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Relativity: X-ray and Auger Transitions
of Highly Charged Ions

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ABSTRACT

Many-electron QED correction is one of the unsolved problems in relativistic atomic structure calculations for many-electron systems. The accuracy of the effective-charged screening approach frequently used in the MCDF model to estimate the many-electron QED corrections is examined. The effects of relativity and configuration interaction are simultaneously important in the treatment of highly-charged ions. These effects can sometimes change the transition rates by orders of magnitude. Numerous irregularities present in Auger rates and oscillator strengths along the isoelectronic sequence due to the level crossings. The spin-orbit mixing and Breit interaction are responsible for the decay of most of the high-spin metastable autoionizing states.

I. INTRODUCTION

Effects of relativity have been found to exert significant influence on the energies and transition rates involving atomic inner shells. The situation for neutral atoms with an inner-shell vacancy has been documented in the recent review articles [1, 2]. For highly-charged ions, relativistic effects may play an increasingly important role due to the increase of the effective charge seen by the bound electrons. In this paper, we will investigate the effects of relativity on the atomic transition energies and rates of highly-charged many-electron ions by analyzing the results obtained using the multiconfiguration Dirac-Fock model (MCDF).

II. RELATIVISTIC ATOMIC STRUCTURE

At the present time, there exists no coherent and accurate solution to the relativistic many-electron problem. Instead, we rely on a calculational prescription, fragments of which are taken from quantum electrodynamic theory [2]. The relativistic Hartree-Fock or Dirac-Fock method is the most widely used calculational procedure in treating the atomic structure of highly-charged ions. The detailed information on the Dirac-Fock method can be found in the review articles [3, 4]. Here, we only outline the essential features of the Dirac-Fock method.

The Dirac-Fock method for an N-electron atom are based on an approximate configuration-space Hamiltonian

$$H = \sum_{i=1}^N h_D(i) + \sum_{i < j} \frac{1}{r_{ij}}, \quad (1)$$

where $h_D(i)$ is the Dirac single-particle Hamiltonian

$$h_D(i) = C\vec{\alpha}_i \cdot \vec{p}_i + \beta_i C^2 + V_n(r_i) \quad (2)$$

Here, $\vec{\alpha}_i$ and β_i are Dirac matrices and $V_n(r_i)$ is the interaction of the electron with nuclear charge which is usually taken as uniform charge or Fermi distribution. Atomic units are used hereafter unless stated otherwise.

The N-electron wave function is approximated by the products of N single-particle central-field Dirac orbitals, which are given by

$$\psi_{n\kappa m}(r) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) & \Omega_{\kappa m} \\ i Q_{n\kappa}(r) & \Omega_{-\kappa m} \end{pmatrix} \quad (3)$$

Here, $P_{n\kappa}$ and $Q_{n\kappa}$ are the large and small components of the radial wavefunctions, respectively. $\Omega_{\kappa m}$ is the j-j coupled wave function of orbital angular momentum and spin. The relativistic quantum number is $\kappa = (l-j)(2j+1)$.

For low- and mid-Z ions with multiple vacancies, j-j coupling is not a correct coupling scheme. Furthermore, spin-orbit mixing and configuration interaction can be quite significant for multiply ionized atoms. To overcome these problems, the many-electron wave function is approximated by multi-configuration wave function.

In the MCDF method [5], the configuration state functions (CSF's) denoted by $\phi(IJM)$ are formed by taking linear combinations of the Slater determinants of the Dirac orbitals; an atomic state function (ASF) for a state i with total angular momentum JM is then constructed from CSF:

$$\psi_i(JM) = \sum_{\lambda=1}^n C_{i\lambda} \phi(I_{\lambda}JM) \quad (4)$$

where n is the number of CSF's included in the expansion and $C_{i\lambda}$ are the mixing

coefficients for state i which are determined by the diagonalization of the energy matrix. In precision calculations of energy levels, one needs to include higher order relativistic corrections : Breit interaction and quantum electrodynamic corrections [2].

A. The Transverse Breit Interaction

The exchange of a virtual photon between two orbital electrons leads to a modification of the instantaneous Coulomb interaction. In Coulomb gauge the transverse Breit interaction is given by [6]

$$H_{Br} = - \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{r_{12}} + (\vec{\alpha}_1 \cdot \vec{\nabla}_1) (\vec{\alpha}_2 \cdot \vec{\nabla}_2) \frac{\cos(\omega r_{12}) - 1}{\omega^2 r_{12}}, \quad (5)$$

where ω is the wave number of the exchange virtual photon. The Breit energy is usually calculated by first order perturbation theory.

