

# Effect of Open Channels on the Isolation of Overlapping Resonances in the Uniformly Perturbed Rydberg Systems Studied by Multichannel Quantum Defect Theory

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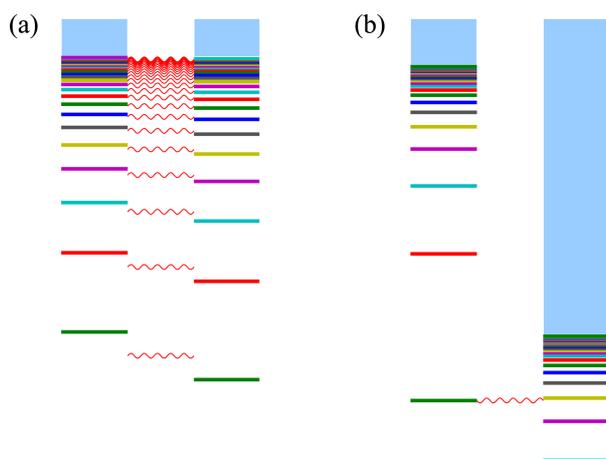
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Received February 10, 2011, Accepted March 8, 2011

A previous study (Lee, C. W. *J. Phys. B* **2010**, *43*, 175002) that isolated the overlapping resonances in the photoionization spectra using multichannel quantum defect theory (MQDT) in systems involving a single open channel was extended to manage many open channels when the closed channels are degenerate. The theory was applied to the dipole allowed  $J = 1^{\circ}$  spectra from the ground state with excitation energies lying between the lowest ionization thresholds for rare gas atoms, Ar, Kr, and Xe, and also for group IV elements, Ge, Sn and Pb.

**Key Words :** Phase-shifted MQDT, Overlapping resonance, Isolation into Beutler-Fano terms, Autoionizing Rydberg series

## Introduction

Autoionization spectra routinely show complex overlapping resonances caused by a perturber.<sup>1</sup> Multichannel quantum defect theory (MQDT) with the implementation of phase renormalization is extremely powerful and is used routinely to deal with the observed overlapping resonances with only a few parameters.<sup>2-4</sup> Different natures of perturbation prevail depending on the series converge to the same ionization threshold as in (a) or to the different thresholds as in (b) in Figure 1.<sup>5</sup> In the perturbed Rydberg series with different ionization thresholds, so that one series appears as an interloper, perturbation is local and shows strong energy dependency on the MQDT parameters. However, perturbation is not local in energy and acts uniformly throughout the entire series if the Rydberg series has the same ionization



**Figure 1.** Different natures of the perturbation prevail depending on whether the autoionizing Rydberg series converge to the same limit as in (a) or to the different limits as in (b). In contrast to the case of (b) for which the perturbation shown by a wiggling line is local in energy and shows strong energy dependency, for case (a), the perturbations shown with a wiggling line are not local and act uniformly throughout the entire series and thus the dynamic parameters are constant functions of energy.

threshold so that the closed channels are degenerate, leading to a constant energy dependency of the spectral parameters normally observed in the spectra of isolated resonances.

The formulation for isolating the overlapping resonances for this uniformly perturbed system involving one open and many degenerate closed channels was developed in Ref. [5]. Unfortunately, that formulation was limited to one open channel and cannot be applied to the most common problem of separating the s and d series in the  $J = 1^{\circ}$  autoionizing Rydberg series of Ar, Kr, and Xe. For that system, Ueda's formula<sup>6</sup>

$$\sigma = \sum_{k \in Q} \sigma_{ak} \frac{(\varepsilon_k + q_k)^2}{1 + \varepsilon_k^2} + \sigma_b \quad (1)$$

was used to fit the experimental data to isolate the s and d series.<sup>7-9</sup> However, his formulation cannot yield the  $q_k$  value from the experimentally obtained MQDT parameters because they neglected the indirect coupling between the closed channels through the open channels. Although restrictive, there are several systems in which his formulation has no serious problems and was used to find  $\sigma_{ak}$ ,  $\sigma_b$  and  $q_k$  by curve fitting of the experimental data.<sup>6,8,10</sup> The other approach is to use Shore's formula, which is based on Feshbach's resonance theory<sup>11-13</sup> and has no such defect. Instead, it has to relinquish the advantages of MQDT. This paper reports the extension of our previous MQDT formulation<sup>5</sup> that can now handle systems involving more than one open channel and does not have the defect that Ueda's formulation has.

## Brief Introduction to the Previous Result

In the previous study,<sup>5</sup> isolation of the overlapping resonances in the photoionization cross sections into the sum of Beutler-Fano terms,

$$\sigma = \sum_{k \in Q} \sigma_{ak} \frac{(\varepsilon_k + q_k)^2}{1 + \varepsilon_k^2} + \sigma_b \quad (2)$$

for systems involving many degenerate closed and one open

channels was attempted in the context of phase-shifted MQDT for which the reactance matrix  $\tilde{K}$  can be represented with a minimal number of elements as follows:

$$\tilde{K} = \begin{pmatrix} \tilde{K}^{cc} & \tilde{K}^{co} \\ \tilde{K}^{oc} & \tilde{K}^{oo} \end{pmatrix} = \begin{pmatrix} 0 & \dots & 0 & \tilde{K}_{1n} \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \dots & 0 & \tilde{K}_{n-1,n} \\ \tilde{K}_{1n} & \dots & \tilde{K}_{n-1,n} & 0 \end{pmatrix} \quad (3)$$

with 1 to  $n-1$  indexing the closed channels and  $n$  indexing an open channel. In (2),  $\sigma_{ak}$ ,  $q_k$  and  $\sigma_b$  are the fitting parameters, and the reduced energy  $\varepsilon_k$  for a closed channel  $k$  is defined by  $\tan\pi(\nu_k + \mu_k)/W_k$  with a reduced spectral width  $W_k$  defined by  $\tilde{K}_{kn}^2$ .  $Q$  denotes the space composed of closed channels. The definitions of  $\nu_k$  and  $\mu_k$  can be found below (4). Each Beutler-Fano term in the sum on the right side of (2) takes the form of resonance scattering devoid of background scattering, suggesting that the index refers to pure resonance eigenchannels. Therefore, the problem of isolating the overlapping resonances in photoionization cross sections into form (2) can be reformulated into the problem of finding the resonance eigenchannels.

