

Hartree-Fock calculation of transition rates for atoms with multiple open shells of the same symmetry and the same occupation number

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X-ray and Auger transition rates and fluorescence yields have been calculated for the $[2p,3p]$ vacancy states of Ar. The standard Hartree-Fock procedure leads to radial $2p$ wave functions with a node in the tail region. The calculated transition rates agree well with experiment. A calculation in which special techniques are employed to obtain nodeless $2p$ wave functions leads to rather poor estimates of the lifetimes, similar to results of earlier Hartree-Fock-Slater calculations. The frozen-core approximation, widely used to calculate Auger rates, yields erroneous results. Reasons for these difficulties are discussed.

I. INTRODUCTION

Radiative and radiationless deexcitation rates of multiply charged atoms have received considerable attention in the past several years.¹⁻⁶ In heavy-ion-atom collisions several outer-shell electrons can be removed in addition to the creation of inner-shell vacancies.⁵⁻⁸ Atomic inner-shell processes, viz., shake-up, shake-off, and Auger transitions following an inner-shell ionization also lead to multiply ionized atoms.⁹⁻¹¹ Astrophysical and high-temperature laboratory plasmas contain such ionized systems,^{12,13} for example. Properties of these highly stripped excited atoms are very interesting from both theoretical and experimental points of view.

Hartree-Fock calculations for ground-state configurations of atoms and ions with a single unfilled shell are a routine procedure, but the calculation for excited states with two incomplete shells of the same symmetry encounters serious problems. For example, the case of the singly excited $1s2s$ configuration of helium is often cited¹⁴ as one of the most interesting and difficult problems in atomic structure and has been studied extensively.¹⁵⁻¹⁷ In the numerical Hartree-Fock approach in which orthogonality among one-electron orbitals is imposed through the introduction of off-diagonal Lagrange multipliers, such calculations often lead to radial wave functions with an unexpected extra node¹⁵⁻¹⁷ and yield energies that may lie below the observed energy. By imposing additional constraints on the radial wave functions it has been possible to remove the extra node and obtain an energy that is an upper bound to the experimental energy.^{15,17}

Calculations of the atomic structure of excited states with two unfilled shells containing p electrons have also been performed¹⁸⁻²¹ through a numerical Hartree-Fock technique. Froese Fischer has studied^{18,19} configurations of the type $2p^n3p$ in Na^+ , Ne^+ , O , and O^+ . She applied the standard Hartree-Fock procedure to some of the states of these configurations and found it to yield $2p$ wave functions with an extra node. Calculations with additional orthogonality constraints resulted in nodeless $2p$ wave functions. The ionization energy was calculated from the

energy difference $E(2p^n3p) - E(2p^n)$, and also using Koopman's theorem. Surprisingly, in each case, the standard Hartree-Fock calculation which yields $2p$ wave functions with an extra node agreed much better with the observed ionization energies¹⁹ than the calculation which leads to nodeless $2p$ wave functions.

In this paper we report on a Hartree-Fock calculation of x-ray and Auger transition rates and fluorescence yields for $[2p,3p]$ vacancy states of Ar. Froese Fischer has already calculated the term energies of this configuration and has discussed in detail the special problems that one encounters in applying a numerical orthogonal Hartree-Fock approach to these states.^{20,21} The present investigation is undertaken for the following two reasons.

(i) To understand the structure of those excited ionic configurations that need special consideration in Hartree-Fock calculations, it is necessary to calculate other properties of these systems that are quite sensitive to the wave functions. Recently, Nordgren *et al.*^{22,23} have been able to measure the absolute deexcitation rates of $[2p,3p]$ vacancy states of Ar from natural x-ray line widths through a high-resolution experiment. Comparison of these observed transition rates with existing Hartree-Fock-Slater calculations^{24,25} reveals a perplexing discrepancy: The measured term intensities differ by a factor of 4 or more from the calculated values. Furthermore, the lifetime of an inner-shell vacancy is found to increase much more rapidly with the creation of outer-shell vacancies than was predicted earlier on the basis of statistical²⁶ and Hartree-Fock-Slater theory. It is interesting to see whether a Hartree-Fock calculation, in spite of its difficulties, leads to better results compared with observations.

