Interaction with Auger continua as a source of atomic-energy-level shifts

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Energy shifts of atomic inner-shell vacancy states caused by interaction with Auger and Coster-Kronig continua are considered. Numerical calculations for the L shell show that L_2- and L_3-subshell-energy shifts due to this effect are negligible, while the L_1-level shift is substantial (~ -4 eV for $30 \leq Z \leq 47$). This $[2s]$ vacancy-state shift is dominated by the interaction with $[LM]\epsilon l$ Coster-Kronig continua and brings *ab initio* self-consistent-field calculations into satisfactory agreement with experiment, for atoms lighter than Sn. For atomic numbers above $Z \cong 50$, discrepancies remain that may be results of errors in quantum-electrodynamic corrections.

I. INTRODUCTION

Comparison of precisely measured atomic-electron binding energies with state-of-the-art self-consistent-field calculations can lead to physical insights regarding the limits of the theoretical model, chemical and physical energy-level shifts, quantum electrodynamic, and other effects. One suitable theoretical basis for such comparison is provided by the comprehensive relativistic (Dirac-Hartree-Slater) *ab initio* calculations of Huang *et al.* of neutral-atom electron binding energies that include complete relaxation and a first-order correction to the local approximation; this tabulation includes the Breit-energy contribution, vacuum polarization, and approximately screened self-energy shifts to the $1s$, $2s$, and $2p_{1/2}$ levels.[1] Generally good agreement is found with traditional[2] as well as more recent[3–7] measurements, in particular if one looks at free atoms[7–9] for which solid-state and chemical shifts are absent, and at inner shells, for which electron correlation effects tend to be small. Experimental binding-energy determinations have recently been compiled and critically evaluated by Sevier.[10]

Even after discrepancies in conversion constants are resolved,[6,11–13] some systematic deviations between *ab initio* theoretical atomic level energies and the most accurate measurements are present.[6,10,13] For outer levels (e.g., Ar $3s$ and $3p$, Kr $4s$ and $4p$, and Xe $5s$ and $5p$), the discrepancies between calculated self-consistent-field (SCF) and measured energies can be removed by including ground-state configuration interaction and hole-state configuration interaction with the nearby bound excited states.[14] The discrepancy between calculated and measured $2s$-level energies (~ 6 eV at $Z \cong 36$), however, cannot be removed by including configuration interaction with nearby bound states.

The excess of the calculated SCF $2s$-level energies of Huang *et al.*[1] over measured energies[2,5,7,10] is not due to the Slater approximation in the atomic potential. We established this fact by repeating K- and L-shell binding-energy calculations for Kr with Dirac-Fock wave functions.[15] The Dirac-Fock energies were found to agree within $\lesssim 1$ eV with the Dirac-Hartree-Slater energies of Ref. 1.

The energy shift due to interaction with the photon continuum was included in our relativistic binding-energy calculations[1] through quantum-electrodynamic corrections. The energy shift due to interaction with the radiationless continua, on the other hand, was not taken into account.

In the present paper, we report on an attempt to estimate the inner-shell level shift produced by interaction with the doubly ionized Auger continua, and show that this shift can account for the remaining discrepancy between theoretical and experimental $2s$-level energies of low- and medium-Z atoms.

II. THEORY

Inner-shell hole states can decay by radiative or radiationless (Auger, Coster-Kronig) transitions. Configuration interaction between a discrete state and the autoionization continuum has been described by Fano.[16] This theoretical technique has recently been extended to calculate Auger transition rates including final-state channel mixing.[17] Here we follow the approach of these earlier developments[16,17] to calculate the energy-level shifts produced by the interaction with the radiationless continua.

The inner-shell hole states of the same symmetry are assumed to be well separated from each other. We only consider an isolated, discrete state superim-

posed on several continua. Let the discrete state be denoted by ϕ, and the doubly ionized Auger continuum states with threshold energies E_i by $\psi_{i\epsilon}(i=1,\ldots,N)$. The energy matrix of the states ϕ and $\psi_{i\epsilon}$ is

$$\langle\phi|H-E|\phi\rangle = E_\phi - E \ , \tag{1a}$$

$$\langle\psi_{i\epsilon}|H-E|\phi\rangle = A_i(\epsilon,E) \ , \tag{1b}$$

$$\langle\psi_{i\epsilon'}|H-E|\psi_{j\epsilon}\rangle = \delta_{ij}\delta(\epsilon'-\epsilon)(\epsilon+E_j-E) + V_{ij}(\epsilon',\epsilon,E) \ . \tag{1c}$$

Here, ϵ and ϵ' are kinetic energies; $\psi_{j\epsilon}$ is normalized per unit energy.

