NONDIPOLE EFFECTS IN PHOTOIONIZATION OF RARE GAS ATOMS

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We present a discussion of octupole and other $O(k^2)$ ($k = 2\pi/\lambda$, where λ is the photon wavelength) corrections to to the angular distribution of photoelectrons from noble-gas atoms. These corrections are characterized by four parameters $\Delta\beta$, λ, μ, and ν constrained by $\lambda+\mu+\nu = 0$. As an example, we consider photoionization of $n = 2$ shell of neon for photon energies below 2 keV. The resulting angular distribution accounts for a significant part of the differences between experimental values of the non-dipole parameters for the $n = 2$ shell of neon and previous theoretical predictions.

1 Introduction

The insufficiencies of the dipole approximation in description of photoionization processes have been noted already at the dawn of quantum mechanics [1]. However, only recently experiments using synchrotron radiation sources have highlighted nondipole effects in photoionization and provided a detailed information at relatively low photon energies $\omega < 1$ keV. The deviations from the dipole approximation are manifested primarily in the angular distributions of photoelectrons. Non-dipole contributions in the angular distributions appearing as interferences between electric dipole and electric quadrupole amplitudes ($O(k)$ effects) were convincingly demonstrated in recent experiments [2,3,4]. Here we focus on the theoretical treatment of next-order $O(k^2)$ corrections to differential cross-sections arising due to an additional inclusion of electric-octupole, magnetic-dipole. magnetic-quadrupole contributions, and retardation effects. These $O(k^2)$ corrections were shown [5] to account for a large part of the previously unexplained differences between theory and experiment [4] in the non-dipole contributions to the angular distribution of photoelectrons ejected from the $n = 2$ shell of neon. In this paper we review our work [5,6,7] and augment it with an extended discussion of results and the employed formalism.

2 Formalism

2.1 Qualitative consideration

The differential cross-section of photoionization process may be expressed as

$$\frac{d\sigma}{d\Omega} = V\frac{\alpha}{2\pi}\frac{pE}{\omega}\left|\langle f|T|i\rangle\right|^2 . \tag{1}$$

Here p is a linear momentum of photoelectron with an energy E, and ω is a frequency of the photon; the initial and final atomic states are designated as $|i\rangle$ and $|f\rangle$, and V is a

normalization volume. T represents an operator of interaction with electromagnetic field

$$T = \sum_i t(\omega, \mathbf{r}_i)\,, \tag{2}$$

with a summation over atomic electrons. Explicitly in the transverse gauge

$$t(\omega, \mathbf{r}_i) = \alpha_i \cdot \hat{\epsilon}\, e^{i\mathbf{k}\cdot\mathbf{r}_i}\,, \tag{3}$$

where $\hat{\epsilon}$ is the photon polarization vector, $\mathbf{k}$ is the photon wave vector $|\mathbf{k}| = \alpha\omega$, and α_i are the Dirac matrices.

The conventional approach is to expand the exponent in Eq. (3) in powers of $\mathbf{k}\cdot\mathbf{r}$

$$e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2!}\left(\mathbf{k}\cdot\mathbf{r}\right)^2 + \cdots \tag{4}$$

The traditional dipole approximation corresponds to setting $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$; then the transition operator reduces to the so-called velocity form of the electric-dipole ($E1$) operator. The above expansion is closely related to the expansion in terms of electromagnetic multipoles designated generically as EJ and MJ, J being the multipolarity. The first order term is related to a linear combination of electric–quadrupole ($E2$) and magnetic–dipoles ($M1$) multipoles. The term quadratic in k corresponds to electric–octupole ($E3$) and magnetic–quadrupole ($M2$) multipoles. The differential cross-section, Eq. (1), is proportional to the square of the transition amplitude and we may write qualitatively

$$\begin{aligned}\frac{d\sigma}{d\Omega} \propto\; & E1\cdot E1 + \\ & + E1\cdot E2 + E1\cdot M1 + \\ & + E1\cdot E3 + E2\cdot E2 + E1\cdot M2 + M1\cdot M1 + \delta(E1\cdot E1)_{\rm ret}\,.\end{aligned}$$

Here we combined interferences between multipoles in such a way that the first line corresponds to the dominant electric-dipole ($O(1)$) contributions, the second line is due to $O(k)$ corrections, and the last line combines $O(k^2)$ terms. We also include effects of retardation in the electric-dipole operator symbolically represented by the term $\delta(E1\cdot E1)_{\rm ret}$. A substantial theoretical work has been carried out for $O(k)$ corrections (see e.g. Ref. [8,9,10,11,12,13,14] and recent studies [15,16,17,18,19,20,21]). Here we focus on $O(k^2)$ contributions to the photoelectron angular distribution. In Ref. [5] we have demonstrated that the $O(k^2)$ corrections account for a substantial fraction of the difference between theory and experiment [4] for the $O(k)$ non-dipole parameter in neon.

