Multiconfiguration Tamm-Dancoff approximation applied to photoionization of the outer shells of Be and Mg

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A multiconfiguration version of the Tamm-Dancoff approximation (MCTD) is developed to study photoexcitation of atoms in cases where the simultaneous excitation of two atomic electrons is important. Starting from a multiconfiguration Dirac-Fock description of the ground state, the variational principle is applied to give equations for a final-state wave function consisting of both singly excited and doubly excited configurations. To illustrate the method, the MCTD equations are applied to determine the $2pns$ and $2pnd$ autoionizing resonances in the low-energy photoionization cross section of Be and the corresponding $3pns$ and $3pnd$ resonances in Mg. The predicted cross sections are found to be in good agreement with previous theoretical results as well as with the available experimental data.

In this paper we present results of a multiconfiguration Tamm-Dancoff calculation of autoionizing resonances involving doubly excited states in Be and Mg atoms. The motivation for the present work is to develop a practical yet accurate method to treat the photoionization of atoms in situations where the simultaneous excitation of two electrons is important. There exist a number of more or less simple, but powerful and elegant schemes such as the R-matrix method[1] and the random-phase approximation (RPA)[2–9] to treat single excitations, while for multielectron excitations the number and power of such schemes is limited. For example, there is the very general approach of configuration interaction, which has been applied to the atoms considered here.[10] Another general approach is many-body perturbation theory[11] which has been applied by Altun, Carter, and Kelly[12] to treat multielectron excitations in Ca and by Chang[13] to treat multielectron excitations in He. Then there is the close-coupling method (see, e.g., Secs. 3 and 4 of Ref. 14), which has been also applied to Be and Mg.[15] There is also the hyperspherical-coordinate approach[16] which has been generalized and applied to treat double excitations of alkaline-earth atoms by Greene.[17] Further, there is the multiconfiguration time-dependent Hartree-Fock approximation (MC-TDHF)[18] and its relativistic generalization, the multiconfiguration relativistic random-phase approximation (MC-RRPA),[19] which have been applied to treat bound-bound excitations in both atomic and molecular systems.[20,21]

The technique described here, the multiconfiguration Tamm-Dancoff approximation (MCTD), is related to the MC-RRPA. As in the MC-RRPA, the linear response to an external electromagnetic field of a system, described in its ground state by a multiconfiguration wave function, is determined variationally. The MCTD excited-state wave function is restricted to include excited-bound configurations constructed from the ground-state orbitals and configurations obtained by single excitations of the ground-state valence orbitals to the continuum. It is just the use of a multiconfiguration ground state that permits us to include automatically the effects of multielectron excitations in our calculations. The single excitations of those configurations which are obtained from the nominal ground state by two-electron, two-hole substitutions, for example, lead to final states with two excited electrons. We use a relativistic multiconfiguration Dirac-Fock (MCDF) wave function to describe the ground state in order to include fine-structure effects automatically: although, in the applications considered below, relativistic effects are not pronounced.

The usual Tamm-Dancoff approximation[22] takes into account many-electron correlations in excited states only, while the RPA, as a further generalization of the Tamm-Dancoff approximation, also includes ground-state correlations through negative-frequency (or time-backward) Feynman-Goldstone diagrams. The MCTD is a somewhat different generalization of the Tamm-Dancoff approximation, in which important ground-state correlations are included by replacing the single-configuration Dirac-Fock (DF) ground-state wave function by a multiconfiguration one. Mathematically, the MCTD approximation can be reduced to the problem of solving a system of coupled integro-differential equations, similar to those of the RRPA,[8] together with an additional system of linear algebraic equations for the weight coefficients of excited bound configurations. Although the detailed formalism and derivation of the MCTD equations will be described elsewhere,[23] we give some elements of the MCTD theory and equations in the paragraphs below.

