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ABSTRACT

An expression for the reduced width of an auto-ionizing level is derived using the R-matrix theory. The electron emission widths are calculated as a function of channel radius. By choosing an appropriate value of channel radius it is found that the electron emission width is 5.885×10^{-3} eV for an outgoing p electron of kinetic energy 1.162 eV. This width is about 3000 times larger than the partial radiation width of the level. It is shown that certain selection rules cause some of the partial widths to vanish. Thus measurements can provide very useful information about the type of coupling. The electronic radial wave functions are obtained by a self-consistent-field calculation. The calculation also shows that the penetrability is not too sensitive to the change in atomic electrical polarizability and the core radius.

I. INTRODUCTION

It is well known in atomic spectroscopy that there are certain energy levels which lie above the ionization limit¹. These discrete levels, because of the interaction with the states in the continuum, undergo spontaneous ionization. We are interested in calculating the widths of these auto-ionizing levels.

According to R-matrix theory² the partial width $\Gamma_{\lambda c}$ for a particular energy level λ and decay mode c is given by the expression

$$\Gamma_{\lambda c} = 2 P_c \gamma_{\lambda c}^2, \quad (1)$$

where P_c is a dimensionless quantity called the penetrability and $\gamma_{\lambda c}^2$ is called the reduced width and has the dimensions of energy. We shall derive an expression for the reduced width amplitude $\gamma_{\lambda c}$ in section 2.

The details of the computer programs which are needed to obtain the numerical values of the partial widths $\Gamma_{\lambda c}$ are given in a technical note³.

II. DERIVATION OF THE EXPRESSION FOR THE REDUCED WIDTH AMPLITUDE

The derivation of the reduced width amplitude will be carried out in L-S coupling, which is valid for not too heavy atoms. We consider an atomic system having $N+1$ electrons which breaks up into an electron-ion pair. Let the set of quantum numbers $L S M_L M_S$ or LSJM label the energy states of the atom and let the primed set label the states of the residual system. Then the separate conservation of $\bar{L}$ and $\bar{S}$ gives the selection rules

$$\bar{S} = \bar{S}' + \frac{1}{2}, \quad \bar{L} = \bar{L}' + \bar{\ell}, \quad (2)$$

where $\bar{\ell}$ is the orbital angular momentum quantum number of the outgoing electron. The conservation of $\bar{J}$ gives the selection rule

$$\bar{J} = \bar{J}' + \bar{\ell} + \frac{1}{2}. \quad (3)$$

We shall now construct the channel spin wave function $\psi_{cs\nu}$ of the R-matrix theory by vector coupling the wave function of the residual system $|L'S'J'M'\rangle$ and the elementary spin function $|\frac{1}{2}m_s\rangle$,

$$\psi_{cs\nu} = \sum_{M' + m_s = \nu} (J' \frac{1}{2} M' m_s | s\nu) |L'S'J'M'\rangle |\frac{1}{2}m_s\rangle, \quad (4)$$

where the channel spin quantum number $\bar{s} = \bar{J}' + \frac{1}{2}$ and ν is its projection. The wave function $|L'S'J'M'\rangle$ can be expressed as a linear combination of the wave functions $|L'S'M_L'M_S'\rangle$ as

$$|L'S'J'M'\rangle = \sum_{M_L' + M_S' = M'} (L'S'M_L'M_S' | J'M') |L'S'M_L'M_S'\rangle. \quad (5)$$

The channel surface wave functions $\varphi_{cs\ell\nu m}$ are defined as

$$\varphi_{cs\ell\nu m} = r_c^{-1} \psi_{cs\nu} Y_{\ell}^m, \quad (6)$$

where r_c is the relative separation of the electron-ion pair and Y_{ℓ}^m is a normalized spherical harmonic. The channel surface wave function in the $slJM$ scheme is obtained by vector coupling $\psi_{cs\nu}$ and Y_{ℓ}^m . Using (4), (5), and (6), $\varphi_{cs\ell JM}$ can be written as

$$\begin{aligned} \varphi_{cs\ell JM} = r_c^{-1} \sum_{\nu + m = M} \sum_{M' + m_s = \nu} \sum_{M_L' + M_S' = M'} (sl\nu m | JM) \\ \times (J' \frac{1}{2} M' m_s | s\nu) (L'S'M_L'M_S' | J'M') |L'S'M_L'M_S'\rangle |\frac{1}{2}m_s\rangle Y_{\ell}^m. \end{aligned} \quad (7)$$

