

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

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Abstract

Core-level photoemission from N₂ can be considered an analogue of Young's double-slit experiment (YDSE) in which the double-slit is replaced by a pair of N 1s orbitals. The measured ratio between the 1σ_g and 1σ_u photoionization cross-sections oscillates as a function of photoelectron momentum, due to two-center YDSE interference, exhibiting a remarkable dependence on the vibrational sub-levels of the core ionized state. We theoretically demonstrate that the recoil of the photoelectron given to the ionized N atom strongly influences this interference pattern. The reason for this is that the momentum transfer affects the phases of the photoionization amplitudes.

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1. Introduction

X-ray photoelectron spectroscopy (XPS) has widely been used in many different fields. Chemical shifts of core levels measured by XPS provide information about chemical environments of specific atomic sites and thus can be used for the chemical analysis of synthesized molecules, surfaces, etc. [1]. In the analysis of the XPS data, recoil of the photoelectron to the emitter, i.e., the atom in the molecule, surface, or solid, has been completely neglected, on the basis of huge mass difference between the emitted electron and the emitting atom. In 1978, Domcke and Cederbaum theoretically investigated the influence of the recoil effect on the high-energy photoelectron spectra of free molecules [2]. As it was shown later [3], the recoil-induced modification of the Franck–Condon (FC) distribution is very weak for photoelectron energies below 2 keV. The reason for this is the small size of the amplitude of vibrations compared to the wavelength of the photoelectron. This ratio can be changed by increasing the amplitude of the vibration using a strong infrared pulse [4]. Observing the quantum interference in

XPS of homonuclear molecules similar to Young's double-slit experiment (YDSE) we have found a strong effect based on the recoil. In contrast to normal XPS measurements this interferometric method is sensitive to the recoil-induced phase-shift between the two one-center photoionization amplitudes which shifts the complete YDSE interference pattern.

Rapid developments of modern synchrotron-radiation-based ultrahigh-resolution XPS opened new research fields such as bulk-sensitive XPS in solid state physics [5], vibrationally resolved XPS in molecular science [6,7], etc. In most cases, the recoil effect has still been neglected in the analysis of the XPS data. Kukk et al. reported the first observation of a very small recoil effect on the vibrational structure of core-level photoelectron spectra of free molecules, taking advantage of unprecedented resolution achieved for soft X-ray (~1 keV) photoelectron spectroscopy at the soft X-ray beam line of SPring-8, Japan [8].

In the present paper, we focus on the theoretical description of the two-center interference in the photoionization of homonuclear diatomics and demonstrate that it is very sensitive to the recoil effect. The largest variation in XPS can be seen when the cross-section of 1σ_g and 1σ_u states are compared instead of the modification of the Franck–Condon (FC) distribution. The reason for this is that when one of them shows constructive interference the other one shows destructive interference. This

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contrast mechanism works so efficiently that one can see the influence of the recoil effect as a shift of the energy where constructive interference occurs for different variational excitations. For the comparison with experimental data we use core-level photoemission from free N_2 molecules as a specific example.

2. Theoretical

Core-level photoemission from the $1\sigma_g$ orbital of the N_2 molecule is conceptually similar to Young's double-slit experiment (YDSE) in which the coherent addition of quantum-mechanical amplitudes leads to interference. Instead of photons passing through slits in a screen, photoelectrons are emitted from non-degenerate molecular σ -orbitals: i.e., from a coherent superposition of atomic $1s$ orbitals localized close to the different N nuclei [9]:

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

The two N atoms in N_2 , $N^{(1)}$ and $N^{(2)}$, play the role of the double-slit that emits coherently phase-shifted electron waves $\propto \exp(i\mathbf{k} \cdot \mathbf{R}_1)$ and $\propto \exp(i\mathbf{k} \cdot \mathbf{R}_2)$, respectively. Here, \mathbf{k} is the momentum of the photoelectron and \mathbf{R}_1 and \mathbf{R}_2 are the coordinates of $N^{(1)}$ and $N^{(2)}$, respectively. The amplitudes for the photoionization $1\sigma_{g,u} \rightarrow \varphi_{\mathbf{k}}$ are

$$F_{g,u} \propto \frac{1}{\sqrt{2}} (e^{i\mathbf{k} \cdot \mathbf{R}_1} \pm e^{i\mathbf{k} \cdot \mathbf{R}_2}) \quad (2)$$

