PHYSICAL REVIEW A **75**, 062703 (2007)

Octupole contributions to the generalized oscillator strengths of discrete dipole transitions in noble-gas atoms

M. Ya. Amusia,[1,2] L. V. Chernysheva,[2] Z. Felfli,[3] and A. Z. Msezane[3]
[1]*Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel*
[2]*A. F. Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia*
[3]*Center for Theoretical Studies of Physical Systems, Clark Atlanta University, Atlanta, Georgia 30314, USA*
(Received 26 December 2006; published 8 June 2007)

The generalized oscillator strengths (GOS's) of discrete excitations $np \rightarrow nd$ and $np \rightarrow (n+1)s,d$, both dipole ($L=1$) and octupole ($L=3$), are studied. We demonstrate that although the relevant transitions in the same atom are closely located in energy, the dependence of their GOS's on the momentum transfer squared q^2 is remarkably different; viz., the GOS's corresponding to $L=3$ have at least one extra maximum as a function of q^2 and dominate over those of the $L=1$, starting from about $q^2=1.5$ a.u. Peculiarities are noted in the GOS of only the Ne dipole $2p \rightarrow 3s$ transition in contrast to the rest of the atoms; viz., the characteristic minimum and the maximum are not obliterated by the dominance of $2p \rightarrow 3d$ GOS dipole and octupole sum as in the other atoms. The depth of the minimum of the GOS for the dipole $2p \rightarrow 3s$ transition is reduced considerably by the $2p \rightarrow 3d$ dipole and octupole GOS sums, while the corresponding maximum is enhanced. In the GOS sum both the minimum and maximum are still identifiable, permitting experimental observation. The calculations were performed in the one particle Hartree-Fock (HF) approximation and with account of many-electron correlations via the random phase approximation with exchange (RPAE). The GOS's are studied for values of q^2 up to 50 a.u. Our calculated RPAE GOS's for the Ar $3p \rightarrow 4s$ dipole transition compare very well with the recently measured data of Zhu *et al.* [Phys. Rev. A **73**, 042703 (2006)].

DOI: 10.1103/PhysRevA.75.062703 PACS number(s): 34.50.−s, 52.20.Hv, 03.65.Nk

I. INTRODUCTION

Here we consider the lowest-energy optically allowed transitions for the outer np subshells of the noble-gas atoms $np \rightarrow nd$ and $np \rightarrow (n+1)s,d$. The former series of transitions in Ne, Ar, Kr, and Xe—namely, $np \rightarrow nd$—can be dipole and octupole, while the latter can only be a pure dipole. The essential feature of the levels considered is that those with the same configurations $np \rightarrow nd$ but different total angular momentum L, $L=1$ and $L=3$, are closely located and hardly separable in existing experiments. This means that they will be excited by electron (or other charged particle) impact simultaneously, but decay via photon emission separately, the decay of the octupole excitation being about eight orders of magnitude slower than the dipole. As a result, soon after excitation of a gas volume by incoming charged particles, only octupole levels will survive. Therefore, separate calculations of octupole generalized oscillator strengths (GOS's) are of importance and interest, presenting the probability of populating and studying the long-living excited levels.

The generalized oscillator strength, introduced by Bethe [1] and reviewed by Inokuti [2], characterizes fast-electron inelastic scattering. It manifests directly the atomic wave functions and the dynamics of scattering. Since then, the GOS has received attention from a variety of perspectives: determination of the correct spectral assignment [3], exploring the excitation dynamics [4], probing the intricate nature of the valence-shell and inner-shell electron excitation [5], investigation of the influence of the angular resolution and pressure effects on the position and amplitude of the GOS minima [6], investigation of the GOS ratio [7] and various correlation effects [8–11], as well as multiple minima [12].

One of the most important utilities of the GOS concept in the limit $q^2 \rightarrow 0$ is in the determination of optical oscillator strengths (OOS's) from absolute differential cross sections (DCS's) [13–16]. Implicit in this is the extrapolation of the measured data through sometimes the unphysical region [17]. The limiting behavior of the GOS as $q^2 \rightarrow 0$ has been a subject of continuing interest because of the difficulty of measuring reliably the electron DCS's for atoms, ions, and molecules at and near zero scattering angles [3,14,18]. This difficulty still plagues measurements of the DCS's [19,20], including the most recent measurements of the DCS's [21,22]. Thus a thorough understanding of the behavior of the GOS's near $q^2=0$ is imperative to guide measurements.

To place the current investigation of the GOS's for the np-nd and np-ns transitions in Ne, Ar, Kr, and Xe in perspective, it is important to highlight some significant manifestations that have been uncovered in recent studies of correlation effects in the GOS's for atomic transitions.

(i) Recently, GOS's for monopole, dipole, and quadrupole transitions of the noble-gas atoms have been investigated in both Hartree-Fock (HF) and random phase approximation with exchange (RPAE) approximations as functions of q and the energy transferred, ω [8]. There it was found that electron correlations, both intrashell and intershell, are important in the GOS's for all values of q and ω investigated and that the variation of the GOS's with q and ω is characterized by maxima and minima, arising entirely from many-electron correlations. These results have been used to understand and interpret [23,24] the first experimental observation of the absolute GOS for the nondipole Ar $3p$-$4p$ transition [5]. Of great significance is that the calculated GOS's for discrete transitions permitted the determination of their multipolarity quite reliably [10]. The interpretation is of particular interest for nondipole transitions since they cannot be observed in photon absorption. Of even greater importance and accomplishment in the recent measurement of the GOS's for the valence-shell excitation of Ar is the separate measurement of the electric monopole and quadrupole of the GOS's for the valence-shell excitation of Ar [25].

(ii) For the outer and intermediate shells of Xe, Cs, and Ba, correlations have been discovered to produce impressive manifestations of the intradoublet interchannel interaction [26], yielding new structures in nondipole parameters and GOS's [9]. GOS results for Xe, Cs, and Ba demonstrated the leveraging role of the spin-orbit interaction—viz., the strong interaction between components of the spin-orbit doublet of the $3d$ electrons in Cs, Ba, and Xe. This leads to the appearance of an additional maximum in the GOS for the $3d_{5/2}$ subshell, due to the action of the $3d_{3/2}$ electrons. The interdoublet correlations were found to be very important in the monopole, dipole, and quadrupole transitions.

(iii) Generalized oscillator strengths for monopole, dipole, and quadrupole transitions in the negative ions I^- and Si^- have been investigated to assess the extent of importance of correlations [27]. It was found that the GOS's for monopole and dipole transitions are generally characterized by two distinct sets of maxima as functions of ω, being most pronounced for the dipole transitions. For the negative ions, there are two interesting and significant peculiarities. First, contrary to the well-known behavior of atomic transitions, the limit of the GOS approaches zero as $q^2 \to 0$ for the dipole transition. Second, in both the monopole and quadrupole transitions, the GOS corresponding to $q=2$ a.u. starts being zero at threshold and becomes dominant beyond about $\omega=6$ Ry.

II. THEORY

In this paper, we consider a relatively simple case where the transition energy can be specified almost entirely by the one-electron nomenclature: namely, by the principal quantum number and angular momentum of the exciting electron in its initial and final states, nl and $n'l'$, respectively, and by the total angular momentum of the excitation, L. Both the energies $\omega_{nl,n'l'}$ and the GOS's are affected by the multi electron correlations, since the one-electron approximation is very often not accurate enough, even for a qualitative, not to mention quantitative, description. With the above in mind, we have performed calculations both in the one-particle Hartree-Fock approximation and with account of many-electron correlations via the RPAE [28].

