moves in a tunneling band whose density of states yields a finite (nonzero) value of u^*. (ii) Hard-core repulsions between adsorbed atoms exclude multiple occupation of the same binding site. Our methods are very closely analogous to those of Callaway and Edwards.[5] The final result is

$$b_1(T) = (kT/\Delta)\, e^{B/kT} , \tag{5a}$$

$$b_2(T) = [(kT/2\Delta) - 4(u^* kT/\Delta^2)]\, e^{2B/kT} , \tag{5b}$$

where B is the binding energy of the substrate. The adsorption isotherms are given by

$$\theta = \left(\frac{\partial \Phi}{\partial \mu}\right)_T = \sum_{l=1}^{\infty} l b_l(T)\, e^{l\mu/kT} , \tag{6a}$$

$$e^{\mu/kT} = \lambda^3 P/kT , \tag{6b}$$

where

$$\lambda = (2\pi\hbar^2/M kT)^{1/2} \tag{7}$$

is the thermal wavelength. The low-pressure data

$$\theta(T, P) \simeq b_1(T)\,(\lambda^3 P/kT) + 2b_2(T)\,(\lambda^3 P/kT)^2 + \cdots \tag{8}$$

would be sufficient for measuring B, Δ, and the critically important inhomogeneity parameter u^*, e.g., via

$$b_2/b_1^2 = (\tfrac{1}{2}\Delta - 4u^*)/kT , \tag{9a}$$

$$b_1 = (kT/\Delta)\, e^{B/kT} , \quad kT \ll \Delta . \tag{9b}$$

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PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Threshold Law for Double Photoionization and Related Processes with $L = 1$ Final States*

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(Received 25 June 1971)

The energy dependence at threshold for the escape of two electrons with total angular momentum $L = 1$ is shown to be the same as that found for $L = 0$ by Rau, and classically by Wannier, for processes that leave the same residual ion. It is suggested that this threshold law will also hold for $L > 1$.

In a recent paper by Rau,[1] the quantum-mechanical energy dependence at threshold of the cross section for ionization by electron impact was established to be the same as that obtained classically by Wannier.[2] Both Rau and Wannier restrict themselves to final states of zero orbital angular momentum ($L = 0$) both because of mathematical simplicity and because as Wannier says "the probability of reaction into an S state has a threshold at least as favorable as the probability of reacting into higher angular momentum states," if a final S state can be reached with conservation of angular momentum.

Wigner[3] has shown that for two-particle reactions the threshold law does not depend on detailed description of the reaction mechanism. Wannier[2] justifies this assumption for three particles. Hence the threshold law for a given L applies equally well to double photoionization, to double ionization by fast electron impact, or, generally, to any process in which two very slow electrons escape to infinity leaving behind an ion with charge Z. In particular, double photoionization of atoms with closed shells gives a final state with $L = 1$. In this paper we examine the two-electron Schrödinger equation for $L = 1$ and find it to be equivalent to that for $L = 0$ for threshold purposes. A numerical approach to the same problem by a classical model has been made by Peterkop and Tsukerman[4]; the results pointed to the conclusions presented in this paper.

The Schrödinger equation takes three different forms for different types of $L = 1$ states. One is for even-parity states, one is for singlet odd-parity states, symmetric under interchange of electron coordinates, and one is for triplet odd-parity states, antisymmetric under interchange of electron coordinates. The equations are given (explicity) by Morse and Feshbach.[5]

The angular parts have been separated out using a set of Euler angles first suggested by Breit[6] in which Θ is the angle between $\vec{r}_1$ and $\hat{z}$, Φ is the angle between $\vec{r}_1$ and the xz plane, and Ψ is the angle between $\vec{r}_2$ and the $\vec{r}_1 z$ plane.

The wave functions are described as functions of the Euler angles (Θ, Φ, Ψ) and of a function $f(r_1, r_2, \vartheta_{12})$ of $|\vec{r}_1|$, $|\vec{r}_2|$ and of the angle between $\vec{r}_1$ and $\vec{r}_2$, ϑ_{12}. To achieve the proper symmetry one considers also the interchanged function $\tilde{f}=f(r_2, r_1, \vartheta_{12})$. For $L=0$ the complete wave function ψ is independent of Θ, Φ, and Ψ and thus $\psi=f$. For $L=1$, $M_L=0$ odd-parity, one has

$$\psi=\cos\Theta(f\pm\cos\vartheta_{12}\tilde{f})\pm\sin\Theta\cos\Psi\sin\vartheta_{12}\tilde{f}, \quad (1)$$

where the upper (lower) sign is for the singlet-symmetric (triplet-antisymmetric) case. For $L=1$, $M_L=0$ even parity, one has

$$\psi=\sin\Psi\sin\Theta f. \quad (2)$$

The presence of the $\sin\Psi$ implies that there is one unit of angular momentum about the axis of r_1 and a centrifugal force which keeps ϑ_{12} away from 0 or π.