Before diagonalizing the whole discrete-continua matrix, we first diagonalize the submatrix involving the continuum states.[16,17] Let us assume that the continuum wave functions $\psi_{j\epsilon}$ $(j=1,\ldots,N)$ diagonlize the submatrix involving continuum states. Then

$$\begin{aligned}&\langle\tilde{\psi}_{i\epsilon'}|H-E|\tilde{\psi}_{j\epsilon}\rangle = \delta_{ij}\delta(\epsilon'-\epsilon)(\epsilon+E_j-E) \ , \\ &\langle\tilde{\psi}_{i\epsilon}|H-E|\phi\rangle = \tilde{A}_i(\epsilon,E) \quad (i=1,\ldots,N) \ .\end{aligned} \tag{2}$$

Here, $\tilde{\psi}_{j\epsilon}$ satisfies the "in-going"-wave boundary conditions.[17]

To determine the eigenvectors which diagonalize the discrete-continua matrix [i.e., Eqs. (1a) and (2)], the eigenvector with eigenvalue E is written

$$\Psi_i(E) = a_i(E)\phi + \sum_{j=1}^{N}\int_0^\infty b_{ij}(E,\epsilon)\tilde{\psi}_{j\epsilon}\,d\epsilon \qquad (i=1,\ldots,N) \ . \tag{3}$$

The coefficients are found as solutions of the system of equations

$$\begin{aligned}&(E_\phi - E)a_i(E) + \sum_{j=1}^{N}\int_0^\infty \tilde{A}_j^*(\epsilon,E)b_{ij}(\epsilon,E)\,d\epsilon = 0 \ , \\ &\tilde{A}_j(\epsilon,E)a_i(E) + (\epsilon+E_j-E)b_{ij} = 0 \ .\end{aligned} \tag{4}$$

The solutions of Eqs. (4) can be obtained by following the Dirac procedure to remove the singularity,[16-18] with the result

$$|a_\lambda(E)|^2 = \frac{\frac{1}{2}\Gamma_\lambda/\pi}{(E-E_r)^2+\Gamma^2/4} \ , \tag{5}$$

where we have

$$\Gamma = 2\pi\sum_{j=1}^{N}|\tilde{A}_j(E-E_j,E)|^2 \tag{6}$$

and

$$E_r = E_\phi + \sum_{j=1}^{N}\mathcal{P}\int\frac{|\tilde{A}_j(\epsilon,E)|^2}{E-E_j-\epsilon}\,d\epsilon \ . \tag{7}$$

Here, Γ and E_r can be identified as the total Auger width and the resonance energy, respectively. The symbol $\mathcal{P}$ indicates the principal value of the integral. These solutions have been obtained previously.[16,17]

From Eq. (7), the energy shift due to the interaction with the Auger continua is

$$\Delta E = E_r - E_\phi = \sum_{j=1}^{N}\mathcal{P}\int\frac{|\tilde{A}_j(\epsilon,E)|^2}{E-E_j-\epsilon}\,d\epsilon \ . \tag{8}$$

This equation is applied in what follows.

III. NUMERICAL CALCULATIONS

We calculated the hole-state energies E_ϕ using Dirac-Hartree-Slater (DHS) wave functions.[1] The same DHS bound-state wave functions are used in calculating the principal-value integrals. In order to simplify the numerical computations, we neglect the effect of channel coupling. The orbital wave functions are assumed to be orthonormal. Only the Coulomb interaction is included in the two-electron operator. Under these approximations, the level-energy shift due to interaction with Auger continua becomes

$$\Delta E = \sum_{\lambda=1}^{N}\mathcal{P}\int\frac{\left|\left\langle\psi_{\lambda\epsilon}\right|\sum_{i<j}r_{ij}^{-1}\left|\phi\right\rangle\right|^2}{E-E_\lambda-\epsilon}\,d\epsilon \ . \tag{9}$$

The Auger matrix element $\langle\psi_{\lambda\epsilon}|\sum_{i<j}r_{ij}^{-1}|\phi\rangle$ is evaluated with the aid of our general relativistic Auger program.[19]

We follow the procedure suggested by Altick and Moore[20] and Chattarji[21] to evaluate the principal-value integrals. These integrals are expressed as finite sums of integrals, each of which extends over three mesh points; the slowly varying part of the integrand is fitted to a quadratic function of the energy. One can then easily determine the basic integrals

$$\begin{aligned}&\int_{E_i}^{E_f}\frac{\epsilon^k}{E-E_\lambda-\epsilon}\,d\epsilon \ , \\ &\mathcal{P}\int_{E_i}^{E_f}\frac{\epsilon^k}{E-E_\lambda-\epsilon}\,d\epsilon, \quad k=0,1,2,3,4 \ .\end{aligned} \tag{10}$$

We take E in Eq. (8) to be the energy E_ϕ of the inner-shell hole state. The Auger energies $E_\phi - E_\lambda$ are obtained from DHS calculations.[22]

IV. RESULTS AND DISCUSSION

On the basis of the theory described in Secs. I–III, we have calculated L-shell level shifts caused by interaction with radiationless continua.

