様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Ultrafast dynamics and resonance effects in photoemission from surfaces

研究課題名（英文）Ultrafast dynamics and resonance effects in photoemission from surfaces

研究代表者
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研究成果の概要（和文）：本研究では時間遅延と内殻励起時の共鳴効果について、光電子放出過程の理解に進展があった。時間依存性シュレーディンガー方程式の解と一次元モデルの多重散乱計算を直接比較することで、ウィグナー遅延理論が原子から固体へと一般化できることを示した。また、銅表面において観測された光電子遅延のエネルギー依存を第一原理計算で説明した。原子多重項モデルと多重散乱理論を組み合わせた、3d金属の内殻共鳴励起における角度分解光電子・光電子回折の理論とコードを開発した。Niの共鳴光電子スペクトルの実験結果を再現し、最近観測された共鳴光電子回折における大門効果を説明した。

研究成果の学術的意義や社会的意義
超高速原子・電子現象の研究は、物質の基本的な動的過程を理解する上で非常に重要なテーマである。　本プロジェクトでは、そのような超高速過程の一つである1フェムト秒以下で起こる表面からの光電子放出遅延現象についての理論的考察に進展が見られた。さらに、共鳴光電子回折の正確な理論を初めて開発した。この手法により、低消費電力電子デバイスの実現が期待されるスピントロニクス材料の磁気的・電子的状態を調べることができる。

研究成果の概要（英文）：In this project we have made good progress in the understanding of the photoemission process for (1) time delay and (2) resonance effect upon core-level excitation. (1) By directly comparing the solution of the time-dependent Schroedinger equation with a multiple scattering calculation in a one-dimensional model, we have shown how Wigner delay theory can be generalized from atoms to solids. Second, we have explained the oscillations of the time delay as a function of energy, observed in photoemission from Cu, by ab initio calculations [Optica 4, 1492]. (2) We have developed a theory and computer code for angle-resolved photoemission/photoelectron diffraction at core-level resonances of 3d metals by combining atomic multiplet theory and multiple scattering [J.Phys.Soc.Jpn 87, 061007]. We have fully reproduced the experimental resonant photoemission spectra of Ni(111), and have explained the recent, first observation of the Daimon effect in resonant photoelectron diffraction.

研究分野：物性Ｉ

キーワード：光物性　表面　界面

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

1. Background（研究開始当初の背景）

Photoemission is one of the most important experimental methods for our understanding of the electronic structure of matter. In recent years, the instrumentation has made tremendous progress, in terms of energy, angle and time resolution as well as the speed of data acquisition. This experimental progress must be matched by advances in theory. Especially (i) the sub-femto-second dynamics of the photoemission process and (ii) core-level resonance effects are still poorly understood. About (i) there is now a rather good understanding for the case of photoemission from gas phase atoms, through direct solution of the time-dependent Schrödinger equation (TDSE). However, for the technologically much more important case of photoemission from solids, the numerically very heavy TDSE cannot be solved, and strong approximations are needed. Usually the true crystal potential by some one-dimensional model potential. While this approach can give good physical insight, it is insufficient for understanding material dependent properties. About (ii), there is a rapidly increasing amount of high-resolution resonant photoemission data for various kinds of materials. At a core-level resonance, the photoemission intensity gives chemically and site-resolved information about the valence electronic states [P. Krüger et al. Phys. Rev. Lett. 108, 126803 (2012)]. However, the interpretation of angle-resolved resonant photoemission is very difficult without comparison with theory. When we started our project, there was no good computational method available.

2. Aim（研究の目的）

In part (i) of the project we tried to find an alternative route for understanding the time-delay in photoemission, such that a realistic description of the surface becomes possible. Rather than solving the numerically very heavy TDSE, we want to obtain the photoemission time-delay from stationary scattering theory. That this is possible in principle was shown long ago by E. Wigner. The Wigner time-delay concept has been successfully applied to gas phase atoms, but never to large molecules or solids. Therefore, the main challenge was to find a way how to generalize the Wigner time-delay theory to solids.

In part (ii) our aim was to develop a theoretical method and a computer code for angle-revolved resonant photoemission spectra for materials relevant for spintronics applications. At project application time, we focused on the topologically (Rashba-type) BiAg surface alloy, where strong resonant effects had apparently been observed recently. However, after reexamination, the resonance effect turned out to be very small, and therefore we changed our plan somewhat, by focusing on nickel, an important ferromagnetic material for which angle-resolved resonant photoemission has recently been measured.

