Wavelengths of the $3p$-$3d$ transitions of the Co-like ions

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Wavelengths of the $3p^6 3d^9\,{}^2D_J - 3p^5 3d^{10}\,{}^2P_{J'}$ transitions of the Co-like ions have been calculated for ions with atomic number $38 \le Z \le 92$. The calculations were performed by using the multiconfiguration Dirac-Fock model with emphasis on the effects of electron correlation. The previously found discrepancies between theory and experiment have been removed due to the inclusion of the correlation effects in the theoretical calculations. A possible misidentification of the $^2D_{3/2}$-$^2P_{1/2}$ transition for the Dy^{39+} ion is noted.

I. INTRODUCTION

The spectra of highly charged ions are of great importance for the development of x-ray laser[1] and laser fusion.[2] The $n=3$ to $n=3$ and $n=4$ to $n=3$ transitions of the Fe, Co, Cu, and Zn isoelectronic sequences have received much attention.[3–6] Recently, the experimental observations of these spectra have been extended to highly charged ions of heavy elements up to uranium ($Z=92$).[7] For the Co-like $3p^6 3d^9\,{}^2D - 3d^5 3d^{10}\,{}^2P$ transitions, comparison between the observed energies and calculated values from the Dirac-Fock model (DF) indicated persistent discrepancies of ~ 3 eV for all ions.[7] In order to shed some light on this situation, we have performed systematic multiconfiguration Dirac-Fock (MCDF)[8,9] calculations for $3p^6 3d^9\,{}^2D - 3p^5 3d^{10}\,{}^2P$ transitions of the Co isoelectronic sequence. In the present work we pay special attention to the effect of electron-electron correlation on the transition energies.

II. THEORY

Systematic relativistic calculations of atomic binding energies or x-ray energies for neutral atoms have previously been performed with Dirac-Fock or Dirac-Hartree-Slater (DHS) wave functions.[10–12] To determine accurately the binding energies, one needs to include the relaxation effect, finite-nuclear-size effect, Breit interaction, and quantum-electrodynamic corrections (QED) and correlation effect. The limitations of the DF model on calculations of the atomic-electron binding energies have been examined.[13] The detailed theoretical treatment of the DF or DHS approaches has been reviewed recently.[14,15] Here, we outline them only briefly.

We use the version of the multiconfiguration Dirac-Fock model due to Grant *et al.*[8,9] In the restricted Hartree-Fock scheme, the N-electron wave function is constructed from the central-field Dirac orbitals given by[8]

$$\psi_{n\kappa m}(r)=\frac{1}{r}\begin{bmatrix} P_{n\kappa}(r)\Omega_{\kappa m} \\ iQ_{n\kappa}(r)\Omega_{-\kappa m}\end{bmatrix}, \tag{1}$$

where

$$\Omega_{\kappa m}=\sum_{\mu} C(l\tfrac{1}{2}j;m-\mu,\mu)Y_{\kappa,m-\mu}(\theta,\phi)\chi_{1/2,\mu} \tag{2}$$

and

$$\kappa=(l-j)(2j+1)\ . \tag{3}$$

In the MCDF model,[8] the configuration-state functions (CSF) denoted by $\phi(\Gamma JM)$ are formed by taking linear combinations of Slater determinants of the Dirac orbitals; the atomic-state function (ASF) for a state i with total angular momentum JM is then constructed from n CSF functions,

$$\Psi_i(JM)=\sum_{\lambda=1}^{n} C_{i\lambda}\phi(\Gamma_\lambda JM)\ , \tag{4}$$

where $C_{i\lambda}$ are the mixing coefficients for state i. The energy of a state β is given by

$$E_\beta=\int \Psi_\beta^\dagger(JM)H\Psi_\beta(JM)d\tau\ . \tag{5}$$

The Dirac-Fock equations are obtained by applying the variation principle and a self-consistent-field (SCF) method is then used to solve the MCDF equations.

