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Core-polarization effects for the intercombination and resonance transitions in Cd-like ions

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Excitation energies and oscillator strengths from the ${}^1S_0$ ground state to the first ${}^3P_1^o$ and ${}^1P_1^o$ excited states of Cd-like ions are calculated by using the multiconfiguration relativistic random-phase approximation including excitation channels from core electrons. The discrepancies among theories and experiments are much reduced but, in general, remain.

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The optical spectrum of Cd-like ions has aroused considerable interest in recent years [1–3]. Systematic studies of oscillator strengths in Cd-like ions were undertaken by measuring the lifetimes of excited atomic states using the level-crossing techniques [4] and beam-foil spectroscopy [2,5–11]. Several calculations for the optical transitions in Cd-like ions were carried out [2,12–14], and large discrepancies existed between theory and experiment. To resolve the discrepancies, the multiconfiguration Dirac-Fock (MCDF) [15] and configuration-interaction (CI) [16,17] calculations were performed with a semiempirical core-polarization (CP) model potential to account for valence-core correlations. Nevertheless, the CP contributions in the excitation energies and oscillator strengths from the available MCDF and CI calculations including semiempirical CP effects depend sensitively on the CP parameters used. In a recent paper [18], we applied the multiconfiguration relativistic random-phase approximation theory (MCRRPA) to the intercombination transition $(5s^2)\,{}^1S_0\rightarrow(5s5p)\,{}^3P_1^o$ and the resonance transition $(5s^2)\,{}^1S_0\rightarrow(5s5p)\,{}^1P_1^o$ in Cd-like ions. Significant discrepancies existed between the MCRRPA and experimental data. The discrepancies may be partly due to the omission of core-excitation channels in the earlier MCRRPA calculation for a practical reason, because the inclusion of core-excitation channels in the calculation would substantially increase the number of coupled differential equations to be solved simultaneously. To investigate the discrepancies, we perform a large-scale MCRRPA calculation including core-excitation channels for the intercombination and resonance transitions in Cd-like ions.

The MCRRPA theory treats both relativistic and correlation effects in open-shell atoms and has been presented in detail in a previous paper [19]. Applications of the MCRRPA to photoexcitations of Be-, Mg-, and Pb-like ions [20–22] and to photoionization of Be, Mg, Zn, and Sr atoms [23–27] were carried out and were in excellent agreement with experiment; however, applications to Zn-, Cd-, and Hg-like ions [18,21,28,29] were less satisfactory. Nevertheless, the MCRRPA approach does have several advantages: First, the MCRRPA results are gauge independent; there is no arbitrariness in choosing the gauge. Second, the MCRRPA simultaneously treats initial- and final-state correlations. In addition, both discrete and continuum correlations are dealt with in the MCRRPA. Finally, the MCRRPA calculation can be performed with core-excitation channels and thus provides an *ab initio* treatment of the CP effects.

In the MCRRPA formulation, the ground reference state of Cd-like ions is described by a multiconfiguration wave function as

$$\Psi=C_1(5s_{1/2}^2)+C_2(5p_{1/2}^2)+C_3(5p_{3/2}^2)\ , \tag{1}$$

where $(5l_j^2)$ symbolically denotes a Slater determinant constructed from the $(5l_j)$ valence orbitals and 14 core orbitals: $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}, \ldots, 4p_{3/2}$, $4d_{3/2}$, and $4d_{5/2}$. The coefficients C_a $(a=1,2,3)$ in Eq. (1) are configuration weights. The configurations $(4f_{5/2}^2)$ and $(4f_{7/2}^2)$ are not included in the ground reference state for ions near the neutral end. Nevertheless, the contribution of the $(4f^2)$ configurations increases with increasing nuclear charges, and, as a matter of fact, the ground configuration for ions around Sm^{14+} is $(4f^2)$ rather than $(5s^2)$. In our previous calculations, we neglected all core-excitation channels. In the present calculation, we include excitation channels from $4s$, $4p$, and $4d$ core electrons. Twenty excitation channels are considered in the electric dipole approximation, as follows.