The RPAE has proved to be very effective in describing the photoionization cross sections and GOS's [8,23,24,28–30] including rather delicate features of the dipole and nondipole angular anisotropy parameters of photoelectrons, where impressive manifestations of electron correlations were recently observed in good accordance with both experiment and calculations (see, e.g., [26,31–36]).

The theoretical consideration in this paper of dipole and octupole excitations is similar to that of quadrupole and monopole excitations [23,24]. However, for the convenience of the reader and for a better understanding of the results, here we repeat the main points considered in the GOS calculation in general and within the one-electron HF and with account of correlations within the RPAE framework in particular. All the necessary formulas are also presented.

There are some discrete excitations considered in this paper that require special attention. Namely, in Kr there are two closely located dipole excitations: $4p$-$4d$ with energy 0.933 30 Ry and $4p$-$6s$ with energy 0.934 03 Ry; the $4p$-$5d$ has energy of 0.984 29 Ry, while for $4p$-$7s$ the energy is 0.984 79 Ry. The method implemented in the computer program [37] and used in [23,24] is suitable for the case of a single relatively isolated discrete excitation for which all others act as perturbations. In the present case the closely located levels are perturbing one another very strongly. Therefore, the corresponding interaction has to be taken into account accurately.

The inelastic scattering cross sections of fast electrons or other charged particles incident upon atoms or molecules are expressed via the GOS $G(\omega,q)$ [1,38] which is a function of the energy ω and the momentum transferred q to the target in the collision process. The GOS is defined as [1] (atomic units are used throughout this paper)

$$G_{fi}(\omega,q) = \frac{2\omega}{q^2}\left| \Sigma_{j=1}^{N} \int \psi_f^*(\vec{r}_1,\ldots,\vec{r}_N) \times \exp(i\vec{q}\cdot\vec{r}_j)\psi_i(\vec{r}_1,\ldots,\vec{r}_N)d\vec{r}_1\cdots d\vec{r}_N \right|^2, \quad (1)$$

where N is the number of atomic electrons and $\psi_{i,f}$ are the atomic wave functions in the initial and final states with energies E_i and E_f, respectively, and $\omega=E_f-E_i$. Because the projectile is assumed to be fast, its wave functions are plane waves and its mass M enters the GOS indirectly: namely, via the energy and momentum conservation law

$$\frac{p^2}{2M} - \frac{(\vec{p}-\vec{q})^2}{2M} = \omega. \quad (2)$$

Here $\vec{p}$ is the momentum of the projectile. It follows from the GOS definition (1) that when $q=0$ the GOS coincides with the OOS or is simply proportional to the photoionization cross section (see, for example, [38]), depending upon whether the final state is a discrete excitation or belongs to the continuous spectrum. The energy ω enters the GOS either via a factor in Eq. (1) or indirectly, via the energy E_f of the final state $|f\rangle$.

In the one-electron Hartree-Fock approximation Eq. (1) simplifies considerably, reducing to

$$g_{fi}^L(q,\omega_{fi}) = \frac{2\omega_{fi}}{q^2}\left| \int \phi_f^*(\vec{r})j_L(qr)P_L(\cos\vartheta)\phi_i(\vec{r})d\vec{r}\right|^2 = \frac{2\omega_{fi}}{q^2}\left|\langle f|j_L(qr)|i\rangle\right|^2, \quad (3)$$

where $\phi_{f,i}(\vec{r})=R_{n_{f,i}}Y_{l_{f,i},m_{f,i}}(\theta_{\vec{r}},\varphi_{\vec{r}})\chi_{s_{f,i}}$ are the HF one-electron wave functions with their radial, angular, and spin parts, respectively, $j_L(qr)$ is the spherical Bessel function, $P_L(\cos\vartheta)$ is the Legendre polynomial, and $\cos\vartheta=\vec{q}\cdot\vec{r}/qr$. The excitation energy of the $i\to f$ transition is denoted as ω_{fi}. The principal quantum number, the angular momentum, its projection, and spin quantum numbers of the initial i and final f states are denoted by $n_{f,i}$, $l_{f,i}$, $m_{f,i}$, and $s_{f,i}$, respectively.

To take into account of many-electron correlations in the RPAE the following system of equations was solved:

$$\langle f|A_L(q,\omega_{fi}^R)|i\rangle = \langle f|j_L(qr)|i\rangle + \left(\sum\int_{n'\leq F,k'>F} - \sum\int_{n'>F,k'\leq F}\right) \times \frac{\langle k'|A_L(q,\omega_{fi}^R)|n'\rangle\langle n'f|U_L|k'i\rangle}{\omega_{fi}^R - \epsilon_{k'} + \epsilon_{n'} + i\eta(1-2n_{k'})}. \qquad (4)$$

Here $\leq F$ ($>F$) denotes occupied (vacant) HF states, ϵ_n are the one-electron HF energies, $\eta \to +0$, and $n_k = l$ (0) for $k \leq F$ ($>F$); $\langle nf|U|ki\rangle_L = \langle nf|V|ki\rangle_L - \langle nf|V|ik\rangle_L$ is the L component of the matrix elements of the Coulomb interelectron interaction V. It is seen that the system of equations for each total angular momentum of an excitation L is separate. The procedure of solving this equation is described in details in [28,38]. Note that the excitation energy of the $i \to f$ transition in RPAE ω_{fi}^R is different from the HF value $\omega_{fi} = \epsilon_f - \epsilon_i$. The procedure of calculating ω_{fi}^R is also described in [28,38].

A relation similar to Eq. (3) determines the GOS's in RPAE $G_{fi}^L(q,\omega_{fi}^R)$:

$$G_{fi}^L(q,\omega_{fi}^R) = \frac{2\omega_{fi}^R}{q^2}\left|\langle f|A_L(q,\omega_{fi}^R)|i\rangle\right|^2. \qquad (5)$$

Here $\langle f|$ and $|i\rangle$ are the final and initial HF states, respectively. Using these formulas the GOS's were calculated for dipole $L=1$ and octupole $L=3$ components.

The operator of the interaction between fast charged particles and atomic electrons can also be represented in another form than $\hat{A}(q) = \hat{A}^r(q) \equiv \exp(i\vec{q}\cdot\vec{r})$. This is analogous to the case of photoionization and can be called the *length* form. The other one is similar to the velocity form in photoionization and looks like [37]

$$\hat{A}^v(\omega,q) = [\exp(i\mathbf{q}\cdot\mathbf{r})(\mathbf{q}\cdot\boldsymbol{\nabla} - \mathbf{q}\cdot\overleftarrow{\boldsymbol{\nabla}})\exp(i\mathbf{q}\cdot\mathbf{r})], \qquad (6)$$

where the upper arrow in $\overleftarrow{\boldsymbol{\nabla}}$ in Eq. (6) implies that the function standing to the left is being operated on.

For the specific case considered in this paper the explicit HF energies are $\omega_{np\to nd,(n+1)s} \equiv \epsilon_{nd,(n+1)s} - \epsilon_{np}$ with ϵ_{np}, ϵ_{nd} and $\epsilon_{(n+1)s}$ being the HF one-electron energies. $R_{np}(r)$, $R_{nd}(r)$, and $R_{(n+1)s}(r)$ are the radial parts of the one-electron wave functions in the HF approximation, and L is the total angular momentum of the excitation, where in our case $L=1$ or 3, $n=2$, 3, 4, and 5 for Ne, Ar, Kr, and Xe, respectively. Symbolically, the RPAE equations can be presented as [28,38]

$$\hat{T} = \hat{t} + \hat{T}\hat{\chi}U, \qquad (7)$$

$$t_{np\to nd,(n+1)s}^L(q) \equiv \langle np|\hat{t}|nd,(n+1)s\rangle = \int R_{np}(r)j_L(qr)R_{nd,(n+1)s}(r)dr, \qquad (8)$$

where U is the Coulomb interelectron interaction, and

$$\hat{\chi} = \hat{1}/(\omega - \omega' + i\gamma) - \hat{1}/(\omega + \omega'), \qquad (9)$$

with $\gamma \to 0$ and ω being the excitation energy parameter of the relevant discrete excitation, while ω' is the energy of any other, including the considered discrete or continuous spectrum excitation of another electron, which is excited by the incoming electron. Its interaction via the potential U leads to the excitation of a given atom under consideration.