The central point of the Wannier-Rau analysis is that the two electrons leave the atom in opposite directions ($\vartheta_{12}=\pi$) to minimize their mutual repulsive energy. Moreover they must be approximately at the same distance from the nucleus ($r_1=r_2$) to minimize their mutual screening. This is the so-called "dynamic" or energy-dependent screening[1]: If one electron has more energy than the other, then the slower electron will fall behind, get screened less, slow down even more, and will end up still bound. The region of space $r_1\sim r_2, \vartheta_{12}\sim\pi$ is called the Wannier line. To take advantage of this intuitive picture we transform the equations into hyperspherical coordinates; $R=(r_1^2+r_2^2)^{1/2}$, $\alpha=\tan^{-1}(r_2/r_1)$. The $L=1$ odd-parity equation becomes

$$H_0 f+\frac{2}{R^2}\left[\frac{1}{\cos^2\alpha}\left(\cot\vartheta_{12}\frac{\partial f}{\partial\vartheta_{12}}-f\right)\mp\frac{1}{\sin^2\alpha\sin\vartheta_{12}}\frac{\partial\tilde{f}}{\partial\vartheta_{12}}\right]=0, \quad (3)$$

where the upper (lower) sign is for the symmetric (antisymmetric) states. H_0 is the operator for the $L=0$ equation, namely,

$$H_0=\frac{\partial^2}{\partial R^2}+\frac{5}{R}\frac{\partial}{\partial R}+\frac{1}{R^2\sin^2 2\alpha}\frac{\partial}{\partial\alpha}\left(\sin^2 2\alpha\frac{\partial}{\partial\alpha}\right)+\frac{4}{R^2\sin^2 2\alpha}\frac{1}{\sin\vartheta_{12}}\frac{\partial}{\partial\vartheta_{12}}\left(\sin\vartheta_{12}\frac{\partial}{\partial\vartheta_{12}}\right)+\frac{2Z}{R}B(\alpha,\vartheta_{12})+k^2, \quad (4)$$

in a.u., where $\frac{1}{2}k^2$ is the total energy and $-ZB/R$ the potential with

$$B(\alpha,\vartheta_{12})=\frac{1}{\cos\alpha}+\frac{1}{\sin\alpha}-\frac{1/Z}{(1-\sin 2\alpha\cos\vartheta_{12})^{1/2}}.$$

We then set $\gamma=\pi-\vartheta_{12}$ and $\beta=\frac{1}{4}\pi-\alpha$. This makes γ and β small parameters in which the equations can be expanded. R will be large to ensure that the electrons are far from the reaction zone.

The operators in all three $L=1$ equations consist of the $L=0$ operator with additional terms. All of the additional terms have a factor $1/R^2$ as expected for a centrifugal potential. It seems reasonable that in the threshold region of large R these terms will affect the wave function less than the potential which goes as $1/R$ (or as $1/R^{3/2}$ after the transformation presented below). This argument suggests that the threshold law holds equally for $L=0$, $L=1$, and for $L>1$ as well. However, the mathematical analysis becomes more complicated for $L>1$ because there is a larger number of coupled equations.

Setting $f=R^{-5/2}\sec(2\beta)\phi$, $\tilde{f}=R^{-5/2}\sec(2\beta)\tilde{\phi}$ and retaining terms to lowest nonvanishing order in β and in γ, Eq. (3) becomes

$$H_0\phi+\frac{4}{R^2}\left\{(1-2\beta)\left[\left(\frac{1}{\gamma}-\frac{\gamma}{2}\right)\frac{\partial\phi}{\partial\gamma}-\phi\right]\pm(1+2\beta)\frac{1}{\gamma}\frac{\partial\tilde{\phi}}{\partial\gamma}\right\}=0, \quad (5)$$

where the upper (lower) sign is for the symmetric (antisymmetric) states and H_0 has become

$$H_0=\frac{\partial^2}{\partial R^2}+k^2+\frac{\frac{1}{4}}{R^2}+\frac{1}{R^2}\left\{\frac{\partial^2}{\partial\beta^2}+4(1+4\beta^2)\left[\frac{\partial^2}{\partial\gamma^2}+\left(\frac{1}{\gamma}-\frac{\gamma}{3}\right)\frac{\partial}{\partial\gamma}\right]-\left[2\xi ZR-4\eta ZR\beta^2+\frac{R\gamma^2}{4\sqrt{2}}\right]\right\}. \quad (6)$$

The term in the second square bracket of (6) comes from the electrostatic potential. We have also defined $\xi=2\sqrt{2}-(\sqrt{2}Z)^{-1}$ and $\eta=3/\sqrt{2}-(4\sqrt{2}Z)^{-1}$ as in Ref. 1.

