Which-pass information in the double-slit experiment of diatomic molecules

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Abstract. Analogy between the double-slit experiment in quantum optics and the photoelectron emission from diatoms is discussed in the light of availabilities of which-pass information and quantum eraser. The availability of which-pass information and the degree of the predictability may be determined by the intrinsic molecular processes involved, whereas the erasing the which-pass information relies on the observation.

1. Introduction
Interference has been continuously capturing imagination of physicists since Young’s double-slit experiment. The present work is concerned with the double-slit interference by the matter wave, i.e., the interference of the coherent photoelectron emission from the diatoms. As the introduction to the double-slit experiment, let us first briefly review two experiments by the coherent light, in order to introduce the concepts of a “which-pass marker” and a “quantum eraser”.

Eichmann et al. investigated interference effects in the light scattering from the two atoms [1]. In this experiment, two $^{198}$Hg$^+$ ions are localized in a linear Paul trap at an appropriate separation, to form a double-slit. The two ions are then irradiated by a linearly polarized, traveling wave laser beam tuned below the resonance frequency of the $^{198}$Hg$^+$ $6s^2S_{1/2} - 6p^2P_{1/2}$ transition at 194 nm. They found that interference fringes appear (disappear) in a distant detection region when the polarization direction of the scattered photon is parallel (perpendicular) to the exciting laser polarization direction. They explained their observation based on the “witch pass” considerations. In case of the perpendicular polarization, the magnetic quantum number of the scattering atom is different from the other one. Thus, the different magnetic quantum number can be regarded as a “which-pass marker”. The interference fringes disappear whenever a which-pass marker is present. Measuring the which-pass marker is not necessary to destroy interference.

The second example is the case where two photons are entangled, as Walborn et al. studied [2]. When one photon of an entangled pair is incident on a double-slit of appropriate dimensions, interference fringes appear in a distant detection region. When quarter-wave plates, oriented so that their fast axes are orthogonal, are placed in front of each slit, the fringes disappear because a which-pass marker is present. If the polarization of the other entangled photon is measured in coincidence with the first photon, the fringes can be recovered because the which-way marker
can be erased by coincident detection of the entangled photon at a certain polarization direction. Such an eraser of the which-way marker is called a “quantum eraser”.

Electron emission from a gerade or ungerade orbital in a homonuclear diatom causes interference that is analogous to double-slit interference. Here, the photoelectron wave is described as a superposition of two phase-coherent waves emitted from the two atoms (slits). Cohen and Fano were the first who predicted that the photoionization cross sections of homonuclear diatomic molecules oscillate as a function of the photoelectron momentum, due to double-slit interference [3]. Cohen-Fano (CF) interference has been first observed in electron emission from H₂ molecules in ion-impact experiments [4, 5]. For photoionization experiments of H₂ molecules, Frankfurt group clearly demonstrated double-slit interference of the coherent photoelectron emission from the two sites [6, 7], fixing the molecule in space using reaction microscope [8, 9].

Coherent photoelectron emission from the 1σ₉ or 1σᵤ core orbital of N₂ is another example that exhibits double-slit interference [10, 11] and indeed Cohen-Fano oscillation has been observed by the author’s group in the ratio of the 1σ₉ and 1σᵤ photoionization cross sections of N₂ [12, 13, 14, 15].

2. Core-level photoemission of N₂

2.1. Cohen-Fano interference

The symmetry-adapted core orbitals in nitrogen molecules are 1σ₂ and 1σₛ, which can be described as a linear combination of the atomic N 1s core orbitals, 1s₁ and 1s₂, localized at two N atoms N(1) and N(2), respectively:

\[ 1σ₂,σ = \frac{1s₁ ± 1s₂}{\sqrt{2}}. \] (1)

*Ab initio* calculations [16, 17] predicts the energy splitting (∼ 100 meV) for the 1σ₂ and 1σₛ core-hole states and high-resolution X-ray photoelectron spectroscopy using synchrotron radiation as a light source indeed confirmed not only this g-u splitting [18] but also the different equilibrium bond lengths for the 1σ₂ and 1σₛ core-hole states [17]. The g-u splitting in the core-hole states was confirmed also in high-resolution Auger electron spectra [19, 20]. If one observes photoelectron emission from the 1σ₂ or 1σₛ orbital, the photoelectron emission can be considered as a coherent superposition of the two waves emitted from the two atoms. As a result, the quantum interference, similar to the Young’s double-slit experiment, may appear. Indeed we have observed CF oscillation in the ratio of the core-level photoemission cross sections for 1σ₂ and 1σₛ single hole creation of N₂ [12, 13, 14, 15].