Sample calculations for $2p$ hole states show that L_2 and L_3 binding energies are affected very little. For example, interaction with $[M_4M_5]\epsilon l$ continua shifts the L_3 level of $_{45}$Rh by only ~ 0.1 eV, while the L_2

TABLE I. Energy shifts of L_1 vacancy states produced by interaction with $[LM]\epsilon$ Coster-Kronig continua and consequent L_1-subshell binding energies (in eV).

Element	$[2s]$ energy shift	$2s$ binding energy
$_{18}$Ar	−0.08	326.6
$_{30}$Zn	−3.3	1 202.7
$_{36}$Kr	−5.0	1 925.5
$_{40}$Zr	−4.8	2 541.7
$_{45}$Rh	−3.7	3 422.9
$_{47}$Ag	−4.4	3 815.9
$_{78}$Pt	−6.2	13 889.5
$_{80}$Hg	−4.2	14 853.4
$_{85}$At	−3.2	17 492.8
$_{90}$Th	−2.2	20 486.1
$_{92}$U	−1.7	21 770.7

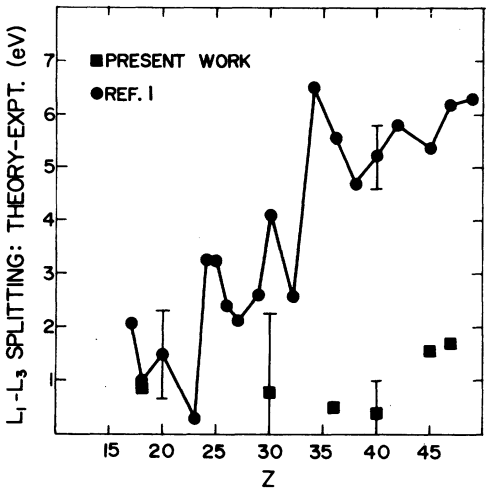

FIG. 1. Energy splitting between atomic $[2s]$ and $[2p_{3/2}]$ vacancy states, as a function of atomic number Z; the plot shows differences between *ab initio* predictions of SCF theory and experimental results from Refs. 2 and 4—dots linked by the solid curve are from the DHS calculations of Ref. 1, squares represent the same energies corrected with the level shifts calculated in the present work. Error bars indicate representative uncertainties introduced by experimental errors.

level of $_{92}$U is shifted by ~ 0.2 eV through the interaction with the $[L_3M_5]\epsilon l$ and $[L_3N]\epsilon l$ Coster-Kronig continua. We therefore concentrate on the L_1 level, for which indeed the most striking systematic discrepancy between theory and experiment exists.

Calculated $2s$-level shifts for 11 elements with atomic numbers $18 \leq Z \leq 92$ are listed in Table I.

Contributions to the L_1-level shifts from interaction with $[MM]\epsilon l$-type Auger continua are found to be negligible. For example, at $Z=36$, $[M_2M_3]\epsilon l$ contributes $\sim 1.4\times10^{-3}$ eV, and $[M_4M_5]\epsilon l$ contributes $\sim 4.8\times10^{-4}$ eV. The reason for the smallness of the effect is that the L_1 hole state lies well above the $[MM]\epsilon l$ double-ionization threshold. The contribution from that portion of the continuum which lies below $E-E_\lambda$ tends to cancel the contribution from that portion of the continuum that lies above $E-E_\lambda$ [Eq. (9)].

The L_1-level shifts are therefore dominated by contributions from the interaction with $[LM]\epsilon l$ Coster-Kronig–type continua, particularly $[L_3M_{4,5}]\epsilon f$. The L_1 hole states lie very close to the thresholds of Coster-Kronig continua. The matrix elements tend to be large and more sensitive to the energy, which accounts for the large contribution to the level shift. The configuration interaction between an L_1 hole state and the Coster-Kronig continua lowers the hole-state energy, which in turn reduces the L_1 binding energy.

To get away from solid-state effects, it is instructive to compare theoretical L_1-L_3 energy *splittings* with experimental results[2,4]; we limit the comparison to $Z<50$ to circumvent uncertainties in the quantum-electrodynamic corrections, which are small in this part of the periodic table. Such a comparison is shown in Fig. 1; good agreement between theory and experiment is seen to result once the L_1-level shift due to interaction with Coster-Kronig continua is included.

For heavier atoms ($Z>50$), however, discrepancies remain.[6,13] It seems likely that these differences at high Z may be traced to errors in the QED corrections.

The effect of interaction with the Auger continua on M- and N-shell binding energies has been the subject of a random-phase-approximation study by Wendin and Ohno,[23] who found a significant shift for the Kr $3p$ and Xe $4s$ and $4p$ shells. Whether inclusion of the shift due to configuration interaction with Auger continua can resolve the discrepancy for M and N shells of heavy elements[10] remains to be investigated.

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