Photoionization of Metallic Lanthanum, Thorium, and Uranium in a Local-Density-Based Random-Phase Approximation

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A nonrelativistic random-phase approximation has been used to introduce exchange interaction between excitations from spin-orbit–split core levels. For relatively deep levels this may lead to nonstatistical intensity ratios of "white line" resonances, while for giant dipole excitations it leads to a narrow peak (triplet excitation) on the low-energy side of the giant resonance. Effects of Auger decay have also been included.

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In this Letter I demonstrate that a nonrelativistic version of the random-phase approximation (RPA)[1] can give a reasonable description of inner-shell photoionization cross sections for heavy elements, provided that spin-orbit splitting Δ_k^{so} of the occupied energy levels ϵ_k is introduced from the beginning.

In the photoionization process, the external potential (photon field) will be screened by the dynamic response of the electronic charge distribution. The electrons will then be excited or emitted by an effective, frequency-dependent potential which may greatly differ from the external one. The RPA (also called the time-dependent Hartree approximation) represents a mean-field approximation to this response: It starts from a one-electron approximation and constructs an induced potential in terms of the Hartree potential from the induced electron-hole pair excitations. The wave functions of the electron-hole pairs are still given by the one-electron model: There is no relaxation and no recognition of the core hole. The only correlations are those built into the one-electron model.

Characteristic for the RPA is that the electron (n)–hole (k) pair interaction (exchange interaction $\langle kn|1/r_{12}|nk\rangle$) shifts the oscillator strength towards higher excitation energies in comparison with the one-electron model. Statistical weighting of spin-orbit–split subshell cross sections will only be valid for sufficiently deep inner shells, where the spin-orbit splitting of the binding energy is much larger than the electron-hole exchange interaction (j-j limit; e.g., $2p$-$5d$ in La, where $\Delta_{2p}^{so} >> \langle 2p5d|1/r_{12}|5d2p\rangle$). In general, the coupling will transfer oscillator strength from the subshell with the lower binding energy ($j=l+\frac{1}{2}$) to the one with the higher binding energy ($j=l-\frac{1}{2}$). In the case of the $3d$-$4f$ resonance peaks in the La absorption spectrum,[2,3] the intensity ratio of the spin-orbit components shows very strong deviation from the statistical value. The same is true for the $2p$-$3d$ "white lines" in CaTi.[4,5] In the case of giant dipole resonances[1] the spin-orbit splitting is small or comparable to the exchange interaction (LS limit). This results in large transfer of oscillator strength and the low-energy resonance peak becomes weak, or very weak, in comparison with the resonance at higher energy. The $4d$ absorption in Ba and La[6] and the $5d$ absorption in Th and U[7–9] are examples of this type of behavior.[10]

In the present calculation I use a local-density (LD)[11] basis to evaluate the diagram expansion for the photoionization amplitude. In particular, I only consider the RPA (bubble) diagrams and call this approximation the LDRPA.[12] Although derived from an atomic charge distribution, the LD potential is not any free-atom potential: It has no Coulomb tail and rather resembles a screened ion-core potential in a metal. However, the inner-well region can support bound, excited levels, the wave functions of which have very large overlap with occupied levels. The oscillator strength in the one-electron model is concentrated in the $5d$-$5f$, $6p$-$6d$, and $7s$-$7p$ resonance transitions, giving rise to giant dipole resonances. Here one finds the strongest induced potentials (largest electron-hole pair exchange integrals) and the strongest modifications of the one-electron model.

In the present LDRPA calculation, the central quantity is the total (effective) potential associated with the photon field. We express this in terms of an effective dipole operator $r(\omega)$, from which we obtain the partial photoionization cross sections

$$\sigma_i(\omega) \propto \omega |\langle \epsilon | r(\omega) | i \rangle|^2. \quad (1)$$

ω is the photon energy and ϵ is the kinetic energy of the photoelectron; $|\epsilon\rangle$ and $|i\rangle$ are one-electron states. The effective dipole operator $r(\omega)$ is obtained from an integral equation

$$r(\omega) = r - \sum_{nk} c_{nk} \frac{\langle k|1/r_{12}|n\rangle \langle n|r(\omega)|k\rangle}{(\omega_{nk}^2 - \omega^2)/2\omega_{nk}}. \quad (2)$$

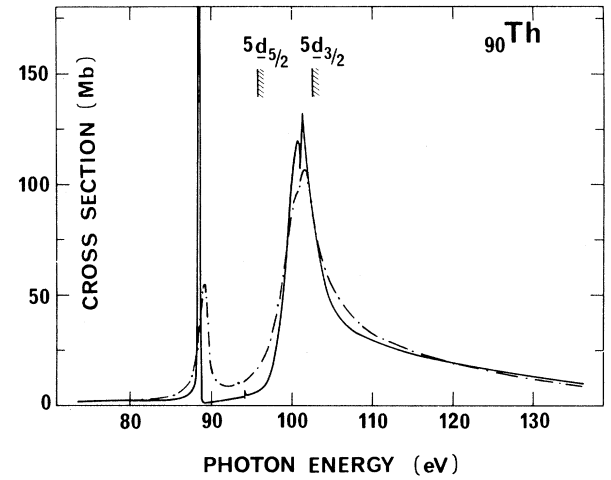

FIG. 1. Total LDRPA photoionization cross section of Th ($7s^26d^25f^0$) in the $5d$ region (solid line); experimental photoabsorption cross section of Th metal (Ref. 8) (dash-dotted line, scaled after removal of a constant background; original maximum ~70 Mb).