Obtaining resonance eigenchannels is not a simple matter but requires a systematic approach. It begins from a factorization of the determinant of the physical scattering matrix  $S$  into background and resonance scattering<sup>14,15</sup>

$$\det(S) = \exp(-2i\delta^o) \frac{\det[\tan\pi(\nu + \mu) + \kappa^{cc*}]}{\det[\tan\pi(\nu + \mu) + \kappa^{cc}]} \quad (4)$$

where  $\nu_k$  is defined as  $E = I_k - \text{Ryd}/\nu_k^2$  with respect to the ionization threshold  $I_k$  for the closed channel  $k$ ;  $\kappa^{cc}$  is a complex reactance matrix<sup>16</sup> defined in terms of the sub reactance matrix by  $K^{cc} - iK^{co}(1 + iK^{oo})^{-1}K^{oc}$ .  $\pi\mu$  denotes the phase shifts introduced by phase renormalization.<sup>3</sup> Equation (4) shows that the resonance eigenchannels can be obtained by the diagonalization of the resonance scattering term,  $\tan\pi(\nu + \mu) + \kappa^{cc}$ . This diagonalization requires two conditions be met. The first condition involves the simultaneous diagonalization of  $\tan\pi(\nu + \mu)$  and  $\kappa^{cc}$ , which is possible only if  $\tan\pi(\nu + \mu)$  is a scalar matrix. If the closed channels have the same ionization threshold, i.e. degenerate,  $\nu$  is a scalar matrix ( $\pi\nu$  is frequently denoted by  $\beta$ ). Therefore, simultaneous diagonalization can be obtained when  $\mu$  is zero, which is achieved by phase renormalization.<sup>3</sup>

The second condition requires that  $\kappa^{cc}$  be a normal matrix that is not met in general. The normal choice for the diagonalization of such a non-normal matrix is to use the biorthogonal base sets used by Feshbach and Shore.<sup>11,17</sup> In the previous study,<sup>5,18</sup> another diagonalization called con-diagonalization was adopted, in which  $\kappa^{cc}$  is diagonalized by a unitary matrix  $V$  into  $\tan\Delta^c = VK^{cc}V^T$  with complex phase shifts  $\Delta_j^c = \delta_j^c - i\gamma_j^c$ .<sup>19</sup>

The resonance eigenchannels obtained by con-diagonalization still contain background scattering that can be removed by the phase renormalization of  $\beta$  into  $\beta + \pi\mu_j^c$ . The "pure" resonance representation obtained by this phase renormalization

was denoted with subscript (cd) and was accented with the tilde like  $\tilde{\beta}_{(cd)j}$  for  $\beta + \pi\mu_j^c$ . (Another tilde representation was encountered in (3)). For convenience, this pure resonance representation will be termed an "intrinsic resonance" representation. The relevant resonance eigenchannels and eigenphase shifts will be called intrinsic resonance eigenchannels and eigenphase shifts, respectively. These were derived in Ref. [5], where the autoionizing states are given as follows:

$$\tilde{\Psi}_{(cd)} = \tilde{\Psi}_{(cd)}^o \cos\tilde{\delta}_{(cd)r} - \sum_{k \in Q} \tilde{\Psi}_{(cd)k}^c \frac{\tilde{\zeta}_{(cd)k}}{\tan\tilde{\beta}_{(cd)k} - i\tilde{\zeta}_{(cd)k}^2} e^{i\tilde{\delta}_{(cd)r}} \quad (5)$$

and the corresponding photoionization cross section  $\sigma = (4\pi^2\alpha\omega/3)|(\tilde{\Psi}_{(cd)}|T|i)|^2$  is given by

$$\sigma = \frac{4\pi^2\alpha\omega}{3} \left| \tilde{D}_{(cd)}^o \cos\tilde{\delta}_{(cd)r} - \sum_{k \in Q} \tilde{D}_{(cd)k}^c \frac{\tilde{\zeta}_{(cd)k}}{\tan\tilde{\beta}_{(cd)k} + i\tilde{\zeta}_{(cd)k}^2} e^{-i\tilde{\delta}_{(cd)r}} \right|^2 \quad (6)$$

where  $\omega$  is the wave-number of an absorbed photon,  $\alpha$  is the hyperfine constant,  $\tilde{D}_{(cd)}^o$  and  $\tilde{D}_{(cd)k}^c$  are the transition dipole moments to the open channel standing wave channel basis function  $\tilde{\Psi}_{(cd)}^o$  (See Ref. [3] for a definition of this function) and the standing wave closed channel basis functions  $\tilde{\Psi}_{(cd)k}^c$ , respectively.  $\tilde{\zeta}_{(cd)k}$  denotes  $\tilde{K}_{(cd)kn}^{co}$ . Considering that the eigenphase shifts  $\tilde{\delta}_{(cd)r}$  can be isolated into the incoherent sum of  $\sum_j \tilde{\delta}_{(cd)rj}$  in this intrinsic resonance representation, (6) was then transformed to

$$\sigma = K \left| \tilde{D}_{(cd)}^o \right|^2 \left| \sum_{j \in Q} \frac{\tilde{\varepsilon}_{(cd)j} + \tilde{q}_{(cd)j}}{\tilde{\varepsilon}_{(cd)j} + i} + i \frac{\left( \sum_{k \in Q} \frac{\partial}{\partial \tilde{\varepsilon}_k} - \mathfrak{I} \right) \prod_{j \in Q} (\tilde{\varepsilon}_{(cd)j} + i)}{\prod_{j \in Q} (\tilde{\varepsilon}_{(cd)j} + i)} - (n_c - 1) \right|^2 \quad (7)$$

and eventually to the sum of Beutler-Fano terms

$$\sigma = K \left| \tilde{D}_{(cd)}^o \right|^2 \sum_{j \in Q} \frac{|\tilde{\varepsilon}_{(cd)j} + \tilde{q}_{(cd)j}|^2}{\tilde{\varepsilon}_{(cd)j}^2 + 1} + \text{interference term} \quad (8)$$

where  $K$  denotes  $4\pi^2\alpha\omega/3$ . In (7),  $n_c$  denotes the number of closed channels, the reduced energy  $\tilde{\varepsilon}_{(cd)j}$  denotes  $\tan\tilde{\beta}_{(cd)j}/\tilde{\zeta}_{(cd)j}^2$ , the line profile index  $\tilde{q}_{(cd)j}$  denotes  $-\tilde{D}_{(cd)j}^c/\tilde{\zeta}_{(cd)j}D_{(cd)}^o$  and  $\partial/\partial\tilde{\varepsilon}_{(cd)k}$  is the partial derivative with respect to  $\tilde{\varepsilon}_{(cd)k}$  with the other  $\tilde{\varepsilon}_{(cd)j}$  fixed.