On dimensional grounds, the relative size of the $O(k)$ non-dipole terms is $\approx ka_b$, where a_b is the radius of the orbit of the ionized electron. For example, for the $n = 2$ shell of neon, ka_b ranges from 0.027 at 100 eV to 0.27 at 1 keV. Therefore, one expects to find substantial corrections to the dipole angular distribution at keV energies. Indeed, in Ref. [4], such large corrections were observed in photoionization of the $n = 2$ shell of neon. Similarly, the ratio of $O((ka_b)^2)$ and $O(ka_b)$ corrections is also in the order of ka_b, i.e. we expect a 30% $O((ka_b)^2)$ correction to the angular distribution truncated at $O(ka_b)$ level.

2.2 Wave functions

We carry out the calculations in the independent particle approximation (IPA). In the IPA the initial state $|i\rangle$ is represented by the Slater determinant constructed from the orbitals

comprising the atomic ground state and the final state $|f\rangle$ – by the determinant where the orbital of the ejected electron is replaced by a continuum orbital of the photoelectron. At large values of electronic coordinate the continuum orbital has to go over to a sum of an incoming spherical and plane waves [22]. Box-normalized scattering wavefunction satisfying this boundary condition may be decomposed in partial waves

$$w_{\mathbf{p}\lambda} = \left(\frac{(2\pi)^3}{\alpha\, E\, p\, V} \right)^{1/2} \sum_{\kappa m} \left(\Omega^{\dagger}_{\kappa m}\left(\widehat{p}\right)\, \chi_\sigma \right)\; i^{l-1} e^{-i\delta_\kappa}\, w_{\kappa m}\left(\mathbf{r}\right) . \tag{5}$$

In this equation $\Omega_{\kappa m}$ is a spherical spinor, χ_σ is a two-component spinor describing spin-polarization of the photoelectron, and $\kappa = (l-j)(2j+1)$ is expressed in terms of the total and orbital angular momenta, and δ_κ is a phase shift. Wave function $w_{\kappa m}\left(\mathbf{r}\right)$ may be expressed in terms of the large (S_κ) and small (T_κ) components satisfying the radial Dirac equations

$$w_{\kappa m}\left(\mathbf{r}\right) = \frac{1}{r} \begin{pmatrix} i S_\kappa(r)\, \Omega_{\kappa m}(\hat{r}) \\ T_\kappa(r)\, \Omega_{-\kappa m}(\hat{r}) \end{pmatrix} . \tag{6}$$

We substitute the continuum, Eq. (5), and bound state b wavefunctions in the expression for the differential cross-section and average over all possible spin polarizations σ and magnetic quantum numbers m_b of the residual ion

$$\begin{aligned} |\langle f|T|i\rangle|^2 = \frac{(2\pi)^3}{\alpha\, E\, p\, V} \sum_{\kappa m\, \kappa' m' m_b \sigma} \left[\Omega^{\dagger}_{\kappa' m'}\left(\widehat{p}\right)\, \chi_\sigma \right] \left[\chi^{\dagger}_\sigma\, \Omega_{\kappa m}\left(\widehat{p}\right) \right] \times \\ \left\{ i^{l-1} e^{-i\delta_\kappa} \langle \kappa m | t | \kappa_b, -m_b \rangle \right\} \left\{ i^{l'-1} e^{-i\delta_{\kappa'}} \langle \kappa' m' | t | \kappa_b, -m_b \rangle \right\}^* . \end{aligned} \tag{7}$$

The angular dependence on the direction of the photoelectron linear momentum becomes more explicit by carrying out the summation over spin projections

$$\sum_\sigma \left[\Omega^{\dagger}_{\kappa' m'}\left(\widehat{p}\right)\, \chi_\sigma \right] \left[\chi^{\dagger}_\sigma\, \Omega_{\kappa m}\left(\widehat{p}\right) \right] = \Omega^{\dagger}_{\kappa' m'}\left(\widehat{p}\right) \Omega_{\kappa m}\left(\widehat{p}\right) = \sum_{L M_L} A^{(\kappa m \kappa' m')}_{L M_L} Y_{L M_L}\left(\widehat{p}\right) , \tag{8}$$

where

$$A^{(\kappa m \kappa' m')}_{L M_L} = (-1)^{j'-m'+M_L} \langle \kappa' || Y_L || \kappa \rangle \begin{pmatrix} j' & L & j \\ -m' & -M_L & m \end{pmatrix} . \tag{9}$$

2.3 Multipole expansion

The electromagnetic vector potential may be expanded in the multipole series (see, e.g., Ref. [23])

$$\hat{\epsilon}\, e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{JM\lambda} i^{J-\lambda} \left(\mathbf{Y}^{(\lambda)}_{JM}(\hat{k}) \cdot \hat{\epsilon} \right) \mathbf{a}^{(\lambda)}_{JM}(\mathbf{r}) . \tag{10}$$

Here $\mathbf{Y}^{(\lambda)}_{JM}$ are the vector spherical harmonics, described, for example, in Ref. [24]. Photon multipolarity is designated as J with associated magnetic quantum numbers M. $\lambda = 0$ and $\lambda = 1$ correspond to magnetic and electric multipoles respectively, and $\mathbf{a}^{(\lambda)}_{JM}(\mathbf{r})$ are the multipole potentials. The parity of a multipole potential ($J\lambda$) is given by $(-1)^{J+1+\lambda}$.