The second term on the right describes the potential induced via excitation of electron (n)–hole (k) pairs: The pairs respond to the effective potential (dipole matrix element $\langle n|r(\omega)|k\rangle$) through the independent-particle response function (frequency factor; $\omega_{nk}=\epsilon_n-\epsilon_k$) and give rise to an induced dipole potential via the dipole part of the Coulomb interaction, $\langle k|1/r_{12}|n\rangle$; this last one-electron integral refers to the variable r' in $1/r_{12}=1/|\vec{r}-\vec{r}'|$, and therefore represents a dipole potential in the variable $\vec{r}$. c_{nk} is an angular coefficient and all matrix elements refer to radial variables only. The hole index k runs over *spin-orbit-split* occupied levels $[\epsilon_k(l+\frac{1}{2})-\epsilon_k(l-\frac{1}{2})=\Delta_k^{so}$, taken from experiment]. In the present work this is the only place where relativistic effects are allowed to enter, since the one-electron potential and wave functions are nonrelativistic. Therefore, if $\Delta_k^{so}\to 0$ the internal dynamics of the kth shell is treated nonrelativistically.

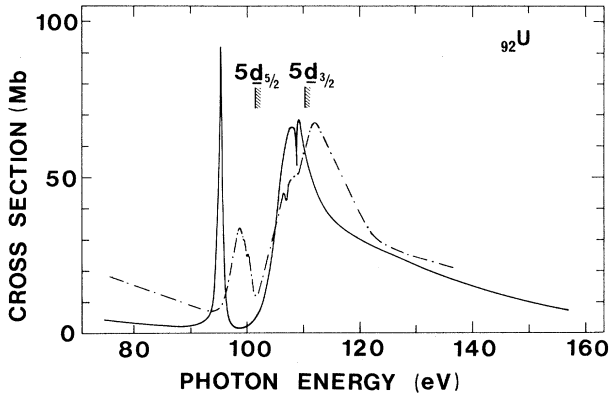

FIG. 2. Total LDRPA photoionization cross section of U ($7s^26d^15f^3$) in the $5d$ region (solid line); experimental photoabsorption cross section of U metal (Ref. 7) (dash-dotted line, scaled; experimental maximum, 40 Mb).

In this Letter I shall only present results for total (absorption) cross sections, obtained by summing all the partial ones, as shown in Figs. 1–4 for Th ($7s^26d^25f^0$), U ($7s^26d5f^3$), and La ($6s^25d^14f^0$). This sequence of figures illustrates the development with increasing spin-orbit to exchange splitting ratio, from ~0.5 in the $5d$ region in Th (Fig. 1), via ~1 in the $6p$ region in Th (Fig. 3), to ~5 in the $3d$ region in La (Fig. 4). In the $4d$ region of

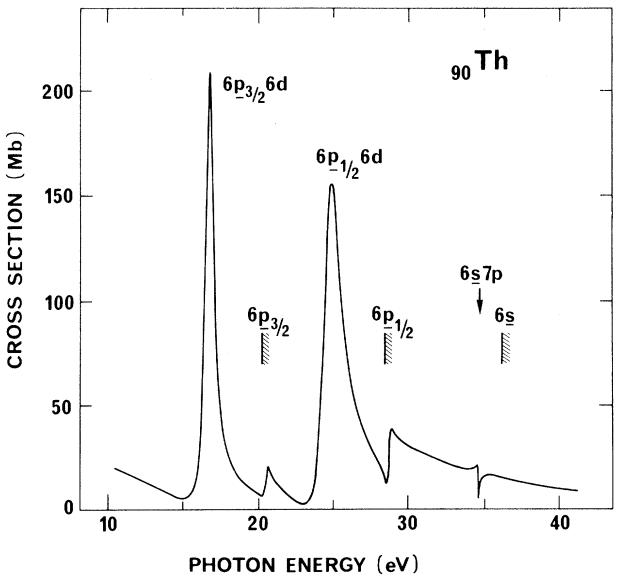

FIG. 3. Total LDRPA photoionization cross section of Th ($7s^26d^25f^0$) in the $6p$ region.

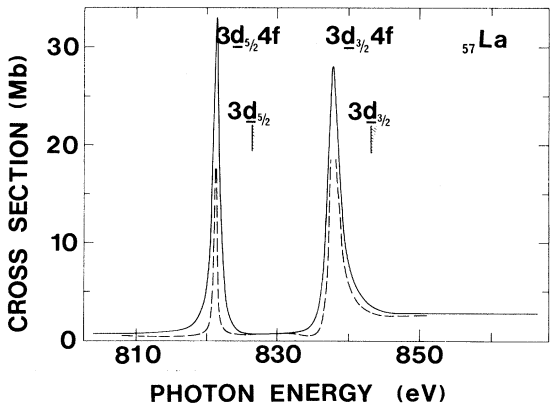

FIG. 4. Total LDRPA photoionization cross section of La ($6s^25d^14f^0$) in the $3d$ region.