There are several different types of calculation available in the program of Grant *et al.*[8] In an optimal-level (OL) calculation, the wave functions and mixing coefficients are simultaneously optimized for a specific level (i.e., term-dependent Hartree-Fock). The average-level (AL) and the extended average-level schemes (EAL) are the least expensive procedures. In AL and EAL calculations, the wave functions are obtained by minimizing the average energy of all the levels with equal and statistical weights, respectively.

The dynamic correction to the electrostatic Coulomb interactions is included through the use of the transverse Breit operator[9,16] in first-order perturbation theory. The finite-nuclear-size effect is taken into account by using uniform charge distribution. The vacuum-polarization correction is obtained by calculating the Uehling potential in first-order perturbation theory.[9] The self-energy corrections for K and L levels are calculated from point-Coulomb values[17] with an effective-charge screening procedure.[9] For levels with principle quantum number $n \ge 3$, the self-energy corrections are estimated with the use of the n^{-3} scaling rule and effective-charge approach.[9]

The correlation energies are much more difficult to estimate. In principle, one should find the correlation contri-

bution to the transition energies by calculating the total correlation energies for the initial and final states and taking the difference. This, however, is a very expensive proposition and a more tractable procedure needs to be chosen. In the present work the correlation energies of the passive electrons from initial and final states are assumed to cancel each other completely. We therefore only need to concern ourselves with the residual correlation corrections which pertain to the characteristic of the initial and final states. This prescription for correlation correction has been shown to be quite adequate in calculation of atomic-electron binding energies for neutral atoms.[13,18]

III. NUMERICAL CALCULATIONS

In the $3p^6 3d^9\,{}^2D - 3p^5 3d^{10}\,{}^2P$ transitions, the initial and final states have a $3p$ and $3d$ electron missing, respectively. These transition energies can also be obtained by taking the differences between $3p_{1/2,3/2}$ and $3d_{3/2,5/2}$ binding energies. Similar to the calculations of $3p$ and $3d$ binding energies of neutral atoms, the most important correlation corrections, which survive after cancellation between the initial and final states, are the ground-state correlation corrections because of the broken pairs and the dynamic relaxation processes due to the $[3p]\leftrightarrow[3d^2]\,nf$ super-Coster-Kronig fluctuation.[13,19] Here $[3l]$ denotes a hole in the $3l$ subshell and nf includes bound and continuum electrons. In the present work, the $[3p]\leftrightarrow[3d^2]\,nf$ interaction was taken into account by using the MCDF-OL method. The CSF functions included for the initial-state calculations are $3p^5 3d^{10}$, $3p^6 3d^8 4f$ and $3p^6 3d^8 4p$. There are 25 and 15 jj-coupled CSF states for $J=\frac{3}{2}$ and $\frac{1}{2}$, respectively. For the $3p^6 3d^9$ final states, single-configuration Dirac-Fock calculations were carried out. The transition energies were obtained by taking the differences between the total energies of the initial and final states. For comparison we also performed single-configuration DF and MCDF-EAL calculations for the initial states with the same CSF functions as for the OL calculations.

The ground-state correlation contributions to the neutral atomic-electron binding energies have been estimated by Chen *et al.*[13] using the pair correlation energies from nonrelativistic theory. In the present work we follow the same procedure as used in Ref. 13. The ground-state correlation correction to the binding energy $E_{\rm GC}(a)$ is evaluated as a sum of pair energies that survive after cancellation between ground and hole states:[13,18]

$$E_{\rm GC}(a)=\frac{1}{2(2l_a+1)}\sum_b E_0(a,b)+\frac{1}{2l_a+1}E_0(a,a)\ , \qquad (6)$$

where $E_0(a,b)$, the total pair energy between two closed shells, is

$$E_0(a,b)=\sum_{L,S}(2S+1)(2L+1)\varepsilon(n_a l_a n_b l_b;SL)\ , \qquad (7)$$

with $\varepsilon(n_a l_a, n_b l_b;SL)$ being the symmetry-adapted pair energy.