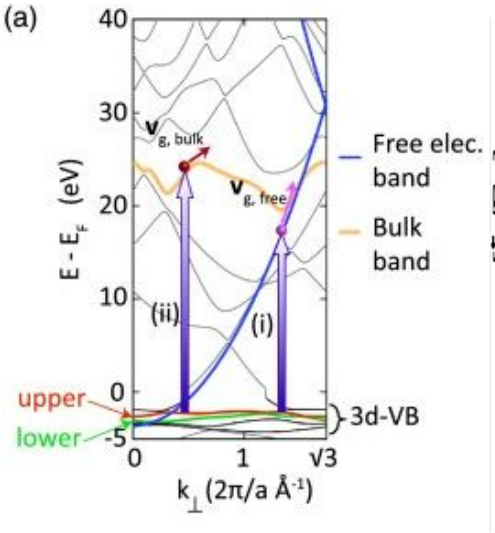
3. Methods（研究の方法）

We have used various theoretical methods, including numerical solution of the time-dependent Schrödinger equation with the Runge-Kutta method, exact diagonalization of the crystal-field multiplet model, as well as multiple scattering theory. For resonant photoemission, we have written a new code and have combined it with the multiple scattering software EDAC for the diffraction of the emitted electron.

4. Results（研究結果）

(1) Theory of time delay in photoemission from surfaces.

① We have met most of our objectives and have made good progress especially along the following two lines. We have done theoretical calculations for estimating the photoemission time-delay from a copper surface, measured through atto-second pump-probe experiments by our colleagues at the ETH and University Zurich, Switzerland. To this end, we have computed the band structure of copper using density functional theory along special, curved lines in the Brillouin zone which correspond to the experimental photoemission angles. The copper bands were calculated over a large energy range from valence band initial states to 40 eV above the Fermi level, see Fig.1. The group velocity of the outgoing photoelectron was computed from the band dispersions of the final state bands, using a computer code that we have written for this purpose. From the calculated group velocity the time-delay of the emitted photoelectron could be estimated. Depending on the energy of the Laser light, good agreement with experiment was obtained with group velocities calculated either from the band structure or from a free electron model, This indicates that the excited electron needs some time before its motion is affected by the crystal potential. If this time is larger than the escape time, the photoelectron dynamics is well described by free electron model. This work was published in the high impact factor (9.3) journal Optica [1].



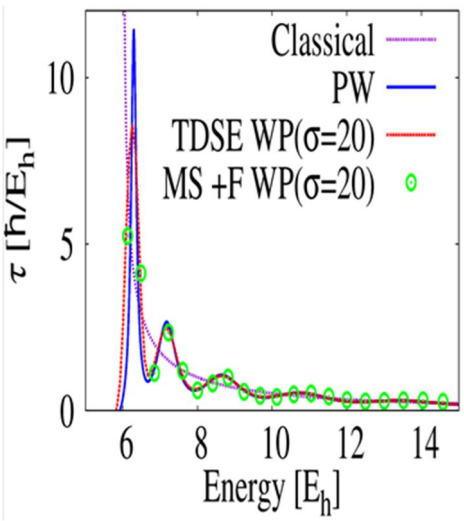


Fig.1 Cu band structure and group velocity　　*Fig.2 Time delay for single barrier scattering*

② We have studied and developed theoretical methods in order to generalize the Wigner time-delay to solids. First, we computed the time-delay of an electron, which is scattered at an array of potential barriers, by numerically solving the time-dependent Schrödinger equation (TDSE) for a wave packet in one dimension (Fig.2). Depending on the width of the wave packet, the time delay of an array of barriers may scale differently with the number of barriers. For largely spaced barriers the total time-delays is just the sum of the time-delays of the individual barriers. For wave packets larger than the barrier spacing, multiple scattering interference effects are strong. We found that for an infinitely large wave packet (i.e. a plane wave), the time delay can be obtained from the scattering phase shifts in a multiple scattering calculation.

This is a simple generalization of the Wigner delay to solids. The only change is that single atom phase shifts are replaced by multiple scattering phase shifts. However, this method is not accurate enough for narrow wave packets or low photoelectron energies. Therefore, a second scheme was developed which consists in computing the wave function amplitudes by multiple scattering over some energy range and then reconstructing the total phase shift of the wave packet as an energy integral. According to our tests, this way always leads to time-delays in agreement with the TDSE. This method will be implemented in our photoemission programs in the near future.