As mentioned previously the MCTD ground state is obtained from an MCDF calculation.[24,25] The MCTD excited-state wave function with the total angular momentum J,M is taken to have the form

$$\Psi(JM)=\sum_{i=1}^{n_c} c_i\chi(\gamma_i JM)+\sum_{j=1}^{n_b} b_j\Phi(\gamma_j JM)\ ,$$

where $\chi(\gamma_i JM)$ and $\Phi(\gamma_j JM)$ are configuration wave functions obtained from one of the ground-state configurations (parent configuration) by photoexciting a valence orbital (hole a) to a continuum orbital $\tilde{a}$, or to another

ground-state (valence) orbital, respectively; γ_i and γ_j represent all other quantum numbers required to define the corresponding configurations uniquely. The parameters c_i are the weight coefficients of the parent configuration, while b_j are the weight coefficients of the excited-bound configuration (XB) composed of ground-state orbitals. The numbers n_c and n_b designate the number of the continuum configurations (photoionization channels) and of the excited-bound configurations, respectively.

The weight coefficients b_j of the XB configurations are solutions of the system of linear algebraic equations

$$\sum_{j=1}^{n_b} [H_{kj}-(E_0+\omega)\delta_{kj}]b_j=F_k \ , \quad k=1,2,\ldots,n_b$$

where $H_{kj}=\langle \Phi(\gamma_k JM) \mid H \mid \Phi(\gamma_j JM)\rangle$ is the atomic Hamiltonian matrix element between XB configurations, E_0 is the ground-state energy, ω is the photon energy, and the terms F_k are given by

$$F_k=-\sum_{i=1}^{n_c} H_{ki}c_i \ ,$$

where $H_{ki}=\langle \chi(\gamma_k JM) \mid H \mid \Phi(\gamma_k JM)\rangle$ is the atomic Hamiltonian matrix element between an XB configuration and a continuum configuration. The continuum orbital function $y_{\tilde{a}}$ for a channel $a\rightarrow\tilde{a}$ is the solution of the following radial integro-differential equation:

$$(h_{\tilde{a}}+V_{\tilde{a}}-\epsilon_a-\omega)y_{\tilde{a}}=R_{\tilde{a}} \ ,$$

where $h_{\tilde{a}}$ is the radial free-particle Dirac Hamiltonian, $V_{\tilde{a}}$ is the Hartree-Fock $V(N-1)$ potential, ϵ_a is the eigenvalue of the ground-state orbital (hole) a, ω is the photon energy, while the term $R_{\tilde{a}}$ describes the interchannel coupling and the coupling to excited-bound configurations.

The photoionization parameters (the cross sections, branching ratios, photoelectric angular distribution asymmetry parameter, and spin polarization parameters) are calculated in terms of the orbital functions as in the RRPA,[8] but modified to account for transitions to XB configurations. We have developed a computer code to solve the necessary equations and to evaluate the photoionization parameters in the MCTD, and we have applied this code to investigate outer-shell photoionization of Be and Mg atoms. For the ground state of these atoms the following configurations are considered: for Be,

$$1s^2(2s^2+2p_{1/2}^2+2p_{3/2}^2) \ , \quad J=0$$

and for Mg,

$$1s^22s^22p^6(3s^2+3p_{1/2}^2+3p_{1/2}^2) \ , \quad J=0 \ .$$

The MCDF code of Desclaux,[24] or that of Grant *et al.*,[25] is suitable for obtaining the ground-state orbitals and weights. The negatives of the valence *ns* and *np* (Be, $n=2$; Mg, $n=3$) eigenvalues represent theoretical values of the corresponding thresholds in the MCTD. These theoretical thresholds are listed in Table I, where they are compared with the corresponding experimental thresholds,[26] as well as with the single-configuration DF eigenvalues which are the theoretical thresholds for the RRPA. The agreement between theoretical and experimental thresholds[26] is seen to be improved using a multiconfiguration description of the ground state. In the calculations of the final-state wave function we include seven excitation channels:

$$ns\rightarrow p_{1/2},p_{3/2} \ ,$$

$$np_{1/2}\rightarrow s,d_{3/2} \ ,$$

$$np_{3/2}\rightarrow s,d_{3/2},d_{5/2} \ ,$$

where $n=2$ for Be and $n=3$ for Mg. The MCTD equations given in the previous paragraph are solved for these seven coupled channels and the resulting transition amplitudes are determined. From these amplitudes the corresponding photoionization parameters are worked out.