Since the all-external pair correlation energies have been shown to be approximately transferable among atoms,[20] the pair energies calculated for the Zn^{2+} ion[21] were used to evaluate the ground-state correlation corrections to the $3p$ and $3d$ binding energies of the other Ni-like ions. The ground-state correlation corrections to the $3p$-$3d$ transition energies of the Co-like ions were then obtained by taking the difference between the corrections for the $3p$ and $3d$ binding energies of the Ni-like ions. In the present work the ground-state correlation corrections to the $3p^6 3d^9$-$3p^5 3d^{10}$ transition energies have been estimated to be -1.41 eV for all ions.

IV. RESULTS AND DISCUSSION

The wavelengths for the $3d^6 3d^9\,{}^2D_J - 3p^5 3d^{10}\,{}^2P_{J'}$ transitions of the Co-like ions were calculated by using the MCDF-OL method[8,9] for ions with atomic number $38 \le Z \le 92$. The relativistic calculations included effects of relaxation and finite nuclear size, transversed Breit interaction, quantum-electrodynamic corrections, and electron-electron correlation. The results are listed in Table I.

For the ${}^2D_{5/2}$-${}^2P_{3/2}$ transitions, the contributions to the transition energies from the various components were displayed in Fig. 1. The Breit interaction contributes -4.4 eV at $Z=92$ and only -0.38 eV at $Z=42$. The QED corrections are quite small for these transitions. They contribute only ~ -1.26 eV even for ions as heavy as uranium ($Z=92$). The effects of correlation can be seen to have quite important contributions (~ -3.5 eV) to the transition energies, and the effects persist to very heavy ions. The finite-nuclear-size effects are quite small

TABLE I. Calculated wavelengths in angstroms for the transition $3p^6 3d^9\,{}^2D_J - 3p^5 3d^{10}\,{}^2P_{J'}$ of the Co-like ions.

Atomic No.	${}^2D_{3/2}$-${}^2P_{1/2}$	${}^2D_{5/2}$-${}^2P_{3/2}$	${}^2D_{3/2}$-${}^2P_{3/2}$
38	86.604	92.250	93.503
39	81.766	87.579	88.910
40	77.382	83.355	84.766
41	73.375	79.502	80.995
42	69.692	75.984	77.562
44	63.131	69.748	71.500
46	57.445	64.387	66.320
48	52.453	59.718	61.839
50	48.027	55.604	57.919
56	37.266	45.699	48.623
57	35.762	44.321	47.350
60	31.632	40.537	43.884
62	29.170	38.270	41.830
64	26.905	36.177	39.950
66	24.820	34.235	38.222
68	22.897	32.428	36.628
70	21.122	30.742	35.153
74	17.969	27.676	32.499
79	14.663	24.347	29.668
82	12.969	22.565	28.167
83	12.446	22.003	27.696
90	9.3156	18.467	24.746
92	8.5689	17.572	24.003

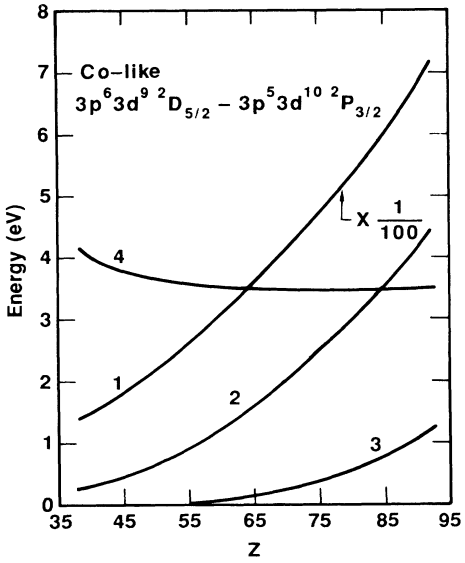

FIG. 1. Contributions of the single-configuration DF Coulomb energy (curve 1), Breit interaction (curve 2), QED corrections (curve 3), and correlation effects (curve 4) to the $3p^6 3d^9\,{}^2D_{5/2}-3p^5 3d^{10}\,{}^2P_{3/2}$ transition energies of the Co-like ions, as functions of atomic number Z. The values for the Breit interaction, QED, and correlation corrections are all negative.

