Partial autoionization widths of inner hole states of O V from the complex-eigenvalue Schrödinger equation

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(Received 10 October 1986)

We have calculated the partial autoionization widths of the O V $1s2s^22p\ ^3P^0$ and $^1P^0$ states which were measured in recent experiments by Bruch *et al.* In order to account for electron correlation and interchannel coupling we have used the state-specific theory of autoionizing states with complex coordinates. Our results correspond to well-defined regions of stability of the widths and yield ratios for the partial widths which, contrary to existing theory, are in agreement with experiment.

I. INTRODUCTION

Recent experiments by Bruch *et al.*[1] on 10-MeV $O^{3+}+He$ collisions have produced Auger spectra for inner-shell excited ionized oxygen of unprecedented accuracy. As compared with previous work,[2] the clarity of the spectra are such that they allow the unambiguous identification of many autoionizing states. Out of the many features, two stand out as most interesting.

(1) The most intense peaks in the O^{4+} spectra are those which correspond to the decay of the O V $1s2s^22p\ ^3P^0$ state to the O VI $1s^22s\ ^2S$ and $1s^22p\ ^2P^0$ channels. Their intensity ratio $^2P^0/^2S$ is deduced to be 1.7 but no absolute numbers for the Auger transition probabilities can be obtained experimentally.

(2) Although in the case of the O V $1s2s^22p\ ^3P^0$ state both channels are intense, in the case of the $^1P^0$ state the $1s^22s\ ^2S$ channel has very small intensity. The experimental ratio $^2P^0/^2S$ is now about 15.7. Since symmetry cannot provide a direct explanation, this result must have a dynamical origin.

The only previous information on these processes comes from the recent theoretical work of Chen,[3] who carried out Dirac-Fock calculations, with the $2s^2\leftrightarrow 2p^2$ near-degeneracy included, where the scattering orbital is computed without exchange and where the effect of nonorthonormality on the Auger transition matrix element is neglected. His results are presented in Table I. Since, in addition to the above, electron correlation is neglected, the reliability of these calculations is limited.

The aforementioned facts suggest that if accurate information became available from a theoretical calculation, it could be utilized for a careful calibration and interpretation of most of the experimental data.

This report presents results on the partial and total autoionization widths of these states from calculations which include electron correlation and interchannel coupling via the application of the many-electron theory of autoionizing states in terms of complex coordinates.[4,5] Since the radiative widths are negligible,[3] the correspondence with the experimental spectrum[1] is direct.

II. THEORY

According to theory,[4-7] the total autoionization width is obtained from the solution of the N-electron Schrödinger equation with complex eigenvalue, $W=E-(i/2)\Gamma$, using an N-electron square-integrable complex wave function, $\Psi(\rho)$, with complex coordinates, $\rho=re^{i\theta}$, of the form

$$\Psi(\rho)=\alpha(\theta)\Psi_0(\rho)+b(\theta)X(\rho)\ . \tag{1}$$

TABLE I. Partial and total autoionization rates (in 10^{13} sec^{-1}) of the O V $1s2s^22p\ ^3P^0$ and $^1P^0$ states.

	$^3P^0$				$^1P^0$			
Experiment	$1s^22s^2S$	Channel Ratio $(^2P^0/^2S)$	$1s^22P^2P^0$	Total	$1s^22p^2P^0$	Channel Ratio $(^2P^0/^2S)$	$1s^22p^3P^0$	Total
Bruch *et al.*, Ref. 1		1.7				15.7		
Dirac-Fock								
Chen, Ref. 3	4.5	1.9	8.5	13.0	0.12	74.1	8.7	8.8
This work[a]			8.3				9.4	
This work[b]	3.2	1.8	5.8	9.0	0.32	14.7	4.7	5.0

[a]Our calculation used the single configuration, Hartree-Fock approximation.
[b]Calculation includes electron correlation and interchannel coupling. Chen's calculation (Ref. 3) took into account only the zeroth order mixing $2s^2\leftrightarrow 2p^2$, in the initial state, while exchange was neglected in the computation of the continuum function, and the calculation of the autoionization matrix element was carried out without taking into account nonorthonormality or any electron correlation.