B. Quantum Electrodynamic Corrections (QED)

There are two main radiative corrections: self energy and vacuum polarization. They arise from the interaction of electron with the radiation field. One electron self-energy corrections are known only for the 1s, 2s and 2p levels of the hydrogenic ions [7]. Self-energy corrections in the many-electron systems are not available except for K shell of heavy neutral atoms [2]. In the MCDF model [5, 8], the many-electron self-energy corrections are estimated using Mohr's point Coulomb values [7] for the 1s, 2s and 2p levels and a n^{-3} scaling rule for the higher- n levels, with an effective-charge approach to take into account the screening effect. The vacuum polarization

corrections are in much better shape. For many-electron atoms or ions, they are determined by evaluating the expectation value of the Uehling potential using self-consistent-field wave functions [2]. Systematic improvement of the electron correlation energies and the ab initio calculation of the many-electron QED corrections are the two remaining problems in the relativistic atomic structure calculations.

C. Comparison With Experiments

Extensive comparison between Dirac-Fock theory and experiment on atomic inner-shell binding energies for neutral atoms have been carried out [9, 10]. In general, theory agrees with experiment within a few eV. For highly charged ions, He- and Li-like ions have received much attention both theoretically and experimentally [11-15]. For the $n = 2 - 2$ and $n = 2 - 1$ transitions of the He-like ions, good agreement between theory and experiment has been found [11-15].

In Fig. 1, the theoretical fine structure splittings of the 2p level in Li-like ions are compared with experiments. To achieve good agreement, theory needs to include electron correlations and higher order relativistic corrections. Furthermore, the effective-charge screening procedure [8] seems to give reasonable accurate many-electron QED corrections. On the other hand, the effective charge approach overcorrects the screening effect on the self-energy corrections for the 3p-3s splittings of the Na-like ions (see Fig. 2).

For the $n = 3 - 2$ transitions of Ne-like ions, MCDF theory agrees with experiment within 1.5 eV [17] for low and mid- Z ions. At $Z = 83$, discrepancy as large as 6 eV exists for transition to the 2s hole state [18].

These discrepancies are partly due to the residual errors in correlation energy and partly due to the treatment of many-electron QED corrections. More precision measurements in high-Z region are needed to resolve these questions.

III. MCDF FORMULATION FOR AUGER AND RADIATIVE TRANSITION

For highly-charged ions, the effects of relativity and configuration interaction are simultaneously important in calculations of transition rates. In the last few years, we have developed general MCDF Auger and radiative codes to treat complex Auger and x-ray spectra for highly ionized atoms [19]

The radiationless transition probability is calculated from perturbation theory [19]. In the MCDF method, the Auger matrix element can be expressed in terms of the CSF basis [19]

$$T_{fi} = 2\pi \left| \sum_{\lambda, \lambda'} C_{i\lambda} C_{f\lambda'} A_{\lambda\lambda'} \right|^2, \quad (6)$$

where

$$A_{\lambda\lambda'} = \langle \phi(\Gamma_{\lambda'} J' M') e j_c : JM | \sum_{\alpha < \beta} V_{\alpha\beta} | \phi(\Gamma_{\lambda} JM) \rangle. \quad (7)$$

Here, the continuum wave function $e j_c$ is normalized in energy; the two-electron operator $V_{\alpha\beta}$ is taken to be the sum of Coulomb and transverse Breit operators.

The spontaneous radiative transition probability is calculated in multipole expansion using perturbation theory. The transition matrix element in the MCDF method can be expressed in terms of CSF basis. The CSF matrix element can then be written as products of angular factor $d_{pq}^L(\beta, \alpha)$ and the one-electron matrix element $\langle p || T_L || q \rangle$ [19, 20]:

$$W_{fi} = \frac{1}{2 J_i + 1} \sum_L \frac{2\pi}{2 L + 1} \sum_{\alpha=1}^{n_i} \sum_{\beta=1}^{n_f} C_{i\alpha} C_{f\beta} \sum_{p,q} d_{p,q}^L(\beta, \alpha) \langle p || T_L || q \rangle. \quad (8)$$

Here, n_i and n_f are the numbers of CSF functions used in the expansion for the initial and final states respectively; the one-electron matrix elements are defined by Grant [20].

IV. MECHANISMS INFLUENCED THE TRANSITION RATES

We have performed systematic relativistic calculations of Auger and radiative transition rates for He, Li, Be, B, O and Na isoelectronic sequences [19, 21-23] using the MCDF method. These results are used to identify the most important factors affecting the transition rates.