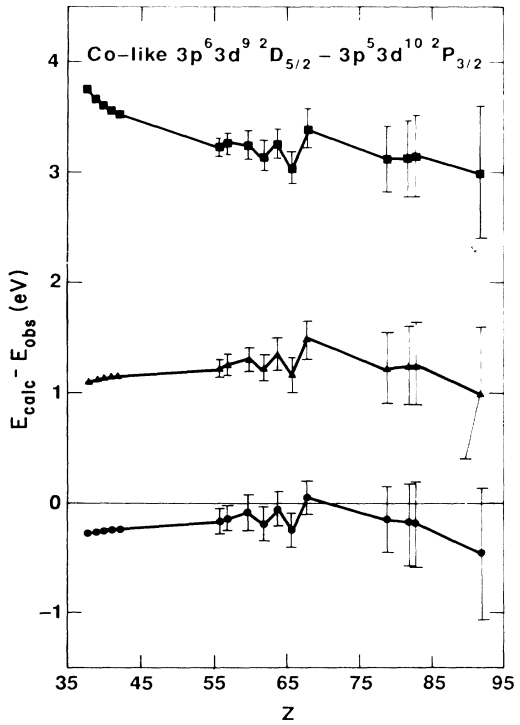

FIG. 2. Comparison of the observed energies ($E_{\rm obs}$) of the $3p^6 3d^9\,{}^2D_{5/2}-3p^5 3d^{10}\,{}^2P_{3/2}$ transitions in Co-like ions with calculated energies ($E_{\rm calc}$): single-configuration DF (squares), MCDF including super-Coster-Kronig fluctuation (triangles), and MCDF with super-Coster-Kronig fluctuation and ground-state correlation corrections (circles). The error bars indicate the experimental uncertainty. The experimental values were taken from Refs. 5, 7, and 22, except for $Z=62$ and 64 which were taken from Ref. 23.

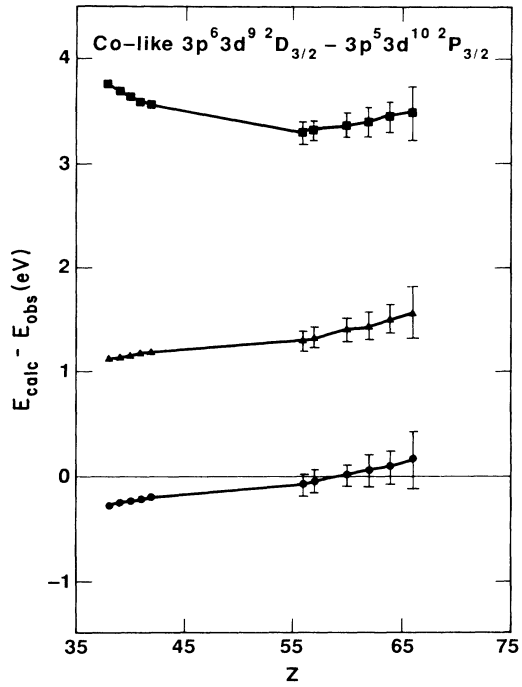

FIG. 3. The same as Fig. 2, except for the $3p^6 3d^9\,{}^2D_{3/2}-3p^5 3d^{10}\,{}^2P_{3/2}$ transitions.

