

# Young's double-slit experiment using two-center core-level photoemission: Photoelectron scattering effects

X.-J. Liu<sup>a</sup>, G. Prümper<sup>a</sup>, F. Gel'mukhanov<sup>a,b</sup>, N.A. Cherepkov<sup>a,c</sup>,  
H. Tanaka<sup>d</sup>, K. Ueda<sup>a,\*</sup>

<sup>a</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

<sup>b</sup> School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden

<sup>c</sup> State University of Aerospace Instrumentation, 190000 St. Petersburg, Russia

<sup>d</sup> Department of Physics, Sophia University, Tokyo 102-8554, Japan

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## Abstract

Core-level photoemission from  $N_2$  can be considered as an analogue of Young's double-slit experiment (YDSE) in which the double-slit is replaced by a pair of N 1s orbitals. N 1s photoelectron spectra of  $N_2$  are measured in the extended photon energy region up to  $\sim 1$  keV at unprecedented resolution. The measured ratio between the  $1\sigma_g$  and  $1\sigma_u$  photoionization cross-sections oscillates as a function of electron momentum due to interference effects analogue to YDSE. We found a shift of the interference pattern with respect to a prediction by a simple model for coherent two-center emission, the Cohen–Fano formula, and attributed it to photoelectron scattering by the neighboring atom. We demonstrate that the shift can be used to determine the scattering phase of the photoelectron.

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## 1. Introduction

Ever since the beginning of quantum mechanics, interference has captured the imagination of physicists. Young's double-slit experiment (YDSE) provides the simplest and most fundamental example in which the coherent addition of quantum-mechanical amplitudes leads to interference. Photoionization of diatomic molecules is conceptually similar, but instead of a photon passing through slits in a screen the photoelectron is ejected from a molecular orbital that is described by a superposition of two localized atomic orbitals—similar to a double-slit. The interference of the electron waves emitted coherently from the two atoms leads to an intrinsic interference effect similar to the one found in the YDSE. Cohen and Fano (CF) [1] were the first who predicted this YDSE interference effect and described it by a simple formula. Stimulated by CF's pioneering work, some experimental studies of ionization were performed for light molecules,  $H_2$  and  $D_2$ , making use of different projectiles, such as heavy ions [2,3], protons [4], and electrons

[5]: the results of these experiments indeed exhibited YDSE interference patterns, or to be more precise, CF interference patterns.

X-ray photoemission spectroscopy of core electrons from heavier molecules like  $N_2$  is another good tool to study the two-center interference [6]. The biggest experimental obstacle for seeing interference effects in K-shell electron spectroscopy of heavier molecules is the presence of the gerade and ungerade ionization channels with similar cross-sections and a very small energy gap between the gerade and ungerade core levels. The double-slit (two-center) interference cannot be observed when the spectral resolution is insufficient to resolve the gerade and ungerade doublet, because the interference contribution has an opposite sign in ionization cross-sections of gerade and ungerade core levels. This means that the photoionization cross-section does not display any interference pattern when the spectral resolution is poor. Modern high-resolution X-ray photoelectron spectroscopy using synchrotron radiation as a light source is indeed able to resolve this very small ( $\sim 100$  meV)  $1\sigma_g-1\sigma_u$  splitting in the core ionization of  $C_2H_2$  [7,8] and  $N_2$  [9] molecules. Recently, partial cross-sections of the  $1\sigma_g$  and  $1\sigma_u$  core-level photoionization of  $C_2H_2$  [8,10] and  $N_2$  [9,11] were measured

\* Corresponding author. Fax: +81 22 217 5380.

E-mail address: [ueda@tagen.tohoku.ac.jp](mailto:ueda@tagen.tohoku.ac.jp) (K. Ueda).

in the shape resonance regions. These observations were, however, limited to the regions rather close to the ionization thresholds.

In the present work, we extend the  $1\sigma_g$ – $1\sigma_u$  resolved measurement for the core-level photoemission from the  $N_2$  molecule to the high energy range up to  $\sim 1$  keV and observe the CF interference pattern. The unprecedented resolutions achieved for both the soft X-ray monochromator and electron energy analyzer make this challenging experiment possible. We find that the experimentally observed interference pattern is shifted with respect to that predicted by the CF formula. Our theoretical analysis reveals that the physical reason of this displacement can be attributed to the scattering of the fast photoelectron by the neighboring atom that is neglected in the CF theory. The common belief is that the scattering correction is small in the high energy region. This is true for the one-center photoionization (from a single atom) due to the small amplitude of backscattering of the electron by the neighboring atom. However, this is not the case for the two-center interference, where the role of photoelectron scattering is enhanced. We show that the phase shift of the CF interference pattern corresponds to twice the scattering phase of the photoelectron by the neighboring atom. Thus the energy dependent scattering phase can be extracted from the measured CF interference pattern by parameter fitting based on the new formula.