The wave function $X_{\lambda JM}$ of $(N+1)$ electrons can be written as a linear combination of the L-S coupled wave functions $|L S M_L M_S\rangle$ as

$$X_{\lambda JM} = \sum_{M_L + M_S = M} (L S M_L M_S | JM) |L S M_L M_S\rangle. \quad (8)$$

The reduced width amplitude $\gamma_{\lambda c}$ is given by

$$\gamma_{\lambda c} = \left(\frac{\frac{1}{2} \hbar^2}{2M_c a_c} \right)^{\frac{1}{2}} \int \varphi_c^* X_{\lambda JM} dS_c, \quad (9)$$

where M_c is the reduced mass, a_c the channel radius, dS_c is an element of channel surface, and φ_c denotes the channel surface wave function φ_{cslJM} which is properly antisymmetrized. To antisymmetrize φ_{cslJM} given by (7) we assume that the outgoing $(N+1)^{st}$ electron is inequivalent to the remaining N electrons, and the wave function of N electrons $|L'S'M_L'M_S'\rangle$ is already antisymmetric. By applying the antisymmetrizing operator $A = \frac{1}{\sqrt{N+1}} \sum_p (-1)^p P$ to expression (7), in which the permutation operator P permutes the $(N+1)^{st}$ electron with the remaining N electrons, we get the properly antisymmetrized channel surface wave function. We make a further simplifying assumption that the state of N electrons is not seriously distorted by the addition of the $(N+1)^{st}$ electron. Then the L-S coupled wave function $|L S M_L M_S\rangle$ of $(N+1)$ electrons can be expressed in terms of the wave function $|L'S'M_L'M_S'\rangle$ of N electrons and the wave function $|\ell \frac{1}{2} m m_s\rangle$ of the $(N+1)^{st}$ electron. Therefore $X_{\lambda JM}$ can be written as

$$X_{\lambda JM} = \sum_{M_L + M_S = M} \sum_{M_L' + m = M_L} \sum_{M_S' + m_s = M_S} (L S M_L M_S | JM) \quad (10)$$

$$\times (L' \ell M_L' m | L M_L) (S' \frac{1}{2} M_S' m_s | S M_S) A |L'S'M_L'M_S'\rangle |\ell \frac{1}{2} m m_s\rangle.$$

We need to evaluate the following integral

$$\int A |L'S'M_L'M_S'\rangle |\frac{1}{2} m_s\rangle Y_\ell^m A |L'S'M_L'M_S'\rangle |\ell \frac{1}{2} m m_s\rangle d\tau_1 \dots d\tau_N, \quad (11)$$

where the integration is over the configuration space of N electrons. Since the antisymmetrizing operator A is self adjoint the integral (11) can be written as

$$\int |L'S'M_L'M_S'\rangle |\frac{1}{2} m_s\rangle Y_\ell^m A^2 |L'S'M_L'M_S'\rangle |\ell \frac{1}{2} m m_s\rangle d\tau_1 \dots d\tau_N.$$

Further $A^2 - \sqrt{N+1} A = 0$; therefore, the above integral reduces to

$$\sqrt{N+1} \int |L'S'M_L'M_S'\rangle |\frac{1}{2} m_s\rangle Y_\ell^m A |L'S'M_L'M_S'\rangle |\ell \frac{1}{2} m m_s\rangle d\tau_1 \dots d\tau_N.$$