The RPAE values for the GOS's $F_{np\to nd,(n+1)s}(q)$ are connected to the matrix elements of $\hat{T}$ similar to the connection of $f_{np\to nd,(n+1)s}$, the HF GOS values, with $\hat{t}$. However, a complication arises for discrete excitations. This results from the fact that one of the intermediate discrete excitation energies consistent with the energy of the excitation of the level under investigation and the corresponding element of $\hat{\chi}$ becomes infinite. To circumvent this singularity an effective interaction matrix has to be created [28,38]:

$$\hat{\tilde{\Gamma}} = U + U\hat{\chi}'\hat{\tilde{\Gamma}}, \qquad (10)$$

where $\hat{\chi}'$ excludes only a single term, with one of the transitions $\omega' = \omega_{np\to nd,(n+1)s}$, from summation over all intermediate states [see Eq. (4)]. Then the total matrix of the effective interaction $\hat{\Gamma}$ is determined by a simple expression

$$\hat{\Gamma} = \hat{\tilde{\Gamma}}(\omega - \omega_{np\to nd,(n+1)s} - \hat{\tilde{\Gamma}})^{-1}. \qquad (11)$$

This is correct only if the interaction between two adjacent levels is sufficiently weak and can be accounted for perturbatively. Then instead of Eq. (3), one can arrive at the following expression for $\hat{T}$:

$$\hat{T} = \hat{t} + \hat{t}\hat{\chi}\hat{\Gamma}. \qquad (12)$$

With the help of Eq. (11) we derive the GOS value in RPAE as

$$F_{np\to nd,(n+1)s}(q) = Z_{np\to nd,(n+1)s}\frac{2\pi\omega_{np\to nd,(n+1)s}}{q^2}|\langle np|\hat{T}|nd,(n+1)s\rangle|^2, \qquad (13)$$

$$\omega_{np\to nd,(n+1)s} = \epsilon_{nd,(n+1)s} - \epsilon_{np} + \tilde{\Gamma}_{np\to nd,(n+1)s}, \qquad (14)$$

$$Z_{np\to nd,(n+1)s} = \left[1 - \left.\frac{\partial\tilde{\Gamma}_{np\to nd,(n+1)s},}{\partial\omega}\right|_{\omega=\omega_{np\to nd,(n+1)s}}\right]^{-1}. \qquad (15)$$

Here $Z_{np\to nd,(n+1)s}$ is the spectroscopic factor of the discrete excitation level.

Equations (10)–(15) determine the RPAE values for both the GOS's and the discrete excitation energies, while Eq. (3) gives the HF GOS, represented simply as $f_{np\to nd,(n+1)s}$ with the appropriate ω_{fi} used.

However, as was mentioned above, at least in Kr one has two very close levels. In this case one must first introduce an

TABLE I. Experimental and theoretical excitation energies in Ry for the dipole and octupole transitions in Ne, Ar, Kr, and Xe.

Atom	Transition	Expt. (Ry)	Dipole (Ry)	Octupole (Ry)
Ne	$2p$-$3d$	1.475248	1.5886	1.5888
	$2p$-$4d$	1.524334	1.6379	1.6379
	$2p$-$5d$	1.547063	1.66065	1.66057
	$2p$-$3s$	1.230844	1.3481	
	$2p$-$4s$	1.447896	1.563	
	$2p$-$5s$	1.513256	1.62799	
Ar	$3p$-$3d$	1.0337	1.00531	0.996454
	$3p$-$4d$	1.089627	1.05508	1.04932
	$3p$-$5d$	1.116365	1.07792	1.1182
	$3p$-$4s$	0.855038	0.834947	
	$3p$-$5s$	1.037901	0.999349	
	$3p$-$6s$	1.094190	1.05268	
Kr	$4p$-$4d$	0.912774	0.9333	0.92127
	$4p$-$5d$	0.972557	0.98429	0.9773
	$4p$-$6d$	0.983380	1.00816	1.00407
	$4p$-$5s$	0.744623	0.7799	
	$4p$-$6s$	0.921292	0.9348	
	$4p$-$7s$	0.975491	0.984969	
Xe	$5p$-$5d$	0.773065	0.801798	0.775117
	$5p$-$6d$	0.812368	0.851733	0.838907
	$5p$-$7d$	0.843888	0.874475	0.86786
	$5p$-$6s$	0.636429	0.675482	
	$5p$-$7s$	0.801240	0.8088	
	$5p$-$8s$	0.828055	0.854632	

TABLE II. GOS's for discrete dipole transitions with $q^2 = 0.00001$ a.u., corresponding essentially to the optical oscillator strengths.

Atom	Transition	HF-L	RPAE-L	Others		
Ne	$2p$-$3d$	0.0282	0.0266	0.0065[a]		0.023[c]
	$2p$-$4d$	0.016	0.015			0.012[c]
	$2p$-$5d$	0.009	0.008			0.007[c]
	$2p$-$3s$	0.156	0.168	0.137[d]	0.1432[b]	0.170[c]
	$2p$-$4s$	0.028	0.029	0.013[a]		0.035[c]
	$2p$-$5s$	0.010	0.011			0.013[c]
Ar	$3p$-$3d$	0.162	0.179	0.302[a]		0.110[c]
	$3p$-$4d$	0.082	0.088			0.059[c]
	$3p$-$5d$	0.045	0.041			0.033[c]
	$3p$-$4s$	0.296	0.316	0.25[a]	0.2214[b]	0.339[c]
	$3p$-$5s$	0.056	0.039	0.034[a]		0.059[c]
	$3p$-$6s$	0.021	0.015			0.033[c]
Kr	$4p$-$4d$	0.133	0.131			
	$4p$-$5d$	0.065	0.063			
	$4p$-$6d$	0.035	0.032			
	$4p$-$5s$	0.187	0.178	0.139[e]	0.1416[b]	
	$4p$-$6s$	0.035	0.033			
	$4p$-$7s$	0.013	0.012			
Xe	$5p$-$5d$	0.242	0.223	0.205[a]		
	$5p$-$6d$	0.115	0.106	0.083[a]		
	$5p$-$7d$	0.062	0.053	0.0217[a]		
	$5p$-$6s$	0.209	0.213	0.251[a]	0.206[f]	
	$5p$-$7s$	0.041	0.062	0.081[a]		
	$5p$-$8s$	0.015	0.023	0.0236[a]		

[a] Reference [39].
[b] Reference [45].
[c] Reference [46].
[d] Reference [15].
[e] Reference [47].
[f] Reference [13].

auxiliary matrix of the effective interelectron interaction $\hat{\Gamma}_{\alpha\beta}$ that is a solution of an equation similar to Eq. (10):

$$\hat{\tilde{\Gamma}} = U + U\hat{\chi}''\hat{\tilde{\Gamma}}, \tag{16}$$

with $\hat{\chi}''$ that excludes the two so-called "time-forward" terms—i.e., those with energy factors $\hat{1}/(\omega-\omega''+i\gamma)$, where ω'' are the energies of two strongly interacting transitions. In our case these are terms with $\omega''=\omega_{4p\to 4d}$ and $\omega''=\omega_{4p\to 6s}$ or $\omega''=\omega_{4p\to 5d}$ and $\omega''=\omega_{4p\to 7s}$. However, the relation that determines $\hat{\Gamma}$ is not that simple as Eq. (11): it is, instead of being a simple algebraic, rather a 2×2 matrix equation.