Atomic units are used throughout the paper unless otherwise specified. The interference of waves emitted coherently from the two localized core orbitals (double-slit) leads to an intrinsic YDSE interference pattern in the cross-section of K-shell photoionization of fixed-in-space molecules, $\sigma_{g,u}(\mathbf{k}) \propto 1 \pm \cos(\mathbf{k} \cdot \mathbf{R})$, which depends on the parity of the molecular core orbital, \mathbf{k} and the internuclear radius vector $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$. In 1966, Cohen and Fano (CF) obtained a simple formula for the XPS cross-section of randomly oriented gas-phase molecules [10]:

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

for $kR \gg 1$. Applying the CF formula (3) to the present N_2 core-level photoemission, $\sigma_0(k)$ is the K-shell photoionization differential cross-section of a single N atom by monochromatic X-rays. We call the interference pattern described by CF formula (3) CF interference pattern.

So far we only considered a fixed internuclear distance. Vibrations change the bond length, $R \rightarrow R + q$, where q is the displacement from the equilibrium internuclear distance R . The standard method to include the effects of nuclear motion within the Born–Oppenheimer approximation is to replace the XPS amplitude for a fixed bond length given by Eq. (2), by the strict XPS amplitude of the transition from the ground $|1\sigma_{g,u}\rangle|0\rangle$ to the final vibronic state $|\varphi_{\mathbf{k}}\rangle|v\rangle_{g,u}$:

$$F_{g,u}^v \propto \frac{1}{\sqrt{2}} \langle 0 | e^{i\mathbf{k} \cdot \mathbf{R}_1} \pm e^{i\mathbf{k} \cdot \mathbf{R}_2} | v \rangle_{g,u} = \frac{1}{\sqrt{2}} [e^{i\mathbf{k} \cdot \mathbf{R}/2} f_1 \pm e^{-i\mathbf{k} \cdot \mathbf{R}/2} f_2] \quad (4)$$

where we wrote the XPS amplitude in the frame of the center of gravity, $\mathbf{R}_1 = (\mathbf{R} + \mathbf{q})/2$ and $\mathbf{R}_2 = -(\mathbf{R} + \mathbf{q})/2$, and introduced the nuclear parts f_1 and f_2 of the photoionization amplitudes of the nitrogen atoms $N^{(1)}$ and $N^{(2)}$, respectively. In contrast to the ordinary FC amplitude $\langle 0 | v \rangle_{g,u}$ which is real, the generalized Franck–Condon (GFC) amplitudes $f_{1,2} \equiv \langle 0 | \exp(\pm i\mathbf{k} \cdot \mathbf{q}/2) | v \rangle_{g,u}$ are complex:

$$f_1 = f e^{i\psi}, \quad f_2 = f e^{-i\psi}, \quad f = |f_1| \quad (5)$$

and have opposite phases $\psi \equiv \psi(v, \mathbf{k})$ and $-\psi$:

$$\psi(v, \mathbf{k}) = \arctan \frac{\langle 0 | \sin((\mathbf{k} \cdot \mathbf{q})/2) | v \rangle_{g,u}}{\langle 0 | \cos((\mathbf{k} \cdot \mathbf{q})/2) | v \rangle_{g,u}} \quad (6)$$

To avoid the ambiguity of the phase of Eq. (6) we have to use in general the strict definition $\psi = \arg(f_1)$. In the above treatment, we ignored the small energy shift of the XPS peak by the recoil energy $E_{\text{rec}} = k^2/2M$, where M is the mass of the molecule. The weak recoil-induced rotational heating is also neglected. The cross-section for the transition from the ground $|1\sigma_{g,u}\rangle|0\rangle$ to the final $|\varphi_{\mathbf{k}}\rangle|v\rangle_{g,u}$ electronic-vibrational states of the oriented molecule is given by

$$\sigma_{g,u}(\mathbf{k}) \propto \frac{1}{2} |e^{i\mathbf{k} \cdot \mathbf{R}/2} f_1 \pm e^{-i\mathbf{k} \cdot \mathbf{R}/2} f_2|^2 = |f_1|^2 \pm \text{Re}[e^{i\mathbf{k} \cdot \mathbf{R}} f_1 f_2^*] \quad (7)$$

The first term of Eq. (7) is the direct term that describes the incoherent sum $|f_1|^2 + |f_2|^2 = 2|f_1|^2$ of the one-center photoionization by the two individual atoms $N^{(1)}$ and $N^{(2)}$, whereas the second term $f_1 f_2^*$ describes the two-center interference.