If we also integrate over the angular coordinates of $(N + 1)^{\text{st}}$ electron and use the orthogonality of N electron functions, then this integral reduces to $R_{N+1}(a_c)$, where $R_{N+1}(a_c)$ is the radial wave function of $(N + 1)^{\text{st}}$ electron evaluated at the channel radius. Substituting the expressions for ϕ_c and $X_{\lambda JM}$ in expression (9), replacing the integral by its value $R_{N+1}(a_c)$, and expressing the summation over magnetic quantum numbers in terms of Racah coefficients, we find

$$\gamma_{\lambda c} = \left(\frac{\hbar^2 a_c^2}{2 M_c} \right)^{\frac{1}{2}} R_{N+1}(a_c) (-1)^{S + S' - s - J'} \sqrt{(2J'+1)(2S+1)(2s+1)(2L+1)} \quad (12)$$

$$W(L'S's\frac{1}{2}; J'S) W(SL'J\ell; sL) .$$

III. ELECTRONIC RADIAL WAVE FUNCTIONS

The electronic radial wave functions $R_{n\ell}(r)$ are obtained by a self-consistent-field calculation. The parameters in the radial wave functions are determined by a variational calculation, in which the radial wave functions $R_{n\ell}(r)$ are expressed as a linear combination of basis orbitals η_i

$$R_a = \sum_{i=1}^M X_{ai} \eta_i, \quad (13)$$

where a is written for $n\ell$.

The orbitals η_i are of the form

$$\eta_i = r^{\ell + A_i} e^{-a_i r}, \quad (14)$$

where A_i is an integer and a_i a variable parameter. To determine these parameters for the unoccupied Hartree-Fock orbitals, the energy of the lowest excited state relative to the ground state is minimized. The various states of the atomic system having a definite value of L and S are constructed by the use of a projection operator technique⁴. The details of self-consistent-field calcu-

lation and the various formulas for the evaluation of matrix elements of the Hamiltonian between Slater determinants are given in reference 5.

The numerical calculation is carried out on the oxygen atom. The lowest excited state 5S was constructed from the excited configuration $(2p)^3(3s)$. Its energy was minimized relative to the ground state 3P of the oxygen atom. The parameters for 3s, 3p electrons are shown in table 1, and the coefficients X are shown in table 2. Using these values the energy of the 5S excited state turns out to be $84\,622.83\text{ cm}^{-1}$ compared to an experimental value of $86\,625.35\text{ cm}^{-1}$, and the energy of the 5P excited state turns out to be $100\,400.85\text{ cm}^{-1}$ compared to an experimental value of $86\,625.35\text{ cm}^{-1}$.

IV. CALCULATION OF PENETRABILITY

The penetrability P_c is given by

$$P_c = \frac{kr}{F^2 + G^2} \bigg|_{r = a_c}, \quad (15)$$

where k is the magnitude of propagation vector in the c.m. system, and F, G are the two linearly independent solutions of the radial wave equation of the relative motion

$$\left\{ \frac{d^2}{dr_c^2} - \frac{l(l+1)}{r_c^2} - \frac{2M_c}{\hbar^2} [V(r_c) - E] \right\} U(r_c) = 0, \quad (16)$$

where $V(r_c)$ is the electron-ion potential energy, E is the energy of the outgoing electron in the c.m. system and $U(r_c)$ is either F or G .

The regular solution F_l starts from zero at the origin and has the asymptotic form

$$F_l \xrightarrow[r \rightarrow \infty]{} \sin \left[kr - \gamma \ln 2kr + \eta_l - \frac{l\pi}{2} \right], \quad (17)$$

where γ is the Coulomb parameter $\frac{ZZ'e^2}{\hbar v}$, v being the relative velocity and η_ℓ is the total phase shift. The irregular solution G_ℓ is the solution which is $\frac{\pi}{2}$ out of phase with F_ℓ at infinity. To get the values of F_ℓ and G_ℓ equation (16) is integrated numerically. The logarithmic derivative of the inside solution is matched to that of the outside Coulomb solution at the boundary which determines the phase shift η_ℓ .