Following Rau[1] we proceed by the following ansatz:

$$\phi=\exp[ic\sqrt{R}(1+\tfrac{1}{2}a\beta^2+ib\gamma^2)]\chi(R), \quad (7)$$

with a, b, and c to be determined later. The interchange $r_1\leftrightarrow r_2$ leads to $R\to R$, $\gamma\to\gamma$, $\beta\to-\beta$ since by our ansatz ϕ is an even function of β and therefore $\tilde{\phi}=\phi$.

Substituting expression (7) of $\phi(=\tilde{\phi})$ in Eq. (5) and neglecting terms of order $\beta^2/R^{3/2}$, $\gamma^2/R^{3/2}$, and of higher order yields

$$\left[\frac{d^2}{dR^2}+k^2+\frac{\frac{1}{4}-(l+\frac{1}{2})^2}{R^2}+\frac{1}{R}\left(2\xi Z-\frac{c^2}{4}\right)+\frac{\beta^2}{R}\left(-a^2c^2-\frac{ac^2}{4}+4\eta Z\right)\right.$$

$$+\frac{\gamma^2}{R}\left(-\frac{\sqrt{2}}{8}+16b^2c^2-\frac{ic^2b}{2}\right)+\frac{ic}{\sqrt{R}}\left(\frac{d}{dR}+\frac{1}{R}(-\tfrac{1}{4}+a+b')\right)\Big]\;\chi(R)=0\;, \tag{8}$$

where $l=\frac{3}{2}$ and $b'=32ib$ for the symmetric case and $b'=16ib$ for the antisymmetric case. The values of a, b, and c which eliminate the $1/R$ terms in (8) are identical to those determined for the $L=0$ case by Rau.[1] The remaining terms of the equation look like a one-electron radial Schrödinger equation with orbital quantum number l and with a $1/R^{3/2}$ potential. This form differs from Rau's equation (A1) only in the value of l, which is $-\frac{1}{2}$ for $L=0$ and $\frac{3}{2}$ for $L=1$, and in the value of b' which is $16ib$ for $L=0$ and is $32ib$ for $L=1$ triplet (antisymmetric) case and is $16ib$ for the $L=1$ singlet (symmetric) case.

At this point we need only note that in Rau's discussion of the threshold law, given in Secs. III and IV in his paper,[1] neither l nor b' affect the threshold law which is

$$\sigma\sim E^{\mu/2\,-1/4}\;, \tag{9}$$

where

$$\mu=\frac{1}{2}\left(\frac{100Z-9}{4Z-1}\right)^{1/2}\;.$$

The equation for the even-parity $L=1$, $M_L=0$ state after setting $f=R^{-5/2}\sec(2\beta)\phi$ and keeping terms to lowest order is

$$\left(H_0-\frac{4}{R^2}\,(1+4\beta^2)\frac{1}{\gamma^2}\right)\phi=0. \tag{10}$$

Owing to the presence of the centrifugal potential $1/\gamma^2$, the ansatz must include a factor γ.

$$\phi=\gamma\exp[ic\sqrt{R}\;(1+\tfrac{1}{2}a\beta^2+ib\gamma^2)]\chi(R). \tag{11}$$

Substituting in Eq. (10) we obtain again Eq. (8) but with $l=\frac{2}{3}\sqrt{3}-\frac{1}{2}$ and $b'=32ib$. Consequently this equation will yield the same threshold law for $L=0$. However the amplitude of the wave function (11) will be small in the far zone due to the node along the Wannier line. This should result in a small cross section.

To connect theory with experiment, it is important to estimate the range of validity of the threshold law. The approximations made in solving our equations involved dropping terms of the order $\gamma^2/R^{3/2}$ and keeping terms of order γ^2/R. Expanding our equations keeping lowest terms in β and γ involved ignoring terms of γ^3/R. To justify such approximations $1/R^{1/2}$, β, and γ must all be $\lesssim 0.1$.

The point $k^2R=2\xi Z$ defines a boundary between the two asymptotic regions considered by Wannier and Rau in deriving the threshold law. With $R>100$ we find that the approximations limit the energy $(\frac{1}{2}k^2)$ to less than 0.02 a.u. = 0.55 eV for $Z=1$ and to less than 0.05 a.u. = 1.3 eV for $Z=2$.

Experiments on double photoionization and ionization by electron impact have been carried out[7,8] that are not inconsistent with the above theory. However the range and accuracy of the data are not sufficient to provide a critical test of the threshold law. In principle, double photoionization is the more accurate of the two.

I wish to thank Professor U. Fano for suggesting this problem to me and for encouragement and support. I wish to thank Dr. A. R. P. Rau for showing me his paper prior to publication and Dr. T. Åberg for interesting discussions. I wish to thank Dr. R. Peterkop for pointing out an error in the manuscript.

*Work supported by the U. S. Atomic Energy Commission under Contract No. C00-1674-50

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