A. Spin-Orbit Interaction

Spin-orbit mixing is very important in calculations of transition rates for complex open-shell ions. As an example, in the LS coupling limit, all the quartet states from the $2p^5 3d 3d'$ configurations of the Na-like ions are Auger and electric-dipole forbidden to decay to fill the L-shell vacancy. The L-shell Auger and radiative transitions are made possible in part by mixing with the doubly states due to the spin-orbit interaction. In Fig. 3, the $2s^2 {}^1S_0 - 1s2p {}^1, {}^3P_1$ E1 transitions are displayed. This E1 transition to the triplet state is the result of configuration interaction between $2s^2$ and $2p^2$ terms and the spin-orbit mixing in the final state. At higher Z, the $1s2p {}^3P_1$ and $1s2p {}^1P_1$ states approach $1s2p_{1/2} J = 1$ and $1s2p_{3/2} J = 1$ states respectively. Since $2s^2 {}^1S_0$ state has much stronger interaction with the $2p_{1/2}^2 J = 0$ than with $2p_{3/2}^2 J = 0$ state, the transition to the 3P_1 state becomes much more favorable than to the 1P_1 state at high-Z region [21].

The Auger transition rates for the $1s2p^4 ({}^2D; {}^2P)$ states of the B-

like ions are shown in Fig. 4. The differences between the transition rates for the fine structure states (e.g., $^2D_{3/2}$ and $^2D_{5/2}$) begin to appear at $Z = 15$ and reach 50% at $Z = 50$ [22].

B. Level Crossing Interaction

Level crossing is a rather common phenomenon in the atomic level structure of highly charged ions along an isoelectronic sequence [24]. It occurs when a spectrum restructures itself to approach its high- Z limit. In a relativistic calculation, effects of relativity can change the level structure and introduce many level crossings. These level crossing configuration interactions can have a pronounced effect on the transition rates.

The effects of level crossing on the systematic trends of the oscillator strengths for the boron, magnesium and aluminum sequences have been analyzed [24]. Here, we give a few examples to illustrate the importance of the level crossing interactions. In Fig. 5, the Auger rates of the $2p^5 3s^2$ states of the Na-like ions are displayed. For the low- Z ions, the $2p^5 3s^2$ $^2P_{1/2}$ state is the lowest level of the $J = 1/2$ odd manifold from the $2\ell^{-1} 3\ell'$ $3\ell''$ complex. As Z increases from 18 to 79, it comes down to cross seven levels from the $2p^5 3p^2$ and $2p^5 3s3d$ configurations. Thus, the Auger rate for the $2p^5 3s^2$ $^2P_{1/2}$ state shows a strong peak at $Z = 47$ and suffers many irregularities in the range $40 < Z < 80$. On the other hand, the transition rates for the $^2P_{3/2}$ state and the nonrelativistic results exhibit normal behavior.

The absorption oscillator strengths for the $2p^4 \ ^3P_1 - 2p^3 3d \ J = 0$ transitions in oxygen isoelectronic sequence are shown in Fig. 6. Numerous

irregularities and sharp discontinuities along the isoelectronic sequence exist in many transitions because of the level crossing interactions between the states from the $2p^3 3d$ configurations and some states from the $2s 2p^4 3p$ configurations. Furthermore, the nonrelativistic oscillator strengths are quite different from the MCDF results for medium and heavy ions, especially for transitions involving level crossings (see Fig. 6).

C. Spin-Induced Autoionization

The effects of magnetic interaction on the Auger transitions for atoms with a single vacancy have been investigated [25]. Recently, we extend the studies to highly-charged ions [21-23]. Similar to the findings for the neutral atoms, inclusion of the Breit interaction in calculations of the Auger matrix elements can have quite different effects on different individual transitions. For some transitions, it can cause drastic change in transition rates. For the others, it introduces very small deviation. In general, Breit interaction is more important for the weak transitions than for the strong ones. In Fig. 7, the Auger rates for the $2s 2p^3 P_0$ state of the He-like ions calculated using nonrelativistic and relativistic Hartree-Fock methods are compared. The change in energy and shift in wave functions because of relativity modify the Auger rate by a factor of 2 while the effect of Breit interaction increases the rate by a factor of 4 at $Z = 42$ [21]. For the L-shell Auger transitions of Na-like ions, Breit interaction has also been found to change the Auger rates for high- Z ions by as much as a factor of 2 [23].