$\Psi_0(\rho)$ contains the terms contributing to the stability of the system and $X(\rho)$ represents the *asymptotic correlation,* i.e., the terms contributing to the decay.

The partial widths γ_i are obtained from the systematic analysis and computation of the electronic structure of $\Psi(\rho)$. The method for computing Ψ_0 and X has already been amply demonstrated.[4-7] Nevertheless, as we have stressed in the past, given the novelty of such computations, more experience is required for the consistent choice and optimization of the function spaces representing $X(\rho)$.[4-7] The approach of this work took the following steps.

(1) The Ψ_0 was obtained as before.[4-7] In the present case of the $^3P^0$ and $^1P^0$ states, it is composed of the following configurations: $1s2s^22p$, $1s2p^3$, $1sv_s^22p$, $1svp^22p$, $1s2s2pv_d$, $1s2s2pv_s$, $1s2sv_pv_d$, $1s2sv_d^2$, and $1s2sv_sv_p$. The v_1 represent optimized virtual orbitals.

(2) The form of the terms in $X(\theta)$ is $1s^22l\epsilon l'$ ($2l=2s,2p$, $\epsilon l'=\epsilon p,\epsilon s$). The rotated bound orbital $\epsilon l'(\theta)$ was expanded in terms of square-integrable functions, $\Phi_m^{l'}(r;\lambda)$, with real coordinates

$$\Phi_m^{l'}(r;\lambda)=(\lambda r)^{l'+1}e^{-\lambda r/2}L_m^{2l'+1}(\lambda r), \quad m=0,1,2,\ldots . \tag{2}$$

$L_m^{2l'+1}$ are the generalized Laguerre polynomials,[8] and λ is a variational parameter.

(3) By carrying out the inverse transformation of $r\rightarrow re^{-i\theta}$, the Hamiltonian matrix is composed of the following diagonal and off-diagonal elements:

$$\langle\Psi_0(\theta)\,|\,H(\theta)\Psi_0(\theta)\rangle=\langle\Psi_0(0)\,|\,H(0)\,|\,\Psi_0(0)\rangle=E_0\ , \tag{3a}$$

$$\langle\Psi_0(\theta)\,|\,H(\theta)\,|\,1s^2(\theta)2l(\theta)\phi_m^{l'}(0)\rangle=\langle\Psi_0(0)\,|\,H(0)\,|\,1s^2(0)2l(0)\phi_m^{l'}(-\theta)\rangle\ , \tag{3b}$$

$$\langle 1s^2(\theta)2l(\theta)\phi_m^{l'}(0)\,|\,H(\theta)\,|\,1s^2(\theta)2l(\theta)\phi_m^{l'}(0)\rangle=\langle 1s^2(0)2l(0)\phi_m^{l'}(-\theta)\,|\,H(0)\,|\,1s^2(0)2l(0)\phi_m^{l'}(-\theta)\rangle\ . \tag{3c}$$

The above implies that only one open channel function is *back-rotated,* and this is expanded in terms of the basis set of Eq. (2).[9]

(4) The complex eigenvalue corresponding to each channel is θ dependent. Therefore, the diagonalization is repeated for values of θ between 0° and 90° [the parameter λ of Eq. (2) is also varied] searching for the region of stability of the complex eigenvalue closest to E_0.

(5) First, the following autoionizing processes were examined separately.

(i) $1s2s^22p\ ^3P^0\rightarrow 1s^22p\ ^2P^0\epsilon s\ ^3P^0$,

(ii) $1s2s^22p\ ^3P^0\rightarrow 1s^22s\ ^2S\epsilon p\ ^3P^0$,

(iii) $1s2s^22p\ ^1P^0\rightarrow 1s^22p\ ^2P^0\epsilon s\ ^1P^0$,

(iv) $1s2s^22p\ ^1P^0\rightarrow 1s^22s\ ^2S\epsilon p\ ^1P^0$.