Let us concentrate on the first two levels $4p\to 4d$ and $4p\to 6s$, denoting them as 1 and 2, respectively. In this case Eq. (16) looks like

$$\begin{pmatrix}\Gamma_{11} & \Gamma_{12}\\ \Gamma_{21} & \Gamma_{22}\end{pmatrix} = \begin{pmatrix}\tilde{\Gamma}_{11} & \tilde{\Gamma}_{12}\\ \tilde{\Gamma}_{21} & \tilde{\Gamma}_{22}\end{pmatrix} + \begin{pmatrix}\tilde{\Gamma}_{11} & \tilde{\Gamma}_{12}\\ \tilde{\Gamma}_{21} & \tilde{\Gamma}_{22}\end{pmatrix} \times \begin{pmatrix}(\omega-\omega_1)^{-1} & 0\\ 0 & (\omega-\omega_2)^{-1}\end{pmatrix}\begin{pmatrix}\Gamma_{11} & \Gamma_{12}\\ \Gamma_{21} & \Gamma_{22}\end{pmatrix} \tag{17}$$

In fact, Eq. (17) describes a two-level system that has two solutions $\omega=\omega'_{1,2}\neq\omega_{1,2}$. Such a system was considered in applications to molecules in [36]. The corresponding solution is also known:

$$\omega'_{1,2} = \frac{1}{2}(\omega_1+\omega_2+\tilde{\Gamma}_{11} + \tilde{\Gamma}_{22}) \pm \sqrt{\frac{1}{4}(\omega_1-\omega_2+\tilde{\Gamma}_{11}-\tilde{\Gamma}_{22})^2 + |\tilde{\Gamma}_{12}|^2}, \tag{18}$$

as it should be, in the absence of a level mixing interaction ($\tilde{\Gamma}_{12}=0$) and $\omega'_{1,2}=\omega_{1,2}$. In principle, each level 1 and 2 has its own spectroscopic factor $Z_{1,2}$. But since these levels are close to each other, the corresponding Z values are close to each other and can be determined by Eq. (15) with $\hat{\tilde{\Gamma}}$ taken from Eq. (16).

III. RESULTS OF CALCULATIONS

The calculations were performed numerically using the programs and procedures described in [37] and for the case

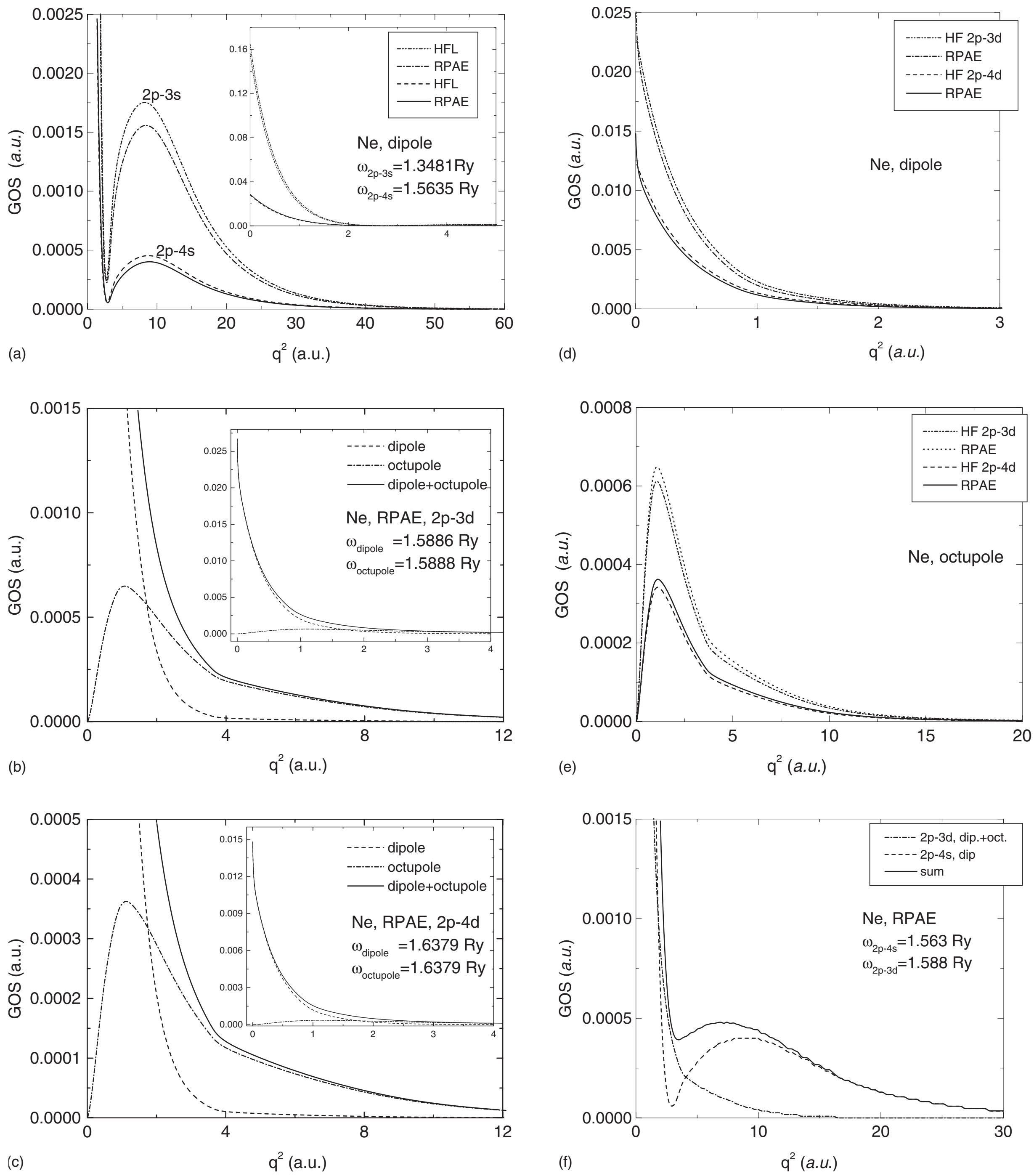

FIG. 1. (a) Comparison between the HF and RPAE GOS's for the Ne $2p \rightarrow 3s$ and $2p \rightarrow 4s$ dipole and octupole transitions and their sum. (b) Calculated RPAE GOS's for the Ne $2p \rightarrow 3d$ dipole and octupole transitions and their sum. (c) Calculated RPAE GOS's for the Ne $2p \rightarrow 4d$ dipole and octupole transitions and their sum. (d) Comparison between the HF and RPAE GOS's for the Ne $2p \rightarrow 3d$ and $2p \rightarrow 4d$ dipole transitions. (e) Comparison between the HF and RPAE GOS's for the Ne $2p \rightarrow 3d$ and $2p \rightarrow 4d$ octupole transitions. (f) Comparison between the GOS for the dipole and octupole sum for the Ne $2p \rightarrow 3d$ transition and the GOS for the Ne $2p \rightarrow 4s$ transition. The GOS sum (Ne $2p \rightarrow 3d$, dipole plus octupole and the Ne $2p \rightarrow 4s$ dipole) is also presented.