High-spin systems present interesting opportunities for tests of theory. The quartet states of the $1s 2s 2p^2$ and the quintet states of the

$1s2p^3$ configurations are all Auger-forbidden in the nonrelativistic limit and dipole-forbidden for K x-ray emission. The Auger transition rates of these states are thus completely determined by the effects of relativity. The Auger decay of these high-spin states may proceed either through the magnetic spin-spin interaction or spin-orbit mixing with low-spin states if present. The quartet states of the Li-like ions have been extensively studied. The previous theoretical and experimental results are summarized in a recent review article [1]. Comparison between theoretical and experimental lifetimes of 4P states of $1s2s2p$ Li-like ions reveals the general good agreement between relativistic theory and experiment (Fig. 8)[26,27]. For the $^4P_{1/2}$ and $^4P_{3/2}$ states of the $1s2s2p$ configuration, more experimental data are needed.

Similar to the $^4P_{5/2}$ state of the $1s2s2p$ Li-like ions, the $2p^53s3p$ $^4D_{7/2}$ state of the Na-like ions can make Auger transitions by magnetic spin-spin interaction, or it can decay radiatively by magnetic-quadrupole emission. The calculated lifetimes for the Ar^{7+} and Fe^{15+} ions using the MCDF method are 3.28 μ sec and 180 nsec respectively. Although the metastability of the $^4D_{7/2}$ state has been established experimentally [28], no measurement of the lifetime has yet been accomplished.

CONCLUSIONS

Energies and transition probabilities of highly-charged ions are influenced by the effects of relativity. Precision measurements of x-ray energies for highly-charged heavy ions, lifetimes and fluorescence yields of high-spin metastable states can test the current relativistic theory and provide a guidance for the future development.

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FIGURE CAPTIONS

- Fig. 1 Differences between experimental and theoretical fine structure splittings for the $1s^2 2p$ Li-like ions as functions of atomic number. The legends for the theoretical results are: the dotted curve-Dirac Fock with Coulomb interaction; the dashed curve-Dirac Fock with Coulomb and Breit interaction; the dash-double-dotted curve- many body perturbation theory plus hydrogenic QED; the solid curve- many body perturbation theory plus screened QED. Experimental points are taken from the tabulation of Ref. 16.
- Fig. 2 Contributions of Lamb shift to the $3p_{3/2} - 3s_{1/2}$ splittings for Na-like ions. The dashed curve represents the hydrogenic values (Ref. 16). The solid curve displays the screened QED corrections from the MCDF model and the semi-empirical results are taken from Ref. 16.
- Fig. 3 Radiative electric-dipole transition rates for the He-like $2s^2 \ ^1S_0$ state as functions of atomic number. The solid curves represent results from MCDF calculations. The dashed curve indicate values from nonrelativistic LS coupling. From Ref. 21.
- Fig. 4 Total Auger rates for the 2P and 2D states of the $1s2p^4$ configuration. The solid curves represent results from MCDF calculations with Coulomb and Breit operator. The dashed curves display values from nonrelativistic calculations in LS coupling. From Ref. 22.

- Fig. 5 Auger rates for the $2p^5 3s^2 \ ^2P$ states of Na-like ions, as functions of atomic number. The solid curves indicate the results from MCDF calculations with Coulomb and Breit interaction. The dash-dotted curves illustrate the values from MCDF calculations with Coulomb operator only. The dashed curve represent the results from nonrelativistic LS coupling.
- Fig. 6 Absorption oscillator strengths for states from oxygen-like ions, as functions of atomic number. The solid curves represent results from MCDF calculations. The triangles indicate the values from nonrelativistic LS coupling.
- Fig. 7 Auger rates for the He-like $2s2p \ ^3P_0$ state. The circles indicate the results from MCDF with the Coulomb-Breit operator. The squares represent the values from the MCDF with Coulomb interaction. The diamonds are the results from the nonrelativistic multiconfiguration Hartree-Fock and the triangles indicate the predictions from single configuration Hartree-Fock. From Ref. 21.
- Fig. 8 Lifetimes of $1s2s2p \ ^4P$ states of Li-like ions as functions of atomic number. The solid curves represent values from MCDF calculations with Coulomb and Breit operator. The dashed curves indicate results from MCDF calculations with Coulomb interaction only. The dashed curves display results from Dirac-Hartree-Slater calculations in intermediate coupling (Ref. 27). The inverted triangles are from Ref. 29. References for other experiments can be found in Ref. 27.

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8