Figure 1 depicts the ratios for the partial cross sections of the υ = 0 → υ′ = 0 and υ = 0 → υ′ = 1 vibrational transitions, as calculated and as measured, as a function of the photoelectron momentum \( k = \sqrt{2E} \), where \( E \) is the kinetic energy of the photoelectron in atomic units. The calculations were carried out using the random-phase approximation (RPA) with the use of the relaxed-core Hartree-Fock (RCHF) wave functions as a zero-order approximation, employing the fractional-charge RCHF method [21]. The measurements [12, 13, 14, 15] were carried out on beam line 27SU [22, 23, 24] at SPring-8, Japan, using a high-resolution electron spectroscopy end station [25], whose heart is 20-cm radius hemispherical electron analyzer SES2002 (GammaData-Sciento). The agreement between the measurements and calculations is reasonable. The peak structure appears at \( k \approx 1 \text{ a.u.} \) It corresponds to the \( σ^* \) shape resonance as discussed in detail in [26]. In the region of 1.5 < k < 6.5 a.u., the ratios exhibit the oscillatory structure, which is due to CF interference.

In the case of photoemission from a nitrogen molecular core orbital, which is a superposition of 1s orbitals localized in two individual N atoms, N⁵(1) and N⁵(2), the two N atoms emit coherently phase-shifted electronic waves \( \propto \exp(ik \cdot R_1) \) and \( \propto \exp(ik \cdot R_2) \), where \( R_1 \) and \( R_2 \) are the
2.2. Role of photoelectron scattering and recoil

We note that CF formula assumes that the wave function of the photoelectron is a plane wave outside of the atom. Thus the shift of the ab initio and experimental oscillatory structure from the CF prediction may be attributed to photoelectron scattering by the neighboring atom [13, 14]. The expression for the interference term is

\[
\chi_{g,u}(k) = \frac{\sin kR}{kR} \]

for \( kR \gg 1 \). Here, \( \sigma_0(\omega) \propto |d(\omega)|^2(e \cdot k)^2 \) is the \( K \)-shell photoionization differential cross section of a single atom by monochromatic x-rays with the frequency \( \omega \) and polarization vector \( e \), and \( d(\omega) \) is the transition dipole moment of atomic photoionization. The prediction by the CF formula is also given in Fig. 1 by the dashed line. Surprisingly, the oscillatory structure is completely out of phase.
where \( \delta_1 \) is the phase of the atomic scattering of the \( p \) electron wave. It is worth noting that the photoelectron scattering does not reduce the amplitude of the oscillatory structure, i.e., the visibility of the fringes, indicating the scattering does not provide any “which-pass” information, or core-hole localization.

Not only the photoelectron diffraction but also the photoelectron recoil cause the shift of the CF oscillation [15]. The recoil phase shift depends strongly on the vibrational quantum number \( v \) of the core hole state. 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:

\[
2\psi_{g,u}(v,k) = \arctan(k\Delta R_v),
\]

where

\[
\Delta R_v = \frac{\langle 0|q|v \rangle_{g,u}}{\langle 0|v \rangle_{g,u}}
\]

is the effective displacement caused by the photoelectron recoil. The final expression for the interference term is

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

where \( \eta_v = \sqrt{1 + (k\Delta R_v)^2} \). We note that the photoelectron recoil also does not reduce the amplitude of the oscillatory structure, or the visibility of the fringes, indicating the recoil does not provide any “which-pass” information, or core-hole localization.

In the conditions described above, one cannot say which atom emitted an electron and thus has a core hole, in the same analogy as Young’s double-slit experiment.

### 2.3. Role of the Auger emission

Recently, we demonstrated, experimentally and theoretically, that a high-resolution Auger electron spectrum, in which the \( 1\sigma_g \) and \( 1\sigma_u \) core-hole states are partially resolved, is accurately described as an incoherent sum of the two separate contributions from the decays of the \( 1\sigma_g \) and \( 1\sigma_u \) core-hole states [20]. Namely, the intensities of the N 1s\( \sigma_{g,u}^- \) Auger transitions to a final state \( |f\rangle \) can be described by

\[
I_{g,u} = |D_{g,u}|^2 |Q_{g,u}|^2
\]

with \( D \) being the dipole matrix element for the photoionization and \( Q \) the Coulomb matrix element for the decay. This finding suggests that the Auger electron alone does not provide any information about the which-pass information, or core-hole localization.