The results of our calculations for the cross section in dipole-length form, in the energy region above the second (*np*) threshold, are shown in Fig. 1 for Be and Fig. 2 for Mg, where they are compared with RRPA results and single-configuration Tamm-Dancoff calculations. In the RRPA and Tamm-Dancoff calculations, just as in the MCTD case, channels obtained by exciting core electrons are not included, i.e., in the single-configuration calculations shown in Figs. 1 and 2, only those two channels arising from excitation of the outer *ns* shell are considered. As seen from Figs. 1 and 2 all of the methods used lead to essentially the same results for the total cross section far above the threshold. The results are somewhat different close to the threshold, however, the general shapes and trends of the cross section curves are very similar. Furthermore, the MCTD results are there closer to the RRPA ones than to the single-configuration Tamm-

TABLE I. Theoretical MCTD and RRPA photoionization thresholds compared with experimental thresholds.

Atom	Shell	MCTD		RRPA		Experiment[a]	
		(a.u.)	(eV)	(a.u.)	(eV)	(a.u.)	(eV)
Be	$2s$	0.3498	9.520	0.309	8.42	0.3426	9.320
	$2p_{1/2}$	0.4927	13.407			0.4881	13.281
	$2p_{3/2}$	0.4927	13.408			0.4881	13.282
Mg	$3s$	0.2827	7.692	0.253	6.88	0.2810	7.644
	$3p_{1/2}$	0.4354	11.848			0.4435	12.069
	$3p_{3/2}$	0.4359	11.861			0.4439	12.080

[a]Moore, Ref. 26.

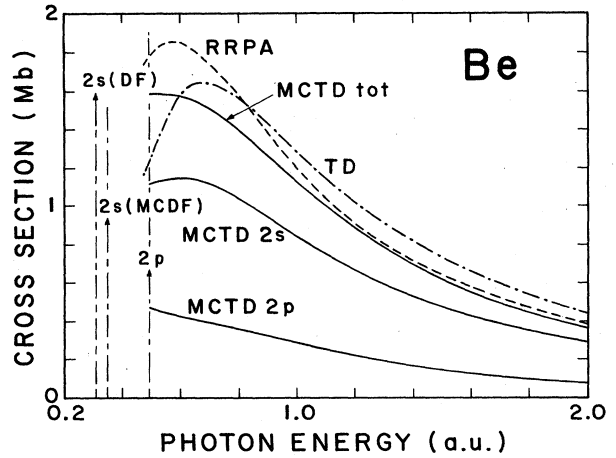

FIG. 1. Photoionization cross section of outer shells of Be in the energy region above the second ($2p$) threshold. Solid curves represent the present results in the MCTD for $2s$ (labeled MCTD $2s$) and $2p$ (labeled MCTD $2p$) shells, and for the sum of both contributions (labeled MCTD tot). Dashed curve represent the $2s$ cross section in the RRPA, while the dotted-dashed curve (labeled TD) is the result for the single-configuration Tamm-Dancoff calculation.

Dancoff results. This is because the present method includes the dominant part of the two-particle two-hole ground-state correlations, which are also included in the RPA through the time-backward Feynman-Goldstone diagrams.

In the energy region between the first (ns) and the second threshold ($np_{1/2}$) only two of seven channels are open ($ns \rightarrow p_{1/2}, p_{3/2}$), while the remaining five exhibit

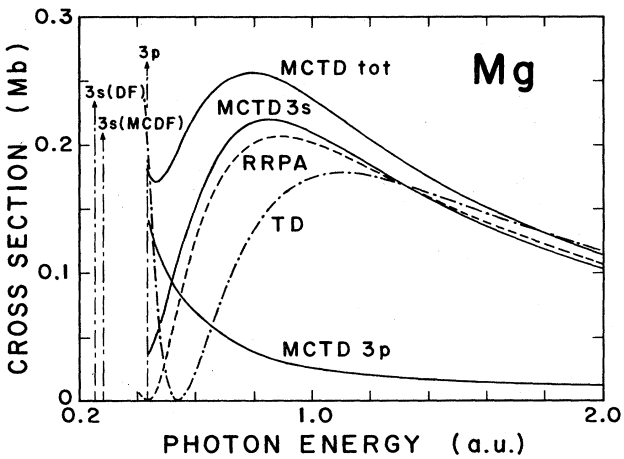

FIG. 2. Photoionization cross section of outer shells of Mg in the energy region above the second ($3p$) threshold. Solid curves represent the present results in the MCTD for $3s$ (labeled MCTD $3s$) and $3p$ (labeled MCTD $3p$) shells, and for the sum of both contributions (labeled MCTD tot). Dashed curve represents the $3s$ cross section in the RRPA, while the dotted-dashed curve (labeled TD) is the result for the single-configuration Tamm-Dancoff calculation.