In practical applications of cross section formula (8), the starting representation is the one in which the minimal number of fitting parameters for the autoionization spectra is used by giving the elements of  $K$  as many null values as possible. Such a representation was achieved using the phase-shifted MQDT and has been the method of choice for the experimentalists to fit their data. For systems involving many open and many degenerate closed channels, the entire  $K^{cc}$  and  $K^{oo}$  submatrices can be made into null matrices  $0^{cc}$  and  $0^{oo}$ .<sup>6</sup>

$$\tilde{K} = \begin{pmatrix} \tilde{K}^{cc} & \tilde{K}^{co} \\ \tilde{K}^{oc} & \tilde{K}^{oo} \end{pmatrix} = \begin{pmatrix} 0^{cc} & \tilde{K}^{co} \\ \tilde{K}^{oc} & 0^{oo} \end{pmatrix} \quad (9)$$

Although the representation where  $\tilde{K}^{oo}$  and  $\tilde{K}^{cc}$  are null is

best, and the fitting procedure is the simplest, it is not the representation where the resonance eigenchannels are obtained by condagonalization. For condagonalization, the phases of the base sets are shifted so that  $\mu$  in (4) becomes zero. After condagonalization,  $\kappa^{\text{cc}}$  becomes a diagonal matrix whose  $(j, k)$ -element is represented by  $\delta_{jk} \tan \Delta_j^{\text{c}}$  with complex  $\Delta_j^{\text{c}} = \delta_j^{\text{c}} - i\gamma_j^{\text{c}}$  and the phase shift due to resonance scattering can be isolated into an incoherent sum of phase shifts<sup>18</sup>

$$\delta_{(\text{cd})r} = \sum_{j \in Q} \delta_{(\text{cd})rj} \quad (10)$$

with  $\tan \delta_{(\text{cd})rj} = \Im(\tan \Delta_j^{\text{c}}) / [\tan \beta_{(\text{cd})j} + \Re(\tan \Delta_j^{\text{c}})]$ , which can be further simplified into

$$\tan \delta_{(\text{cd})rj} = \frac{\Im(\tan \Delta_j^{\text{c}})}{\tan \tilde{\beta}_{(\text{cd})j}} \quad (11)$$

with another phase renormalization that restores  $\Re(\tilde{\kappa}_{(\text{cd})}^{\text{cc}}) = 0$  and consequently the tilde notation. The procedure described thus far can be summarized into the following diagram (see Ref. [5] for further details):

$$\begin{array}{c} \left. \begin{array}{l} \tilde{\kappa}^{\text{oo}} = 0, \tilde{\kappa}^{\text{cc}} = 0 \\ (\tilde{\kappa}^{\text{co}}: \text{expt.}) \\ \tilde{\delta}_r \\ \tilde{\beta}_j = \beta + \pi\tilde{\mu}_j^{\text{c}} \\ (\tilde{\mu}_j^{\text{c}}: \text{expt.}) \end{array} \right\} \xrightarrow{[-\tilde{\mu}^{\text{c}}0]} \left\{ \begin{array}{l} \kappa^{\text{cc}} \\ \delta_r \\ \beta \end{array} \right\} \\ (12) \end{array}$$

$$\xrightarrow{\text{condiag.}} \left\{ \begin{array}{l} \kappa_{(\text{cd})}^{\text{cc}} = \tan \Delta^{\text{c}} = V^T \kappa^{\text{cc}} V \\ (\Delta_j^{\text{c}} = \delta_j^{\text{c}} - i\gamma_j^{\text{c}}) \\ \delta_{(\text{cd})r} = \sum_j \delta_{(\text{cd})rj} \\ \beta \end{array} \right\} \xrightarrow{[\mu^{\text{c}}\mu^{\text{c}}]} \left\{ \begin{array}{l} \Re(\tilde{\kappa}_{(\text{cd})}^{\text{cc}}) = 0, \tilde{\kappa}_{(\text{cd})}^{\text{oo}} = 0 \\ (\Delta_j^{\text{c}} = -i\gamma_j^{\text{c}}) \\ \tilde{\delta}_{(\text{cd})r} = \sum_j \tilde{\delta}_{(\text{cd})rj} \\ \tilde{\beta}_{(\text{cd})j} = \beta + \pi\mu_j^{\text{c}} \end{array} \right\}$$

### Extension to the Systems Involving Many Open Channels

The previous section summarized the formulation for the isolation of overlapping resonances into the autoionizing Rydberg eigenseries developed in Ref. [5]. Now consider its extension into the system involving more than one open channel. In this case, the procedures shown in (12) still hold but, Eqs. (5), (6), (7) and (8) should be modified to incorporate more than one open channel. If more than one open channel is involved, the number of independent degenerate autoionizing states becomes larger than one; actually equal to  $n_o$ , the number of open channels. Autoionization can occur in  $n_o$  different ways but the interferences between the  $n_o$  different processes are cancelled out in the total ionization cross section. The total ionization cross section is given by the incoherent sum of partial cross sections, which means that any independent set of physical channel basis functions that satisfy the boundary conditions at  $R \rightarrow \infty$  can be used to represent the partial cross sections as far as they are related by unitary transformation. Let  $\tilde{\Psi}_{(\text{cd})\rho}$  denote the physical eigenchannel basis functions. The total photoionization cross section  $\sigma$  is obtained as a sum of the partial cross

section  $\sigma_\rho$ :

$$\sigma = \sum_{\rho \in P} \sigma_\rho = \frac{4\pi^2 \alpha \omega}{3} \sum_{\rho \in P} |\tilde{\mathbf{D}}_\rho|^2 \quad (13)$$

where  $\tilde{\mathbf{D}}_\rho$  denotes  $(\tilde{\Psi}_{(\text{cd})\rho} | T | i)$  and  $P$  denotes the subspace composed of open channels. It is not difficult to modify the previous derivation to obtain  $\tilde{\Psi}_{(\text{cd})\rho}$  as follows:

$$\tilde{\Psi}_{(\text{cd})\rho} = \sum_{j \in P} (\tilde{\Psi}_{(\text{cd})j}^{\text{oo}} \tilde{Z}_{j\rho}^{\text{oo}} \cos \tilde{\delta}_{(\text{cd})r\rho}) - \sum_{k \in Q} \tilde{\Psi}_{(\text{cd})k}^{\text{c}} \frac{(\tilde{K}^{\text{co}} \tilde{Z}^{\text{oo}})_{k\rho}}{\tan \tilde{\beta}_{(\text{cd})k} - i\tilde{\zeta}_{(\text{cd})k}^2} e^{i\tilde{\delta}_{(\text{cd})r\rho}} \quad (14)$$

where the expansion coefficient matrix  $\tilde{Z}_{j\rho}^{\text{oo}}$  is obtained by solving

$$\sum_{j \in Q} \tilde{\mathbf{K}}_{(\text{cd})ij} \tilde{Z}_{j\rho}^{\text{oo}} = \tilde{Z}_{i\rho}^{\text{oo}} \tan \tilde{\delta}_{(\text{cd})r\rho} \quad (15)$$

By substituting the eigenchannel open channel basis functions,  $\tilde{\Psi}_{(\text{cd})}^{\text{c}}$  is defined as

$$\tilde{\Psi}_{(\text{cd})\rho}^{\text{c}} = \sum_{j \in P} \tilde{\Psi}_{(\text{cd})j}^{\text{oo}} \tilde{Z}_{j\rho}^{\text{oo}} \quad (16)$$