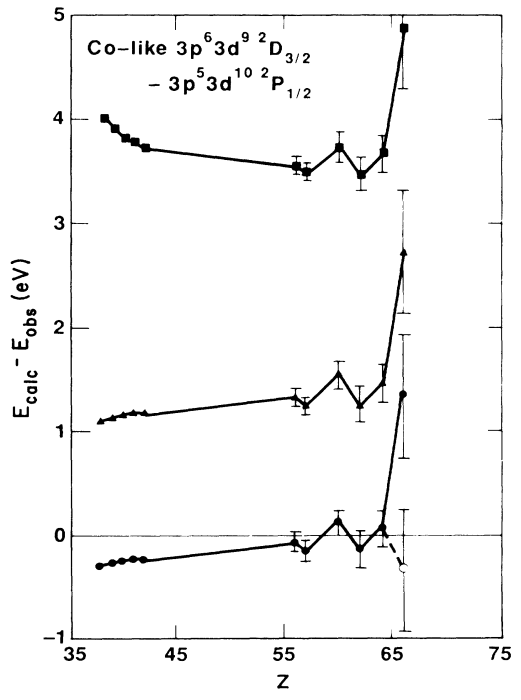

FIG. 4. The same as Fig. 2, except for the $3p^6 3d^9\,{}^2D_{3/2}-3p^5 3d^{10}\,{}^2P_{1/2}$ transitions. The open circle at $Z=66$ indicates the results if the 24.803-Å line was adopted (see text).

for the $3p$-$3d$ transitions. They are not shown in Fig. 1.

The theoretical wavelengths for the $3p^6 3d^9\,{}^2D_J - 3p^5 3d^{10}\,{}^2P_{J'}$ transitions of the Co-like ions were compared with experiments[5,7,22,23] in Figs. 2–4. The single-configuration DF calculations overestimate the transition energies by ~ 3.3 eV. The interaction between $3p^5 3d^{10}$ and $3p^6 3d^8 nf$ reduces the transition energies by ~ 2 eV. The ground-state correlation corrections further reduce the transition energies by 1.41 eV. For the $^2D_{5/2}$-$^2P_{3/2}$ and $^2D_{3/2}$-$^2P_{3/2}$ transitions, theoretical results agree very well with measurements.[5–7,22,23] For the $^2D_{3/2}$-$^2P_{1/2}$ transitions, good agreement between theory and experiment has been obtained for $Z < 50$. For $62 < Z < 66$, discrepancies up to 1.4 eV have been observed between theoretical results and experimental values from Ref. 5. The discrepancies at $Z = 62$ and 64 have mostly been removed by new measurements.[23] For the Dy^{39+} ion, a deviation of 1.4 eV still remains. However, in the spectrum of Dy^{39+}, there are two lines (24.886 and 24.803 Å) in this region that might be considered for the $^2D_{3/2}$-$^2P_{1/2}$ transition. The 24.886-Å line was identified as the $^2D_{3/2}$-$^2P_{1/2}$ transition in Ref. 5. If one took the other line (24.803 Å) as the $^2D_{3/2}$-$^2P_{1/2}$ transition instead, one would obtain good agreement between theory and experiment (see Fig. 4). The residual discrepancies between theory and experiments for $Z < 45$ are probably due to the inadequacy in the treatment of the ground-state correlation corrections.

In the calculations of the initial $3p$ hole states, it is essential to employ the MCDF-OL procedure instead of the widely used AL or EAL options. The MCDF-AL calculations for the $3p$ hole states, with the same number of CSF functions as used for OL calculations, have been found to overestimate the transition energies by as much as 8 eV. Therefore, the AL or EAL approximation is not suitable to treat interacting levels which are far apart in energy.

For the $3p^6 3d^{n-1}$-$3p^5 3d^n$ ($n \geq 2$) transitions of the other neighboring isoelectronic sequences, similar correlation effects as those found in the present work exist. They should be included in the precision calculations of transition energies.

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