(i) Core-excitation channels:

$$\begin{aligned}
&4s_{1/2}\rightarrow np_{1/2},\ np_{3/2}\ ,\\
&4p_{1/2}\rightarrow ns_{1/2},\ nd_{3/2}\ ,\\
&4p_{3/2}\rightarrow ns_{1/2},\ nd_{3/2},\ nd_{5/2}\ ,\\
&4d_{3/2}\rightarrow np_{1/2},\ np_{3/2},\ nf_{5/2}\ ,\\
&4d_{5/2}\rightarrow np_{3/2},\ nf_{5/2},\ nf_{7/2}\ ,
\end{aligned} \tag{2}$$

and (ii) valence-excitation channels:

$$\begin{aligned}
&5s_{1/2}\rightarrow np_{1/2},\ np_{3/2}\ ,\\
&5p_{1/2}\rightarrow ns_{1/2},\ nd_{3/2}\ ,\\
&5p_{3/2}\rightarrow ns_{1/2},\ nd_{3/2},\ nd_{5/2}\ .
\end{aligned} \tag{3}$$

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TABLE I. Excitation energies (in cm^{-1}, 1 a.u.=219 474.6306 cm^{-1}) for the intercombination transition $(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$ and the resonance transition $(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$ in Cd-like ions.

	MCDF[a]			CI[b]			MCRRPA[c]		Expt.
	I	II	III	I	II	III	I	II	
				$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$					
Cd	26 766.5	29 627.1	30 359.3	29 558.2	28 582.6	27 799.1	25 902	25 700	30 656.130[d]
In^{1+}	39 482.6	42 266.9	42 904.0	42 071.5	40 528.2	41 196.5	38 511	38 252	43 349[d]
Sn^{2+}	51 290.8	54 035.1	54 529.8	53 685.0	51 925.7	52 701.6	50 260	49 959	55 196.4[d]
Sb^{3+}	62 731.3	65 463.8	65 873.1	65 023.1	63 190.0	63 956.2	61 646	61 301	66 700[d]
Te^{4+}	73 995.0	76 729.6	76 980.3	76 135.5	74 299.4	75 051.5	72 855	72 457	78 023[d]
I^{5+}	85 175.7	87 924.6	88 190.2	87 343.7	85 531.9	86 250.7	83 978	83 519	89 210[e]
Xe^{6+}	96 325.0	99 096.7	99 357.0	98 507.2	96 734.8	97 424.6	95 065	94 534	101 000[f]
				$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$					
Sn^{2+}	86 925.6	84 476.2	84 136.3	83 964.2	79 208.2	78 149.4	80 723	75 782	79 911.3[d]
Sb^{3+}	104 534	101 488	101 131	100 768	95 313.9	94 633.9	97 673	91 692	95 952[d]
Te^{4+}	121 476	118 046	117 794	117 333	111 386	110 940	114 164	107 295	117 707[d]
I^{5+}	138 170	134 466	134 177	133 639	127 364	127 078	130 506	122 858	128 000[e]
Xe^{6+}	154 844	150 932	150 634	150 035	143 517	143 352	146 888	138 541	143 000[f]

[a] Reference [15]. I, without CP effects; II and III, with semiempirical CP effects. Calculations II and III differ in the CP parameters used.

[b] Reference [17]. Calculations I, II, and III all include semiempirical CP effects, and they differ in the size of the basis set used. Calculation III employs the largest basis set.

[c] The present MCRRPA results, where I and II are calculations without and with core-excitation channels.

[d] Reference [1].

[e] Reference [2].

[f] Reference [3].

The first 13 excitation channels associated with the excitations of 4*s*, 4*p*, and 4*d* orbitals account for the CP effects.

In Table I, excitation energies for the intercombination transition $(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$ and the resonance transition $(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$ in the Cd-like ions from the MCRRPA theory, including excitation channels from the 4*s*, 4*p*, and 4*d* core electrons, are compared with those from the MCDF [15] and CI [16,17] calculations including semiempirical CP effects. In all calculations, excitation energies for both the intercombination and resonance transitions increase with increasing nuclear charges. Incidentally, the MCRRPA excitation energies with CP effects are in poorer agreement with experiment [1–3] than those without CP effects. The contributions from CP effects and their percentages in the excitation energies are presented in Table II. In the MCDF calculation, the CP effects increase the intercombination excitation energies, but decrease the resonance excitation energies, while, in the MCRRPA calculations, excitation energies for both transitions are reduced by the CP effects. In the MCDF calculation the CP effects affect the intercombination excitation energies more strongly than the resonance excitation energies. On the other hand, in the MCRRPA calculation the CP effects have a larger influence on the resonance transition. For the intercombination transition, the percentages of contributions of CP effects in the MCDF excitation energies are larger than those from the MCRRPA calculation by a factor of 6–15, whereas for the resonance transition the percentages of contributions of CP effects in the MCDF calculation are less than those from the MCRRPA calculation by a factor of 2. In both the MCDF and MCRRPA calculations the percentages of contributions of CP effects in the excitation energies decrease with increasing nuclear charges.