For the open channel basis functions,  $\tilde{\Psi}_{(\text{cd})}^{\text{oo}}$  and  $\tilde{K}^{\text{cc}}$  are defined by  $\tilde{K}^{\text{co}} \tilde{Z}^{\text{oo}}$ . For  $\tilde{K}^{\text{co}}$ , (13) can be simplified as follows:

$$\tilde{\Psi}_{(\text{cd})\rho} = \tilde{\Psi}_{(\text{cd})\rho}^{\text{c}} \cos \tilde{\delta}_{(\text{cd})r\rho} - \sum_{k \in Q} \tilde{\Psi}_{(\text{cd})k}^{\text{c}} (\tan \tilde{\beta}_{(\text{cd})k} - i\tilde{\zeta}_{(\text{cd})k}^2)^{-1} \tilde{K}_{(\text{cd})k\rho}^{\text{cc}} e^{i\tilde{\delta}_{(\text{cd})r\rho}} \quad (17)$$

Consequently, the corresponding transition dipole moment is obtained as follows:

$$\tilde{\mathbf{D}}_{(\text{cd})\rho} = \tilde{\mathbf{D}}_{(\text{cd})\rho}^{\text{c}} \cos \tilde{\delta}_{(\text{cd})r\rho} - \sum_{k \in Q} \tilde{\mathbf{D}}_{(\text{cd})k}^{\text{c}} (\tan \tilde{\beta}_{(\text{cd})k} + i\tilde{\zeta}_{(\text{cd})k}^2)^{-1} \tilde{K}_{(\text{cd})k\rho}^{\text{cc}} e^{-i\tilde{\delta}_{(\text{cd})r\rho}} \quad (18)$$

and the total ionization cross section (13) can be obtained as follows:

$$\sigma = \frac{4\pi^2 \alpha \omega}{3} \sum_{\rho} \left| \tilde{\mathbf{D}}_{(\text{cd})\rho}^{\text{c}} \cos \tilde{\delta}_{(\text{cd})r\rho} - \sum_{k \in Q} \tilde{\mathbf{D}}_{(\text{cd})k}^{\text{c}} \frac{\tilde{K}_{(\text{cd})k\rho}^{\text{cc}}}{\tan \tilde{\beta}_{(\text{cd})k} + i\tilde{\zeta}_{(\text{cd})k}^2} e^{-i\tilde{\delta}_{(\text{cd})r\rho}} \right|^2 \quad (19)$$

Although (19) has the same form as (6) except for the summation over  $\rho$ , it cannot be transformed into (7) without a further assumption. The transformation of (6) into (7) relies on the isolation equation (10), which does not hold for the physical eigenphase shifts  $\tilde{\delta}_{(\text{cd})r\rho}$ . Although both physical  $\tilde{\delta}_{(\text{cd})r\rho}$  and intrinsic  $\tilde{\delta}_{(\text{cd})rj}$  eigenphase shifts are phase shifts due to resonance scattering, they are defined in different subspaces. The former is for the process along the physical eigenchannel  $\rho$  in the open channel space  $P$  and the latter is for the process along the intrinsic resonance eigenchannel  $k$  in closed channel space  $Q$ . Note that their sum should be equal:

$$\sum_{\rho \in P} \tilde{\delta}_{(\text{cd})r\rho} = \sum_{j \in Q} \tilde{\delta}_{(\text{cd})rj} \quad (20)$$

### Limiting Behaviors of Eigenphase Shifts

Two limiting behaviors of the eigenphase shifts are fre-

quently observed in the autoionization spectra. One limiting behavior frequently observed is that only one eigenphase shift contains most of the resonance contributions and the remaining eigenphase shifts contains mostly background ones.<sup>20-22</sup> [The latter phase shifts should be close to zero in the present formulation (12) because background phase shifts become zero as  $\tilde{K}_{(cd)}^{\text{oc}}$  approaches zero by the phase renormalization.] In other words, in this limit, the eigenchannels are classified as a single resonance eigenchannel and the remaining non-resonance background eigenchannels. Let  $\tilde{\delta}_{(cd)\text{res}}$  denote the phaseshift corresponding to the eigenchannel that contains most of the resonance contributions in the resonance eigenchannel. Equation (20) becomes in this limit as follows:

$$\tilde{\delta}_{(cd)\text{res}} \approx \sum_{j \in Q} \tilde{\delta}_{(cd)rj} \quad (21)$$

Although this case is expected to occur in strongly coupled systems, as frequently observed in systems involving non-degenerate closed channels, such as in Ba and Cu,<sup>21,22</sup> there is no system available involving degenerate closed channels instead of non-degenerate ones and for which the MQDT parameters were obtained by data-fitting.

Another limiting behavior of the eigenphase shifts is that each  $\tilde{\delta}_{(cd)rj}$  is a one-to-one correspondence with  $\tilde{\delta}_{(cd)r\rho}$ . If the number of involved open channels is larger than the number of involved closed channels, the eigenphase shifts in the physical eigenframe which has no correspondence in the intrinsic resonance eigenframe are zero, meaning that the corresponding channels are of a background nature. Let  $\rho = \rho(k)$  denote the one-to-one correspondence between the index  $\rho$  in the physical eigenframe and index  $k$  in the intrinsic resonance eigenframe. The total cross section can then be approximated as follows:

$$\sigma = \sum_{\rho \in \text{res}} \sigma_{a\rho(k)} \frac{|\tilde{\epsilon}_k + \tilde{q}_{\rho(k)}|^2}{1 + \tilde{\epsilon}_k^2} + K \sum_{\rho \notin \text{res}} |\tilde{D}_{(cd)r\rho}^e|^2 \quad (22)$$

with

$$\sigma_{a\rho(k)} = K |\tilde{D}_{(cd)r\rho(k)}^e|^2 \quad (23)$$

$$q_{\rho(k)} = -\frac{\tilde{D}_{(cd)k}^c}{\tilde{\zeta}_{(cd)k} \tilde{D}_{(cd)\rho(k)}^c} \quad (24)$$

where  $\tilde{D}_{(cd)r\rho(k)}^e$  is the transition dipole moment to the physical eigenchannel  $\rho$  corresponding to intrinsic resonance eigenchannel  $k$ . Note that  $\tilde{D}_{(cd)r\rho(k)}^e$  is defined as  $\sum_{j \in P} \tilde{D}_{(cd)rj}^o \tilde{Z}_{j\rho(k)}^o$  with  $\tilde{Z}_{j\rho(k)}^o$  obtained by solving (15). Note that  $\tilde{Z}_{j\rho(k)}^o$  is in general a function of energy. As noted in the introduction, the periodic nature of the uniform perturbation in the systems involving degenerate closed channels imposes constancy on the parameters  $\tilde{D}_{(cd)r\rho(k)}^e$  and  $\tilde{q}_{\rho(k)}$ , meaning that  $\tilde{Z}_{j\rho(k)}^o$  should be a constant function of energy. Indeed, the energy dependency of  $\tilde{Z}_{j\rho(k)}^o$  is introduced at the avoided crossing points of the eigenchannels of  $\tilde{\mathbf{K}}_{(cd)}$ , which is accidental and irrelevant to the nature of the overlapping resonance and should be removed. The energy dependency can be removed easily by substituting the eigenvectors of

$-\text{const} \tilde{\mathbf{K}}_{(cd)}^{\text{oc}} \tilde{\mathbf{K}}_{(cd)}^{\text{co}}$  for the eigenvectors  $\tilde{\mathbf{Z}}_{j\rho(k)}^o$  of the full physical reactance matrix,  $\tilde{\mathbf{K}}_{(cd)} = -\tilde{\mathbf{K}}_{(cd)}^{\text{oc}} (\tan \tilde{\beta}_{(cd)} + \tilde{\mathbf{K}}_{(cd)}^{\text{co}})^{-1} \tilde{\mathbf{K}}_{(cd)}^{\text{co}}$ .