The multipole expansion of the electromagnetic vector potential, Eq. (10), leads to a corresponding multipole expansion of the transition matrix element

$$t(\omega, \mathbf{r}) = 4\pi \sum_{JM\lambda} i^{J-\lambda} \left(\mathbf{Y}^{(\lambda)}_{JM}(\hat{k}) \cdot \hat{\epsilon} \right) \tau^{(J\lambda)}_{M} \,, \tag{11}$$

with the spherical tensor operator

$$\tau^{(J\lambda)}_{M} = \left(\alpha \cdot \mathbf{a}^{(\lambda)}_{JM}(\mathbf{r}) \right) \,. \tag{12}$$

The operators $\tau^{(J\lambda)}_{M}$ are related to the conventional multipole operators $q^{(J\lambda)}_{M}$ as

$$\tau^{(J\lambda)}_{M} = i \sqrt{\frac{(2J+1)(J+1)}{4\pi J}} \frac{k^J}{(2J+1)!!} q^{(J\lambda)}_{M} \,. \tag{13}$$

For example, the traditional electric-dipole operator $\mathbf{r}$ is recovered in the long-wavelength limit $kr \gg 1$ of $q^{(1\,1)}_{M}$.

The differential cross-section may be represented as

$$\frac{d\sigma}{d\Omega} = \sum_{LM_L} Y_{LM_L}(\hat{p}) \sum_{(J\lambda),(J'\lambda')} B^{(J\lambda)(J'\lambda')}_{LM_L} \tag{14}$$

with

$$\begin{aligned} B^{(J\lambda)(J'\lambda')}_{LM_L} = \frac{(2\pi)^4}{\omega} \, i^{J-\lambda-J'+\lambda'} \sum_{\kappa m \, \kappa' m'} A^{(\kappa m \kappa' m')}_{LM_L} \times \\ \sum_{MM'} \left(\mathbf{Y}^{(\lambda)}_{JM}(\hat{k}) \cdot \hat{\epsilon} \right) \left(\mathbf{Y}^{(\lambda')}_{J'M'}(\hat{k}) \cdot \hat{\epsilon} \right)^* \times \\ \sum_{m_b} \left\{ i^{l-1} e^{-i\delta_\kappa} \langle \kappa m | \tau^{(J\lambda)}_{M} | \kappa_b, -m_b \rangle \right\} \left\{ i^{l'-1} e^{-i\delta_{\kappa'}} \langle \kappa' m' | \tau^{(J'\lambda')}_{M'} | \kappa_b, -m_b \rangle \right\}^* \end{aligned} \tag{15}$$

By applying the Wigner-Eckart theorem and summing over the magnetic quantum numbers m_b of the residual ion and m, m' of the photoelectron we arrive at

$$\begin{aligned} B^{(J\lambda)(J'\lambda')}_{LM_L} = \frac{(2\pi)^4}{\omega} \, C^{(J\lambda)(J'\lambda')}_{LM_L} \, i^{J+\lambda+J'+\lambda'} (-1)^{\lambda+J'} \times \\ \sum_{\kappa \, \kappa'} (-1)^{j_b+j'} \begin{Bmatrix} J & J' & L \\ j' & j & j_b \end{Bmatrix} \langle \kappa' || Y_L || \kappa \rangle \left\{ i^{l-1} e^{-i\delta_\kappa} \tau^{(J\lambda)}_{\kappa\kappa_b} \right\} \left\{ i^{l'-1} e^{-i\delta_{\kappa'}} \tau^{(J'\lambda')}_{\kappa'\kappa_b} \right\}^* \,. \end{aligned} \tag{16}$$

Here $\tau^{(J\lambda)}_{\kappa\kappa_b}$ are reduced matrix elements and

$$C^{(J\lambda)(J'\lambda')}_{LM_L} = (-1)^{J+J'+L} \sum_{MM'} (-1)^{M'+M_L} \begin{pmatrix} J' & L & J \\ -M' & -M_L & M \end{pmatrix} \left(\mathbf{Y}^{(\lambda)}_{JM}(\hat{k}) \cdot \hat{\epsilon} \right) \left(\mathbf{Y}^{(\lambda')}_{J'M'}(\hat{k}) \cdot \hat{\epsilon} \right)^* \tag{17}$$

contains the angular dependence on propagation direction and polarization of the photon.

