag{11}$$

where the $J_{ij}^- = (\partial\alpha_i/\partial\gamma_1)(\partial\gamma_1/\partial\eta_j)$ form a (time independent) matrix of coordinate transformation. Through Eq. (8) the radial instability is related to the excess energy ϵ. Using Eq. (8) and the time dependence of the radial instability Eq. (10) to replace time by energy ϵ in Eq. (9) the probability Eq. (2) for fragmentation into N free charged particles reads finally

$$P_N(\epsilon \to 0) \propto \epsilon^{(N-2)\beta}, \tag{12}$$

where $\beta = 2\lambda_1/p^*$.

So far we have assumed that all the eigenvalues λ_i are different. In case of degeneracy of eigenvalues the monodromy matrix $\mathcal{M}$ cannot be fully diagonalized in general and the solutions $\delta\gamma_i(\tau)$ from Eq. (9) are modified. If n eigenvalues are degenerate, the general solution contains additional terms $\tau^k\exp(\lambda\tau)$, $(k < n)$ [15]. Hence, if λ_1 is n-fold degenerate, the dominating term for large τ is of the form $\delta\gamma_1(\tau) \to \tau^{n-1}\exp(\lambda_1\tau)\delta\gamma_n^-$. As a consequence, the modified threshold law reads

$$\sigma_N(\epsilon) \propto \epsilon^{(N-2)\beta}|\ln\epsilon|^{-(N-2)(n-1)}, \tag{13}$$

i.e., the cross section in the case of degeneracy is smaller by a logarithmic correction compared to the nondegenerate case.

As an application we have investigated the triple ionization of oxygen and neon, i.e., the formation of $N = 4$ charged fragments. The largest (degenerate) eigenvalue for the in-plane departure from the equilibrium configuration of Fig. 1 leads to the exponent

$$2\beta = 4\lambda_1/p^* = (a + 2\sqrt{b})^{1/2}, \tag{14}$$

where a and b are functions of the nuclear charge Z and mass M,

$$a = -11 + 13\sqrt{3}Z + 6\sqrt{3}Z/M , \tag{15}$$

$$b = 1 + 108Z^2 + 6\sqrt{3}Z/M + 324Z^2/M + 27(Z/M)^2. \tag{16}$$

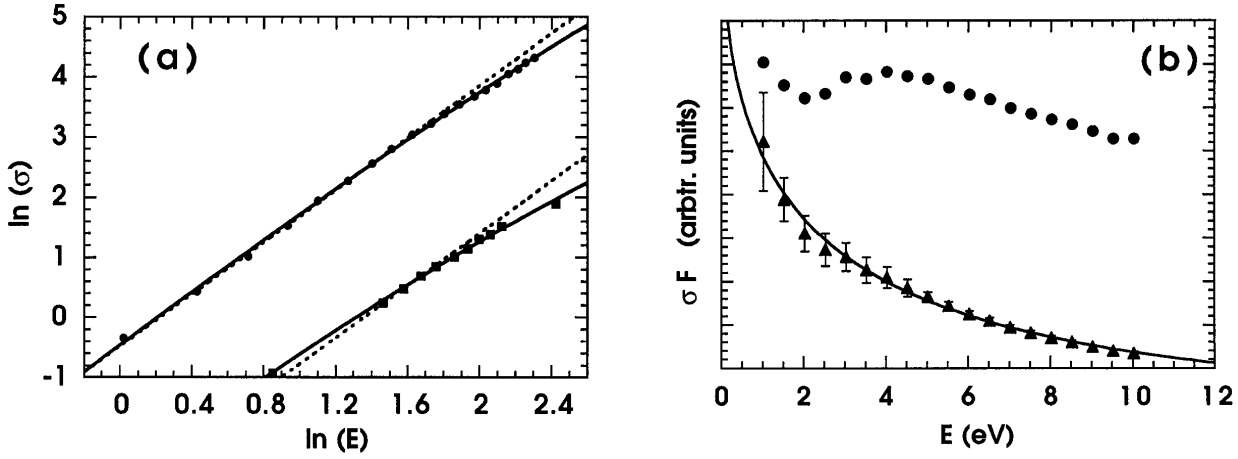

FIG. 2. Threshold ionization cross section from [10]. Part (a) shows the best fit with a pure power law (dashed lines) according to [10], where $\beta = 2.170$ for Ne^{3+} and $\beta = 2.176$ for O^{3+}. The solid lines are fits with Eq. (17) where the absolute magnitude of the cross section and a are fitting parameters. Part (b) shows σF for neon where for the circles $F(\epsilon) = (\epsilon)^{-2.162}$ and for the triangles $F(\epsilon) = (\epsilon)^{-2.162}\ln(\epsilon)^2$. Experimental errors [16] are given and the solid line is from the fit of the neon data in (a).

In the limit $M \to \infty$ Eq. (14) coincides with Klar's result [11]. As expected the largest (real) Liapunov exponent is degenerate, $\lambda_1 = \lambda_2$. Incorporating recent results from the 4th order Wannier theory [6] and the hidden crossing approach [7] along with the logarithmic terms derived here, we obtain the explicit form of the threshold law for triple ionization

$$\sigma_4(\epsilon) \propto \epsilon^{2.162}/(\ln \epsilon)^2 \exp(-a\sqrt{\epsilon}) . \qquad (17)$$

The constant a has been analytically derived for two-electron escape [6,7], but is unknown for three-electron escape. Figure 2a shows that a fit with Eq. (17) improves the agreement with the experiment considerably compared to the pure power law $\sigma \propto \epsilon^m$. However, this is not a stringent test of the logarithmic terms in Eq. (17). Fortunately, the experimental data set for neon from [10] was still available [16] and enabled us to plot the threshold cross section data in the form $\sigma\epsilon^{-2.162}$ (circles in Fig. 2b). A clearly visible structure emerges which is not present in any two-electron escape data we are aware of. If we go one step further and plot $\sigma\epsilon^{-2.162}(\ln \epsilon)^2$, i.e., if we take out the predicted logarithmic dependence, the cross section assumes a regular form (triangles in Fig. 2b), similar to two-electron escape cross sections.

Hence to the accuracy which the experimental data permit there is evidence for a logarithmic energy dependence in the triple ionization cross section of neon. With the advanced experimental possibilities of modern synchrotron facilities it should be possible to examine the logarithmic corrections in greater detail in the future.

To summarize we have presented a formulation for the probability of multiple breakup into charged particles near threshold in terms of the stability matrix of the classical fixed point in energy scaled coordinates. This formulation clarifies the phase space factor with which the so called Wannier exponent β must be multiplied in the case of N-fold fragmentation to yield the total exponent $m = (N - 2)\beta$. More importantly, we have shown that the threshold law for ionization of more than two electrons involves logarithmic correction terms. Their existence is a consequence of degenerate eigenmodes in the dynamics about the fixed point which governs threshold ionization. Since the fixed point equilibrium configuration of a many-particle system is highly symmetric the degenerate case will be the generic one for three and more identical fragments.

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