Autoionizing levels of beryllium from the multiconfiguration relativistic random-phase approximation

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(Received 30 July 1990)

Autoionizing levels of beryllium near its first ionization threshold are investigated using the multiconfiguration relativistic random-phase approximation. The $2pns\ ^1P^o_1$ and $2pnd\ ^1P^o_1$ Rydberg series of doubly excited states manifest as autoionization resonances in the $2s$ photoionization cross section. Theoretical predictions and available experimental data are in excellent agreement within 0.05 eV.

In recent years, a great deal of attention has been paid to multielectron excitations in open-shell atoms. Double-electron excitations are the most prominent feature in the photoionization of alkaline-earth atoms with photon energies near their first ionization thresholds. Among theoretical approaches, there are the many-body perturbation theory,[1–4] the close-coupling method,[5–9] the configuration-interaction formalism,[10–14] the model-potential calculation,[15] the complex-basis expansion method,[16] the generalized hyperspherical coordinate method,[17,18] the random-phase approximation,[19,20] the relativistic random-phase approximation,[21,22] the multiconfiguration relativistic Tamm-Dancoff approximation,[23] the multiconfiguration Hartree-Fock theory,[24] and the R-matrix method.[25] Extensive experimental results on alkaline-earth atoms have also been reported.[26–35] These investigations have enhanced our understanding of multielectron excitations in open-shell atoms.

The random-phase approximation[19,20,36–38] has been very successful in explaining cross sections for low-energy photoionization of light closed-shell atoms. By incorporating relativity, the relativistic random-phase approximation[21,39–44] (RRPA) is capable of treating heavy closed-shell atoms and explaining more refined details of atomic photoionization, such as angular distributions for individual subshells, subshell branching ratios, and spin polarizations of photoelectrons, which are sensitive to both relativistic and correlation effects. However, the RRPA theory is limited in applicability to closed-shell atoms for which a single configuration description of the atomic system is appropriate; consequently, only single-electron excitations are dealt with. For open-shell atoms, multielectron excitations become more important and therefore we need a formalism to treat multielectron excitations.

The multiconfiguration relativistic random-phase approximation theory[45] (MCRRPA) is a generalization of the RRPA theory by employing a multiconfiguration reference state. As in the RRPA theory, the MCRRPA theory takes into account all single-electron excitations. The existence of the "real" doubly excited configurations in the reference state makes possible a natural realization of the double-electron excitations because single-electron excitations from these "real" doubly excited configurations will result in final states with two excited electrons. We describe an open-shell atom or ion in its ground state by a multiconfiguration Dirac-Fock (MCDF) wave function. An applied external field excites particle-hole pairs from the MCDF ground state. The lowest-order correlation corrections to the particle-hole excitation amplitude are those due to one-particle–one-hole and two-particle–two-hole final-state processes and those due to two-particle–two-hole initial-state processes. The mixing among the doubly excited configurations is accomplished through interchannel couplings. Therefore the MCRRPA theory provides a natural framework for analyzing autoionization resonance profiles involving multielectron excitations. The MCRRPA theory preserves all advantages of the RRPA theory. First, the relativistic formulation builds in all the fine structures from the outset. Second, the theory is independent of the gauge of the applied field. Third, core polarization can be treated readily. The merits of the MCRRPA theory have been demonstrated in its applications to resonance transitions in the Be-, Mg-, and Zn-isoelectronic sequences[46,47] and to photoionization of the Be atom above its $2p_{3/2}$ ionization threshold.[48] In this Brief Report, we will report the application of the MCRRPA theory to the photoionization of the Be atom, where autoionization resonances dominate the cross sections and make comparisons with experiment and other theories.