The following selection rules may be imposed on L

$$|J - J'| \le L \le J + J' \,, \;\; (-1)^L = (-1)^{J+\lambda+J'+\lambda'} \,. \tag{18}$$

The triangular condition follows, e.g., from the examination of the $3j$-symbol in Eq. (17) and the parity rule comes from the inspection of matrix elements in Eq. (16). Indeed, the

parities of the intermediate states are $\mathcal{P}_\kappa = (-1)^{J+1+\lambda}\mathcal{P}_b$ and $\mathcal{P}_{\kappa'} = (-1)^{J'+1+\lambda'}\mathcal{P}_b$ and the reduced matrix element $\langle\kappa'||Y_L||\kappa\rangle$ requires $(-1)^L = \mathcal{P}_\kappa\mathcal{P}_{\kappa'}$.

We choose the coordinate system in such a way that the photon propagation direction $\hat{k}$ is along the z-axis and the polarization $\hat{\epsilon}$ is along the x-axis (see Fig. 1(a)). Then

$$\left(\mathbf{Y}^{(\lambda)}_{JM}(\hat{k})\cdot\hat{\epsilon}\right) = \frac{1}{4}\sqrt{\frac{[J]}{\pi}}\left((-1)^\lambda\delta_{M,1}+\delta_{M,-1}\right)\,, \tag{19}$$

where we used a conventional abbreviation $[J] = 2J+1$. Further

$$C^{(J\lambda)(J'\lambda')}_{LM_L} = \frac{-1}{16\pi}\sqrt{[J][J']}\times \left\{2\begin{pmatrix} J & L & J' \\ -1 & 0 & 1\end{pmatrix}\delta_{M_L,0} + (-1)^{\lambda'}\begin{pmatrix} J & L & J' \\ -1 & 2 & -1\end{pmatrix}(\delta_{M_L,2}+\delta_{M_L,-2})\right\}\,. \tag{20}$$

To simplify this formula we invoked the parity selection rule, Eq. (18).

2.4 All-multipole angular distribution

By substituting Eq. (20) into Eq. (14), we see that on very general grounds, the photoelectron angular distribution by a linearly polarized photon averaged over photoelectron spin and magnetic states of the residual ion may be expressed as

$$\frac{d\sigma}{d\Omega} = \sum_{L=0}^{\infty} a_L P_L(\cos\theta_p) + \sum_{L=2}^{\infty} b_L P^2_L(\cos\theta_p)\cos 2\phi_p\,. \tag{21}$$

Here $P_L(z)$ are the Legendre polynomials and $P^2_L(z)$ are the second-order associated Legendre polynomials of the first kind. Such an all-multipole formula has been originally derived by Scofield [13]. The angular photoelectron distribution from an unpolarized light is

$$\left.\frac{d\sigma}{d\Omega}\right|_{\rm unpol} = \sum_{L=0}^{\infty} a_L P_L(\cos\theta_p)\,. \tag{22}$$

Therefore the second sum in Eq. (21) is associated with the light polarization. The Eq. (22) was originally derived by Bechler and Pratt [8] and by Scofield [13]. Total photoionization cross-section is given by

$$\sigma = 4\pi a_0\,. \tag{23}$$

The angles θ_p and ϕ_p are spherical angles of photoelectron linear momentum $\hat{p}$ in the coordinate system where photon propagation direction $\hat{k}$ is along the z-axis and the polarization $\hat{\epsilon}$ is along the x-axis (see Fig. 1(a)). The general expression (21) may be rewritten using spherical angles employed by Cooper [11] and elsewhere (see Fig. 1(b))

$$\frac{d\sigma}{d\Omega} = \sum_{L=0}^{\infty} a_L P_L(\sin\theta\cos\phi) + \sum_{L=2}^{\infty} b_L P^2_L(\sin\theta\cos\phi)\,\frac{\cos^2\theta-\sin^2\phi\sin^2\theta}{\cos^2\theta+\sin^2\phi\sin^2\theta}\,. \tag{24}$$

It is worth emphasizing that the expression for angular distribution, Eq. (21), exhausts all possible multipoles. The L-dependent coefficients may be expressed as

$$a_L = \sum_{(J'\lambda')\geq(J\lambda)} a^{(J'\lambda')(J\lambda)}_L =$$

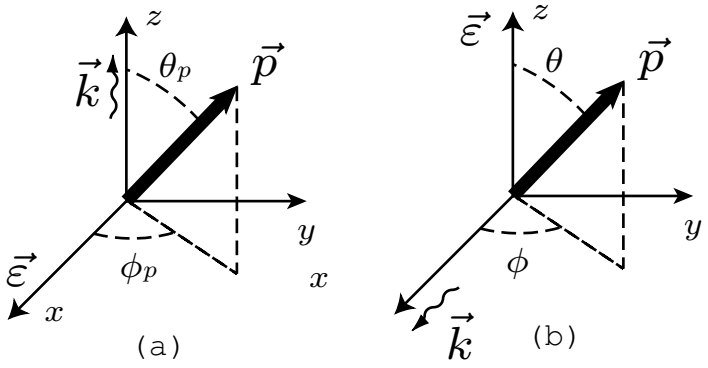

Figure 1. Employed reference systems. **k** is the photon propagation direction and ϵ is its polarization.