On the other hand, if the number of closed channels is larger than the number of open channels, a many-to-one correspondence between  $\tilde{\delta}_{(cd)rj}$  and  $\tilde{\delta}_{(cd)r\rho}$  occurs so that several intrinsic resonance eigenchannels can correspond to a single physical eigenchannel. Let  $k = k(\rho)$  denote the many-to-one correspondence between the index  $k$  in the intrinsic resonance eigenframe and the index  $\rho$  in the physical eigenframe. In this case, interference between the intrinsic resonance eigenchannels belonging to a single physical eigenchannel  $\rho$  occurs. In accordance with this change, two modifications to (22) should be performed. One is that the same  $\sigma_{a\rho}$  should be used for the intrinsic resonance eigenchannel  $k(\rho)$  belonging to the same physical eigenchannel  $\rho$ , the other modification is that interference terms should be added as follows:

$$\sigma = \sum_{\rho \in \text{res}} \left( \sigma_{a\rho} \sum_{k \in \rho} \frac{|\tilde{\epsilon}_k + \tilde{q}_{k(\rho)}|^2}{1 + \tilde{\epsilon}_k^2} + \sigma_{\text{interference}}(\rho) \right) + K \sum_{\rho \notin \text{res}} |\tilde{D}_{(cd)r\rho}^e|^2 \quad (25)$$

(Obtain the explicit formula for  $\sigma_{\text{interference}}$  from (7). For example, for  $n_c$  equal to 2 and 3, it is a simple matter and will be omitted). This case is observed in the autoionization spectra of group IV elements.<sup>23,24</sup>

### General Cases for the Behaviors of Eigenphase Shifts

Generally, the behavior of the physical eigenphase shifts, which are obtained by the diagonalization of physical reactance matrix  $\tilde{\mathbf{K}}_{(cd)}$  in the condiagonalized and phase-renormalized pure-resonance representation, may deviate significantly from the limiting cases considered in the previous section. Interestingly, many systems examined experimentally are very close to the limiting cases. Although they are close to the limiting cases, the deviations from the limiting cases cannot be ignored for some systems. Therefore, it might be important to have an analysis tool that can tell when the deviation from the limiting cases is large and what is the cause of the deviation.

The answer to this question can be obtained from a previous study<sup>5</sup> of the systems involving only one open channel. According to this study, a decomposition of the cross section into the sum of Beutler-Fano terms is based on the feasibility of the isolation (10) of the resonance eigenphase shift into the intrinsic resonance eigenphase shifts. This means that the same relation should hold if the decomposition of the cross section into the Beutler-Fano terms is possible. This can be true when one physical eigenchannel contains all the resonance contributions because of equation (20). For the limiting case of a one-to-one correspondence between the physical eigenchannels and intrinsic resonance eigenchannels, the only way equation (10) holds is that both eigenframes should be identical. In the latter case, the feasibility of the decomposition of the total cross section into

the Beutler-Fano terms can be assessed by examining how closely resembled the one-to-one corresponding physical resonance eigenchannels and intrinsic resonance eigenchannels are with each other.

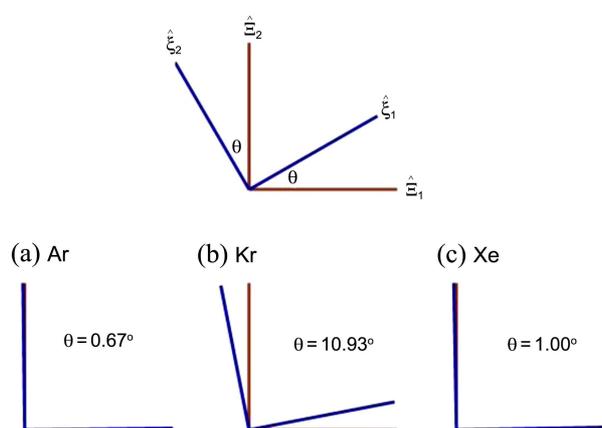
To provide an analysis tool to determine the extent of the difference between two one-to-one correspondent resonance eigenframes, consider the 2-by- $n_0$  reactance matrix  $\tilde{K}_{(cd)}^{ce}$  as a simple example. For convenience, let the physical eigenchannels 1 and 2 be one-to-one correspondent with the intrinsic resonance eigenchannels 1 and 2, respectively and the remaining physical eigenchannels from 3 to  $n_0$  are of a background nature. For concreteness, in the case of 2-by-3, the reactance matrix  $\tilde{K}_{(cd)}^{ce}$  can be represented as

$$\tilde{K}_{(cd)}^{ce} = \begin{pmatrix} \tilde{K}_{11} & \tilde{K}_{12} & 0 \\ \tilde{K}_{21} & \tilde{K}_{22} & 0 \end{pmatrix} \equiv (\Xi_1 \ \Xi_2 \ 0) \quad (26)$$

where  $\Xi_j$  ( $j=1,2$ ) denotes the vector in the intrinsic resonance eigenframe containing the coupling strength of a physical eigenchannel  $j$  with other channels. If the one-to-one correspondence is exact,  $\tilde{K}_{21} = \tilde{K}_{12} = 0$  is expected because the two frames are identical. In this case,  $\Xi_1 \cdot \Xi_2 = 0$  holds, indicating that the indirect coupling between the two physical eigenchannels 1 and 2 through the intrinsic resonance eigenchannels is zero. In a real system,  $\tilde{K}_{21} = \tilde{K}_{12} = 0$  is unlikely to hold and the two resonance frames are not identical. Since the two frames are related rotationally, the compatibility of the two frames can be quantified by the rotation angle  $\theta$  between them, as shown in Figure 2. If the unit axis vectors for the intrinsic resonance eigenframe are denoted as  $\hat{\xi}_1$  and  $\hat{\xi}_2$  and the unit axis vectors for the physical resonance eigenframe as  $\hat{\Xi}_1$  and  $\hat{\Xi}_2$ , the following equation can be derived:

$$(\Xi_1 \ \Xi_2) = (\hat{\xi}_1 \ \hat{\xi}_2) \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad (27)$$

If the number of closed channels is larger than the number of open channels, at least one physical eigenchannel should correspond to several intrinsic resonance eigenchannels. Note that the intrinsic resonance eigenframes are the frame