A detailed derivation of the MCRRPA equations has been given in a previous paper.[45] Here we concentrate on the application of this theory to the Be atom. In principle, once the MCRRPA equations are solved, photoionization parameters for the angular distribution and spin polarization of photoelectrons are evaluated easily. Formulas of these parameters for photons of arbitrary polarization have been given explicitly.[49] In the present

MCRRPA calculation, the $J=0$ even reference state of the Be atom is taken to be

$$\Psi = C_1(2s_{1/2}^2) + C_2(2p_{1/2}^2) + C_3(2p_{3/2}^2) ,$$

where the symbols $(2l_j)^2$ represent coupled Slater determinants constructed from two core $1s_{1/2}$ and two valence $2l_j$ electrons, and C_i are the configuration weights. The ground-state orbitals and weights can be obtained from a MCDF computer code[50] and we present the values of the weights in Table I. The ground-state wave function is still dominated by the $2s_{1/2}^2$ configuration, but the contributions from the $2p_{1/2}^2$ and $2p_{3/2}^2$ configurations are also significant. We list theoretical thresholds of these valence orbitals from the MCDF and DF calculations together with experimental values in Table II. From Table II, we see that the agreement between theoretical and experimental thresholds is improved by adopting a multiconfiguration wave function for the ground state. Because we are interested in low-energy photoionization, we restrict our attention to dipole excitations. The single-electron excitation spectrum consists of seven interacting Rydberg series and corresponding continua. Two of the series result from the excitation of a $2s_{1/2}$ valence electron to $np_{1/2}$ or $np_{3/2}$ states; these series converge to the $^2S_{1/2}$ ground state of the ion. Two series arise from the excitation of a $2p_{1/2}$ valence electron to $ns_{1/2}$ or $nd_{3/2}$ states; these series converge to the $^2P^o_{1/2}$ state of the ion. The remaining three series arise from the excitation a $2p_{3/2}$ valence electron to $ns_{1/2}$,$nd_{3/2}$, or $nd_{5/2}$ states and converge to the $^2P^o_{3/2}$ state of the ion. We summarize these direct-ionization channels in the following:

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2s_{1/2}\ ^2S_{1/2}) + e^-(\epsilon p_{1/2}) , \quad (1)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2s_{1/2}\ ^2S_{1/2}) + e^-(\epsilon p_{3/2}) , \quad (2)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2p_{1/2}\ ^2P^o_{1/2}) + e^-(\epsilon s_{1/2}) , \quad (3)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2p_{1/2}\ ^2P^o_{1/2}) + e^-(\epsilon d_{3/2}) , \quad (4)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2p_{3/2}\ ^2P^o_{3/2}) + e^-(\epsilon s_{1/2}) , \quad (5)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2p_{3/2}\ ^2P^o_{3/2}) + e^-(\epsilon d_{3/2}) , \quad (6)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}^+(2p_{3/2}\ ^2P^o_{3/2}) + e^-(\epsilon d_{5/2}) . \quad (7)$$

We consider photon energies between $2s_{1/2}$ and $2p_{1/2}$ ionization thresholds, from 9.52 to 13.407 eV, where only the first two of the seven direct-ionization channels considered above are open. The remaining five closed channels (3)–(7) provide five autoionization channels,

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}(2pns\ ^1P^o_1, ^3P^o_1) \rightarrow \mathrm{Be}^+(2s_{1/2}\ ^2S_{1/2}) + e^-(\epsilon p_{1/2} \text{ or } \epsilon p_{3/2}) , \quad (8)$$

$$\mathrm{Be}+h\nu \rightarrow \mathrm{Be}(2pnd\ ^1P^o_1, ^3P^o_1, ^3D^o_1) \rightarrow \mathrm{Be}^+(2s_{1/2}\ ^2S_{1/2}) + e^-(\epsilon p_{1/2} \text{ or } \epsilon p_{3/2}) , \quad (9)$$

which interfere strongly with the two open channels (1) and (2). This strong interference yields five Rydberg series of autoionization resonance profiles in the $2s_{1/2}$ photoionization cross sections. A practical method to obtain the autoionization resonance profiles is to apply the multichannel quantum-defect theory[52] (MQDT) to analyze the solutions of the MCRRPA equations. We first calculate the eigenchannel quantum-defect parameters near the $2p_{1/2}$ ionization threshold. Then we use the MQDT theory to interpolate or extrapolate these dynamical parameters to the resonance region; photoionization amplitudes in this region are thus evaluated. Because of