$$b_L = \sum_{(J'\lambda')\geq(J\lambda)} b_L^{(J'\lambda')(J\lambda)} = \begin{array}{l} \frac{\pi}{k} \sum_{(J'\lambda')\geq(J\lambda)} \left(1-\frac{1}{2}\delta_{JJ'}\delta_{\lambda\lambda'}\right)(-1)^{\lambda+J'} \begin{pmatrix} J & L & J' \\ -1 & 0 & 1 \end{pmatrix} c_L^{(J\lambda)(J'\lambda')}, \\ \frac{\pi}{\omega}\sqrt{\frac{(L-2)!}{(L+2)!}} \sum_{(J'\lambda')\geq(J\lambda)} \left(1-\frac{1}{2}\delta_{JJ'}\delta_{\lambda\lambda'}\right)(-1)^{L+J} \begin{pmatrix} J & L & J' \\ -1 & 2 & -1 \end{pmatrix} c_L^{(J\lambda)(J'\lambda')}, \end{array} \tag{25}$$

with

$$c_L^{(J\lambda)(J'\lambda')} = \frac{k^{J+J'}}{(2J-1)!!(2J'-1)!!}\sqrt{\frac{(J+1)(J'+1)}{JJ'}}[L]\times \tag{26}$$

$$\sum_{\kappa\,\kappa'} \begin{Bmatrix} J & J' & L \\ j' & j & j_b \end{Bmatrix} (-1)^{j'-j_b}\langle\kappa'||C_L||\kappa\rangle \times$$

$$\mathcal{RI}_L\left[\left(i^{l-1}e^{-i\delta_\kappa}\langle\kappa||q^{(J\lambda)}||n_b\kappa_b\rangle\right)\left(i^{l'-1}e^{-i\delta_{\kappa'}}\langle\kappa'||q^{(J'\lambda')}||n_b\kappa_b\rangle\right)^*\right]. \tag{27}$$

Here we introduced a function

$$\mathcal{RI}_L[z] = \begin{cases} (-1)^{\frac{J+J'+\lambda+\lambda'}{2}}\ \Re[z] & : \text{ even } L \\ (-1)^{\frac{J+J'+\lambda+\lambda'+1}{2}}\ \Im[z] & : \text{ odd } L \end{cases}. \tag{28}$$

Similar relativistic all-multipole formula has been derived by Scofield [13]. Total photoionization cross-section is given by

$$\sigma = 4\pi a_0\,. \tag{29}$$

The term a_0 contains no interferences between various multipoles, i.e. it is a sum over $J = J'$, $\lambda' = \lambda$.

2.5 High-order interference effects

We introduce a characteristic size of the bound electron orbit a_b. In atomic units, this size is approximately given by $1/Z_{\rm eff}$, $Z_{\rm eff}$ being the effective charge felt by the bound electron. $Z_{\rm eff}$ is in the order of 1 for valence shells.

The matrix elements scale as

$$q^{(J\lambda)} \sim a_b^J (\alpha/a_b)^{1-\lambda}\,, \tag{30}$$

i.e. compared to the EJ multipoles, the matrix elements of magnetic multipoles MJ are suppressed by a factor of $\alpha/a_b \sim \alpha Z_{\rm eff}$. (We remind that the matrix elements of magnetic-dipole $M1$ operator are further reduced by a factor of $(\alpha Z_{\rm eff})^2$.)

$$c_L^{(J\lambda)(J'\lambda')} \sim (ka_b)^{J+J'+2-\lambda-\lambda'} \left(\frac{1}{\omega a_b^2}\right)^{2-\lambda-\lambda'}\,. \tag{31}$$

We choose (ka_b) as a "smallness" parameter and designate the leading E1-E1 contribution ($\propto k^2$) as $O(1)$. According to this classification the $O(ka)$ contributions arise from interferences of multipoles $E1E2$ and $E1M1$, and $O((ka)^2)$ from $E1E3, E2E2, E1M2$, and $M1M1$. Using the selection rules (18) we restrict the values of L characterizing contributions to the angular distribution (21); these values are listed in Table 1.

Table 1. Allowed values of L characterizing contributions to general angular distribution, Eq.(21).