**Figure 2.** Physical and intrinsic eigenframes in Ar, Xe and Kr. See the text for the explanations.

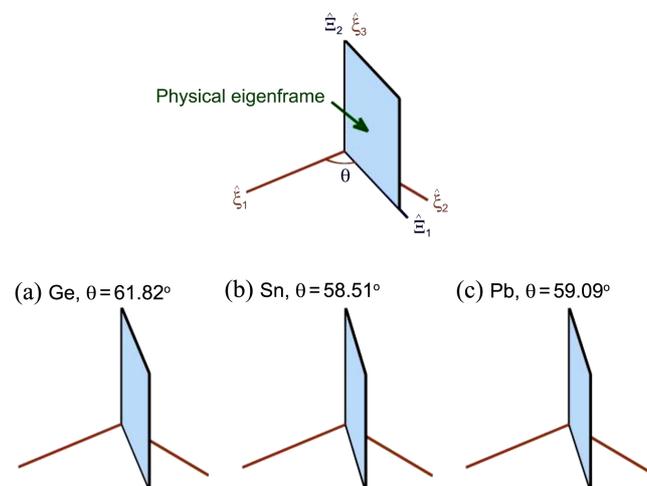
that contains all the information of the coupling nature of possible resonance scattering. On the other hand, the coupling nature of this resonance scattering cannot be observed in the real spectra. The real spectra provide information on the coupling nature of resonance scattering only through the physical resonance frame, which acts as a gate to the real world. In the case of many-to-one correspondence, several intrinsic processes pass simultaneously through the same gate, subsequently leading to interference. For concreteness, consider the form of  $\tilde{K}_{(cd)}^{ce}$  taken from a study of the group IV elements described in the next section:

$$\tilde{K}_{(cd)}^{ce} = \begin{pmatrix} \tilde{K}_{11} & 0 \\ \tilde{K}_{21} & 0 \\ 0 & \tilde{K}_{32} \end{pmatrix} \equiv (\Xi_1 \ \Xi_2) \quad (28)$$

In this case, the intrinsic resonance eigenchannels 1 and 2 are 2-to-1-correspondant to the physical eigenchannel 1. Figure 3 shows the geometrical realization of the relevant eigenframes along with their unit axes. If either  $\tilde{K}_{21}$  or  $\tilde{K}_{11}$  is zero, only one intrinsic eigenchannel corresponds to a physical eigenchannel and thus no interference will occur. The largest interference is expected when both intrinsic eigenchannels contribute equally to the 2-to-1 correspondence, i.e., when  $\Xi_1$  makes an angle of  $45^\circ$  with  $\hat{\xi}_1$ .

### Application to Experimental Spectra

Consider the application of the formulation developed in the previous section to the rare gas atoms, Ar, Kr and Xe, and also to the group IV elements, Ge, Sn and Pb. Although the two groups appear unrelated judging from their relative position in the periodic table, their dipole allowed  $J=1^o$  spectra from the ground states in the excitation energies lying between the lowest ionization thresholds share many common features. For example, their autoionizing Rydberg series are composed of s and d series with negligible s-d coupling.<sup>8,23,24</sup> However, because of the difference in occupancy in the outmost subshells, the ordering of the ionization

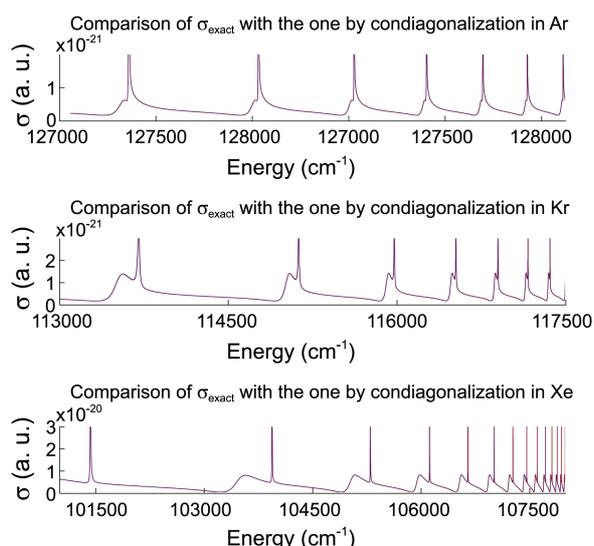


**Figure 3.** Physical and intrinsic eigenframes in Ge, Sn and Pb. See the text for the explanations.

thresholds is in reverse to each other. Consequently, there is a different inequality between the number of open and closed channels and subsequently different spectra.

**Rare Gases.** One-photon photoionization spectra of the rare gas atoms, Ar, Kr and Xe, from the ground states with excitation energies between the two lowest ionization thresholds,  $^2P_{3/2}^0$  and  $^2P_{1/2}^0$ , have been of interest both experimentally and theoretically.<sup>1</sup> The spectra allowed studies of the  $ns'[1/2]_1^0$  and  $nd'[3/2]_1^0$  autoionizing Rydberg series. In this dipole-allowed excitation leading to the  $J = 1$  odd-parity levels, in addition to the two closed channels,  $^2P_{1/2}ns'[1/2]_1^0$  and  $^2P_{1/2}nd'[3/2]_1^0$ , three more open channels,  $^2P_{3/2}ns[3/2]_1^0$ ,  $^2P_{3/2}nd[1/2]_1^0$  and  $^2P_{3/2}nd[3/2]_1^0$ , are involved. Several studies of Ueda type's MQDT analysis (1) have been performed on these systems.<sup>7,8,10</sup> Unlike these studies, where indirect coupling of closed channels through the open channels are ignored and the line profile index cannot be calculated from the other MQDT parameters, the formula (22) developed in this study has no such defect and the line profile index  $q$  can be obtained from other MQDT parameters. Moreover, the relative contributions of the relevant dynamic factors can be assessed and the goodness of the various approximations can be evaluated.

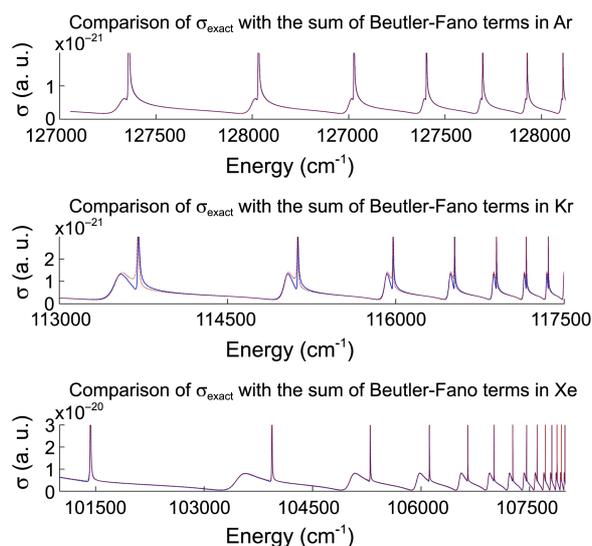
In the time-delay study on the same system done in Ref. [18], the condiagonalization with the approximation  $V^T V = 1$  was shown to be an excellent approximation. This conclusion also holds for the autoionization spectra, as shown in Figure 4. Figure 5 compares the exact cross section with the sum (22) of the Beutler-Fano terms. The sum of the Beutler-Fano terms given by (22) is an excellent approximation for Ar and Xe but not so good for Kr. This indicates that isolation of the autoionization spectra into the  $ns'$  and  $nd'$  series, as shown in