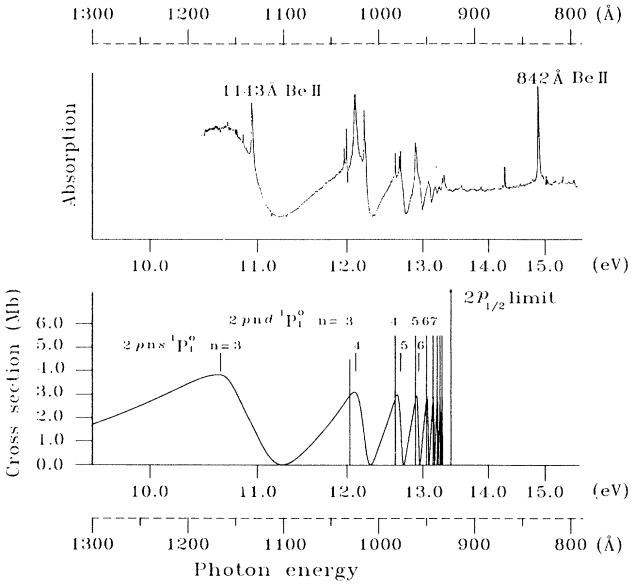

FIG. 1. Comparison of the $2s_{1/2}$ photoionization cross section of beryllium from the present MCRRPA calculation with the photoabsorption spectra of Mehlman-Ballofet and Esteva (Ref. 28).

TABLE I. Configuration weights of the Be atom in its $J=0$ even ground state.

Configuration	Weight	Square of the weight
$2s_{1/2}$	0.950	0.903
$2p_{1/2}$	0.180	0.032
$2p_{3/2}$	0.255	0.065

TABLE II. Ionization thresholds (in eV) of the Be atom in its $J=0$ even ground state.

	Theory		
Shell	DF	MCDF	Experiment[a]
$2s_{1/2}$	8.42	9.520	9.32
$2p_{1/2}$	12.305	13.407	13.281
$2p_{3/2}$	12.306	13.408	13.282

[a]Reference 51.

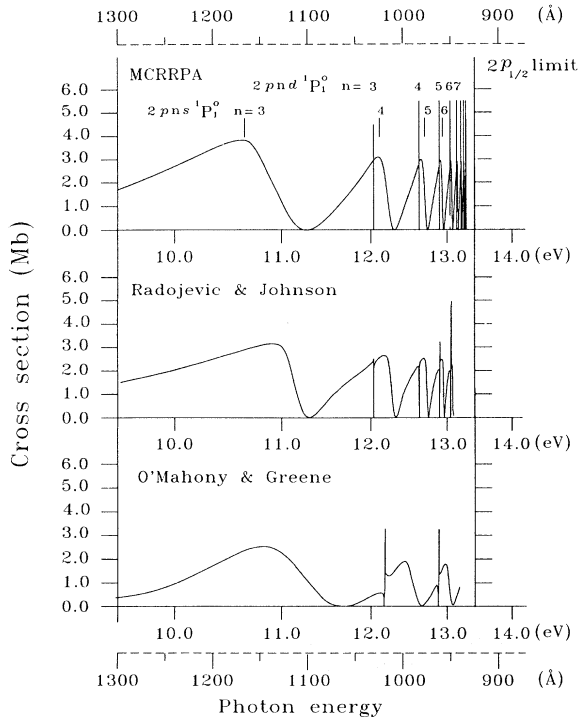

FIG. 2. Comparison of the $2s_{1/2}$ photoionization cross section of beryllium from the present MCRRPA calculation with those from Radojevic and Johnson (Ref. 23) and O'Mahony and Greene (Ref. 18).

TABLE III. Positions (in eV) of autoionization resonances in the $2s_{1/2}$ photoionization cross section of Be.

