Enhanced Nondipole Effects in Low Energy Photoionization

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(Received 26 October 1998)

It is found that electric-dipole–electric-quadrupole $E1$-$E2$ interference effects at low photon energies, of the order of tens of eV, in photoelectron angular distributions can be significant, comparable to, or even larger than, effects at energies of hundreds to thousands of eV, owing to quadrupole autoionizing resonances. This is illustrated both for Ne $2p$ photoionization around 51 eV and Ar $3p$ photoionization around 33 eV, where random phase approximation with exchange calculations are performed with allowance for correlations in both dipole and quadrupole channels.

PACS numbers: 32.80.Dz, 32.80.Fb

Nondipole effects resulting from electric-dipole–electric-quadrupole $E1$-$E2$ interference in photoelectron angular distribution spectra have become a subject of active experimental investigations in recent years [1–3]. The effect arises from the first-order correction to the dipole approximation for a photoionization matrix element between initial and final states: $M_{if} = (f|(1 + i\mathbf{k}\cdot\mathbf{r})\mathbf{e}\cdot\mathbf{p}|i)$, with $\mathbf{k}$ and $\mathbf{e}$ being the photon momentum (in atomic units) and polarization vector, and $\mathbf{r}$ and $\mathbf{p}$ being the electron position vector and the electron momentum operator. The correction term $i\mathbf{k}\cdot\mathbf{r}$ in this expression gives rise to the appearance of an electric dipole($E1$)–electric quadrupole($E2$) interference term in the differential photoionization cross section $d\sigma_{nl}/d\Omega$ of a nl-subshell of the atom [4–7].

It has tacitly been believed for many years that nondipole $E1$-$E2$ interference effects are undetectable against the background of purely dipole ($E1$) effects at photon energies of the order of tens of eV; due to the small value of the photon momentum at these energies ($k \approx \alpha \approx 1/137$, α being the fine structure constant), the $E1$-$E2$ interference effects were expected to be only of the order of 1% or less of the dipole effects. Consequently, until recently, nondipole effects were sought after at photon energies of hundreds to thousands of eV. Very recently, however, Martin *et al.* [3], have demonstrated the possibility of detecting experimentally (with accuracy of 0.5%) $E1$-$E2$ interference effects even at extremely low photon energies (<15 eV). Clearly, theoretical investigations of these effects at low photon energies of tens of eV, where the present knowledge is largely lacking, are in order.

With the impetus of the work of Martin *et al.* [3], we have extended the dipole version of the random phase approximation with exchange (RPAE) [8] to treat the $E1$-$E2$ interference effects with allowance for correlation including interchannel coupling in both dipole D and quadrupole Q photoionization amplitudes, and applied it to a study of the nondipole asymmetry parameters in the vicinity of quadrupole and dipole autoionizing resonances emerging from the $2s^2$ subshell of Ne around 51 eV and from the $3s^2$ subshell of Ar around 33 eV. It is the aim of this paper to demonstrate that owing to *quadrupole* resonances, the photoelectron nondipole angular asymmetry parameters, and the size of the $E1$-$E2$ interference correction term to the differential photoionization cross section at low photon energies, are comparable with, and may even be larger than, those observed at high photon energies. RPAE was utilized because it has been so successful in including the important correlations in dipole photoionization [8].

In the present work the RPAE was employed with allowance for electron correlation between ns^2 and np^6 electrons in the calculation of both the dipole and quadrupole photoionization channels of Ne ($n = 2$) and Ar ($n = 3$). For the sake of consistency of application of RPAE, Hartree-Fock (HF) values of ionization potentials I_{nl} were used in these calculations: $I_{2s} = 52.53$ eV and $I_{2p} = 23.14$ eV for Ne, and $I_{3s} = 34.76$ eV and $I_{3p} = 16.08$ eV for Ar.

Explicit expressions for the differential photoionization cross section $d\sigma_{nl}/d\Omega$, including the lowest order $E1$-$E2$ interference correction have been given for unpolarized light [4], for 100% linearly polarized light [5,6], and for general polarization [7]. For 100% linearly polarized light,

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\sigma_{nl}}{4\pi}\left[1 + \frac{\beta_{nl}}{2}(3\cos^2\theta - 1)\right] + \Delta E_{12}. \quad (1)$$

Here σ_{nl} is the dipole photoionization cross section of the subshell nl, β_{nl} is the dipole photoelectron angular asymmetry parameter, ΔE_{12} is the $E1$-$E2$ interference correction term,

$$\Delta E_{12} = \frac{\sigma_{nl}}{4\pi}(\delta_{nl} + \gamma_{nl}\cos^2\theta)\sin\theta\cos\phi, \quad (2)$$

where the spherical angles θ and ϕ are defined in relation to directions of the photon momentum $\mathbf{k}$, photoelectron momentum $\mathbf{p}$, and photon polarization vector $\mathbf{e}$ as specified in Fig. 1, and γ_{nl} and δ_{nl} are the nondipole angular