(ii) In experiments involving heavy-ion-atom collisions, the charge state of the collision products is usually investigated by looking at the x-ray emission spectrum. To determine the relative populations from line intensities, a knowledge of fluorescence yields for various multiple vacancy states is essential. Experimental values of fluorescence yields for such states are not usually available, placing added importance on theory. Since most multiple-vacancy states predominantly decay by radiation-

less transitions, an accurate value of nonradiative transition rates is crucial in determining fluorescence yields. In the light of poor performance by the statistical and Hartree-Fock-Slater calculations in predicting such rates it is instructive to try other approaches.

II. THEORY

The x-ray and Auger transition rates W can be calculated using time-dependent perturbation theory,

$$W = 2\pi |\langle \psi_f | O | \psi_i \rangle|^2 \rho(E_f), \quad (1)$$

where ψ_i and ψ_f are the initial and final states of the sys-

$$\langle \gamma'J' || D || \gamma J \rangle = -3^{-1/2} (-1)^{S+L+J'} [(2J+1)(2L+1)(2J'+1)]^{1/2} \begin{Bmatrix} J' & 1 & J \\ L & S & 1 \end{Bmatrix} \int P_{2p}(r) r P_{3s}(r) dr, \quad (3)$$

where R_{2p} and R_{3s} are the radial wave functions. Summing over all J' in Eq. (3) and substituting into Eq. (2) we find

$$W = (4\Delta E^3/9c^3) \left| \int P_{2p}(r) r P_{3s}(r) dr \right|^2. \quad (4)$$

To calculate nonradiative transition rates, the operator O in Eq. (1) is replaced by $H - E$,²⁷ where E is the initial total energy and H is the total Hamiltonian of the system. If we assume that the initial and final one-electron orbitals are orthogonal, we can make the following approximations:

$$W = 2\pi |\langle \psi_f | H - E | \psi_i \rangle|^2 \rho(E_f) \quad (5a)$$

$$\approx 2\pi \left| \langle \psi_f | \sum_{i>j} (1/r_{ij}) | \psi_i \rangle \right|^2 \rho(E_f) \quad (5b)$$

$$= 2\pi \left| \sum_k a_k R^k(n_1 l_1 n_2 l_2; n_3 l_3 n_c l_c) \right|^2. \quad (5c)$$

In Eq. (5c) the $R^k(n_1 l_1 n_2 l_2; n_3 l_3 n_c l_c)$ are Slater integrals, and the a_k are the angular coefficients.²⁸ The quantum numbers $n_c l_c$ characterize the continuum-electron orbital which is normalized per unit energy.

Auger decay of $[2p, 3p]$ vacancy states of Ar includes transitions from the initial states

$$1s^2 2s^2 2p^5 3s^2 3p^5 1,3(SPD) \quad (6a)$$

to the final states

$$(1s^2 2s^2 2p^6 3p^5) \epsilon p^1,3(SPD); \epsilon f^1,3D, \quad (6b)$$

$$(1s^2 2s^2 2p^6 3s 3p^4) \epsilon s^1,3(SPD); \epsilon d^1,3(SPD), \quad (6c)$$

and

$$(1s^2 2s^2 2p^6 3s^2 3p^3) \epsilon p^1,3(SPD); \epsilon f^1,3(PD). \quad (6d)$$

The processes in Eqs. (6b), (6c), and (6d), respectively, are $L_{23}M_{23}-M_1M_1M_{23}$, $L_{23}M_{23}-M_1M_{23}M_{23}$, and $L_{23}M_{23}-M_{23}M_{23}M_{23}$ Auger transitions.

III. NUMERICAL CALCULATIONS

The initial and final one-electron orbitals and energies were obtained using the Hartree-Fock computer code of

tem, respectively; $\rho(E_f)$ is the density of final states, and O is the appropriate operator. For E1 transitions we have

$$W = \frac{4}{3} \left[\frac{\Delta E}{c} \right]^3 \frac{1}{(2J+1)} |\langle \gamma'J' || D || \gamma J \rangle|^2, \quad (2)$$

where $|\gamma J\rangle$ and $|\gamma'J'\rangle$ represent the initial and final states of the system, respectively, E is the energy difference between the initial and final states, c is the velocity of light, D is the electric dipole operator, and $\langle \gamma'J' || D || \gamma J \rangle$ is the reduced matrix element. For the $2p^5 3s^2 3p^5(SLJ) - 2p^6 3s 3p^5(S'L'J')$ transition in Ar, the reduced matrix element is