Oscillator strengths of the Cd-like ions are presented in Table III for both transitions. In the MCDF and CI calculations the trend of oscillator strengths along the Cd-like ions is less regular than in the MCRRPA calculation,

TABLE II. The CP contributions and their percentages in the excitation energies for the intercombination and resonance transitions in Cd-like ions.

	MCDF[a] (cm^{-1})	CP contribution (cm^{-1})	CP contribution (%)	MCRRPA[b] (cm^{-1})	CP contribution (cm^{-1})	CP contribution (%)
			$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$			
Cd	30 359.3	3592.8	11.8	25 700	−202	−0.786
In^{1+}	42 904.0	3421.4	7.97	38 252	−259	−0.677
Sn^{2+}	54 529.8	3239.0	5.94	49 959	−301	−0.602
Sb^{3+}	65 873.1	3141.8	4.77	61 301	−345	−0.563
Te^{4+}	76 980.3	2985.3	3.88	72 457	−398	−0.549
I^{5+}	88 190.2	3014.5	3.42	83 519	−459	−0.549
			$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$			
Sn^{2+}	84 136.3	−2789.3	−3.32	75 782	−4941	−6.52
Sb^{3+}	101 131	−3403.0	−3.36	91 692	−5981	−6.52
Te^{4+}	117 794	−3682.0	−3.13	107 295	−6865	−6.40
I^{5+}	134 177	−3993.0	−2.98	122 858	−7648	−6.23
Xe^{6+}	150 634	−4210.0	−2.79	138 541	−8347	−6.02

[a] Reference [15].

[b] The present MCRRPA results.

TABLE III. Oscillator strengths for the intercombination and resonance transitions in Cd-like ions. Numbers in brackets denote powers of 10.

	MCDF[a]			CI[b]			MCRRPA[c]		Expt.
	I	II	III	I	II	III	I	II	
					$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$				
Cd	5.49[−4]	1.07[−3]	1.24[−3]	9.6[−4]	1.05[−3]	7.36[−3]	1.002[−3]	1.304[−3]	0.002 00±0.000 03[d]
In^{1+}	1.97[−3]	2.97[−3]	3.22[−3]	2.78[−3]	3.29[−3]	5.73[−3]	3.170[−3]	3.999[−3]	0.019±0.004[e]
Sn^{2+}	4.24[−3]	5.66[−3]	5.92[−3]	5.34[−3]	6.51[−3]	8.33[−3]	6.383[−3]	7.896[−3]	
Sb^{3+}	7.34[−3]	9.12[−3]	9.39[−3]	8.68[−3]	1.068[−2]	1.232[−2]	1.058[−2]	1.287[−2]	
Te^{4+}	1.13[−2]	1.33[−2]	1.35[−2]	1.27[−2]	1.56[−2]	1.78[−2]	1.570[−2]	1.880[−2]	0.0185±0.0045[f]
I^{5+}	1.60[−2]	1.83[−2]	1.85[−2]	1.75[−2]	2.15[−2]	2.36[−2]	2.168[−2]	2.554[−2]	0.0230±0.001[g]
					$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$				
Sn^{2+}	2.286	1.771	1.694	1.64	1.60	1.57	2.222	1.748	1.50±0.1[h]
Sb^{3+}	2.292	1.767	1.702	1.65	1.61	1.60	2.221	1.717	1.29±0.14[i]
Te^{4+}	2.274	1.754	1.715	1.67	1.63	1.56	2.204	1.685	1.31±0.1[j]
I^{5+}	2.247	1.739	1.698	1.66	1.62	1.57	2.181	1.655	1.29±0.07[k]
Xe^{6+}	2.218	1.721	1.682	1.64	1.61	1.57	2.154	1.626	1.45±0.10[i]

[a] Reference [15]. I, without CP effects; II and III, with semiempirical CP effects. Calculations II and III differ in the CP parameters used.

[b] Reference [17]. Calculations I, II, and III all include semiempirical CP effects, and they differ in the size of the basis set used. Calculation III employs the largest basis set.