of Kr corrected according to the formulas (16)–(18). The results of the calculations are presented in the Tables I and II and the figures below. It is important to bear in mind that at small $q^2 (q^2 \rightarrow 0)$ the dipole GOS is absolutely dominant, since the GOS dipole component is nonzero at $q^2 \rightarrow 0$, corresponding to the OOS. However, with increasing q^2 the situation changes considerably and in some cases even dramatically, since $f^{L=1}_{np \rightarrow nd,(n+1)s}(q)$ rapidly decreases with increasing q^2 while $f^{L=3}_{np \rightarrow nd,(n+1)s}(q)$ rapidly increases as q^2 at least for small q. Then $f^{L=3}_{np \rightarrow nd,(n+1)s}(q)$ has to reach its maximum before subsequent decrease. The q^2 dependence of f proved to

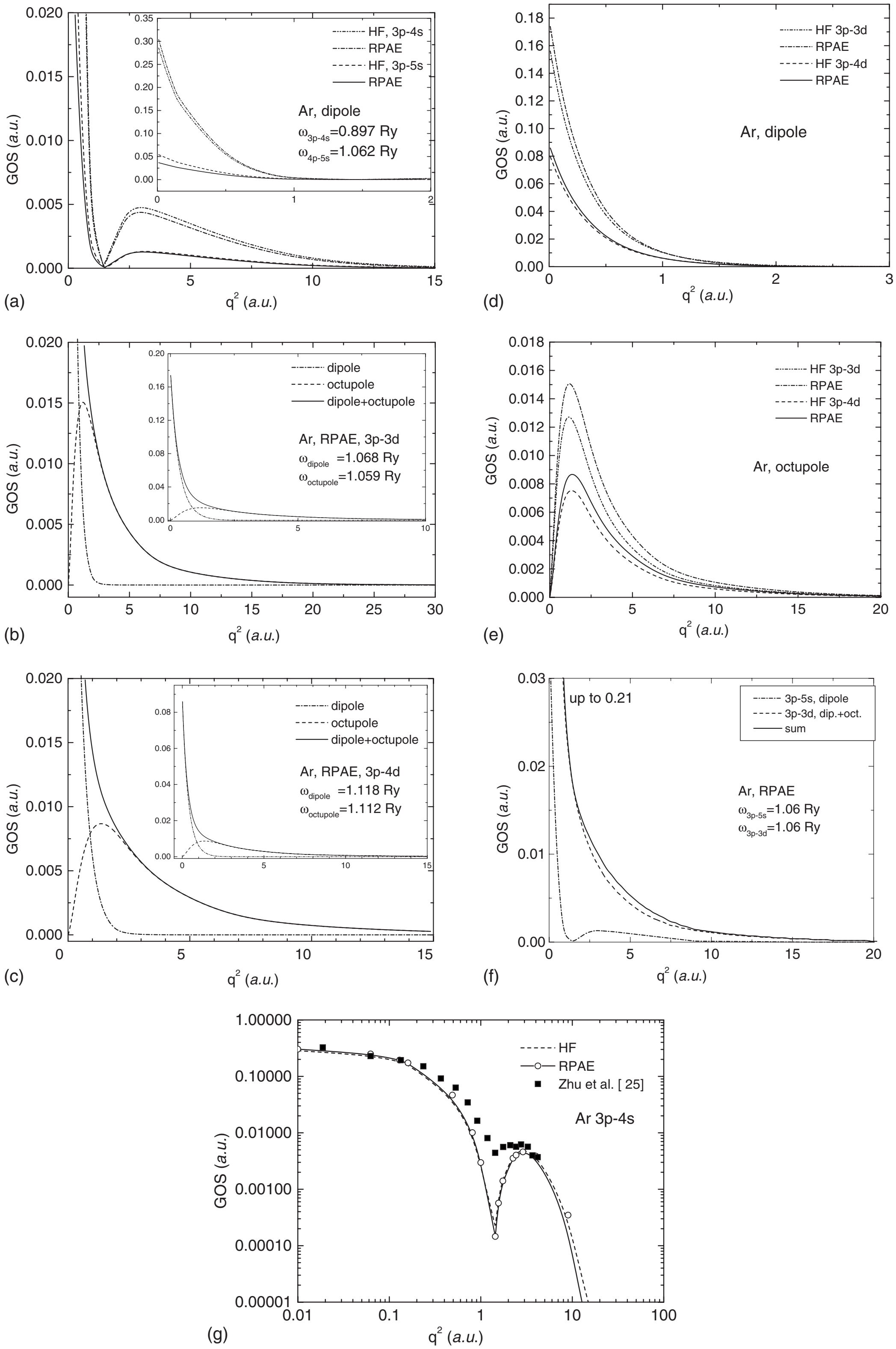

FIG. 2. (a) Comparison between the HF and RPAE GOS's for the Ar $3p \rightarrow 4s$ and $3p \rightarrow 5s$ dipole transitions. (b) Calculated RPAE GOS's for the Ar $3p \rightarrow 3d$ dipole and octupole transitions and their sum. (c) Calculated RPAE GOS's for the Ar $3p \rightarrow 4d$ dipole and octupole transitions and their sum. (d) Comparison between the HF and RPAE GOS's for the Ar $3p \rightarrow 3d$ and $3p \rightarrow 4d$ dipole transitions. (e) Comparison between the HF and RPAE GOS's for the Ar $3p \rightarrow 3d$ and $3p \rightarrow 4d$ octupole transitions. (f) Comparison between the GOS for the dipole and octupole sum for the Ar $3p \rightarrow 3d$ transition and the GOS for the Ar $3p \rightarrow 5s$ transition. The GOS sum (Ar $3p \rightarrow 3d$, dipole plus octupole and the Ar $3p \rightarrow 5s$ dipole) is also presented. (g) Comparison of our calculated HF and RPAE GOS's for the Ar $3p \rightarrow 4s$ dipole transition with those measured by Zhu *et al.* [25].