(2) Resonant photoemission of spintronics materials

In this part of the project we have met our main objective by developing a new theory for angle-resolved resonant photoemission. Resonant photoelectron and Auger electron emission is a second order process, including an optical excitation and an Auger-type decay due to electron-electron scattering. We have focused on photoemission at the core-valence resonance of a transition element, where the resonance effect is large and gives information about the magnetic state of the ion. Because of the atomic-like nature of the core-level, the resonant spectra provide an atom-projected picture of the valence state which is very useful for active site analysis. For the energy and angle-dependence of the resonant spectra, the following two points are crucial. (i) The strong electron correlation effect in the 2p-3d excitation and Auger decay process which gives rise to a complex energy spectrum with many-electron multiplet splittings. (ii) The scattering of the photoemitted electron by the neighboring atoms which leads to clear diffraction patterns at single crystal surfaces and can be used to identify the emitter site. In this project we have developed the first theory of resonant photoemission which describes well both effects (i,ii). This was done by combining a many-electron atomic multiplet calculation program for the local resonant process, with a single or multiplet scattering calculation for the propagation of the emitted electron. The multiplet program was written from scratch. The final state energies and photoelectron wave function amplitudes so obtained were used as input for a photoelectron diffraction calculation carried out with the EDAC software. We have applied the new method to 2p3d3d and 2p3p3d resonant Auger emission from a Nickel (111) surface, which has been measured recently [F. Matsui et al. Phys. Rev. B 97, 035424 (2018)]. As seen in Fig. 3, the energy spectrum is well reproduced in the calculations, which proves that the atomic multiplet approach is well justified. We next focused on excitation with circularly polarized light, because circular dichroism is a good probe of local magnetic moments. We have analyzed the angular momemtum transfer from the light to the resonantly emitted electron. We found that the amount of angular momentum transfer depends very much on the binding energy through the final state multiplet, i.e. the spin and orbital moment of the ionized atom. For certain energies, the angular momentum of the emitted electron can even be opposite to that of absorbed light. Such a reversed angular momentum transfer has been observed by F. Matsui et al. in the Ni 2p3p3d spectra and our theory fully explains the experimental data. A publication summarizing our results is in preparation.

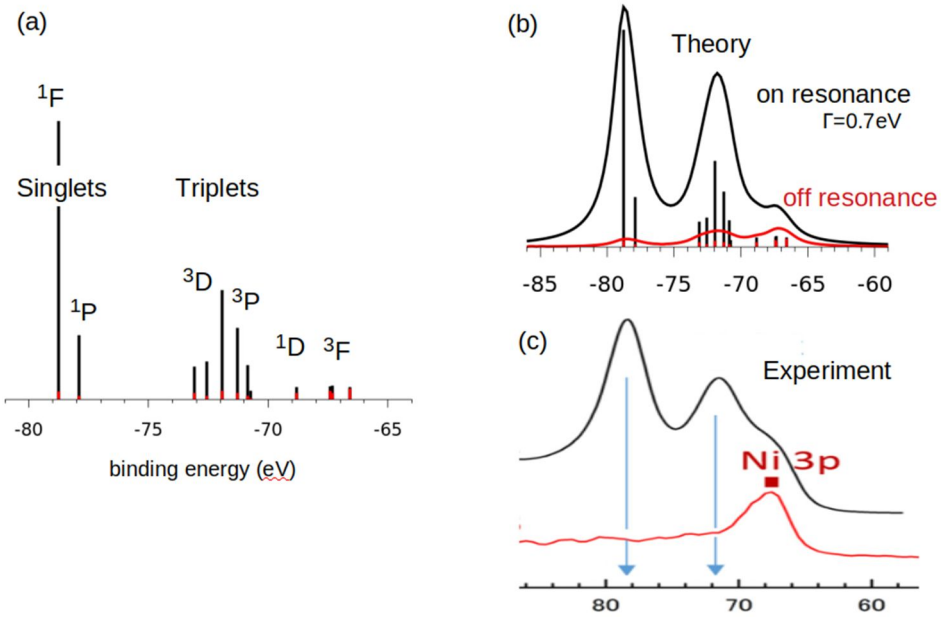


Fig.3 Ni 2p3p3d resonant photoemission: (a) calculated line spectra (b) broadened spectra (c) experiment.

(3) Further results obtained in the process of developing new theories for (1,2)

① In the search for a good calculation method for angle-resolved photoemission, we have conceived a new scheme, where the photoelectron wave function is constructed from density functional theory supercell calculations, which is very accurate and flexible. All wave functions are computed in the supercell method and matched to the free-electron photoelectron states at some distances from the surface. The method was implemented in a one-dimensional model and gave good results for normal emission from graphene [3].

② Focusing on oriented molecules, we have compared different schemes used for final state wave function, namely the plane-wave approximation, the independent atom approximation and full multiple scattering calculations. We have found that the popular plane-wave approximation can give good results for parallel emission but completely fails to account for the polarization dependence of the intensity patterns [4].

③ For the atomic multiplet calculations, we have developed a method for computing ligand field parameters. Usually, these parameters are obtained by a fit to the experimental data. This is impossible for low-symmetry or multi-site systems. In our new method, the parameters are easily obtained from a standard density functional theory calculation. We have tested the method for transition metal oxides and metal phthalocyanines and have obtained very good results in all cases [5].

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１．著者名 C. R. Natoli, P. Krueger, Y. Yoshimoto, J. Bartolome and F. Bartolome	４．巻 98
２．論文標題 Simple model of the ground state and spin-orbital excitations of free and adsorbed Fe(II) phthalocyanine molecules	５．発行年 2018年
３．雑誌名 Phys. Rev. B	６．最初と最後の頁 195108
掲載論文のDOI（デジタルオブジェクト識別子） 10.1103/PhysRevB.98.195108	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Peter Krueger,	４．巻 175
２．論文標題 Ab initio calculation of ligand field multiplet parameters for transition metal L-edge spectra	５．発行年 2020年
３．雑誌名 Radiat. Phys. Chem.	６．最初と最後の頁 108051
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

―

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考