## 2. Experimental and fitting procedure

The experiment was carried out at the high-resolution soft X-ray photochemistry beam line 27SU [12,13] at SPring-8, Japan. The resolution of the monochromator was set to  $\sim 10,000$ . The light source of the beam line is a figure-8 undulator [14]. In the present high energy measurement where the value of the anisotropic parameter  $\beta$  becomes nearly identical for  $1\sigma_g$  and  $1\sigma_u$  and approaches the limiting value two [6,11], only horizontally polarized radiation was used. The electron spectroscopy apparatus has been described elsewhere [15]. The lens axis of the analyzer is set in a horizontal direction. The analyzer bandwidth was set to  $\sim 31$  meV in most cases. The overall bandwidth, i.e., a convolution of the monochromator and analyzer bandwidths was determined separately by measuring Xe 5p photoelectrons at the same monochromator and analyzer settings.

Fig. 1 shows the N 1s photoelectron spectrum recorded at a photon energy of 831 eV. Note that the y-axis is in “counts” after compensation by the multiple counting factor intrinsic to the detection system of the SES2002 analyzer. The experimental spectra recorded at different energies up to  $\sim 1$  keV have been decomposed by least-squares curve fitting [16] into  $1\sigma_g$  and  $1\sigma_u$  components with the individual vibrational progressions, as seen in Fig. 1. The Lorentzian widths were fixed to the values previously determined; 120 meV for both  $1\sigma_g$  and  $1\sigma_u$  [17]. The Gaussian widths were fixed to the values obtained from the separate measurements; the difference of the Doppler broadening between Xe and  $N_2$  molecules was taken into account. The  $1\sigma_g$ – $1\sigma_u$  splitting of the  $v' = 1$  vibrational components was 97 meV [18]. The vibrational spacings were also fixed to 298 meV for

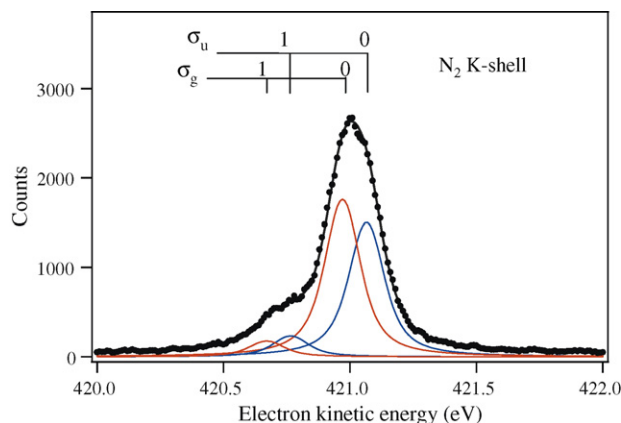


Fig. 1. Photoelectron spectrum at photon energy of 831 eV, parallel to the polarization vector. Dots: experiment; thick solid lines: fitted spectrum; thin lines: individual peaks.

$1\sigma_g$  and 300 meV for  $1\sigma_u$  [18]. The position of the  $1\sigma_u v' = 0$  component and the intensities of the individual vibrational components were treated as fitting parameters.

## 3. Ab initio theory

We have also performed the calculations [17] in the random-phase approximation (RPA) by the method described earlier in [19,20] with the use of the relaxed-core Hartree–Fock (RCHF) wave functions as a zero order approximation. Since the RCHF method overestimates the influence of the relaxation effects for K-shells [21], we employed the fractional charge RCHF method described in [22]. In this method the relaxed-core wave functions are calculated as solutions of the HF equation with the fractional charge  $z_e$  of the molecular ion. The fractional charge  $z_e$  is set to a value to maximize the agreement with the experimental data. The frozen-core HF approximation corresponds to  $z_e = 0$ , while the standard RCHF method corresponds to  $z_e = 1$ . We chose  $z_e = 0.7$ , which gives the correct position of the shape resonance [11]. The RPA calculations were carried out below  $k \simeq 3$  a.u. At higher energies the contribution of many-electron correlations is small. We checked that the RCHF calculations agree well with the RPA calculations in the region  $2 < k < 3$  a.u. Thus the RCHF calculations have been extended to higher energy range. In the present calculation, the effect of the vibrations was not taken into account.