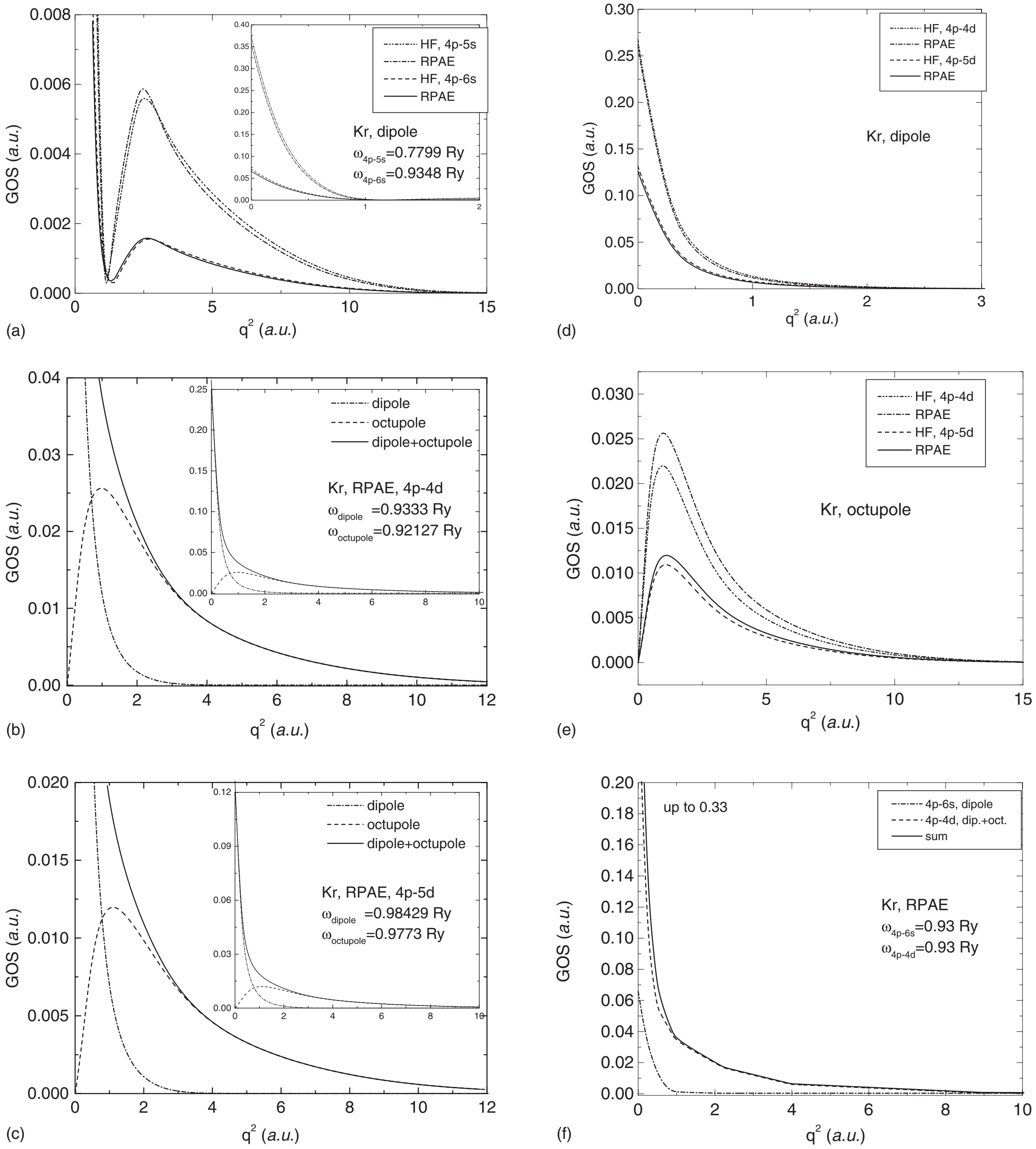

FIG. 3. (a) Comparison between the HF and RPAE GOS's for the Kr $4p \rightarrow 4s$ and $4p \rightarrow 6s$ dipole transitions. (b) Calculated RPAE GOS's for the Kr $4p \rightarrow 4d$ dipole and octupole transitions and their sum. (c) Calculated RPAE GOS's for the Kr $4p \rightarrow 5d$ dipole and octupole transitions and their sum. (d) Comparison between the HF and RPAE GOS's for the Kr $4p \rightarrow 4d$ and $4p \rightarrow 5d$ dipole transitions. (e) Comparison between the HF and RPAE GOS's for the Kr $4p \rightarrow 4d$ and $4p \rightarrow 5d$ octupole transitions. (f) Comparison between the GOS for the dipole and octupole sum for the Kr $4p \rightarrow 4d$ transition and the GOS for the Kr $4p \rightarrow 6s$ transition. The GOS sum (Kr $4p \rightarrow 4d$, dipole plus octupole and the Kr $4p \rightarrow 6s$ dipole) is also presented.

be more complicated, exhibiting maxima for all the cases considered.

The calculated excitation energies are presented in Table I, along with the existing experimental data [39]. In Table I we compare the experimental from Ref. [39] with the present RPAE-L excitation energies for the various dipole transitions in Ne, Ar, Kr, and Xe. Also included in the table are the excitation energies for some of the relevant octupole transitions in these atoms. As seen from the table, indeed the octupole excitations energies are quite close to their dipole counterparts. The agreement between the experimental and the RPAE values is better than 5% for the transitions in most of the atoms, except in Ne where the agreement is better than 10%. Overall, the agreement is acceptable because the main interest is the calculation of the GOS's for the indicated transitions.

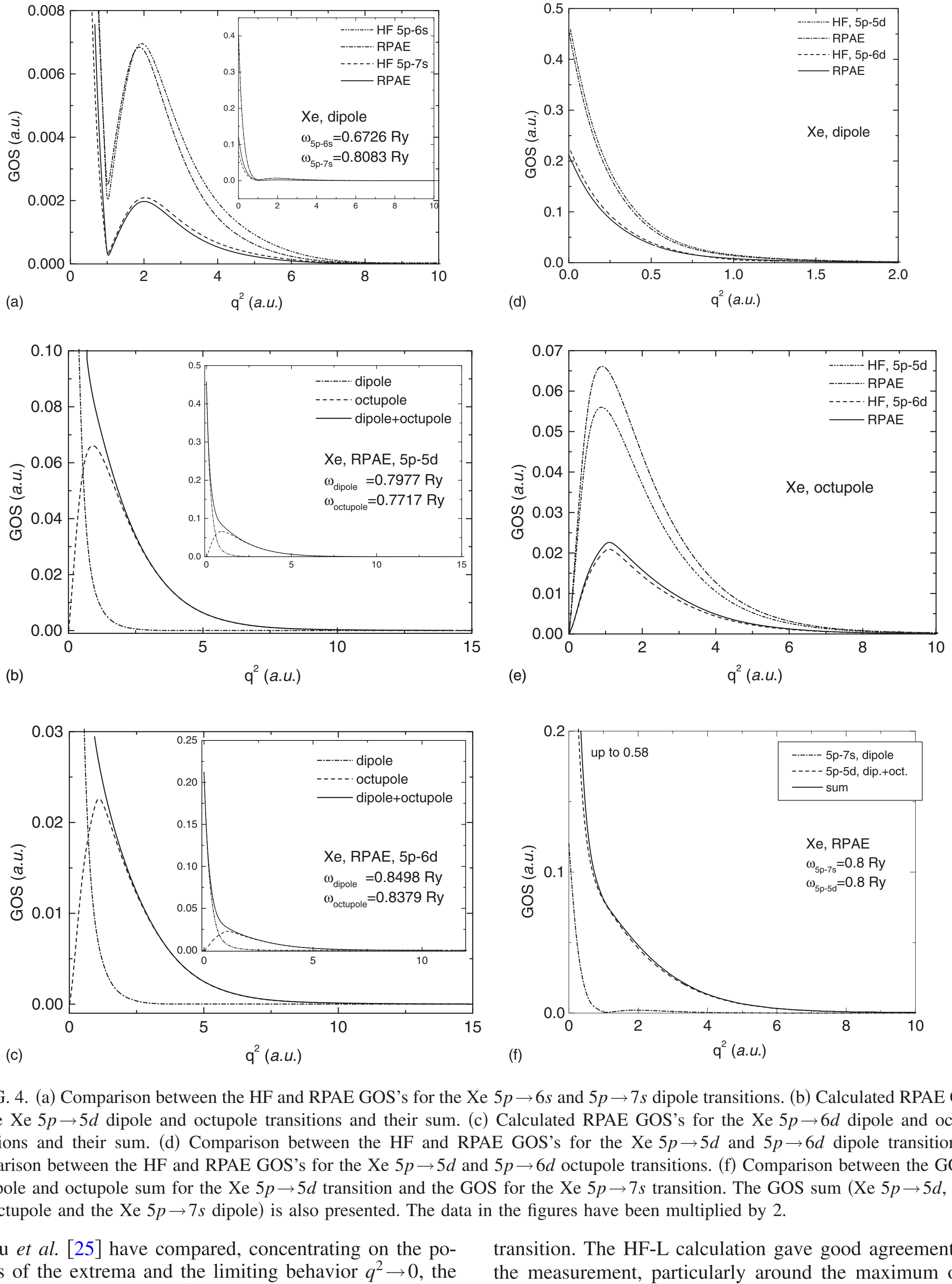

FIG. 4. (a) Comparison between the HF and RPAE GOS's for the Xe $5p \to 6s$ and $5p \to 7s$ dipole transitions. (b) Calculated RPAE GOS's for the Xe $5p \to 5d$ dipole and octupole transitions and their sum. (c) Calculated RPAE GOS's for the Xe $5p \to 6d$ dipole and octupole transitions and their sum. (d) Comparison between the HF and RPAE GOS's for the Xe $5p \to 5d$ and $5p \to 6d$ dipole transitions. (e) Comparison between the HF and RPAE GOS's for the Xe $5p \to 5d$ and $5p \to 6d$ octupole transitions. (f) Comparison between the GOS for the dipole and octupole sum for the Xe $5p \to 5d$ transition and the GOS for the Xe $5p \to 7s$ transition. The GOS sum (Xe $5p \to 5d$, dipole plus octupole and the Xe $5p \to 7s$ dipole) is also presented. The data in the figures have been multiplied by 2.