At first sight the transition from Eq. (2) with fixed nuclei to the strict XPS amplitude (4) within the Born–Oppenheimer approximation looks merely like a formal step to average over the contributions of various internuclear distances. The integration in Eq. (4) is performed over amplitudes and not over cross-sections. Therefore the implications are more subtle: even though Eq. (4) is based on the Born–Oppenheimer approximation, it implicitly links the dynamics of the nuclear wave packet and the electron wave. The momentum exchange (recoil) between the electron and nuclear motion is already included. This is seen immediately from the GFC amplitude f_1 written in the momentum space:

$$\langle 0 | e^{i\mathbf{k} \cdot \mathbf{q}/2} | v \rangle_{g,u} = \int_{-\infty}^{\infty} \Phi_0^*(p) \Phi_v^{(g,u)} \left(p - \frac{k \cos \theta}{2} \right) dp \quad (8)$$

using the momentum representation $\Phi_v^{(g,u)}(p)$ for vibrational wave function, where p is the momentum of relative nuclear motion and θ is the angle between \mathbf{k} and molecular axis \mathbf{R} . The link (8) between the phase factor $\exp(i\mathbf{k} \cdot \mathbf{q}/2)$ and the recoil effect, $p \rightarrow p - (k \cos \theta)/2$, is evident. Thus, we arrive at an important conclusion: the momentum transfer from the photoelectron to the nuclei makes the amplitudes f_1 and f_2 of the photoelectron ejection from different nitrogen atoms $N^{(1)}$ and $N^{(2)}$ complex. According to Eqs. (5) and (7), the recoil-induced counter rotation (Fig. 1) of the amplitudes f_1 and f_2 results in

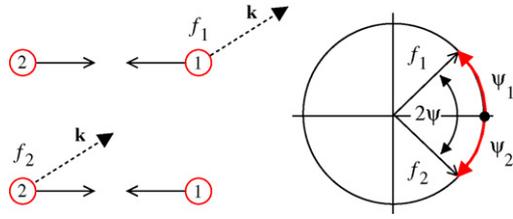


Fig. 1. Illustration of the recoil-induced *rotation* of the partial photoionization amplitudes f_n of Eq. (5) in the complex f -plane.

a phase-shift of 2ψ for the YDSE interference pattern:

$$\sigma_{g,u}(\mathbf{k}) \propto f^2 \{1 \pm \cos[\mathbf{k} \cdot \mathbf{R} + 2\psi(v, \mathbf{k})]\} \quad (9)$$

This is our key result. The phase-shift $2\psi(v, \mathbf{k})$ in Eq. (9) can be large even for a relatively small photoelectron momentum k ($kq < 1$) because it is a first order effect over k , contrary to the small recoil energy $E_{\text{rec}} = k^2/2M$ which is quadratic over k . It is worth noting that the recoil-induced correction for the prefactor f^2 in Eq. (9) is also proportional to $(kq)^2$. This explains why the role of the recoil is so small in ordinary one-center photoionization (from a single atom in a molecule) that is described by $|f_1|^2$.