State	MCRRPA[a]	MCRRPA[b]	Expt.[c]	Expt.[d]
$2p3s\ ^1P_1^\circ$	10.63	10.52	10.71	10.93
$2p4s\ ^1P_1^\circ$	12.09	11.98	11.97	12.10
$2p5s\ ^1P_1^\circ$	12.64	12.53	12.53	12.57
$2p6s\ ^1P_1^\circ$	12.91	12.79	12.78	12.81
$2p7s\ ^1P_1^\circ$	13.06	12.94	12.92	12.94
$2p8s\ ^1P_1^\circ$	13.15	13.03	13.00	13.03
$2p9s\ ^1P_1^\circ$	13.21	13.09		
$2p10s\ ^1P_1^\circ$	13.25	13.13		
$2p3d\ ^1P_1^\circ$	12.03	11.92	11.86	11.86
$2p4d\ ^1P_1^\circ$	12.61	12.50	12.47	12.50
$2p5d\ ^1P_1^\circ$	12.89	12.78	12.77	12.79
$2p6d\ ^1P_1^\circ$	13.05	12.93	12.89	12.95
$2p7d\ ^1P_1^\circ$	13.14	13.02		
$2p8d\ ^1P_1^\circ$	13.20	13.09		
$2p9d\ ^1P_1^\circ$	13.24	13.13		

[a]Using the ground-state energy as the reference energy.
[b]Using the $2p_{1/2}$ ionization threshold as the reference energy. $\mathrm{MCRRPA}^b = \mathrm{MCRRPA}^a - \Delta I_{2p_{1/2}}$, $\Delta I_{2p_{1/2}} = I_{2p_{1/2}}(\text{theory}) - I_{2p_{1/2}}(\text{experiment}) = 13.407 - 13.281 = 0.116$ eV.
[c]Mehlman-Ballofet and Esteva (absorption spectra, Ref. 28).
[d]Esteva, Mehlman-Ballofet, and Romand (emission spectra, Ref. 29). The precision for both experiments is at best ±0.5 Å (0.01 eV) and is much worse for the $2p3s\ ^1P^\circ_1$ resonance.

small relativistic effects in Be, only two Rydberg series, the broad $2pns\ ^1P_1^\circ$ series and the narrow $2pnd\ ^1P_1^\circ$ series, are prominent in our calculation. The broad and narrow resonance profiles reveal the short and long lifetimes of the respective doubly excited series. We plot our photoionization cross sections as well as the absorption spectra in Fig. 1. The characteristics of our theoretical curve in this energy range are very similar to those of the absorption spectra. Comparisons with other recent theories are presented in Fig. 2. Our predictions of resonance positions together with the experimental data are presented in Table III. The first column in this table is our predictions relative to the ground-state level. By choosing the $Be^+(2p_{1/2}\ ^2P_{1/2})$ ionization threshold as the reference energy, the corresponding predictions are listed in the second column of Table III. We see that by using such a reference energy, the overall agreement with experiment is substantially improved except for the $2p3s$ resonance. The asymmetry parameter $\beta_{2s_{1/2}}$ for subshell $2s_{1/2}$ is perturbed from its normal value 2.0 very sharply at the Cooper minima, where the relative amplitudes of the two open channels vary rapidly with respect to the photon energy. The spin-polarization parameters have features similar to the asymmetry parameter. They are nearly zero in the order 10^{-4} in this energy range except at the Cooper minima.

The merits of the MCRRPA theory in treating photoionization of Be, where double-electron excitations play important roles, are demonstrated above. To obtain autoionization resonance profiles, we have utilized the MQDT theory to analyze *ab initio* dynamical parameters determined from the MCRRPA theory. The characteristics of the profiles are in good agreement with existing experimental data. The predictions of resonance positions are in excellent agreement with available experimental data within 0.05 eV and are in good agreement with other theories. Furthermore, the relativistic formulation of the present theory provides a proper treatment of heavy atoms or ions for which relativistic effects are large.

This work was supported in part by the National Science Council of the Republic of China.

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