## 4. Results

Ratios for the partial cross-sections of  $1\sigma_g$  and  $1\sigma_u$  extracted from the fitting are plotted in Fig. 2 as a function of the photoelectron momentum  $k = \sqrt{2E}$ , with  $E$  being the kinetic energy of the photoelectron in atomic units. Here, we determined the ratio of the sums of the areas for the individual  $g$  and  $u$  vibrational components so that we can compare the result with theoretical predictions that do not take vibrations into account. The uncertainties of the data points as given by the error bars in the figure were obtained using the error estimate routine [16] that allows us to take account of cross-correlations of the parameters; the uncertainty of the fitted energy of the  $1\sigma_u v' = 0$

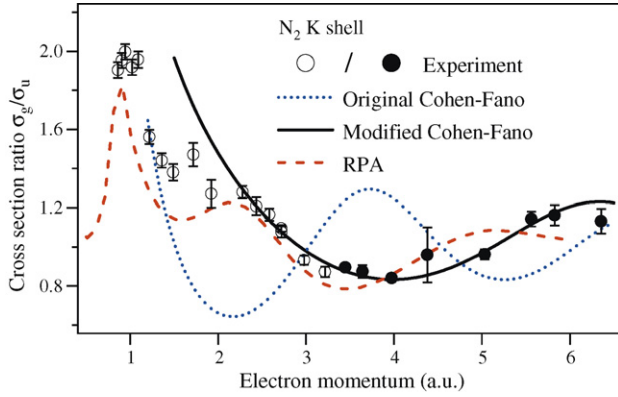


Fig. 2. Ratios of  $1\sigma_g$  and  $1\sigma_u$  partial photoionization cross-sections of  $N_2$ . Open and closed circles: previous [11,18,17] and present experiments, respectively. Dashed red line: present *ab initio* result. Dotted blue line: CF formula. Solid black line: fitted curve by the present modified CF formula. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

component was propagated to the final result. In this connection, it is worth noting that the uncertainty of the point at  $\sim 4.4$  a.u. from the preliminary measurement is significantly larger than those of other points. The large uncertainty stems from the two reasons. First, the band width of the electron energy analyzer was set by a factor of two larger than that of the measurement of other points. Second, the measurement for the instrumental width using the Xe photoelectron was not available and thus the Gaussian width was also regarded as a fitting parameter. This illustrates the importance of the narrow instrumental width and its characterization by a separate measurement.

In both the experimental and *ab initio* ratios of Fig. 2, the peak structure appears at  $k \simeq 1$  a.u. This peak corresponds to the shape resonance as discussed in detail in [11]. In the region of  $1.5 < k < 6.3$  a.u., both experimental and *ab initio* ratios exhibit the oscillatory structure. This oscillatory structure is the CF interference pattern. The experimental and *ab initio* CF interference patterns agree reasonably well. The discrepancy for  $k > 3.5$  a.u. may at least partly be attributed to the neglect of the vibrations in the present calculation. The dotted line in Fig. 2 is the CF interference pattern calculated by the CF formula described below. Apparently, the phase of the interference pattern is displaced from both experimental and *ab initio* interference patterns. In the rest of this paper, we elucidate the origin of this displacement and demonstrate that one can determine the scattering phase of photoelectrons from this displacement.

## 5. Discussion

Let us briefly review the essence of CF theory. When a nitrogen molecule is irradiated by monochromatic X-rays, K-shell photoemission takes place from a molecular core orbital, which is a superposition of  $1s$  orbitals localized in two individual N atoms,  $N^{(1)}$  and  $N^{(2)}$ :

$$1\sigma_{g,u} = \frac{1s_1 \pm 1s_2}{\sqrt{2}}. \quad (1)$$

Here, the two N atoms play the role of the *slits* in YDSE: the two slits emit coherently phase-shifted electronic waves  $\propto \exp(i\mathbf{k} \cdot \mathbf{R}_1)$  and  $\propto \exp(i\mathbf{k} \cdot \mathbf{R}_2)$ , with  $\mathbf{R}_1$  and  $\mathbf{R}_2$  being the position vectors of  $N^{(1)}$  and  $N^{(2)}$ . When the electron with the momentum  $\mathbf{k}$  is ejected from the delocalized coherent gerade or ungerade core orbital given by Eq. (1), the interference of waves emitted coherently from the two atoms (slits) leads to intrinsic YDSE interference pattern in the cross-section of K-shell photoionization:

$$\sigma_{g,u}(\omega) \propto \frac{1}{2} |e^{i\mathbf{k} \cdot \mathbf{R}_1} \pm e^{i\mathbf{k} \cdot \mathbf{R}_2}|^2 = 1 \pm \cos(\mathbf{k} \cdot \mathbf{R}), \quad (2)$$

which depends on the parity of the core orbital,  $\mathbf{k}$  and internuclear radius vector  $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ . Molecules are randomly oriented in gas phase. The orientational averaging of the cross-section of Eq. (2) results in the CF interference pattern [1]:

$$\sigma_{g,u}(\omega) = \sigma_0(\omega) [1 \pm \chi_{CF}(k)], \quad (3)$$

where

$$\chi_{CF}(k) = \frac{\sin kR}{kR} \quad (4)$$

for  $kR \gg 1$ . Here,  $\sigma_0(\omega) \propto |d(\omega)|^2 (\mathbf{e} \cdot \mathbf{k})^2$  is the K-shell photoionization differential cross-section of a single atom by monochromatic X-rays with the frequency  $\omega$  and polarization vector  $\mathbf{e}$ , and  $d(\omega)$  is the transition dipole moment of atomic photoionization. We note that CF formula assumes that the wave function of the photoelectron is a plane wave outside of the atom. In other words, the electron scattering by the neighboring atom is ignored in CF theory.

Now let us look at what happens if we improve the wave function of the fast photoelectron taking into account the scattering of the electron by the neighboring atom. According to the dipole selection rules, the photoelectron wave  $\psi_i$  should be the p electronic wave in the case of the K-shell photoionization of the atom  $N^{(i)}$  ( $i = 1, 2$ ). The first and major contribution in this p wave near  $N^{(1)}$  is the incident plane wave  $\hat{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_1)$  (see Fig. 3A<sub>1</sub>). The scattering of the incident wave by  $N^{(2)}$  with the amplitude  $f(\vartheta)$  towards  $N^{(1)}$   $\hat{\mathbf{R}} = \mathbf{R}/R$  gives the second contribution as it is shown in Fig. 3B<sub>1</sub>. Thus, the amplitude of the p wave of the photoelectron near  $N^{(1)}$  reads

$$\psi_1 = \hat{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_1} + \hat{\mathbf{R}} \frac{e^{ikR}}{R} f(\vartheta) e^{i\mathbf{k} \cdot \mathbf{R}_2}. \quad (5)$$

The amplitude of the p wave near  $N^{(2)}$ ,  $\psi_2$ , is obtained from  $\psi_1$  by replacing  $1 \rightleftharpoons 2$ ,  $\mathbf{R} \rightarrow -\mathbf{R}$  and  $\vartheta \rightarrow \pi - \vartheta$ .

The calculation of the differential cross-section,  $|\mathbf{e} \cdot (\psi_1 \pm \psi_2)|^2$ , of randomly oriented molecules is straightforward in high energy limit,  $kR \gg 1$ :

$$\frac{\sigma_{g,u}(\omega)}{\sigma_0(\omega)} = 1 - \frac{1}{kR^2} \text{Im} \left\{ f(\pi) e^{2i[kR + \delta_1(k)]} \right\} \pm \chi(k), \quad (6)$$

where

$$\chi(k) = \frac{1}{kR} \sin [kR + 2\delta_1(k)], \quad (7)$$

and  $\delta_1(k)$  is the phase shift of the single-scattered wave by the neighboring atom. Eq. (7) is based on the multiple scattering expansion over powers of  $1/(kR)$  and neglects terms  $\sim 1/(kR)^2$ .