Order	Interference	L
$O(1)$	$E1E1$	$0, 2$
$O(ka)$	$E1E2$	$1, 3$
	$E1M1$	1
$O((ka)^2)$	$E1E3$	$2, 4$
	$E2E2$	$0, 2, 4$
	$E1M2$	2
	$M1M1$	$0, 2$

With the aid of this Table we obtain the following contributions to the differential cross-section:

$$\frac{d\sigma}{d\Omega}[O(1)] = a_0^{E1E1} + a_2^{E1E1} P_2(\cos\theta_p) + b_2^{E1E1} P_2^2(\cos\theta_p)\cos 2\phi_p\,, \tag{32}$$

$$\frac{d\sigma}{d\Omega}[O(ka)] = (a_1^{E1E2} + a_1^{E1M1}) P_1(\cos\theta_p) + a_3^{E1E2} P_3(\cos\theta_p) + b_3^{E1E2} P_3^2(\cos\theta_p)\cos 2\phi_p\,, \tag{33}$$

$$\begin{aligned}\frac{d\sigma}{d\Omega}[O((ka)^2)] = {} & a_0^{E2E2} + a_0^{M1M1} + \\ & \left(a_2^{E1E3} + a_2^{E2E2} + a_2^{E1M2} + a_2^{M1M1}\right) P_2(\cos\theta_p) + \\ & \left(a_4^{E1E3} + a_4^{E2E2}\right) P_4(\cos\theta_p) + \\ & \left(b_2^{E1E3} + b_2^{E2E2} + b_2^{E1M2} + b_2^{M1M1}\right) P_2^2(\cos\theta_p)\cos 2\phi_p +\end{aligned} \tag{34}$$

$$\left(b_4^{E1E3} + b_4^{E2E2}\right) P_4^2(\cos\theta_p)\cos 2\phi_p \,.$$

The above differential cross-section may be transformed to the "Cooper" reference frame (θ, ϕ) shown in Fig. 1(b)

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \frac{d\sigma}{d\Omega}[O(1)] + \frac{d\sigma}{d\Omega}[O(ka)] + \frac{d\sigma}{d\Omega}[O((ka)^2)] = \\ &= \frac{\bar{\sigma}}{4\pi}\left\{1 + (\beta + \Delta\beta)\ P_2(\cos\theta) + \left(\delta + \gamma\cos^2\theta\right)\ \sin\theta\cos\phi\ + \right. \\ &+ \left.\ \lambda\, P_2(\cos\theta)\cos 2\phi + \mu\ \cos 2\phi + \nu\ (1 + \cos 2\phi)\ P_4(\cos\theta)\right\}\ . \end{aligned} \tag{35}$$

Here we introduced the total cross-section truncated at $O((ka)^2)$ level

$$\bar{\sigma} = 4\pi\bar{a}_0 = 4\pi(a_0^{E1E1} + a_0^{E2E2} + a_0^{M1M1})\,. \tag{36}$$

The conventional dipole $O(1)$ parameter β is

$$\beta = -2a_2^{E1E1}/\bar{a}_0\,. \tag{37}$$

The $O(ka)$ parameters are

$$\delta = \frac{1}{\bar{a}_0}\left(a_1^{E1E2} + a_1^{E1M1} + a_3^{E1E2}\right)\ . \tag{38}$$

$$\gamma = -5\frac{a_3^{E1E2}}{\bar{a}_0}\,, \tag{39}$$

and the $O((ka)^2)$ parameters are

$$\Delta\beta = \frac{1}{\bar{a}_0}\left(-\frac{3}{4}a_2^{E1E3} + a_2^{E2E2}\right)\,, \tag{40}$$

$$\lambda = -\frac{1}{\bar{a}_0}\left(\frac{2}{3}a_2^{E1M2} + \frac{5}{12}a_2^{E1E3} + a_2^{E2E2} + \frac{5}{6}(a_4^{E1E3} + a_4^{E2E2})\right)\,, \tag{41}$$

$$\mu = \frac{1}{\bar{a}_0}\left(\frac{2}{3}a_2^{E1M2} + \frac{5}{12}a_2^{E1E3} + a_2^{E2E2} - \frac{1}{6}(a_4^{E1E3} + a_4^{E2E2})\right)\,, \tag{42}$$

$$\nu = \frac{1}{\bar{a}_0}\left(a_4^{E1E3} + a_4^{E2E2}\right)\ . \tag{43}$$

We note that the last three parameters satisfy a relation

$$\nu + \lambda + \mu = 0\,. \tag{44}$$

Corrections of $O(k)$ to the photoionization differential cross section have been studied previously in Refs. [8,9,10,11,12,13,14]. The M_1 amplitude (consequently a_1^{E1M1}) is found to be negligibly small in the present relativistic calculations and vanishes identically in the nonrelativistic limit, as pointed out by Cooper [10,11]. In Eq. (35), we followed the notation of Ref. [10,11] for the $O(k)$ non-dipole corrections to the angular distribution. In [10,11], one can also find translations to alternative parameterizations of non-dipole angular distributions used in Refs. [8,9,12,13,14]. It should be mentioned that $a_1^{E1E2} = -a_3^{E1E2}$ for photoionization of ns subshells in nonrelatvistic calculations, and consequently $\delta_{ns} = 0$ nonrelativistically. In the present relativistic calculations, δ_{ns} is negligibly small for the $2s$ shell of neon.