The energy separation between the \( 1\sigma_g \) and \( 1\sigma_u \) core-hole states of N2 is 100 meV, which is in fact smaller than the lifetime width of 120 meV. Thus, the separations in the photoelectron and Auger electron spectra are possible only via least-squares curve fitting. The Cohen-Fano oscillation disappears when \( 1\sigma_g \) and \( 1\sigma_u \) core-hole states are not resolved. Without resolving the \( 1\sigma_g \) and \( 1\sigma_u \) core-hole states, Schöffler et al. measured molecular-frame N 1s photoelectron angular distributions (MFPAD) of N2, resolving also the direction of the Auger electron emission [27]. They demonstrated that, depending on the direction of the Auger electron emission, the MFPAD exhibits the emission from the non-localized \( 1\sigma_g \) or \( 1\sigma_u \) orbital as well as from the atomic orbital localized to the right or left atom.

In the atomic sequential doublephotoionization, it is well known that the angular correlations between the photoelectron and the Auger electron are well described by a general expression in which the sequential double-photoionization is treated as a single scattering process [28, 29, 30, 31, 32]:

\[
M_f(\epsilon, \epsilon_A) = \langle f \epsilon, \epsilon_A | D | 0 \rangle + \sum_n \int \frac{\langle f \epsilon, \epsilon_A | Q | n \tau \rangle Q | n \tau | D | 0 \rangle d\tau}{\hbar \omega - E_n + i\Gamma_n/2},
\]

where \( \hbar \), \( \omega \), and \( \Gamma_n \) are the reduced Planck constant, energy, and lifetime of the \( n \)th state, respectively.
Here the summation is over the intermediate states $|n\tau\rangle$, which are characterized by their energy $E_{n\tau}$ and life-time width $\Gamma_{n\tau}$. The total intermediate-state energy is $E_{\tau} = E_0 + I_{\tau} + \tau$, where $E_0$ is the energy of the ground state $|0\rangle$. These states, excited by the dipole photon with the energy $\hbar\omega$ from the ground state $|0\rangle$, further decay to the Auger final state $|f\rangle$ via the Coulomb interaction $Q$. The total final-state energy is $E_f = E_0 + I_f + \epsilon + \epsilon_A$, with $\epsilon$ and $\epsilon_A$ being photoelectron and Auger electron kinetic energies. This general formula is often called Kramers-Heisenberg formula. From this general formula it is straightforward to obtain the expression for the current $N_2 1s$ photoemission:

$$M_f(\epsilon, \epsilon_A, \tau) \propto \langle f\epsilon, \epsilon_A | V | g\tau \rangle \langle g\tau | D | 0 \rangle + \langle f\epsilon, \epsilon_A | V | u\tau \rangle \langle u\tau | D | 0 \rangle . \tag{10}$$

Here we neglected direct double photoionization term and the energy splitting of $N_2 1s\sigma_{g,u}$. It is clear that the photoelectron and the Auger electron are entangled to form a Bell state.

The above situation reminds us the quantum eraser experiment with the two entangled photons described in the introduction. In the quantum eraser experiment, quarter-wave plates oriented so that their fast axes are orthogonal are placed in front of each slit and one photon of an entangled pair is incident on the double-slit. The polarization of the other entangled photon is measured in coincidence. Then the double-slit interference fringes appear and disappear depending on the direction of the polarization of the entangled photon detected in coincidence. Analogously, in the experiment by Schöffler et al., the photoelectron angular distributions in the molecular frame mimic the localized core-hole or non-localized core-hole, depending on the direction of the Auger emission detected in coincidence. Thus, the experiment by Schöffler et al. is in a sense an analog of the quantum eraser experiment.

3. Concluding remark
We have discussed analogy of the double slit in quantum optics with coherent electron emission from diatoms, using the $N_2$ molecule as a specific example. We have observed a separated g or u core-hole level both in the core-level photoemission and Auger emission. We have observed Cohen-Fano interference oscillation in the g-u split partial cross sections or randomly oriented molecules. This oscillation is equivalent to Young’s double slit interference “fringes”, indicating that the core-level photoemission is indeed a coherent two-center emission. Intramolecular elastic scattering and photoelectron recoil shift the phase of the interference fringes but hardly affect the fringe visibility, illustrating that these effects would not provide the which-pass information. If we do not resolve g and u states, double slit interference fringes disappear. Even if one does not resolve g and u symmetry of the intermediate core-hole state but detects the entangled Auger electrons with well defined g or u final state, one can restore or destroy the double slit interference, as demonstrated by Schöffler et al.. Here the observation plays a vital role. On the other hand, in certain cases, atomic ion left after the photoemission may provide a partial which-pass information, as demonstrated for the Ne$_2$ case [33, 34]. The availability of which-pass information and the degree of the predictability by the atomic ion may be determined by the intrinsic molecular processes involved, such as interatomic Coulombic decay and dissociation. Here the molecular process plays a vital role. It is important to differentiate the role of the observation and molecular dynamics.

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