[c] The present MCRRPA results, where I and II are calculations without and with core-excitation channels.

[d] Reference [4].

[e] Reference [10].

[f] Reference [11].

[g] Reference [2].

[h] Reference [5].

[i] Reference [6].

[j] Reference [7].

[k] Reference [8].

where the intercombination oscillator strengths increase and the resonance oscillator strengths decrease with increasing nuclear charges. The inclusion of CP effects in general improves the agreement between the MCRRPA oscillator strengths and the cascade-corrected experimental results from Pinnington and co-workers [5–8,11]. For the intercombination transition, the discrepancy between the MCRRPA and cascade-corrected experimental results for Te^{4+} is resolved by including CP effects in the MCRRPA calculation. The large discrepancies between the MCRRPA and experimental results for Cd and In^{1+} may be partly due to experimental errors. For the resonance transition, the discrepancies between the MCRRPA and experimental results are greatly reduced. The MCRRPA results with CP effects are in reasonable agreement with the cascade-corrected experimental results. The CP contributions and their percentages in the oscillator strengths are presented in Table IV. In both the MCDF and MCRRPA calculations the CP effects increase the intercombination oscillator strengths, but decrease the resonance oscillator strengths. In the MCDF calculation the percentages of contributions of CP effects in both the intercombination and resonance oscillator strengths decrease with increasing nuclear charges. In the MCRRPA calculation the percentages of contributions of CP effects in the intercombination oscillator strengths decrease with increasing nuclear charges, whereas the percentages of contributions of CP effects in the resonance oscillator strengths increase with increasing nuclear charges. For the resonance transition both the MCDF and MCRRPA calculations give about the same CP contributions in the oscillator strengths, while for the intercombination transition there is no consistent agreement between the MCDF and MCRRPA calculations.

We conclude that the MCRRPA calculation including core-excitation channels provides a satisfactory and gauge-independent description of the intercombination and resonance transitions in Cd-like ions and demonstrates the importance of the CP effects. In general, we should start with more configurations in the reference ground state when double-excitation effects are important, and should include more core-excitation channels when CP effects are important. Core-excitation channels in addition to those included in the present calculation make only slight contributions to the results. The remaining discrepancies may be due to the omission of other valence configurations such as $(4f^2)$ and $(5d^2)$ in the description of the ground reference state, and due to electron correlations not included in the RPA-type calculation. While the MCDF [15] and CI [16,17] calculations with semiempirical CP model potentials seem to yield largely different results depending on the gauge and on the CP parameters used, our MCRRPA approach offers, to our knowledge, the only *ab initio* gauge-independent results. Because of insufficient experimental data and the difference in systematic trends of the CP contributions from the MCDF, CI, and MCRRPA calculations, further and more extensive investigations are certainly needed to understand fully, as well as remove, the remaining discrepancies.

TABLE IV. The CP contributions and their percentages in the oscillator strengths for the intercombination and resonance transitions in Cd-like ions. Numbers in brackets denote powers of 10.

	MCDF[a]	CP contribution		MCRRPA[b]	CP contribution	
			(%)			(%)
			$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^3P_1^o$			
Cd	1.24[−3]	6.91[−4]	55.7	1.304[−3]	3.02[−4]	23.2
In^{1+}	3.22[−3]	1.25[−3]	38.8	3.999[−3]	8.29[−4]	20.7
Sn^{2+}	5.92[−3]	1.68[−3]	28.4	7.896[−3]	1.513[−3]	19.2
Sb^{3+}	9.39[−3]	2.05[−3]	21.8	1.287[−2]	2.29[−3]	17.8
Te^{4+}	1.35[−2]	2.20[−3]	16.3	1.880[−2]	3.10[−3]	16.5
I^{5+}	1.85[−2]	2.50[−3]	13.5	2.554[−2]	3.86[−3]	15.1
			$(5s^2)\,^1S_0 \rightarrow (5s5p)\,^1P_1^o$			
Sn^{2+}	1.694	−0.592	−34.9	1.748	−0.474	−27.1
Sb^{3+}	1.702	−0.590	−34.7	1.717	−0.504	−29.4
Te^{4+}	1.715	−0.559	−32.6	1.685	−0.519	−30.8
I^{5+}	1.698	−0.549	−32.3	1.655	−0.526	−31.8
Xe^{6+}	1.682	−0.536	−31.9	1.626	−0.528	−32.5

[a] Reference [15].

[b] The present MCRRPA results.

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