To reiterate, the $O(k^2)$ corrections to Eq. (35) arise from interference between $E1-E3$, $E1-M2$, $E2-E2$, $E2-M1$, $M1-M1$, and from retardation corrections to the $E1-E1$ amplitudes. In our calculations, we do not expand out the retardation corrections to the $E1$ amplitude in powers of k; rather, we include retardation in the $E1$ amplitude fully.

3 Example: photoionization of neon

We have carried out detailed numerical studies of the $O(k^2)$ corrections for noble-gas atoms in the independent-particle approximation [7]. Wave functions for bound-state and continuum electrons were obtained by solving the radial Dirac equation in a Hartree potential modified to produce an orthonormal set of orbitals. Values of the two $O(k)$ parameters $\delta_{n\kappa}$ and $\gamma_{n\kappa}$, and the four $O(k^2)$ parameters $\Delta\beta_{n\kappa}$, $\lambda_{n\kappa}$, $\mu_{n\kappa}$, and $\nu_{n\kappa}$ were calculated for energies up to 2 keV ; these results are tabulated and presented graphically in Ref. [7].

The experimental values [4] of the non-dipole parameter for the $2s$ shell of neon was found to be somewhat larger than predictions based on theoretical independent-particle approximation (IPA) calculations of the $O(k)$ corrections [8,9,10,11], while the measured value of the non-dipole parameter for the $2p$ subshell was found to be 30% larger than $O(k)$ theoretical predictions, for energies above 1 keV. It was also found in [4] that the dipole angular-distribution parameter β disagreed substantially with IPA calculations, but was in close agreement with correlated calculations carried out in the random-phase approximation (RPA) [25,26,12]. Electron correlation was thereby found to be responsible for the differences between IPA calculations of β and experiment. Investigations to determine whether or not the differences between IPA calculations and experiment for the non-dipole parameters γ and δ were also the results of correlation [6] were negative. In Ref. [6], the correlated RPA calculations of the non-dipole parameters were found to be in close agreement with the uncorrelated IPA calculations; both calculations disagreed with the measurements reported in Ref. [4]. The differences between experimental measurements and calculations were *not* explained by including correlation in the $O(k)$ calculations.

The $O(k^2)$ corrections were shown [5] to account for the disagreement between theory and experiment for the neon $2s$ non-dipole parameter γ_{2s} and to account for a substantial fraction of the difference between theory and experiment for the $2p$ non-dipole parameter $\gamma_{2p}+3\delta_{2p}$ in neon.

The present values of the two $O(k)$ parameters are in good agrement with the nonrelativistic IPA calculations of Cooper [10,11], which were carried out using Hartree-Slater wave functions. In Fig. 2, we present values of the $O(k^2)$ parameters $\Delta\beta$, λ, and μ obtained from our calculations for photon energies below 2 keV. The remaining parameter λ can be obtained from the values given in Fig. 2 using the relation $\nu=-\lambda-\mu$.

We do not expect correlations to modify the IPA values significantly. Following Ref. [6], we note that the contributions to $O(k^2)$ coefficients are from terms of the form

$$\rho_l\rho_{l'}\cos\left(\delta_l-\delta_{l'}-\frac{\pi}{2}(l-l')\right), \tag{45}$$

where ρ_l and $\rho_{l'}$ are radial multipole matrix elements and where δ_l and $\delta_{l'}$ are continuum orbital phase shifts. The dominant contributions arise when l and l' take on the *maximum* values allowed by angular-momenta selection rules. Thus, the largest contribution to the E_1-E_3 term for $2p$ photoionization arises from interference of amplitudes involving d and

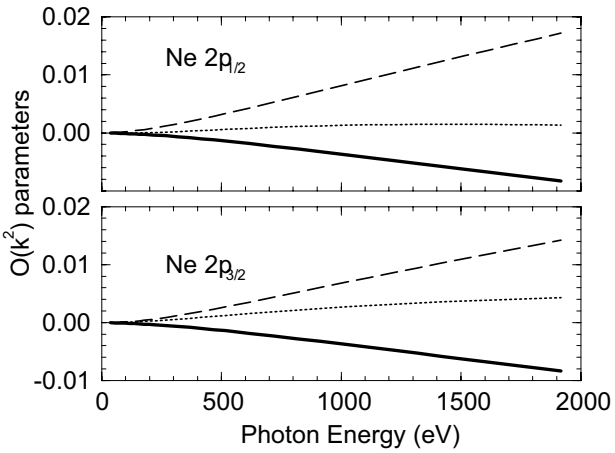

Figure 2. $O((ka)^2)$ parameters for the $2p$ shell of neon. We plot $\Delta\beta$ (solid line), λ (dotted line), and μ (dashed line). Note that $\nu = -\lambda - \mu$. Upper panel: $2p_{1/2}$ subshell; Lower panel: $2p_{3/2}$ subshell.