We shall now calculate the electron-ion potential which is to be used in equation (16). The charge density for the ion can be written as

$$\rho(\vec{r}) = Ze \delta(\vec{r}) - \sum_{i=1}^{Z-1} e P_i(\vec{r}), \quad (18)$$

where Z is the atomic number, $\delta(\vec{r})$ is the three dimensional Dirac delta function and $P_i(\vec{r})$ is the probability density for the i^{th} electron. It is given by

$$P_i(\vec{r}) = \int |\psi(\vec{r}_1, \dots, \vec{r}_{i-1}, \vec{r}, \vec{r}_{i+1}, \dots, \vec{r}_{Z-1})|^2 d\tau_1 \dots d\tau_{i-1} d\tau_{i+1} \dots d\tau_{Z-1}. \quad (19)$$

From (16) and (17) we get

$$\int \rho(\vec{r}) d^3r = e,$$

as it should be.

The potential $\phi(\vec{r})$ due to the ion at $\vec{r}$ satisfies Poisson's equation

$$\nabla^2 \phi = -4\pi\rho, \quad (20)$$

and is given by

$$\phi(\vec{r}) = \int \frac{\rho(\vec{r}') d^3r'}{|\vec{r} - \vec{r}'|}. \quad (21)$$

Using (18) and expanding $\frac{1}{|\vec{r} - \vec{r}'|}$, $\phi(\vec{r})$ can be written as

$$\varphi(\bar{r}) = \frac{Ze}{r} - e \sum_{i=1}^{Z-1} \sum_{k=0}^{\infty} \sum_{m=-k}^{+k} \frac{4\pi}{2k+1} Y_k^m(\theta, \varphi) \int \frac{r_{<}^k}{r_{>^{k+1}}} Y_k^{m*}(\theta', \varphi') P_i(\bar{r}') d^3r', \quad (22)$$

where $r_{<}$, $r_{>}$ is the smaller or the larger of r, r' .

We now average $\varphi(\bar{r})$ over the angles and simplify it using the determinantal functions. This gives the following expression for the electron-ion potential energy $V(r)$

$$V(r) = -\frac{Ze^2}{r} + e^2 \sum_{j=1}^{Z-1} \left[\frac{1}{r} \int_0^r |R_j(r')|^2 r'^2 dr' + \int_r^\infty |R_j(r')|^2 r' dr' \right] - \frac{\alpha}{2(r^2 + b^2)^2}, \quad (23)$$

where the last term is added to take into account the electrical polarization, α is the polarizability and b is the core radius. To get a simpler expression for $V(r)$, $R_j(r')$'s are replaced by approximate radial orbitals obtained by Slater's method⁶. Thus for the $e-O^{II}$ system, $V(r)$ can be written as

$$V(r) = -\frac{1}{r} - \frac{1}{r} (2e^{-15.4r} + 5e^{-4.9r}) - 15.4e^{-15.4r} - 1.02e^{-4.9r} (18 + 29.4r + 24.01r^2) - \frac{\alpha}{2(r^2 + b^2)^2}, \quad (24)$$

where we have used atomic units (a.u.). 1 a.u. of energy = 27.210 eV and 1 a.u. of distance = 5.292×10^{-9} cm.

V. RESULTS AND CONCLUSIONS

The potential energy $V(r)$ calculated for various values of α and b is shown in figure 1. These values were used in the ABACUS-2 code to print out the phase shifts and the numerical values of F_ℓ . The values of the irregular function were obtained by a separate FORTRAN program. The numerical calculation shows that the penetrability P_c is not very sensitive to the values of α and b .

In subsequent calculations α was taken to be 3.47 a.u. and b was taken to be 1.23 a.u. A plot of P_c for this set of values of α and b is shown in figure 2.

Because of the selection rules described in Section 2, a number of levels which lie above the series limit in O^I have zero width. Thus all of the auto-ionizing levels which can emit a 3s electron have zero widths. The calculation shows that a number of excited states which are obtained from the configuration $(2p)^3(3p)$ can emit a 3p electron. The values of partial widths for these levels are obtained as a function of channel radius. These values are shown in table 3. The values of $\Gamma_{\lambda c}$ continue to decrease with increasing channel radius not shown in Table 3.