Frøese Fischer.²⁹ Following her work,^{20,21} we have performed a Hartree-Fock calculation of the statistically weighted average energies of the 3S , 1P , and 3D states. To obtain accurate initial estimates, a Hartree-Fock calculation was first performed with the off-diagonal Lagrange multipliers λ_{2p3p} and λ_{3p2p} set equal to zero. The Gram-Schmidt procedure was employed to ensure orthogonalization of one-electron orbitals. This calculation yields nodeless radial $2p$ wave functions. These wave functions were fed as initial estimates into the standard Hartree-Fock routine.²⁹ The calculation produced radial $2p$ wave functions with a node in the tail. The radial $2p$, $3s$, and $3p$ wave functions from both of these calculations are shown in Fig. 1. It is seen that the $2p$ and $3p$ wave functions differ greatly, but that there is hardly any change in the $3s$ wave function.

The wave function of the continuum electron was determined in the field of the final ionic state. The exchange interaction among the continuum and the final-bound-

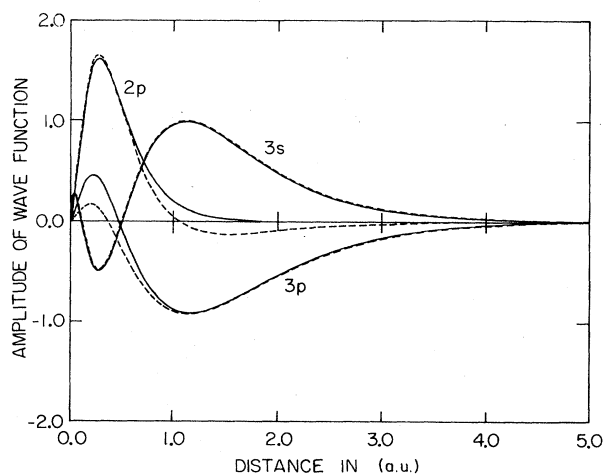


FIG. 1. Radial $2p$, $3s$, and $3p$ wave functions of Ar. The dashed curve indicates the result of a standard Hartree-Fock calculation which yields $2p$ wave functions with a node in the tail; the solid curve represents the result of a Hartree-Fock calculation in which the Lagrange multipliers λ_{2p3p} and λ_{3p2p} were set equal to zero.

state electrons³⁰ was taken into account. The continuum orbitals were made orthogonal to the bound-state one-electron orbitals by using the Gram-Schmidt orthogonalization procedure. The angular coefficients a_k in Eq. (5c) were evaluated using Hibbert's computer program.³¹ These coefficients agree with those reported by Chen and Crasemann.²⁴

IV. RESULTS AND DISCUSSION

A. Auger transition rates

Auger transition rates were calculated using wave functions both from the special Hartree-Fock procedure in which off-diagonal Lagrange multipliers are set equal to zero to get nodeless $2p$ wave functions, and from the standard Hartree-Fock approach as described above. The Auger transition rates and fluorescence yields from these calculations are listed in Table I. The transition rates from the Hartree-Fock-Slater calculation of Chen and Crasemann²⁴ and the experimental rates obtained by Nordgren *et al.*^{22,23} from natural linewidth measurements are also listed. It is seen that results of the standard Hartree-Fock calculation which yields a radial $2p$ wave function with a node in its tail agrees well with the experimental rates. The Auger term intensities obtained from the Hartree-Fock-Slater calculation are off by factors of ~ 4 or more from the experimental intensities, but agree well with the special Hartree-Fock calculation that yields nodeless $2p$ wave functions. To investigate any term dependence, Auger transition rates were also calculated using wave functions of 1S and 3D states. The radial $2p$ wave functions from these calculations exhibit similar behavior in relation to the special and standard Hartree-Fock approach. Auger rates from these calculations do not vary more than 4% from the rates reported in Table I.

Auger-electron energies can be calculated from the differences of total term energies of the initial states and

the final ionic states. These energies are needed to calculate Hartree-Fock wave functions of the continuum electron. In the present calculation, however, we used Auger-electron energies that are the differences between configuration-average energies. The maximum difference in Auger-electron energies due to multiplet splitting of the initial and final states is ~ 12 eV. It was found that variation over this energy does not cause significant changes in the Auger matrix elements. The exchange interaction between the outgoing Auger electron and the final bound-state electrons was found to be small for most terms.