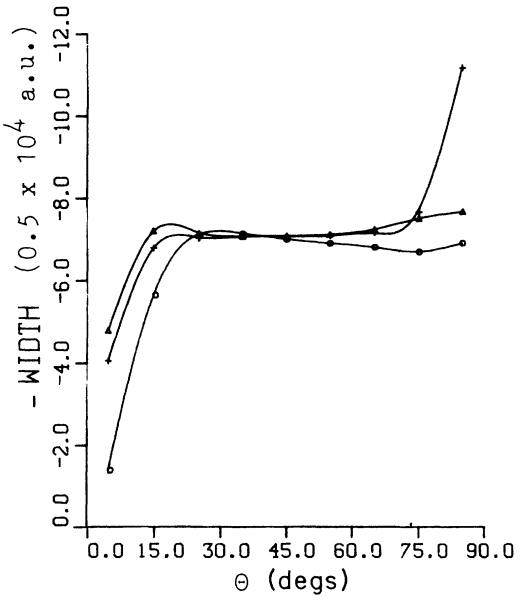

FIG. 1. $1s2s^22p\ ^3P^0\rightarrow 1s^22p\ ^2P^0\epsilon s\ ^3P^0$. Stability of the autoionization half-width (in a.u.) as a function of the rotation angle θ, for $\lambda=4.0$, 6.0, 8.0 [Eq. (2)].

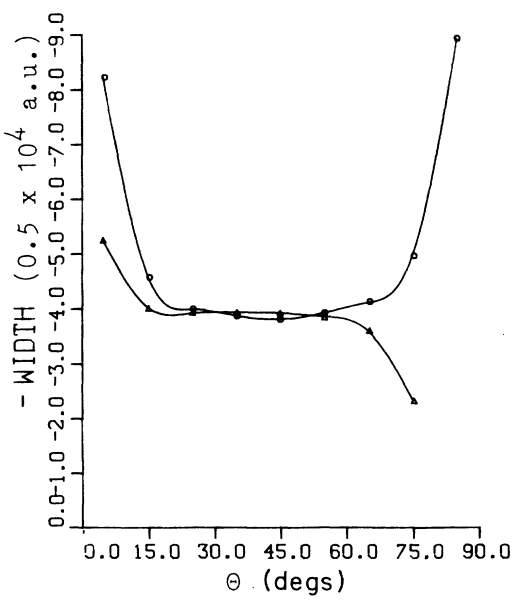

FIG. 2. $1s2s^22p\ ^3P^0\rightarrow 1s^22s\ ^2S\epsilon p\ ^3P^0$. Stability of the autoionization half-width (in a.u.) as a function of the rotation angle θ, for $\lambda=4.0$, 6.0 [Eq. (2)].

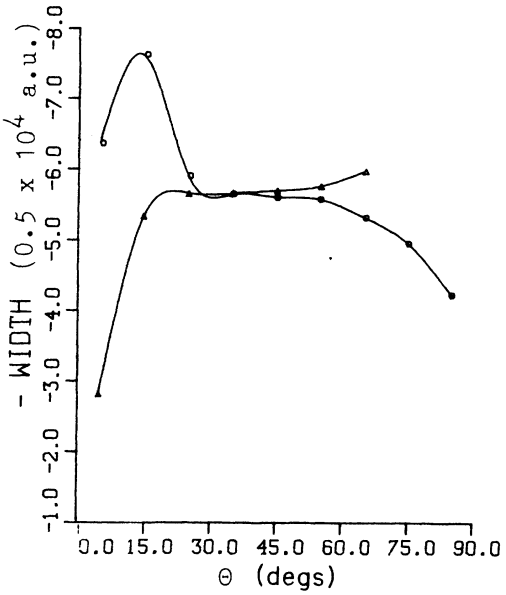

FIG. 3. $1s2s^22p\ ^1P^0 \rightarrow 1s^22p\ ^2P^0\epsilon s\ ^1P^0$. Stability of the autoionization half-width (in a.u.) as a function of the rotation angle θ, for $\lambda=4.0$, 6.0 [Eq. (2)].