It is interesting to compare the electron emission width obtained by choosing an appropriate channel radius, with the radiation width. The appropriate channel radius can either be chosen by plotting the electron-ion potential energy as a function of r , or by plotting $\Gamma_{\lambda c}$ as a function of channel radius. In the former case we have to choose a point somewhere outside the potential well and in the latter case we have to choose a point where $\Gamma_{\lambda c}$ does not change very rapidly with the channel radius. Figure 3 shows a plot of $\Gamma_{\lambda c}$ as a function of channel radius a_c for the emission of a 3p electron of kinetic energy 1.162 eV. By using a channel radius of 8.787 a.u., the partial width for the emission of a 3p electron having kinetic energy 1.1624 eV turns out to be 5.885×10^{-3} eV. Using the methods given in reference 7, the radiative width for the same level is estimated to be 1.721×10^{-6} eV. Thus the particle width is about 3000 times larger than radiation width.

The selection rules on L,S cause a number of partial widths to vanish. The measurements of these widths can therefore give information about the type of coupling. It is interesting to note that the partial width can also be used to test the accuracy of the electronic radial wave function, since any change in the wave

function produces a significant change in the partial width. Using the techniques given in this paper, it is now possible to get the electron widths of a large number of auto-ionizing levels for a number of atoms. These widths can then be used to obtain statistical distributions in the atomic case⁸.

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TABLE 1

parameters A_i, a_i for the basis orbitals η_i

η_i	l	A_i	a_i (atomic units)
η_1	0	0	7.658
η_2	0	1	2.995
η_3	0	1	1.497
η_4	0	2	1.800
η_5	0	2	0.900
η_6	1	0	2.968
η_7	1	0	1.484
η_8	1	1	1.800
η_9	1	1	0.900

TABLE 2

coefficients X_{ai} for 3s,3p electrons

R_a	X_{a1}	X_{a2}	X_{a3}	X_{a4}	X_{a5}
3s	0.05447	-0.34707	1.06127	-1.34775	1.25635
	X_{a6}	X_{a7}	X_{a8}	X_{a9}	
3p	-0.61580	2.13333	-2.35741	1.30707	

TABLE 3

values of $\Gamma_{\lambda c}$ as a function of channel radius a_c

Kinetic energy of 3p electron (eV)	1.1865	2.8797	1.2978	1.1623	1.0709
	$\Gamma_{\lambda c}$ in eV				
a_c (a.u.)					
1.228	0.4439	0.4294	0.4485	0.0298	0.3984
1.984	0.0274	0.0272	0.0280	0.0019	0.0247
2.740	1.5790	1.5773	1.5987	0.1059	1.4187
3.496	3.6534	3.6638	3.6666	0.2433	3.2755
4.252	3.9666	4.0222	3.9770	0.2637	3.5458
5.007	2.9686	3.0663	2.9992	0.1982	2.6485
5.763	1.7933	1.8859	1.8290	0.1204	1.5993
6.520	0.9471	1.0069	0.9702	0.0638	0.8452
7.275	0.4572	0.4879	0.4670	0.0307	0.4082
8.031	0.2066	0.2209	0.2096	0.0138	0.1843
8.787	0.0886	0.0952	0.0893	0.0059	0.0789

FIGURE CAPTIONS

Fig. 1. Electron- O^{II} potential energy $V(r)$ as a function of r . α is varied from 3.47 to 5.59 and b from 1.23 to 3.23 a.u. The values of $V(r)$ for different sets of values of α and b lie between the two curves shown in the figure.

Fig. 2. Penetrability P_c vs separation distance r_c . $\alpha = 3.47$
 $b = 1.23$ a.u.

Fig. 3. Partial width $\Gamma_{\lambda c}$ as a function of channel radius a_c for the emission of a 3p electron of K.E. 1.162 eV.

FIGURE 1

FIGURE 2

FIGURE 3