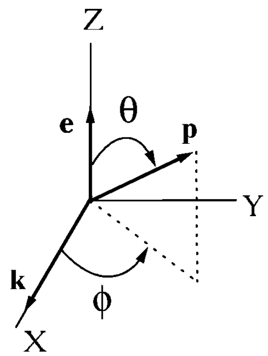

FIG. 1. Definition of the angles θ and ϕ from Eqs. (1) and (2) relative to directions of the photoelectron momentum **p**, photon momentum **k**, and photon polirization vector **e**.

distribution asymmetry parameters

$$\gamma_{nl} = \frac{3k}{2[lD_{l-1}^2 + (l+1)D_{l+1}^2]} \times \sum_{l',l''} A_{l',l''} D_{l'} Q_{l''} \cos(\delta_{l''} - \delta_{l'}),$$
$$\delta_{nl} = \frac{3k}{2[lD_{l-1}^2 + (l+1)D_{l+1}^2]} \times \sum_{l',l''} B_{l',l''} D_{l'} Q_{l''} \cos(\delta_{l''} - \delta_{l'}). \tag{3}$$

Here $D_{l'}$ and $Q_{l''}$ are the radial dipole and quadrupole photoionization amplitudes, respectively, $l' = l \pm 1$, $l'' = l, l \pm 2$, δ_λ are the phase shifts of the wave functions of photoelectrons in the field of the positive ionic core, and the coefficients $A_{l',l''}$ and $B_{l',l''}$ are given in Ref. [6]. For the analyzer located at the magic angle $\theta = 54.7°$ in the $\phi = 0°$ plane, which is the geometry used in Ref. [2], Eqs. (1) and (2) reduce to

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\sigma_{nl}}{4\pi} + \Delta E'_{12}, \tag{4}$$

$$\Delta E'_{12} = \frac{\sigma_{nl}}{4\pi}\sqrt{\frac{2}{27}}(3\delta_{nl} + \gamma_{nl}). \tag{5}$$

Displayed in Fig. 2 are the parameters γ_{nl}, δ_{nl}, their combination $\zeta_{nl} = 3\delta_{nl} + \gamma_{nl}$ as well as the interference term $\Delta E'_{12}$, calculated using our modified RPAE in the vicinity of quadrupole $2s \to 3d$ and dipole $2s \to 4p$ autoionizing resonances in the Ne $2p \to \varepsilon p, \varepsilon f$ and $2p \to \varepsilon s, \varepsilon d$ photoionization channels, respectively. The outstanding feature of the results is that all of the nondipole parameters are enhanced in the neighborhood of the resonance. Even more important is that quadrupole peak values of the nondipole parameters are comparable to those at much higher photon energies (200 to 500 eV) for the Ne $2p$ photoionization [6]. The nondipole interference term in Fig. 2 is seen to maximize in the vicinity of the quadrupole resonances at a value of about 0.05 Mb sr^{-1}; this represents a correction to the differential cross section, in the specified direction, of 7%, or more than an order of magnitude larger than observed recently at low energies for Cd [3].