After an Auger transition, the atomic orbitals relax in the new potential. Auger transition rates are, however, usually calculated in the frozen-core approximation, under the assumption that the effect of orbital relaxation can be neglected and the final bound-state wave functions in Eq. (5c) can be replaced by those of the initial configuration. In view of the differences, in the present case, between the initial- and final-state $2p$ and $3p$ orbitals, Auger transition rates were also calculated from Eq. (5c) with radial wave functions of the final states replaced by those of the initial states, and vice versa. Both these approximations were found to yield erroneous results. The Auger rates computed by replacing the final wave functions with initial ones underestimates the experimental rates by a factor of ~ 3 , while the rates obtained by replacing the initial wave functions with the final ones overestimate the experimental rates by a factor of ~ 4 . The latter results agree approximately with those from Hartree-Fock-Slater calculation.

B. Radiative rates and fluorescence yields

The $[2p,3p]$ vacancy states in Ar can decay through various radiative channels. The total x-ray transition rate summed over all final channels is the same for each initial state if configuration-average energies are used in Eq. (4).

TABLE I. Auger transition rates (in milliatomic units) and fluorescence yield (in multiples of 10^{-4}) for $[2p,3p]$ vacancy states of Ar.

	Initial states					
	1D	3D	1S	1P	3P	3S
	Auger transition rates					
Experiment ^a	2.57	1.47	1.84	< 1.47		
HFS calculation ^b	10.235	0.347	9.210	0.479	10.906	0.133
Present calculation ^c	8.195	0.336	7.812	0.376	8.701	0.088
Present calculation ^d	2.601	0.761	2.213	0.472	2.652	0.083
	Fluorescence yields					
HFS calculation ^b	0.859	25.310	0.954	18.340	0.806	66.150
Present calculation ^d	4.542	15.508	5.338	24.980	4.455	140.410

^aReferences 22 and 23.

^bHartree-Fock-Slater calculation, Ref. 24.

^cPresent Hartree-Fock calculation in which off-diagonal Lagrange multipliers were set equal to zero to obtain nodeless radial $2p$ wave functions.

^dPresent Hartree-Fock calculation which yields radial $2p$ wave functions with a node in their tail.

This rate was found to be 11.83×10^{-7} a.u. The rate agrees reasonably well with results from the statistical approach,²⁶ the Hartree-Fock-Slater calculation of Chen and Crasemann.²⁴ The fluorescence yields for all the initial vacancy states are listed in Table I. The average fluorescence yield for the $[2p, 3p]$ configuration, calculated as²⁴

$$\bar{\omega} = \frac{\sum_{L,S} (2L+1)(2S+1)\omega(L,S)}{\sum_{L,S} (2L+1)(2S+1)}, \quad (7)$$

was found to be 22.13×10^{-4} . Fluorescence yields of individual terms from the present work differ widely from the Hartree-Fock-Slater results of Chen and Crasemann;²⁴ the average fluorescence yields remain, however, in fair agreement.

V. CONCLUSION

The requirements of stationary energy and the constraints of orthogonality of one-electron orbitals in the numerical Hartree-Fock calculation of excited configurations with two open shells of the same symmetry and the same occupation number can force the appearance of an additional node in the tail region of radial wave functions. Appearance of these nodes can be avoided by imposing additional constraints on the wave functions. For the $[2p, 3p]$ configuration of Ar, the $2p$ wave functions con-

tain an extra node in their tail. The Auger transition rates calculated with these wave functions agree extremely well with experimental rates, at least compared with the Hartree-Fock-Slater calculations which differ by a factor of ~ 4 from the measured rates.

A great deal of effort has been reported in the literature on numerical Hartree-Fock calculations of the structure and energetics of excited configurations of the type $nln'l$, $2p^n 3p$, and $[2p, 3p]$. Here we have attempted to extend this approach to calculate other properties of such excited states. Auger transition rates are extremely sensitive probes of atomic structure. In view of the success of the present calculation we can conclude that the numerical Hartree-Fock approach, in spite of certain difficulties, can lead to an adequate approximate description of excited configurations with unfilled shells of the same symmetry and the same occupation number.