g continuum wave functions, while for the $E_1 - M_2$ and $E_2 - E_2$ terms, the largest contributions are from continuum states with $l = l' = d$. Therefore, the $E_1 - E_3$ contributions are potentially sensitive to correlations, since $\delta_l - \delta_{l'} - \pi(l - l')/2$ is nonvaninshing. However, in the 1 keV region of photon energies, the value of the cosine in Eq. (45) stays close to -1 and is, therefore, insensitive to small changes in its argument. It follows that the correlation corrections to the continuum wave function will have little influence on the leading contributions to the interference terms. The question of the importance of correlation corrections could be answered more fully in the RPA approach.

In Ref. [4], the $O(k)$ non-dipole parameters γ_{2s} and $\gamma_{2p}+3\delta_{2p}$ in Eq. (35) were determined by making measurements of the differential cross section for several values of ϕ at the "magic angle" $\bar{\theta}$, where $P_2(\cos\bar{\theta}) = 0$. Indeed, one can define an effective value of $\gamma + 3\delta$ from Eq. (35) as

$$(\gamma + 3\delta)_{\rm eff} = \sqrt{\frac{27}{2}}\left[\frac{\sigma(\bar{\theta}, 0)}{\sigma(\bar{\theta}, \pi/2)} - 1\right], \tag{46}$$

$$\approx \frac{\gamma + 3\delta + \sqrt{54}(\mu - 7\nu/18)}{1 - \mu}. \tag{47}$$

In Eq. (46), we use the notation $\sigma(\theta, \phi) = \frac{d\sigma}{d\Omega}(\theta, \phi)$. The expression in Eq. (47) is obtained from Eq. (35) and omits terms of $O(k^3)$ in the cross section. In Fig. 3, we compare values of $(\gamma + 3\delta)_{\rm eff}$ and $\gamma + 3\delta$ for the $2s$ and $2p$ subshells of neon calculated in the IPA with experimental results from Hemmers *et al.* [4]. We see that the experimental results are uniformly higher than the calculated values of $\gamma+3\delta$, for energies above 1 keV, but that the $O(k^2)$ corrections contained in $(\gamma+3\delta)_{\rm eff}$ account for a substantial fraction of the differences between the uncorrected theoretical values of $\gamma + 3\delta$ and experiment.

The contribution from $E1 - E3$, $E2 - E2$, and $E1 - M2$ interferences to the $O(k^2)$ correction are comparable in size. The $E1 - E3$ contributions a_2^{E1E3} and a_4^{E1E3} account

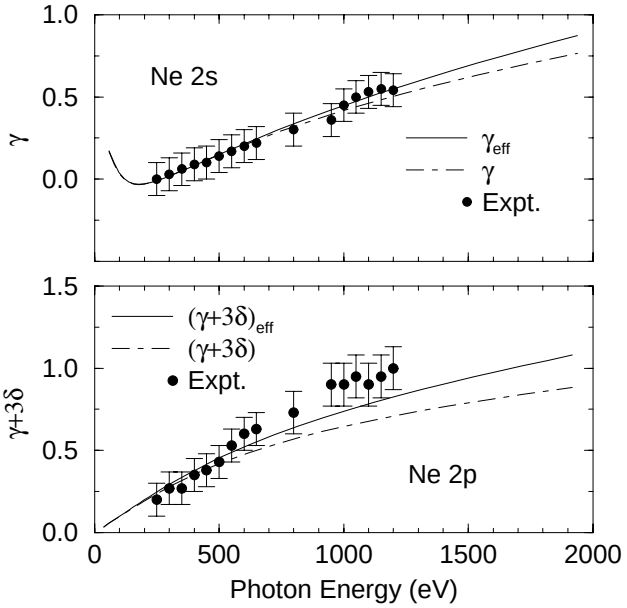

Figure 3. Comparison of theoretical values of of γ_{2s} and $\gamma_{2p}+3\delta_{2p}$ with experiment for neon. The quantities with subscript "eff" are corrected for $O(k^2)$ effects.

for almost 65% of the total value at 1 keV. The least important contribution is from the $E1-M2$ parameter a_2^{E1M2} which reduces $\Delta(\gamma+3\delta)$ by 10%.

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