Many Body Effects in Elementary Processes Occurring at Solid Surfaces

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INTRODUCTION

In this talk we will give a brief survey of some elementary processes observable at surfaces that manifest many body effects. We begin our survey by discussing how the electron ground-state would look like in real-space at surfaces and also the mechanism behind why the surface electrons behave and look (in reference to their real-space image) as they do in the ground-state. Next we will discuss how these electrons behave when perturbed by external fields lasting for ultrashort periods of time. We then follow this with a discussion of how the dynamics of electrons would then affect the motion of adsorbates (atoms/molecules on a solid surface). Finally we will cite some possible immediate technological applications possible with this knowledge of elementary processes involving the so-called many-body effects. We will also discuss some of the possible trends or directions in doing scientific research in this century.

OVERVIEW & MOTIVATION

Recent and future trend in surface science is and will be towards an understanding of the dynamical nature rather than the static nature of processes occurring on surfaces. The latter is of course important and gives support to the study of the former. The basic rationale as to why we need to study the dynamical nature of these processes and why this would be of general interest is as follows:

Let us consider how dynamical processes proceed around us. A slight change (e.g., induced by light irradiation) in electronic states making up a solid surface interacting with atoms or molecules gives rise to a slight change in the position of atoms and molecules which in turn initiates further a marked change in the electronic states. Eventually the dynamical process of atoms or molecules proceeds on the surface. This is properly regarded as the development of surface dynamics and could be an essential mechanism behind all kinds of dynamics involving complex systems around us on the earth including those concerning various life forms. Thus in order to deepen our understanding of dynamics in complex systems it is necessary to clarify the fundamental mechanism behind the dynamics that is to study each elementary process. The most important breakthrough we can achieve towards a thorough understanding of all the dynamics occurring around us would come from an accurate understanding of the elementary processes in which mass charge and energy transport play important roles.

Now with recent advances in experimental techniques in the field of surface science we are at the stage where we can prepare well characterized solid surfaces which in a sense serve as *playgrounds* for physics. The solid surface provides us with a stage to study the dynamics of complex systems where state transitions of the corresponding electron system are closely connected with changes of atomic and molecular motion on various scales of magnitude with respect to time, space and energy. For this reason it is not only interesting but also necessary and important to study the excited as well as the ground states of the electron system making up a system of interacting surface and atoms and molecules.

We will start off by considering the dyr.amics of surface electrons as the temperature $T \rightarrow 0$ K (the electron ground state!) in Part 3. We will then consider the

dynamics of electrons perturbed by external fields with ultrashort time scales in Part 4. We then follow this by considering how the dynamics of atoms or molecules adsorbed on surfaces is affected by these ultrafast electron dynamics.

HOW ELECTRONS AT SURFACES LOOK AS $T \rightarrow 0K$

One manifestation of the effect of magnetic impurities has been known since the early 1930s. This is the observation of a resistance minimum (van den Berg, 1964) as a function of temperature T in some metals. The electric resistance monotonically decreases with decreasing temperature until some critical temperature at which it increases with further decrease in temperature. A very significant advance in the theory of magnetic impurities was an explanation of this phenomenon by J. Kondo in 1964. Kondo showed, using perturbation theory, that this was a result of many body effects (scattering of conduction electrons near the Fermi level) due to local and dynamical interactions of the conduction electrons with a single magnetic impurity with an associated spin moment which leads to a - ln T contribution to the resistance. The - ln T term increases at low temperatures and when this term is included with the phonon contribution to the electric resistance (in most metals the resistance monotonically decreases with decreasing temperature because of the dominance of phonon scattering which decreases rapidly at low temperatures) it is sufficient to explain the observed resistance minimum. Hence the solution of a long-standing puzzle.