Zhu *et al.* [25] have compared, concentrating on the positions of the extrema and the limiting behavior $q^2 \to 0$, the variation of the GOS with q^2 for the various transitions in Ar, including the $4s$ [3/2]+$4s'$ [1/2] dipole-allowed transition. For the latter, they found generally good agreement with the other data [5,40–44]. Included in the comparison were also the GOS's for the electric-quadrupole excitation of the $3p$-$4p$ transition. The HF-L calculation gave good agreement with the measurement, particularly around the maximum of the GOS, while agreement with the monopole GOS was reasonable [10].

Table II presents the limiting behavior of the GOS's as $q^2 \to 0$, corresponding essentially to the OOS's as required by the Lassettre limit theorem [48], for the various dipole-allowed transitions in Ne, Ar, Kr, and Xe, calculated in both HF-L and RPAE-L. For these atoms, the RPAE-L and RPAE-V GOS's as $q^2 \rightarrow 0$ agree very well, implying that the RPAE correlation effects have been accounted for adequately. So in the table we present only the HF-L and RPAE-L values to create more space for including data from experiments and other calculations for easier comparison. The general reasonable agreement between our HF-L and RPAE-L on the one hand and the many other available OOS's on the other gives credence to our calculated GOS's. We note, however, that there is a great need for measured and calculated data to fill the void in the various transitions in Kr and that our Xe $5p$-$7d$ OOS, both HF-L and RPAE-L, are about a factor of 2 larger than that of Ref. [39]. This could be explained in the context of the possible need for the inclusion of more correlation terms from higher orbitals.

Suffice it to state that the tabulated data will certainly prove useful, particularly in guiding measurements, and that the main interest of this paper is the investigation of the contribution of the octupole transition to the GOS sum.

Figure 2(g), below, compares the measured GOS by Zhu *et al.* [25] with those calculated via the HF and RPAE. It is seen that indeed the $L=1$ and $L=3$ transitions are rather close together. The general feature for all of the GOS's is the presence of maxima for the $L=3$ transitions while the $L=1$ have only one maximum, not counting the one at $q^2 \rightarrow 0$. We note that the results for the dipole components of the $3p \rightarrow 4s$ level in Ar were obtained earlier [23]. Here our previous results are complemented by those from the octupole contributions.

The calculated GOS's are presented in Figs. 1–4 for each atom. Note that in Figs. 3 and 4 the GOS's have been multiplied by a factor of 2. The general feature for all of them is that the dipole ($L=1$) transitions are characterized by the presence of a maximum, not counting the one which is at $q^2 \rightarrow 0$, corresponding to the OOS. The Ar, Kr, and Xe octupole ($L=3$) transitions are characterized by a single maximum near $q^2 \rightarrow 0$, approximately at $q^2 \approx 1.2$ a.u. Beyond this maximum, the octupole GOS's dominate the dipole GOS's.

For the $3p \rightarrow 3d$ and $3p \rightarrow 4d$ transitions of Ar, the $4p \rightarrow 4d$ and $4p \rightarrow 5d$ of Kr, and the $5p \rightarrow 5d$ and $5p \rightarrow 6d$ of Xe, the RPAE effects enhance the HF GOS's by approximately 20% at their respective maxima. In Kr, the combined dipole plus octupole GOS's for the $4p \rightarrow 4d$ transition dominate the dipole GOS for the $4p \rightarrow 6s$ transition beyond approximately $q^2 > 1$ a.u. For the Xe $5p \rightarrow 7s$ transition, a second maximum appears at about $q^2 \approx 2$ a.u., but interestingly, even very close to $q^2=0$, the combined dipole plus octupole GOS for the $5p \rightarrow 5d$ transition overwhelms the dipole GOS for the $5p \rightarrow 7s$ transition [see Fig. 4(f) for Xe].

The results of Fig. 1(f) of Ne and Fig. 2(f) of Ar provide interesting comparison and contrast. In both the GOS's exhibit the expected dipole behavior near threshold because of the strength of the dipole GOS. Namely, the maximum at threshold ($q^2=0$) is followed by a second maximum at around 8.2 a.u. for Ne and at about 3 a.u. for Ar. However, in Ne the combined dipole plus octupole GOS for the $2p \rightarrow 3d$ transition decreases, becoming smaller than the dipole GOS beyond the minimum of the dipole GOS; so the minimum of the dipole GOS remains visible, somewhat slightly shifted to a larger value of q^2. Beyond about $q^2 > 5$ a.u. the dipole GOS remains the dominant component of the sum. The maximum is the combined GOS for the dipole and the dipole plus octupole for the $2p \rightarrow 3d$ transition, but only the dipole GOS contributes to the sum for $q^2 \geq 15$ a.u., whereas that of the $2p \rightarrow 3s$ is at about 8.2 a.u.

In summary, peculiarities are noted in the GOS of only the Ne dipole $2p \rightarrow 3s$ transition in contrast to the rest of the atoms; viz., the characteristic minimum and the maximum are not obliterated by the dominance of the $2p \rightarrow 3d$ GOS dipole and octupole sums as in the other atoms. The depth of the minimum of the GOS for the dipole $2p \rightarrow 3s$ transition is reduced considerably by the $2p \rightarrow 3d$ dipole and octupole GOS sums, while the corresponding maximum is enhanced. In the GOS sum both the minimum and the maximum are still identifiable, permitting experimental observation. Our calculated HF and RPAE GOS's for the $3p \rightarrow 4s$ dipole transition are compared with those measured by Zhu *et al.* [25] in Fig. 7. As seen, the agreement with the measurement in shape, including the position of the characteristic minimum and maximum, is quite good, giving credence to the calculational methodologies.

IV. DISCUSSION AND CONCLUSION

We have investigated the GOS's of discrete excitations $np \rightarrow nd$ and $np \rightarrow (n+1)s$ both dipole ($L=1$) and octupole ($L=3$), in Ne, Ar, Kr, and Xe. We demonstrated using both Hartree-Fock and random phase approximation with exchange that although the relevant transitions in the same atom are closely located in energy, their GOS dependence on q^2 is remarkably different. The GOS's for the octupole transitions are characterized by maxima as a function of q^2 and dominate those for the dipole, starting from about $q^2 \approx 1.5$ a.u. For the Ar $3p \rightarrow 4s$ dipole transition, our calculated HF and RPAE GOS's compare very well with the recently measured data of Zhu *et al.*, in both shape and position of the characteristic minimum found at $q^2=1.4$ a.u. This gives credence to our calculated GOS data.

ACKNOWLEDGMENTS

Research is funded by U.S. DOE Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research. M.Ya.A. is grateful for support of this research by the Israeli Science Foundation under Grant No. 174/03 and by the Hebrew University Intramural fund.