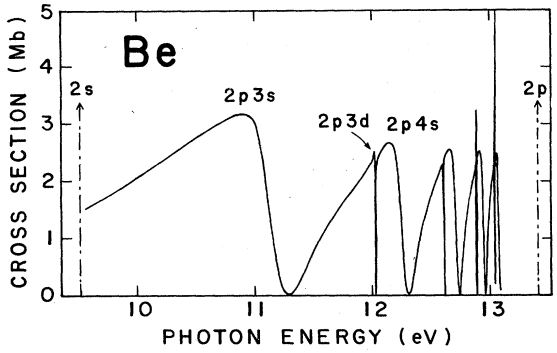

FIG. 3. Cross section for Be in the resonance region between the first ($2s_{1/2}$) and second ($2p_{1/2}$) thresholds.

five Rydberg series of discrete (bound) states producing autoionizing resonance profiles in the ns cross section.

To study these resonances, we first calculated the multichannel quantum-defect parameters, which are slowly varying functions of energy. We extrapolated or interpolated these parameters to the region of interest and then applied the multichannel quantum-defect theory (MQDT) analysis[27] to obtain the resulting cross sections. The calculated cross section in the resonance region is presented in Fig. 3 for Be and in Fig. 4 for Mg. We did not calculate the cross section for Mg in the vicinity of the first threshold, since extrapolation from the region near the second threshold becomes inaccurate in the vicinity of the first threshold. Because of low values of nuclear charge for both atoms, they behave rather nonrelativistically, and only two of five series of resonances show up distinctly in the figures. However, due to the gradual onset of relativistic effects with the increase of nuclear charge, for Mg a third series of resonances can be seen on the left shoulder of the broad $2pns$ profiles in Fig. 4. If LS coupling were valid for Mg, only two series of resonances would appear, the series $3pns\ ^1P_1$ and $3pnd\ ^1P_1$. The shapes on the resonances in Figs. 3 and 4 are very similar to previous configuration-interaction[10] results, and to those obtained

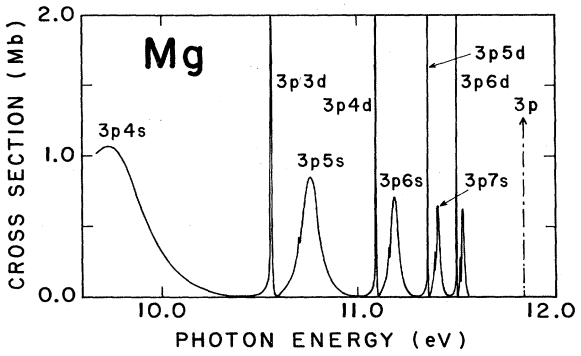

FIG. 4. Cross section for Mg in the resonance region below the second ($3p_{1/2}$) threshold. Respective heights of sharp $3snd$, $n = 4,5,6,7$ resonances are 13.6, 16.5, 15.9, and 13.0 Mb.

from close-coupling calculations using quantum-defect theory,[15] as well as to the results obtained using hyperspherical coordinates,[17] apart from the additional $3pns\ ^3P_1$ series of resonances, which cannot appear in the nonrelativistic LS-coupled calculations with which we compare our results. The calculated resonance positions agree well with the predictions of these alternative approaches and with the available experimental data.[28,29]

We have put forth the MCTD as a simple yet powerful alternative to the RPA to treat problems of photoexcitation in atomic systems where double excitations play a significant role. Final-state electron-electron correlations are included in the MCTD in the same way as they are included in the RPA, while initial-state correlations are included by adopting a multiconfiguration initial-state wave function as an alternative to summing time-backward Feynman diagrams. Using this hybrid procedure it is possible to study situations where two-electron excitations play an important role in determining the behavior of photoexcitation amplitudes. Calculations of the low-energy photoionization cross sections of Be and Mg illustrate the potential of the MCTD to predict photoionization parameters in cases where two-electron excitations dominate the cross section. Also, the MCTD as a relativistic approach accounts automatically for spin orbit interaction and consequently for breakdown of LS coupling, and thus can be used for systems with higher nuclear charge where these effects are important.