However there were difficulties with the theory. Note that because ln T terms diverge as $T \rightarrow 0$ Kondo's perturbation calculations could not be valid at low temperatures. A more comprehensive theory was needed to explain questions such as—What would be the actual low temperature ($T \rightarrow 0$) behavior of electron systems showing resistance minima, i.e., what would be the ground state of the electron system of a dilute magnetic alloy? The search for such a theory opened a new and fascinating field of research for many body condensed matter physics and became known as the *Kondo problem* (Yosida, 1996; Hewson, 1993; Cox & Zadowski, 1999). From then on starting with the ground state properties and resistance near absolute zero temperature several physical quantities were clarified. Starting with Wilson's solution (Wilson, 1975) which was valid for all temperature ranges, one after the other exact solutions (Andrei et al., 1983; Tsvelick & Wiegmann, 1983; Okiji, 1988) to the two basic models used to study dilute magnetic alloys *viz.* the *s-d* model and the Anderson model were discovered in the early 1980s. These studies confirmed the generality of earlier perturbation theory results and further resolved fundamental problems related to the Kondo effect relevant to a single magnetic impurity. Since then numerous systematic and extensive studies of a variety of physical properties e.g., magnetism and superconductivity of heavy electron systems were made as an extension of the Kondo impurity system. Results of these studies have greatly benefited other fields of condensed matter physics especially studies on high critical temperature T_c superconductivity.

Surface science has also made, and is continuing to make, major contributions to a better understanding of the Kondo problem. True to the saying— *A picture is worth more than a thousand words* we are now at the stage where a real space image of the Kondo effect could be realized with the aid of the scanning tunneling microscope (STM). In 1993, almost 30 years after Kondo solved the puzzle regarding the resistance minimum phenomenon, Crommie et al. (1993) studied the behavior of an Fe adsorbed on Cu(111) with the aid of an STM. Operating the STM at constant-current mode at temperature $T = 4$ K, they scanned a region of the surface 130 Å × 130 Å in area with the Fe centered in this region. The corresponding STM image of this region showed a central main peak structure at the location of the Fe and concentric standing waves about Fe. These concentric standing waves are a result of the in-teraction/interference between the conduction electrons scattered by the Fe. The height of the standing wave is distinguishable to within 0.01 Å which gives us an idea of the high degree of resolution attainable with STMs! By modelling the Fe as a cylindrically symmetric scattering potential they were able to derive an expression for the change in the local density of states (LDOS) at the Fermi level $\in_F$ surrounding the Fe, and reproduce the standing wave structure observed *far from the Fe* (with surface lateral distances r [Å] > 20 Å from Fe) in the STM image. In addition to this they also

measured the corresponding density of states distribution (*dI/dV vs. V* curve). Since the Fe/Cu(111) system is one *classic* example of a dilute magnetic alloy showing the Kondo effect, the measured density of states distribution as well as the *sharp peak structure* observed at the position of the Fe motivated studies (Kawasaka et al., 1998; 1999; Kasai et al., 2000; Diño et al., 2000) on finding a means of observing the Kondo effect, in particular the Yosida-Kondo peak (Yosida singlet state) in real space with the aid of the STM. A few years later Manoharan et al., (2000) actually succeeded in obtaining a real-space image of the Yosida-Kondo peak for the system Co/Cu(111) (*cf.* Fig. 1(c) of Manoharan et al., 2000) using the same procedure suggested earlier (Kawasaka et al., 1998; 1999; Kasai et al., 2000; Diño et al., 2000). For a more detailed discussion on "How Electrons at Surfaces Look as $T \rightarrow 0$K" we refer the readers to Kawasaka et al. (1998 & 1999); Kasai et al. (2000) and Diño et al. (2000).

ULTRAFAST ELECTRON DYNAMICS STUDIED BY TIME-RESOLVED TWO-PHOTON PHOTOEMISSION SPECTROSCOPY

How would electrons on metal surfaces respond when perturbed with external fields with ultrashort time scales? It has been one of the long-standing dreams of surface scientists to resolve this fundamental question since ultrafast dynamical processes involving electron dynamics in the metal affect chemical reactions and optical responses at the surface. Let us consider for example photon-stimulated desorption. Initially we photoexcite the electrons of the metal surface at/on which atoms and molecules (adsorbate) are adsorbed. Subsequently the adsorbate gains enough kinetic energy to desorb from the surface through energy and charge transfer between the metal and the adsorbate due to electronic transitions (Mizuno et al., 1994; Tsuchiura et al., 1997). However since the excited electrons relax in a very short time—femtosecond (10^{-15} seconds) time scale—it is very difficult to track down the dynamics of electrons in ultrafast surface processes. Fortunately recent progress in femtosecond laser technology has revolutionized the study of ultrafast dynamics. One effective experimental method for studying ultrafast electron dynamics is time-resolved two-photon photoemission (time-resolved 2PPE TR2PPE) spectroscopy.