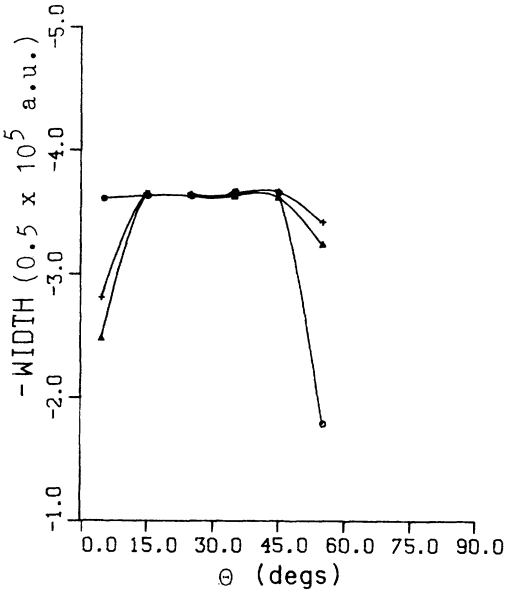

FIG. 4. $1s2s^22p\ ^1P^0 \rightarrow 1s^22s\ ^2S\epsilon p\ ^1P^0$. Stability of the autoionization half-width (in a.u.) as a function of the rotation angle θ, for $\lambda=4.0$, 6.0, 8.0 [Eq. (2)].

Orbitals $1s,2s,2p$, for each decay channel, were in analytic form. For $\epsilon l'(-\theta)$ we used eight to eleven functions of Eq. (2) and diagonalized 9×9 to 12×12 matrices, whose matrix elements are as in Eq. (3). The calculation was repeated for $\theta=5°,15°,\ldots,85°$ and $\lambda=4.0$, 6.0, 8.0, following the root corresponding to E_0. The stability region for the widths is found to be between $\theta=30°$ and $\theta=50°$. (See Figs. 1, 2, 3, and 4.)

(6) By using the assumption that interchannel coupling does not affect significantly the radial characteristics of each asymptotic pair correlation function which yields the partial width in the independent asymptotic pair approximation,[4] we construct the total non-Hermitian matrix and diagonalize it. The diagonalization yields the total resonance wave function for each spin multiplicity:

$$\Psi=\alpha\Psi_0+C_1 1s^2 2p\epsilon s+C_2 1s^2 2s\epsilon p\ . \tag{4}$$

In this computation ϵs and ϵp are held fixed (θ and λ are the stability region) and each partial complex eigenvalue W^i is given by[4]

$$W^i-E_0=\frac{C_i}{\alpha}\langle\Psi_0\,|\,H\,|\,1s^2 2l\epsilon l'\rangle$$
$$=\delta^i-(i/2)\gamma^i,\quad i=1,2$$
$$(2l=2s,2p,\quad \epsilon l'=\epsilon p,\epsilon s)\ . \tag{5}$$

The total width and energy shift are given by

$$\Gamma=\sum_i \gamma^i\ ,$$
$$\Delta=\sum_i \delta^i\ . \tag{6}$$

III. RESULTS

Our results are presented in Table I, where they are compared with those of Chen[3] from Dirac-Fock calculations and the golden rule formula, and with the experimental values of Bruch *et al.*[1] The agreement with experiment is very good. We note that we present only our final results, with interchannel coupling included. The method for doing so was first presented in Refs. 4 and 6.

The explicit consideration of interchannel coupling must be within the practical reach of a fully correlated many-body theory. This is why the present calculation constitutes a good test for the complex eigenvalue many-electron approach. On the other hand, a useful result has emerged, i.e., that its effect on the partial widths in the present and previous cases[4] has been very small. For example, whereas before coupling the partial widths ($\gamma_i/2$ in electron volts) for the $^3P^0$ and $^1P^0$ states are ^2S: 0.01 72, $^2P^0$: 0.019 25 and ^2S: 0.9875×10^{-3}, $^2P^0$: 0.015 41, respectively, after coupling they become ^2S: 0.10 67, $^2P^0$: 0.019 20 and ^2S: 1.056×10^{-3} and $^2P^0$: 0.015 47 eV, respectively.

IV. CONCLUSION

The herein timely, new application of the state-specific theory of autoionizing states in terms of real or complex coordinates[4–7,10–12] has yielded results (Table I) which concur with the recent experimental findings[1] about the ratio of the partial Auger rates. This favorable comparison suggests once again that for the reliable description of the phenomenon of autoionization, the theory must be capable of incorporating systematically both the localized as well as the asymptotic correlation.

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