[1] H. A. Bethe, Ann. Phys. **5**, 325 (1930).
[2] M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971).
[3] C. C. Turci, J. T. Francis, T. Tyliszczak, G. G. B. de Souza, and A. P. Hitchcock, Phys. Rev. A **52**, 4678 (1995).
[4] X. J. Liu, L. F. Zhu, Z. S. Yuan, W. B. Li, H. D. Cheng, Y. P. Huang, Z. P. Zhong, K. Z. Xu, and J. M. Li, Phys. Rev. Lett. **91**, 193203 (2003).
[5] X. W. Fan and K. T. Leung, Phys. Rev. A **62**, 062703 (2000).
[6] W. B. Li, L. F. Zhu, X. J. Liu, Z. S. Yuan, J. M. Sun, H. D. Cheng, Z. P. Zhong, and K. Z. Xu, Phys. Rev. A **67**, 062708 (2003).
[7] H. D. Cheng, L. F. Zhu, Z. S. Yuan, X. J. Liu, J. M. Sun, W. C. Jiang, and K. Z. Xu, Phys. Rev. A **72**, 012715 (2005).
[8] M. Ya. Amusia, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, Phys. Rev. A **64**, 032711 (2001) and references therein.
[9] M. Ya. Amusia, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, Phys. Rev. A **73**, 062716 (2006) and references therein.
[10] M. Ya. Amusia, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, Phys. Rev. A **67**, 022703 (2003).
[11] Zhifan Chen and A. Z. Msezane, Phys. Rev. A **70**, 032714 (2004) and references therein.
[12] N. B. Avdonina, D. Fursa, A. Z. Msezane, and R. H. Pratt, Phys. Rev. A **71**, 062711 (2005).
[13] T. Y. Suzuki, Y. Sakai, B. S. Min, T. Takayanagi, K. Wakiya, H. Suzuki, T. Inaba, and H. Takuma, Phys. Rev. A **43**, 5867 (1991).
[14] T. Ester and K. Kessler, J. Phys. B **27**, 4295 (1994).
[15] T. Y. Suzuki, H. Suzuki, S. Ohtani, B. S. Min, T. Takayanagi, and K. Wakiya, Phys. Rev. A **49**, 4578 (1994).
[16] K. Z. Xu, R. F. Feng, S. L. Wu, Q. Ji, X. J. Zhang, Z. P. Zhong, and Y. Zheng, Phys. Rev. A **53**, 3081 (1996).
[17] Z. Felfli, A. Z. Msezane, and D. Bessis, Phys. Rev. Lett. **81**, 963 (1998).
[18] S. J. Buckman and J. P. Sullivan, Nucl. Instrum. Methods Phys. Res. A **247**, 5 (2006).
[19] V. Karaganov, I. Bray, and P. J. O Teubner, Phys. Rev. A **59**, 4407 (1999).
[20] M. A. Khakoo, M. Larsen, B. Paolini, X. Guo, I. Bray, A. Stelbovics, I. Kanik, S. Trajmar, and G. K. James, Phys. Rev. A **61**, 012701 (2000).
[21] B. Predojevic, D. Sevic, V. Pejcev, B. P. Marinkovic, and D. M. Filipovic, J. Phys. B **38**, 3489 (2005) and references therein.
[22] B. Predojevic, D. Sevic, V. Pejcev, B. P. Marinkovic, and D. M. Filipovic, J. Phys. B **38**, 1329 (2005) and references therein.
[23] A. Z. Msezane, Z. Felfli, M. Ya. Amusia, Zhifan Chen, and L. V. Chernysheva, Phys. Rev. A **65**, 054701 (2002).
[24] M. Ya. Amusia, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, Phys. Rev. A **65**, 062705 (2002).
[25] L. F. Zhu, H. D. Cheng, Z. S. Yuan, X. J. Liu, J. M. Sun, and K. Z. Xu, Phys. Rev. A **73**, 042703 (2006).
[26] M. Ya. Amusia, L. V. Chernysheva, S. T. Manson, A. M. Msezane, and V. Radojević, Phys. Rev. Lett. **88**, 093002 (2002).
[27] L. V. Chernysheva, M. Ya. Amusia, Z. Felfli, and A. Z. Msezane (unpublished).
[28] M. Ya. Amusia, *Atomic Photoeffect* (Plenum Press, New York, 1990).
[29] Zhifan Chen and A. Z. Msezane, Phys. Rev. A **72**, 050702(R) (2005); J. Phys. B **39**, 4355 (2006).
[30] Zhifan Chen and A. Z. Msezane, Phys. Rev. A **68**, 054701 (2003); J. Phys. B **33**, 5397 (2000).
[31] M. Ya. Amusia, A. S. Baltenkov, L. V. Chernysheva, Z. Felfli, S. T. Manson, and A. Z. Msezane, J. Phys. B **37**, 937 (2004) and references therein.
[32] M. Ya. Amusia, N. A. Cherepkov, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, Phys. Rev. A **70**, 062709 (2004).
[33] A. Kivimäki, U. Hergenhahn, B. Kempgens, R. Hentges, M. N. Piancastelli, K. Maier, A. Rudel, J. J. Tulkki, and A. M. Bradshaw, Phys. Rev. A **63**, 012716 (2000).
[34] O. Hemmers, R. Guillemin, E. P. Kanter, B. Krässig, D. W. Lindle, S. H. Southworth, R. Wehlitz, J. Baker, A. Hudson, M. Lotrakul, D. Rolles, W. C. Stolte, I. C. Tran, A. Wolska, S. W. Yu, M. Ya. Amusia, K. T. Cheng, L. V. Chernysheva, W. R. Johnson, and S. T. Manson, Phys. Rev. Lett. **91**, 053002 (2003).
[35] S. Ricz, R. Sankari, Á. Kövér, M. Jurvansuu, D. Varga, J. Nikkinen, T. Ricsoka, H. Aksela, and S. Aksela, Phys. Rev. A **67**, 012712 (2003).
[36] M. Ya. Amusia, A. S. Baltenkov, L. V. Chernysheva, Z. Felfli, S. T. Manson, and A. Z. Msezane, Phys. Rev. A **67**, 060702 (2003).
[37] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Oxford: Butterworth-Heinemann, 1999), Vol. 3.
[38] M. Ya. Amusia and L. V. Chernysheva, *Computation of Atomic Processes* (IOP, Bristol, 1997).
[39] http://physics.nist.gov/cgi-bin/AtData/main-asd
[40] C. E. Bielschowsky, G. G. B. de Souza, C. A. Lucas, and H. M. Boechat Roberty, Phys. Rev. A **38**, 3405 (1988).
[41] Q. Ji, S. L. Wu, R. F. Feng, X. J. Zhang, L. F. Zhu, Z. P. Zhong, K. Z. Xu, and Y. Zheng, Phys. Rev. A **54**, 2786 (1996).
[42] T. C. Wong, J. S. Lee, and R. A. Bonham, Phys. Rev. A **11**, 1963 (1975).
[43] I. Shimamura, J. Phys. Soc. Jpn. **30**, 824 (1971).
[44] Zhifan Chen, A. Z. Msezane, and M. Ya. Amusia, Phys. Rev. A **60**, 5115 (1999).
[45] N. D. Gibson and J. S. Risley, Phys. Rev. A **52**, 4451 (1995).
[46] http://vizier.u-strasbg.fr/topbase/fvalues.html
[47] T. Takayanagi, G. P. Li, K. Wakiya, H. Suzuki, T. Ajiro, T. Inaba, S. S. Kano, and H. Takuma, Phys. Rev. A **41**, 5948 (1990).
[48] E. N. Lassettre, A. Skerbele, and M. A. Dillon, J. Chem. Phys. **50**, 1829 (1969).