In TR2PPE spectroscopy, the metal surface is irradiated with pump and probe laser pulses, and then the intensity of the photoelectron emitted from the surface is measured as a function of the photoelectron energy and pump-probe delay time (TR2PPE spectrum). First a pump photon excites an electron from an initial state below the Fermi level into an intermediate state above the Fermi level (hence a hole is excited/created at the initial state level). Then the electron density in the intermediate state decreases at a rate described by a lifetime due to electron hopping between the substrate metal and the adsorbate and various scattering processes, e.g., electron-electron and electron-phonon scattering and electron scattering at impurities and defects. Next, a probe photon excites the electron in the intermediate state into a final state above the vacuum level and hence the electron is emitted from the surface.

By analyzing (Sakaue et al., 1998; 2000; 2001; Sakai et al., 2001) the correlation trace (photoelectron intensity as a function of the pump-probe delay time) in the TR2PPE spectrum, we can obtain information on the temporal evolution of the electron density in the intermediate state. The correlation trace becomes symmetric (auto-correlation trace) when the pump and probe photons have the same energy and polarization and it becomes asymmetric (cross-correlation trace) when the pump and probe photons have different energies or polarizations. Usually the auto-correlation trace is considered to contain information on both *energy relaxation* and *dephasing* while the cross-correlation trace is considered to contain information on energy relaxation only (Petek & Ogawa, 1997). In quantum optics of atoms and molecules in the gas phase insulators and semiconductors, relaxation of the photoexcited electron and the hole is mainly due to recombination of the electron and the hole. Energy relaxation describes decay of the density of the electron-hole pair due to recombination. On the other hand dephasing describes loss of coherence of the partial system consisting of the electron-hole pair due to elastic scattering of the electron-hole pair by quasiparticles in the reservoir, e.g., scattering by other atoms and molecules in the gas phase and that by phonons in the

insulators and semiconductors. In metals on the other hand, the picture of energy relaxation and dephasing is not convenient for analysis of the TR2PPE spectrum. The photoexcited electron and the hole in the metal are scattered by the *cold Fermi sea* (electrons below the Fermi level) and hence new electrons and holes are excited. As a result the electrons and the holes have energy dependent lifetimes whose qualitative features can be understood from Landau's Fermi liquid theory (Abrisokov et al., 1965). In general 2PPE processes in metals are more complicated than outlined above since the probe photon not only excites the photoexcited electron but it can also excite new electrons as a result of scattering. Therefore it is a crucial theoretical problem to develop the method of analysis (Sakaue et al., 1998; 2000; 2001; Sakai et al., 2001) of the TR2PPE spectrum. For a more detailed discussion of the theory on Ultrafast Electron Dynamics Studied by Time Resolved Two-Photon Photoemission Spectroscopy we refer the readers to Sakaue et al. (1998; 2000; 2001), and Sakai et al. (2001). For a list of some of the notable achievements in experimental studies of electron dynamics in metals by TR2PPE spectroscopy and theoretical studies on the analysis of the TR2PPE spectrum, we refer the readers to Petek & Ogawa, 1997.

ADSORBATE DYNAMICS INDUCED BY STM — E.G., CO DESORPTION FROM CU(111) AND ACETYLENE ROTATION ON CU(001)—

Continuing on and developing over the question we asked earlier in the beginning of Part 4 how would adsorbates respond in turn when the corresponding electron system is perturbed by some external fields and forced to make a transition from the ground state of the electron system to an excited state? What physical mechanism governs the motion induced?

As we have mentioned earlier with the emergence of the STM, it is now possible to perform highly accurate spectroscopic and spatial studies of electronic transition induced adsorbate motion. For our discussion of electronic transition induced adsorbate motion we will consider two systems which are of particular interest to us *viz.* the STM-induced desorption of a single CO from Cu(111) (Bartels et al., 1998) and the STM-induced rotation of a single acetylene on Cu(001) (Stipe et al., 1998) and discuss the mechanism behind the corresponding adsorbate motion induced from a microscopic point of view (Hasegawa et al., 1998; 1999; 2000; 2001) where state transitions of the corresponding electron systems are closely connected with changes of molecular motion on various scales of magnitude with respect to time space and energy.

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