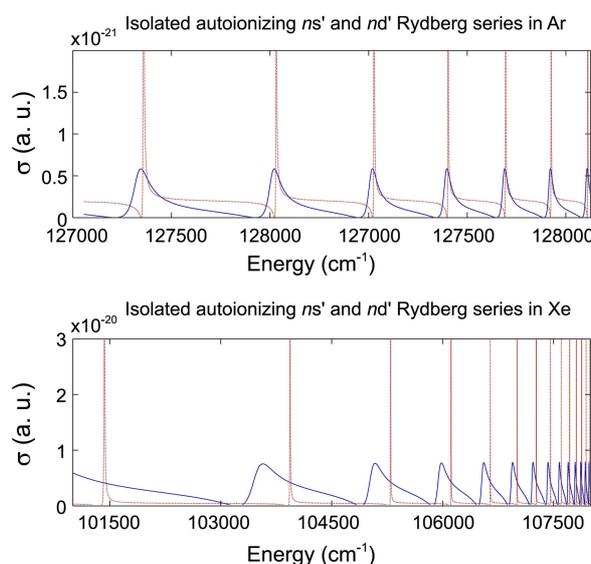
**Figure 4.** Comparison of the dipole allowed  $J = 1^0$  autoionization cross sections from the ground states with excitation energies between the two lowest ionization thresholds for Ar, Kr and Xe calculated without any approximation using the experimentally obtained MQDT parameters in Ref. [18], and the one obtained from condiagonalization with the approximation  $V^T V = 1$ . Note that two types of calculations are similar and the differences cannot be discernible in the spectra.

Figure 6 for Ar and Xe are meaningful, but the same type of isolation for Kr may not be accepted.

The reason why the autoionization spectra for Kr cannot be represented as an incoherent sum of Beutler-Fano terms lies in the intrinsic and physical resonance eigenframes for the one-to-one corresponding  $\tilde{\delta}_{(cd)TJ}$  and  $\tilde{\delta}_{(cd)TP}$ , respectively, are markedly different for Kr, whereas the two frames are almost identical for Ar and Xe. The extent of the difference between the two corresponding frames can be evaluated by the deviation of rotation angle from zero, as described around (26) and (27). For Ar,  $K_{(cd)}^{cc}$  is calculated as



**Figure 5.** Comparison of the autoionization cross sections calculated without any approximation using the experimentally obtained MQDT parameters in Ref. [18] plotted as a dotted line and the ones from the sum of Beutler-Fano terms in (22) plotted as a solid line for the same systems as the ones in Figure 4. Note that the two types of calculations yield similar results except for the one for Kr.



**Figure 6.**  $ns'$  and  $nd'$  autoionizing Rydberg series isolated by (22) and plotted as dotted and solid lines, respectively, for Ar and Xe. A similar isolation was not performed for Kr because the isolation (22) is not an excellent approximation for Kr.

$$\tilde{K}_{(cd)}^{ce} = \begin{pmatrix} 0.4272 & -0.0009 & 0 \\ -0.0050 & -0.0755 & 0 \end{pmatrix}$$

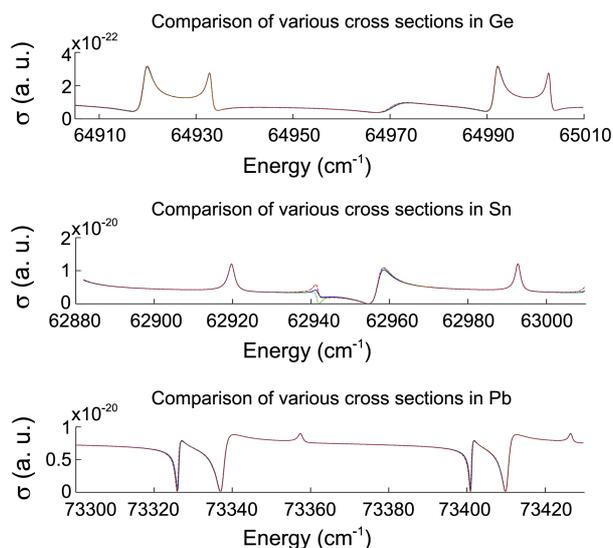
which is the form given in (26) and indicates that the rotation angle that physical resonance eigenframe ( $\tilde{\xi}_1$ ,  $\tilde{\xi}_2$ ) makes with the intrinsic frame ( $\xi_1$ ,  $\xi_2$ ) is given by  $0.67^\circ$ . Similarly, the rotation angles for the Kr and Xe systems were calculated to be  $10.93^\circ$  and  $1.00^\circ$ , respectively. Hence, for Ar and Xe, the two eigenframes are almost identical, whereas there is a significant difference for Kr. These angles show that the decomposition of an autoionization cross section into the Beutler-Fano terms will be very excellent for Ar and Xe but poor for Kr.

Surprisingly, the physical and intrinsic resonance eigenframes are coplanar but the reason for this coplanarity is unclear.

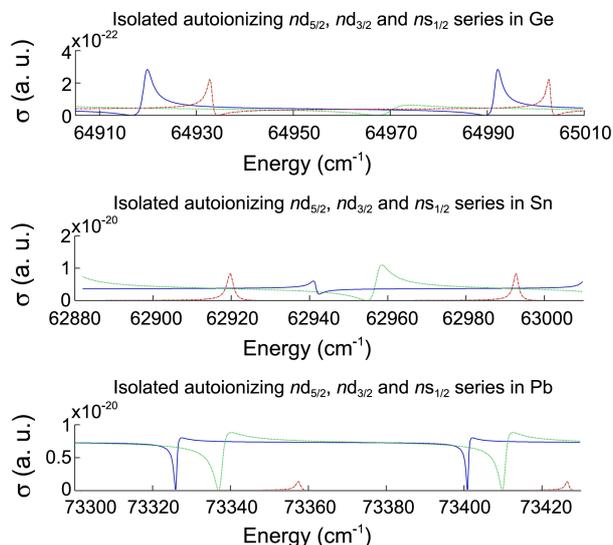
**Group IV Elements.** The dipole-allowed  $J=1^o$  photoionization spectra from the  $p^2 \ ^3P^o$  ground states of group IV elements, Ge, Sn and Pb, involve 5 Rydberg series associated with  $P_{1/2}nd_{3/2}$ ,  $P_{1/2}ns_{1/2}$ ,  $P_{3/2}nd_{5/2}$ ,  $P_{3/2}nd_{3/2}$  and  $P_{3/2}ns_{1/2}$ . In the excitation energy lying between two lowest ionization thresholds  $I_{1/2}$  and  $I_{3/2}$ , the autoionizing systems involve two open channels associated with the first 2 series, whereas the remaining 3 series belong to the closed channels. Therefore, the number of open channels in group IV elements is smaller than the number of closed channels. Since 3 closed channels are involved in group IV elements, the photoionization spectra show 3 autoionizing Rydberg series consisting of two d and one s series, as shown in Figure 7, which also shows that the condiaagonalization with the approximation,  $V^T V = 1$ , is an excellent approximation except for Sn. (The origin of the bad behavior for Sn is unclear and will be the topic for future research.)