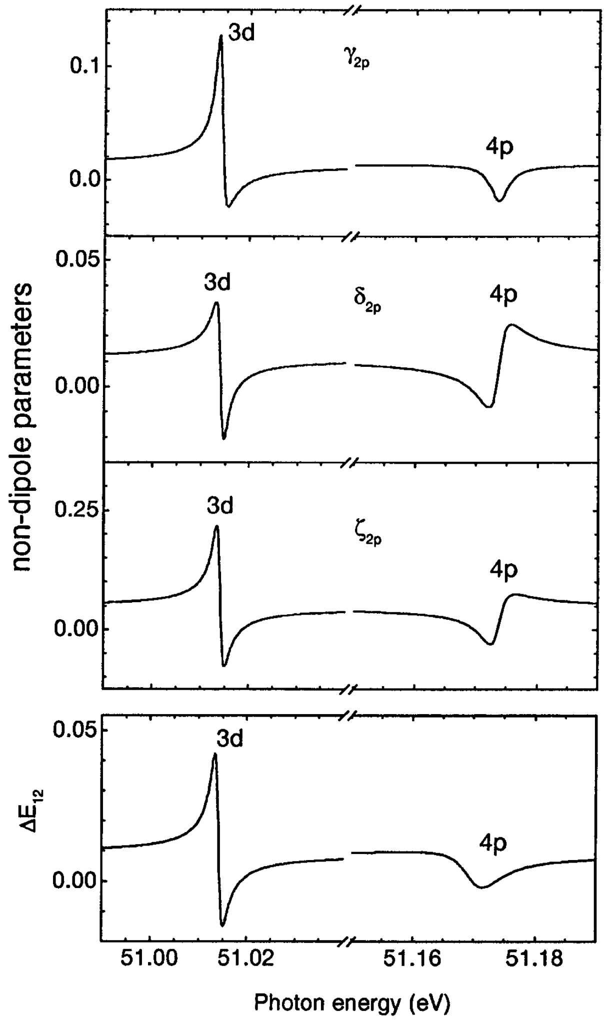

FIG. 2. Nondipole $E1$-$E2$ interference parameters γ_{2p}, δ_{2p}, $\zeta_{2p} = 3\delta_{2p} + \gamma_{2p}$, as well as $\Delta E'_{12}$ (Mb sr^{-1}) of Eq. (5) calculated in the framework of RPAE in the energy region of the quadrupole $2s \to 3d$ and dipole $2s \to 4p$ autoionizing resonances in the Ne $2p$ photoionization.

The case of Ne, however, is likely to pose certain experimental difficulties because the quadrupole resonances are very narrow. Hence, other species might be more suitable for experimental investigation. An outstanding candidate is Ar where there are $\Delta n = 0$ quadrupole resonances, e.g., $3s \to 3d$, which are likely to be quite strong.

Displayed in Fig. 3 are the parameters γ_{nl}, δ_{nl}, $\zeta_{nl} = 3\delta_{nl} + \gamma_{nl}$ as well as the interference term $\Delta E'_{12}$, calculated in the framework of RPAE in the vicinity of quadrupole $3s \to 3d, 4d$ and dipole $3s \to 4p, 5p$ autoionizing resonances for Ar $3p$ photoionization. The enhancement of the nondipole effects in this case is profoundly more significant than in the above case of Ne; in addition,

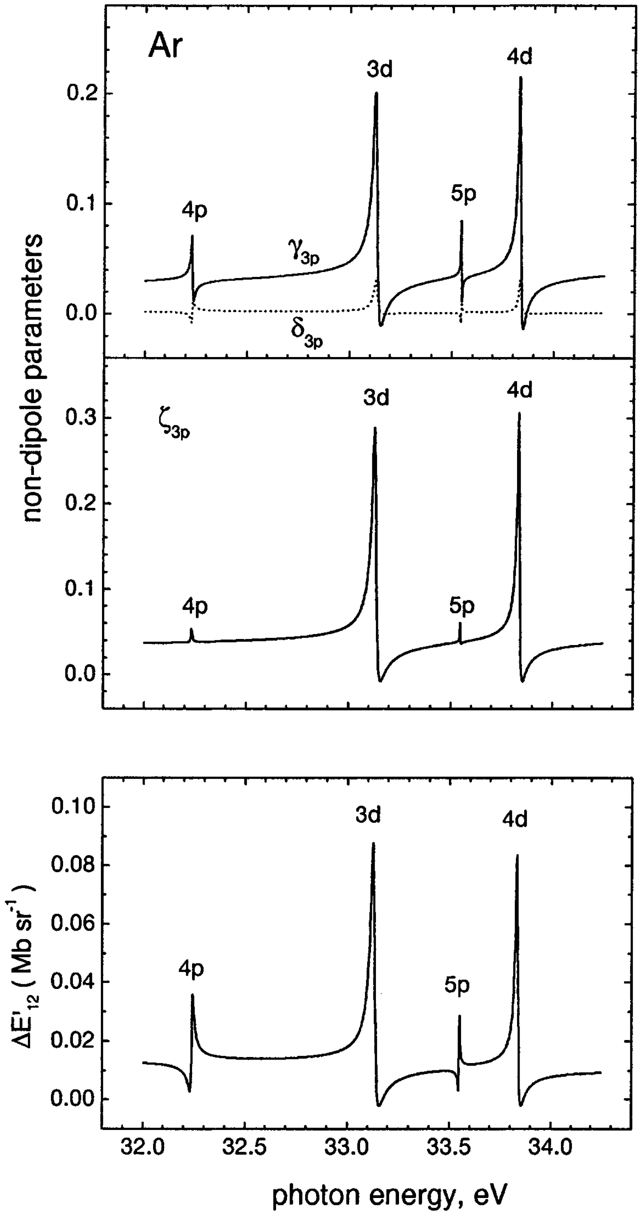

FIG. 3. Nondipole $E1$-$E2$ interference parameters γ_{3p}, δ_{3p}, ζ_{3p}, as well as $\Delta E'_{12}$ (Mb sr^{-1}) of Eq. (5) calculated in the framework of RPAE in the energy region of the quadrupole $3s \rightarrow 3d, 4d$ and dipole $3s \rightarrow 4p, 5p$ autoionizing resonances in the Ar $3p$ photoionization.

the widths of the quadrupole resonance oscillations in γ_{3p}, δ_{3p}, ζ_{3p}, and $\Delta E'_{12}$ are very much larger as well. This eliminates experimental problems related to the finite experimental resolution for these nondipole effects to be observed, which, in turn, tremendously facilitates the possibility of penetrating into the physics of low energy $E1$-$E2$ interference effects in photoelectron angular distributions.