If the experiment is performed with gas-phase molecules, the cross-section of Eq. (9) for fixed-in-space molecules must be averaged over all molecular orientations. In the energy region of interest, the displacement is shorter than the photoelectron wavelength, $kq < 1$. Hence, we may expand the phase factors in a series $e^{\pm i\mathbf{k} \cdot \mathbf{q}/2} \approx 1 \pm i\mathbf{k} \cdot \mathbf{q}/2$. Using this approximation, we can perform the orientational averaging of the cross-section of Eq. (7):

$$\sigma_{g,u}(k, v) = \sigma_0(k) \langle 0|v \rangle_{g,u}^2 [1 \pm \chi_{g,u}(k, v)] \quad (10)$$

As it was seen for fixed-in-space molecules [see Eq. (9)], the photoelectron recoil shifts the CF interference pattern of Eq. (3) for randomly oriented molecules as well. Contrary to the CF formula (3), the interference term $\chi_{g,u}(k, v)$ experiences a phase-shift due to the recoil which is twice the phase of the one-center amplitude:

$$2\psi_{g,u}(v, k) = \arctan(k\Delta R_v) \quad (11)$$

where the effective *displacement*

$$\Delta R_v = \frac{\langle 0|q|v \rangle_{g,u}}{\langle 0|v \rangle_{g,u}} \quad (12)$$

is the same as the one obtained in the theory of the shape resonances [11,12]. As one can see from the expression for ΔR_v of Eq. (12), the recoil-induced phase-shift $2\psi_{g,u}(v, k)$ of Eq. (11) in the CF interference pattern is very sensitive to the vibrational state $|v\rangle$.

So far, we have neglected the electron scattering effect. Recently, we found that the CF interference pattern of Eq. (3) is shifted also by twice the scattering phase of the photoelectron [13]. Here, we only formulate our main result. As it is well known in the EXAFS theory [14,15] the electron scattering by the neighboring atoms changes the cross-section of one-center photoionization and gives a minor correction due to the small

backscattering amplitude, $|f(\pi)|/R \ll 1$. The two-center interference enhances anomalously the role of electron scattering, similar to the recoil effect studied here. The electron scattering causes an additional phase-shift of the interference pattern, which is twice the phase $\delta_1(k)$ of the atomic scattering of the p electronic wave. This extra shift is large [14,15] and changes drastically the CF interference pattern [13]. The final expression for the interference term is

$$\chi_{g,u}(k, v) = \frac{\eta_v}{kR} \sin[kR + 2\psi_{g,u}(v, k) + 2\delta_1(k)] \quad (13)$$

where $\eta_v = \sqrt{1 + (k\Delta R_v)^2}$. We want to point out that the recoil effect gives a new and very important opportunity to determine the sign of the nuclear displacement due to core ionization, ΔR , because the phase $\psi_{g,u}(v, k)$ changes the sign just like ΔR .

3. Experimental data

Some experimental studies on the CF interference effect have been reported. They were focused on ionization of the lightest molecules H_2 and D_2 , with different projectiles [17–20]. In this paper we focus on the core-level photoemission from free N_2 molecules. The main experimental difficulty for seeing a CF interference effect for the core-level photoemission from the heavier molecule N_2 is the presence of both gerade and ungerade ionization channels with a very small energy gap between the corresponding core levels. The CF interference cannot be observed when the spectral resolution is insufficient to resolve the gerade and ungerade doublet. The $1\sigma_g - 1\sigma_u$ resolved partial cross-section measurements have so far been limited to the regions rather close the ionization threshold [21–24]. Recently we have extended 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 ~ 1 keV and observed the CF interference pattern [13,16]. The details of the experiment and data analysis are described elsewhere [8,22].

The core-level photoelectron spectrum of N_2 consists of two spectral bands $1\sigma_g \rightarrow \varphi_{\mathbf{k}}$ and $1\sigma_u \rightarrow \varphi_{\mathbf{k}}$ because both gerade and ungerade core levels in N_2 are occupied. The relative intensities of the transitions to the final vibrational states v are given by

$$\frac{\sigma_g(k)}{\sigma_u(k)} = \frac{\langle 0|v \rangle_g^2}{\langle 0|v \rangle_u^2} \rho_v(k) \quad (14)$$

$$\rho_v(k) = \frac{1 + \chi_g(k, v)}{1 - \chi_u(k, v)} \quad (15)$$

To compare the experimental data with theory [Eqs. (13)–(15)], we used a combined approach. The FC factors in Eq. (14) and the effective displacement of Eq. (12) are calculated from the spectroscopic constants given in Ref. [23], employing the harmonic oscillator approximation. The scattering phase $\delta_1(k)$ is determined using a least-squares fitting [13] of Eqs. (13)–(15) to the experimental data. Following Teo and Lee [15], we use a quadratic approximation for the phase-shift:

$$2\delta_1 = a + bk + ck^2 \quad (16)$$

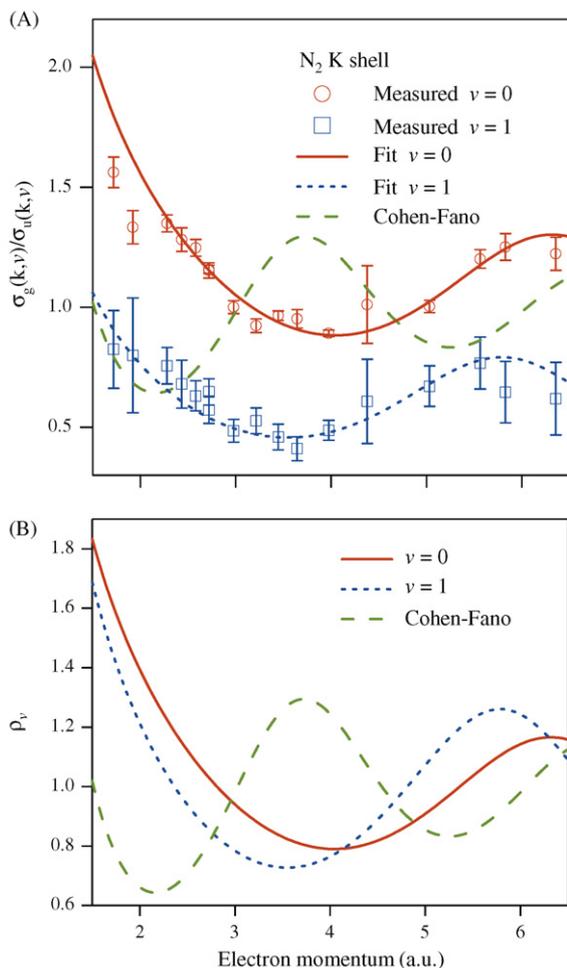


Fig. 2. (A) Comparison of experimental [16] and theoretical cross-section ratios of Eq. (14) and (B) the ρ_ν function of Eq. (15) for vibrational levels $\nu = 0, 1$ and the CF ratio of the cross-sections σ_g and σ_u .

The fitting results are $a = -5.2 \pm 0.6$, $b = -1.6 \pm 0.4$, and $c = 0.09 \pm 0.05$ a.u. Note that there is no independent adjustable parameter between $\nu = 0$ and 1. The remarkable agreement between theory and experiment shown in Fig. 2A for the cross-section ratios both of $\nu = 0$ and 1 strongly supports the presented recoil theory. The theoretical ratio $\sigma_g(k, \nu)/\sigma_u(k, \nu)$ was computed with FC factors ratios ($\langle 0|0\rangle_g^2/\langle 0|0\rangle_u^2 = 1.07$, $\langle 0|1\rangle_g^2/\langle 0|1\rangle_u^2 = 0.60$). The origin of this factor can be a slight difference of one-center cross-section $\sigma_0(k)$ for gerade and ungerade core holes. It is easy to spot the failure of the CF formula (3). Fig. 2B shows a significant difference between $\rho_{\nu=0}(k)$ and $\rho_{\nu=1}(k)$ (up to 20%) due to the recoil. We emphasize that the strong enhancement of the recoil effect (up to 20%) caused by the CF interference is in sharp contrast to the conventional measurements of the vibrational distribution, where the effect is about 1% of the cross-section in the studied energy region [8].

4. Conclusions

We studied theoretically the core-level photoionization of the nitrogen molecule and compared the results to experimental

data. Both the experiment and theory show interference oscillations in the ratio of the $1\sigma_g$ and $1\sigma_u$ cross-sections. The measured cross-section ratio between $1\sigma_g$ and $1\sigma_u$ for the vibrationally excited level $\nu = 1$ of the core ionized state deviates significantly from that of vibrationally ground level $\nu = 0$. The reason for it is the recoil effect. Namely, the recoil induces a phase-shift of the amplitude of the one center core ionization. The recoil-induced phase-shift of the Cohen-Fano fringe offers a unique opportunity to define the sign of the shift for the equilibrium distance under core ionization.

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