Using the formalism developed in the previous section, these 3 series can be isolated, as shown in Figure 8. Figure 9 shows a comparison of the exact cross section with the sum (22) of the Beutler-Fano terms without including an interference terms between the two  $nd$  closed channels. The figure shows that the effect of interference on the cross section for these group IV elements is significant for all cases. In particular, it is much larger in Sn and Pb than in Ge. The closeness to  $45^\circ$  of the angle that  $\tilde{\xi}_1$  makes with  $\xi_1$  indicates the magnitude of interference. The angles are  $61.8^\circ$ ,  $58.5^\circ$  and  $59.1^\circ$  for Ge, Sn and Pb, respectively. This suggests that interference is large for all cases. In particular, it is larger for Sn  $\cong$  Pb and smaller for Ge, which is in agreement with Figure 9, because the departure of the angles from  $45^\circ$  is given by  $16.8^\circ$ ,  $13.5^\circ$  and  $14.1^\circ$ , respectively.

In contrast to the rare gas atoms, where the contributions of complex parts in rare gas atoms are negligible, the contributions of the complex parts in the group IV elements cannot be ignored. All the figures for the group IV elements were drawn with real parts alone because they agree better with the exact results. Physically, discarding the complex part of the calculation might be reasonable but there is no fundamental argument available for this.



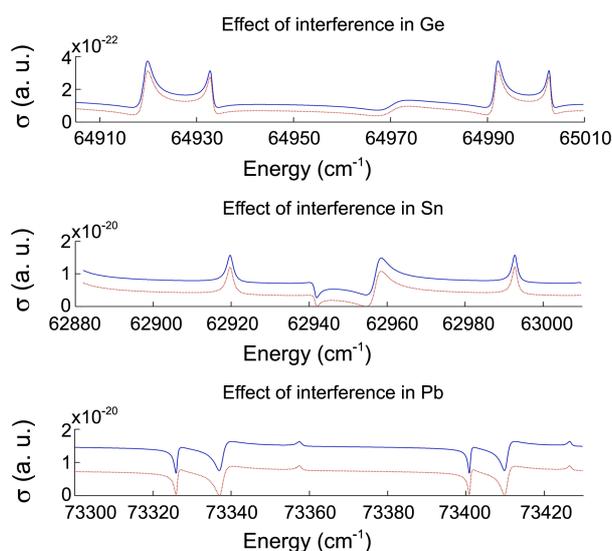
**Figure 7.** Comparison of the dipole allowed  $J=1^o$  autoionization cross sections from the ground states with excitation energies between the two lowest ionization thresholds calculated (1) without any approximation using the experimentally obtained MQDT parameters by Ueda,<sup>23,24</sup> plotted as a dashed line (2) the one obtained from condiaagonalization with the approximation  $V^T V = 1$  plotted as a solid line and (3) the ones from the sum of Beutler-Fano terms with interference included in (25) plotted as dashed-dotted line for the group IV elements, Ge, Sn and Pb. Note that the 3 types of calculations yield almost the same results except for Sn.



**Figure 8.**  $nd_{5/2}$ ,  $nd_{3/2}$  and  $ns_{1/2}$  autoionizing Rydberg series isolated by (25) and plotted with a solid, dash-dotted and dotted lines, respectively, for the same systems as those shown in Figure 7 for Ge, Sn and Pb. Note that, at approximately  $62940 \text{ cm}^{-1}$  for Sn where the method of (25) breaks down, unexpected behavior of the  $nd_{5/2}$  series occurs in that its minimum does not approach zero.

## Results and Discussion

In the overlapping resonances between the Rydberg series with the same ionization threshold, the perturbation between the series is not local in energy and acts uniformly throughout the entire series. The fact that uniform perturbation imposes



**Figure 9.** Comparison of the cross sections calculated without any approximation using the experimentally obtained MQDT parameters by Ueda<sup>23,24</sup> plotted as a dotted line and the one obtained from the sum of the Beutler-Fano terms in (25) without including interference terms plotted as a solid line. Therefore, the difference between the two curves in each spectrum is due mainly to interference.

constancy upon the energy dependence of the MQDT parameters was used to isolate the overlapping resonances in the previous study<sup>5</sup> as well as to express the photoionization cross section into the following form:

$$\sigma = K|D^0|^2 \sum_{k \in Q} \frac{|\varepsilon_k + q_k|^2}{1 + \varepsilon_k^2} + \text{interference term}$$

This was extended in this study to deal with systems involving more than one open channel to handle the most prominent problem of separating the s and d series in the  $J=1^0$  autoionizing Rydberg series of Ar, Kr, and Xe.

More than one open channel introduces more than one physical eigenchannel through which photoionization can occur. The presence of more than one physical eigenchannels brings about a wide range of ways in which the resonance scattering caused by the intrinsic resonance eigenchannels can affect the photoionization process. Therefore, the physical eigenchannels play the role of doorway or gate through which intrinsic resonance scattering can affect the real world photoionization process. According to this point of view, the previous study<sup>5</sup> dealt with the case of a single doorway through which many intrinsic resonance processes can affect the real photoionization process and provided the formulation that can handle such a case. Thus previous study<sup>5</sup> provided the extension to Fano's resonance theory<sup>3,25</sup> that handles only a single intrinsic resonance process. The previous formalism can be regarded as providing a basic building block for the mechanisms in general cases involving many

doorways to photoionization processes. An additional basic mechanism through which the intrinsic resonance processes can affect the photoionization processes was also found. The additional mechanism is that the distortion to the photoionization spectra can be brought about by the geometrical incompatibility between the intrinsic resonance eigenframe and physical resonance eigenframe.

This theory was applied to the autoionization spectra of the rare gas atoms Ar, Kr, and Xe and also of the group IV elements Ge, Sn and Pb to obtain the isolated autoionizing Rydberg spectra. Unlike the other studies on rare gas atoms, which rely on data fitting to experimental data using Ueda's formulation,<sup>6,7</sup> the present study produced the spectral parameters in terms of the MQDT parameters. In contrast to the rare gas spectra, Ueda's formulation cannot be used for group IV elements to decompose the total photoionization cross sections into Beutler-Fano terms. The present formulation can handle this case, showing that the interferences between autoionizing Rydberg series are significant in the photoionization spectra of group IV elements

**Acknowledgments.** This study was supported by the Ajou university research fellowship of 2011.

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