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[1]P. G. Burke and K. T. Taylor, J. Phys. B 2620 (1975).

[2]There are a number of equivalent approaches which fall under the rubric RPA. There is first the pioneering work on photoionization of atoms by P. L. Altick and A. E. Glassgold, Phys. Rev. **113**, A632 (1964), then there is the RPA with exchange (RPAE) (Refs. 3—6), and the time-dependent Hartree-Fock approximation (Ref. 7). Closely related to the present approach is the relativistic RPA (RRPA) (Refs. 8 and 9).

[3]M. Ya. Amusia and N. A. Cherepkov, Case Stud. At. Phys. **5**, 47 (1975).

[4]G. Wendin, in *Photoionization and Other Probes of Many-Electron Interactions,* edited by F. J. Wuilleumier (Plenum, New York, 1976), pp. 61—82.

[5]M. Ya. Amusia, N. A. Cherepkov, Dj. Živanović, and V. Radojević, Phys. Rev. A **13**, 1466 (1976).

[6]M. Ya. Amusia, N. A. Cherepkov, I. Pavlin, V. Radojević, and Dj. Živanović, J. Phys. B **10**, 1413 (1979).

[7]A. Dalgarno and G. A. Victor, Proc. R. Soc. London, Ser. A **291**, 219 (1966).

[8]W. R. Johnson and C. D. Lin, Phys. Rev. A **20**, 964 (1979).

[9]W. R. Johnson and K. T. Cheng, Phys. Rev. A **20**, 978 (1979).

[10]P. L. Altick, Phys. Rev. **169**, 21 (1968); G. N. Bates and P. L. Altick, J. Phys. B **6**, 653 (1973).

[11]H. P. Kelly and R. L. Symons, Phys. Rev. Lett. **30**, 529 (1973).

[12]Z. Altun, S. L. Carter, and H. P. Kelly, Phys. Rev. A **27**, 1943 (1983).

[13]T. N. Chang, J. Phys. B **13**, L551 (1980).

[14]M. J. Seaton, Rep. Prog. Phys. **43**, 167 (1983).

[15]J. Dubau and J. Wells, J. Phys. B **6**, L31 (1973); J. Dubau and J. Wells, *ibid.* **6**, 1452 (1973); J. M. Preses, C. E. Burkhard, W. P. Garver, and J. J. Leventhal, Phys. Rev. A **29**, 985 (1984).

[16]C. D. Lin, Phys. Rev. A **10**, 1986 (1974); **12**, 493 (1975); Phys. Rev. Lett. **35**, 1150 (1975).

[17]C. H. Greene, Phys. Rev. A **23**, 661 (1981).

[18]E. Dalgaard, J. Chem. Phys. **22**, 348 (1980).

[19]K.-N. Huang and W. R. Johnson, Phys. Rev. A **25**, 634 (1982).

[20]W. R. Johnson and K.-N. Huang, Phys. Rev. Lett. **48**, 315 (1982).

[21]D. L. Yeager and P. Jørgensen, Chem. Phys. Lett. **65**, 77 (1979).

[22]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[23]V. Radojević and W. R. Johnson (unpublished).

[24]J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).

[25]I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Meyers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[26]C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1971), Vol. I.

[27]C. M. Lee and W. R. Johnson, Phys. Rev. A **22**, 979 (1980).

[28]R. W. Dichburn and G. B. Marr, Proc. Phys. Soc. London, Ser. A **66**, 655 (1953).

[29]G. Mehlman-Ballofet and J. M. Esteva, Astrophys. J. **157**, 945 (1969); J. M. Esteva, G. Mehlman-Ballofet, and J. Romand, J. Quant. Spectrosc. Radiat. Transfer **12**, 1291 (1972).