La this ratio is about 0.2: As a consequence, in La the first peak is much weaker than in Th (Fig. 1) because more intensity has been transferred to higher energies.

In the case of giant dipole resonances (e.g., $4d$ and $5p$ regions in La, $5d$ and $6p$ regions in Th, U) the very large dipole moment results in autoionization (direct electron-hole recombination) as the dominant decay. This is described within the RPA. Comparison of the LDRPA with experimental absorption[7-9] and photoemission[13-15] spectra for Th and U in the $5d$-resonance region shows good qualitative agreement.[16,17] In particular in Th, however, it is clear that additional broadening has to be included for the low-energy resonance peak. There is competition with $5d$-Auger decay processes (beyond the RPA) and with effects due to $5f$ hybridization (beyond an atomic model). In U, the $5f^3$ configuration introduces considerable broadening already in the atomic model through $5f$ emission. In the $6p$ region in Th (Fig. 3) inclusion of the $6d$ bandwidth will probably give qualitative agreement with experimental results for Th metal.[8]

The comparison with experiment in Figs. 1 and 2 is highly nontrivial: In the experimental data there is a background (e.g., from higher-order light and stray light), and the absolute cross sections are not well determined. Figures 1 and 2 therefore only represent different examples of possible (or perhaps impossible) ways of comparison. In Fig. 2, the original experimental data for uranium have been scaled to the same maximum value as theory around 110 eV. However, the present theory neglects multiplet splitting which would lead to a broader and lower maximum. In Fig. 1, the thorium data have been scaled after removal of a constant background, leading to excellent, but perhaps too good, agreement with the present LDRPA theory. An atomic approach is certainly adequate for describing the gross distribution of oscillator strength in the metals in the $5d$ region.

Proceeding to deep inner shells, the autoionization rate decreases because of reduced electron-hole overlap, while the Auger rate in general increases, often to become the principal decay mode. Figure 4 (dashed curve) shows the LDRPA result for the total $3d$-photoionization cross section in La without $3d$-Auger broadening. The $(3d_{5/2}\text{-}4f)/(3d_{3/2}\text{-}4f)$ oscillator strength ratio is ~ 0.75 in the present LDRPA calculation (statistical value 1.5). This agrees reasonably well with the experimental value[2] of 0.63 and with the $^3D_1/^1P_1$ ratio of ~ 0.65 from other calculations[18,19] using intermediate coupling starting from the LS limit. The autoionization width of the $3d_{5/2}\text{-}4f$ resonance is much smaller than the $3d$-Auger width. On the other hand, the $3d_{3/2}\text{-}4f$ resonance strongly autoionizes into the $3d_{5/2}\text{-}\epsilon f$ continuum and acquires a substantial width ($\Gamma_a \simeq 0.6$ eV) and a pronounced asymmetric profile because of interference (Fano profile).

In the present calculation, Auger broadening has been introduced by adding an imaginary part $-\Gamma_A/2$ to the $3d$ core-hole energy. $\Gamma_A = 1.1$ eV is taken from experiment[2] for metallic La (width of the first line in the photoabsorption spectrum).

The partial photoionization cross sections now have reasonable resonance linewidths and intensities. However, they no longer add up to the total cross section in the neighborhood of the resonances, because a fraction $\Gamma_A/(\Gamma_a+\Gamma_A)$ of the oscillator strength has been lost. We pick up this fraction of the total cross section taken away from single-hole final states by the Auger mechanism through addition of a Lorentzian-like term for each of the resonances. The result is given by the full line in Fig. 4 and is in quite good agreement with experiment.[2,3,20] We emphasize that the larger width of the second resonance in Fig. 4 is due to autoionization of the $3d_{3/2}\text{-}4f$ electron-hole pair into the $3d_{5/2}\text{-}\epsilon f$ continuum and *not* due to different $3d$ core-hole widths. This does not exclude that the $3d_{3/2}$ hole could be slightly broader than $3d_{5/2}$ because of Coster-Kronig decay which would be allowed in the metal.

Analogous results are found for the $2p\text{-}3d$ resonance region in Ca metal,[21] in which case the LDRPA gives a $(2p_{3/2}\text{-}3d)/(2p_{1/2}\text{-}3d)$ ratio of ~ 1.0 instead of the statistical value of 2.0.

In conclusion, nonrelativistic RPA gives a good account of the coupling between the components of spin-orbit–split subshells. RPA describes nonstatistical weighting of photoionization cross sections by introducing the electron-hole pair exchange interaction from the j-j limit. With a local-density basis (LDRPA) one obtains a good overall description of the oscillator-strength distribution of photoabsorption spectra for metals. As regards subshell photoemission cross sections, in regions of giant dipole resonances, autoionization (direct recombination) is the dominant mode of decay and the LDRPA works well. In other resonance regions there may be important competition from Auger processes and bandwidth (hybridization) effects, and atomic RPA methods may have to be augmented.

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