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¹K. R. Karim, M. H. Chen, and B. Crasemann, *Phys. Rev. A* **28**, 3355 (1983).

²Itoh, T. Schneider, G. Schiwietz, Z. Roller, H. Platten, G. Nolte, D. Schneider, and N. Stolterfoht, *J. Phys. B* **16**, 3965 (1983).

³D. Ridder and D. Schneider, *Phys. Rev. A* **25**, 921 (1982).

⁴M. H. Chen, B. Crasemann, K. R. Karim, and H. Mark, *Phys. Rev. A* **24**, 1845 (1981).

⁵D. Schneider, M. Prost, B. Dubois, and N. Stolterfoht, *Phys. Rev. A* **25**, 3102 (1981).

⁶R. S. Peterson, W. W. Smith, H. C. Hayden, and M. Furst, *IEEE Trans. Nucl. Sci.* **NS-28**, 1114 (1981).

⁷D. Schneider, R. Bruch, W. H. E. Schwarz, T. C. Chang, and C. F. Moore, *Phys. Rev. A* **15**, 926 (1977).

⁸P. Dahl, M. Rødbro, G. Herman, B. Fastrup, and M. E. Rudd, *J. Phys. B* **9**, 1581 (1976).

⁹G. Armen, T. Åberg, K. R. Karim, J. C. Levin, B. Crasemann, G. S. Brown, M. H. Chen, and G. E. Ice, *Phys. Rev. Lett.* **54**, 182 (1985).

¹⁰P. H. Kobrin, S. Southworth, C. M. Truesdale, D. W. Lindle, U. Becker, and D. A. Shirley, *Phys. Rev. A* **29**, 194 (1984).

¹¹R. D. Deslattes, R. E. LaVilla, P. L. Cowan, and A. Henins, *Phys. Rev. A* **27**, 923 (1983).

¹²N. J. Peacock, M. F. Stamp, and J. D. Silver, *Phys. Scr.* **T8**, 10 (1984).

¹³V. A. Boikov, A. Ya. Faenov, and S. A. Pikuz, *J. Quant. Spectrosc. Radiat. Transfer* **19**, 11 (1978).

¹⁴A. S. Coolidge and H. M. James, *Phys. Rev.* **49**, 676 (1936).

¹⁵C. Froese Fischer, *Can. J. Phys.* **45**, 7 (1967).

¹⁶C. Froese Fischer, *Can. J. Phys.* **51**, 1238 (1973).

¹⁷C. Froese Fischer, *J. Phys. B* **5**, 1302 (1972).

¹⁸C. Froese Fischer, *Phys. Rev.* **137**, A1644 (1965).

¹⁹C. Froese Fischer, *Can. J. Phys.* **46**, 2435 (1968).

²⁰C. Froese Fischer, *Phys. Rev. Lett.* **38**, 1075 (1977).

²¹C. Froese Fischer, *J. Phys. B* **11**, 2267 (1978).

²²J. Nordgren, H. Ågren, L. Selander, C. Nordling, and K. Siegbahn, *Phys. Scr.* **16**, 70 (1977).

²³J. Nordgren, H. Ågren, C. Nordling, and K. Siegbahn, *Phys. Scr.* **19**, 5 (1979).

²⁴M. H. Chen and B. Crasemann, *Phys. Rev. A* **10**, 2232 (1974).

²⁵E. J. McGuire, *Phys. Rev. A* **11**, 1880 (1975).

²⁶E. J. McGuire, *Phys. Rev.* **185**, 1 (1969); F. P. Larkins, *J. Phys. B* **4**, L29 (1971).

²⁷T. Åberg and G. Howat, in *Corpuscles and Radiation in Matter I*, Vol. 31 of *Handbuch der Physik*, edited by W. Mehlhorn (Springer, Berlin, 1982), p. 469.

²⁸K. R. Karim, M. H. Chen, and B. Crasemann, *Phys. Rev. A* **31**, 709 (1985).

²⁹C. Froese Fischer, *Comput. Phys. Commun.* **14**, 145 (1978).

³⁰K. R. Karim, M. H. Chen, and B. Crasemann, *Phys. Rev. A* **29**, 2605 (1984).

³¹A. Hibbert, *Comput. Phys. Commun.* **2**, 180 (1971).