Of particular importance is that this significant enhancement occurs at quadrupole resonances, not dipole resonances. In the vicinity of the dipole resonances, the nondipole parameters are damped (or masked [9]), owing to the minimum of the resonance cross section occurring near the maximum in γ_{nl} and δ_{nl}; indeed, one can see from Figs. 2 and 3 that the dipole resonances in the $\Delta E'_{12}$ are rather small as compared to the quadrupole resonances. In any case, it is remarkable that nondipole interference could have so large an effect upon differential cross section at such low photon energies.

It is important to consider the applicability of RPAE to the Ar $3s \rightarrow nd$ quadrupole resonances since it is known that RPAE fails to correctly describe the *dipole* $3s \rightarrow np$ autoionizing resonances in Ar [8]. The latter is because the $3s \rightarrow np$ transitions are very weak and the RPAE dipole corrections in Ar are so strong that they cause a change of several hundred percent to these transition strengths, e.g., the $3s \rightarrow 4p$ reduced matrix element, which is -0.033 in the HF approximation, rises to $+0.075$ in RPAE (note that even the sign of the matrix element is changed). This more than 300% change, brought about principally by interchannel coupling with the $3p \rightarrow kd$ dipole channels, implies that even *weaker* ionization plus excitation channels affect the $3s \rightarrow np$ autoionizing resonances, and the omission of these channels in RPAE causes the failure. The quadrupole $3s \rightarrow nd$ resonances, on the other hand, are quite strong and, as our calculations show, the RPAE quadrupole corrections, in contrast to dipole, are small; the $3s \rightarrow 3d$ reduced matrix element, $Q_{3s \rightarrow 3d} = \langle 3s \parallel r^2 \parallel 3d \rangle$, 1.08 in the HF approximation, is reduced to 0.86 due to the RPAE corrections, only a 20% change. Clearly, then, the non-RPAE quadrupole ionization plus excitation channels will have an even smaller effect. Thus, while RPAE is inadequate for the description of the dipole autoionization of Ar, it appears to be quite applicable to $3s \rightarrow 3d$ quadrupole autoionization, and hence predictions related to quadrupole photoionization made in this paper should be substantially correct.

The importance of the results of this paper is that significant quadrupole resonance enhancement of the $E1$-$E2$ interference spectra will be a general occurrence for atoms, ions, molecules, clusters, and solids. Ne and Ar are just the first cases studied. For other species the effect described is expected to be at least as significant or even much larger in certain cases. Some of them may be found among those already mentioned (heavier atoms with $\Delta n = 0$ quadrupole resonances, e.g., $4s \rightarrow 4d$ of Kr, etc.), as well as among transition-metal and rare-earth elements where the outer nd and nf orbitals are collapsed. Another possibility for great enhancement of nondipole effects can occur in situations where quadrupole resonance widths are narrowed by electron correlation, but without significantly changing the oscillator strengths, as in the valence $nd \rightarrow n'p$ dipole autoionizing resonances in the ns photoionization of all semifilled nd^5 atoms and ions [10]. Under such conditions, the peak values of the nondipole angular distribution parameters γ_{nl} and δ_{nl}, as well as that of ΔE_{12}, will be increased by one to several orders of magnitude, thus dominating over the dipole effects even at low photon energies. We are presently searching for such atoms and conditions.

It is important to reemphasize that these nondipole effects are entirely measurable with current technology [2,3], and such measurements will give important information about the $E1$-$E2$ interference, along with how correlation affects quadrupole amplitudes, a virtually unexplored area. And, since the resonance enhancement of the $E1$-$E2$ interference effects will also affect, as shown previously [5,11,12], a related phenomenon—the electrical current appearing in gaseous environment upon photoionization of its atoms [4], these effects may be studied by the measurements of the currents as well. In addition, low energy enhancement of nondipole effects may have astrophysical consequences [13], owing to the momentum transferred to the photoelectron in the nondipole photoionization process. Note also, that these effects will not only be seen in photoelectron angular distributions, but in spin-polarization parameters as well. One of our future directions is to pursue this by direct calculation.

This work was supported by the National Science Foundation and NASA. V. K. D. expresses thanks for the hospitality of the Department of Physics and Astronomy, Georgia State University, Atlanta, where this work was performed.

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