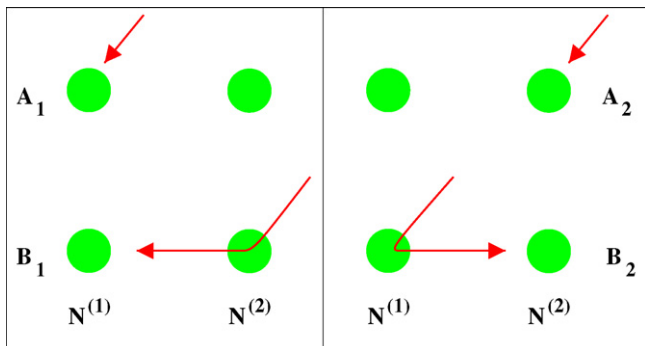


Fig. 3. In high energy limit,  $kR \gg 1$ , the incident wave on the  $n$ th atom  $N^{(n)}$  is formed mainly by plane wave ( $A_n$ ) and by wave single scattered by another atom ( $B_n$ ).

This means that the  $\chi$  function is calculated with the precision about 1% in the region  $k \gtrsim 2$ . The first two terms in Eq. (6) describe the incoherent sum of the one-center photoionization by the two individual atoms  $N^{(1)}$  and  $N^{(2)}$ . The second term in this one-center contribution is a scattering correction, i.e., interference of free  $A_i$  and single-scattered  $B_i$  waves that are incident on the same atom  $N^{(i)}$ . This scattering term is well-known EXAFS contribution [23] and is very small for light elements in high energy region ( $|f(\pi)|/kR^2 \leq 10^{-2}$ ) and give negligible contribution in our experiment. Thus we have

$$\frac{\sigma_{g,u}(\omega)}{\sigma_0(\omega)} \approx 1 \pm \chi(k). \quad (8)$$

This expression is analogous to CF formula given by Eq. (3). However, the phase shift  $2\delta_1(k)$ , which is absent in  $\chi_{CF}$  of Eq. (4) in the original CF formula, appears in  $\chi(k)$  given by Eq. (7). This phase shift arises as a result of interference of the free ( $A_1$ ) and scattered ( $B_2$ ) waves incident on different atoms (see Fig. 3). This phase shift influences drastically the interference pattern in the high energy region. Contrary to the one-center term, the role of scattering in the two-center interference term is surprisingly huge. A large phase shift of  $2\delta_1(k)$  displaces the interference pattern as compared to the CF formula and brings the result in coincidence with the experiment and the *ab initio* solution (see Fig. 2).

Noting that the displacement of the CF interference pattern is due to photoelectron scattering by the neighboring atom, one can obtain the scattering phase  $2\delta_1(k)$  from the experimental CF interference pattern. From Eq. (8) we have

$$\frac{\sigma_g}{\sigma_u} = \frac{1 + \chi(k)}{1 - \chi(k)}. \quad (9)$$

$\delta(k)$  in Eq. (7) can be well approximated by a quadratic polynomial in the momentum region of  $k < 7$  a.u. [24]:

$$2\delta(k) = a + bk + ck^2. \quad (10)$$

We have performed the least-squares fit to the experimental ratios of  $\sigma_g/\sigma_u$ , using Eqs. (9), (7), and (10). In order to avoid the influence of the shape resonance to the analysis of the interference modulation, the fitting has been performed within a range of  $2.2 < k < 6.3$  a.u. The resulting values  $a$ ,  $b$ , and  $c$  in Eq. (10) obtained via fitting are  $-5.2 \pm 0.6$ ,  $-1.6 \pm 0.4$ , and

$0.09 \pm 0.05$  a.u., respectively. These values are to be compared with the values  $a = -4.8$ ,  $b = -1.15$ , and  $c = 0.069$  a.u., obtained via interpolation of *ab initio* estimates for the scattering phases  $2\delta(k)$  for C and O [24]. The resulting curve of the fitting is given in Fig. 2. The agreement between the experimental and fitted curves is excellent, indicating the validity of the present modified Cohen–Fano model used for the fitting.

## 6. Conclusions

We have studied experimentally and theoretically photoionization of core electrons in  $N_2$  molecule. The present experimental and *ab initio* ratios between the  $1\sigma_g$  and  $1\sigma_u$  cross-sections display interference patterns, analogous to Young's double-slit experiment, with considerable displacement in phase from the one predicted by the CF formula. To explain this displacement we derived an analytical formula for the high energy region making use of multiple-scattering theory. We show that the CF interference pattern is shifted by twice the phase of the photoelectron scattering. The shift of the CF interference pattern gives new opportunity to measure directly the scattering phase of photoelectron, which is needed in different applications, for example, in EXAFS studies of molecular structure.

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