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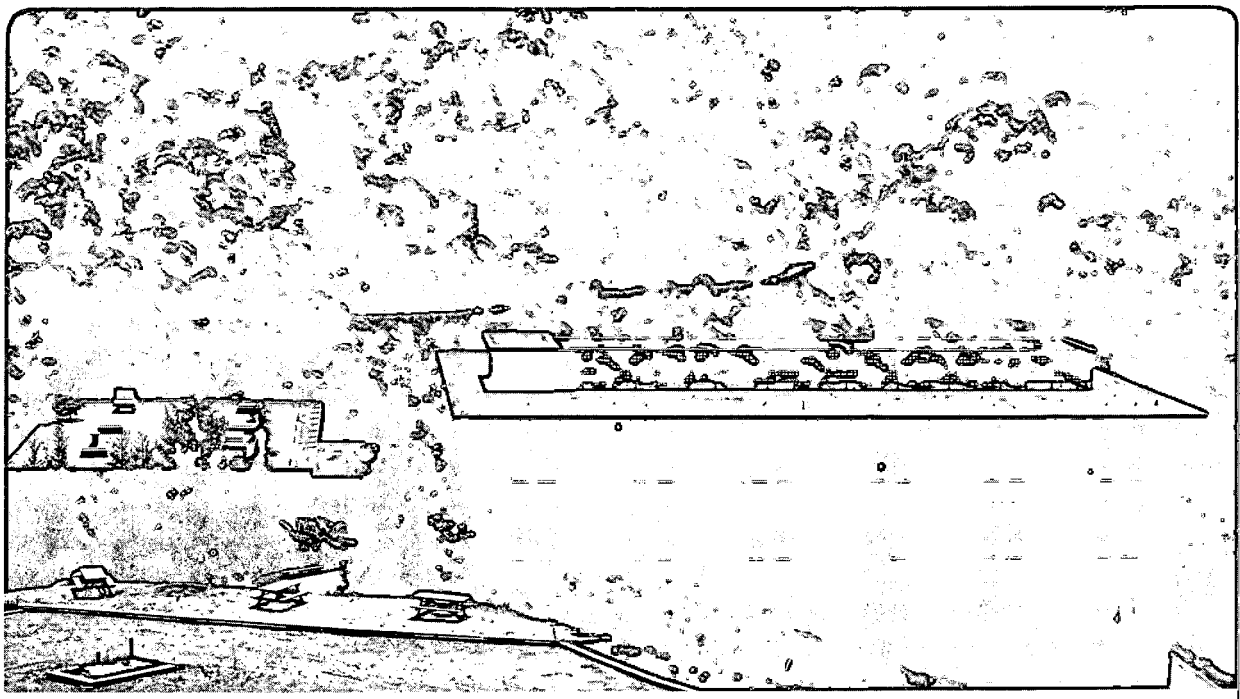

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THEORY FOR SPIN-POLARIZED ELECTRON CAPTURE SPECTROSCOPY IN FERROMAGNETIC NICKEL*

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THEORY FOR SPIN–POLARIZED ELECTRON CAPTURE SPECTROSCOPY IN FERROMAGNETIC NICKEL

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A time-dependent many-body theory is developed for the study of spin-polarized electron capture spectroscopy. As a model system we choose the head-on collision of protons with a nickel atom. For the electronic part of the Hamiltonian we use the most general on-site interaction terms allowed by atomic symmetry. The total electronic many-body states are group-theoretically classified with respect to the conserved quantum numbers L, L_z and S_z. The time-dependent Schrödinger equation for this system is solved exactly. The zero-, one- and two- electron capture probabilities which are treated on the same footing are monitored along the trajectories of the scattering species on the femtosecond time scale. In good agreement with experiments on surfaces we find probabilities of 22% and 0.33% for one- and two-electron capture respectively and spin polarizations between - 60% and -100%. The predominant capture of minority electrons is enhanced due to electronic correlations. This implies that the probing of magnetism occurs on a significantly longer time scale than the probing of single electron properties.

1. Introduction

For more than one decade spin-polarized electron capture spectroscopy (ECS) has been used to study various magnetic properties of ferromagnetic surfaces of transition and rare earth metals, as well as thin magnetic epitaxial structures[1]. In ECS, energetic (typically 1 to 200 keV) cations (typically H^+, D^+, or He^{++}) are scattered from surfaces or thin films under grazing incidence angles (below 1°). The outgoing channels consist of ions scattered without change of their charge state as well as of particles having picked up one electron of either spin (one-electron capture, OEC) or two electrons at a time (two-electron capture, TEC) from the substrate. ECS is surface sensitive as electrons can escape only from the first few substrate layers and it probes long-range *ferro*magnetic order in OEC as well as short-range order(in TEC). The interpretation of the existing ECS experiments is hampered considerably: i) The final state analysis is difficult and not always reliable. ii) The correspondence between the electronic structure of the solid surface or heterostructure and the spin polarization of the captured electrons is unclear. There is a considerable lack of theoretical understanding of the electron capture process.

In this paper, we address the latter question in a fundamental way. Thus, we study the head-on scattering of protons from a single nickel atom in detail. For this model system, we formulate the time-dependent many-body theory and solve the Schrödinger equation exactly on the femtosecond time scale. This approach has three advantages: i) By the restriction to head-on collisions we separate the artifact of kinematic selection rules[2,3] from the physics of the electron capture process itself. ii) We do not rely on any perturbational expansion neither in the hopping integral between the nickel atom and the proton[4] nor in the Coulomb correlation on the nickel or hydrogen atom[4] but treat the correlations exactly[5]. Thus we need not know the relevant correlations in advance (as in the case of Auger processes[6]). In our case of electron capture spectroscopy the nickel–hydrogen hopping probes these correlations on a characteristic time scale of 10^{-15} seconds. iii) In solving the exact time-dependent many-body Schrödinger equation along the projectile trajectory we do not resort to approximations like the infinite Landau–Zener or complex Born–Oppenheimer theory. The complex Born–Oppenheimer theory, although simple in its form and easy to handle, violates –strictly speaking– quantum mechanics as the optical potential of the Hamiltonian is not norm-conserving[4].

2. Theory

The many-body Hamiltonian which governs the time evolution of our system reads in the hole picture

$$
\begin{aligned}
H = \quad & E_d \sum_{m,\sigma} d^+_{m\sigma} d_{m\sigma} + \sum_{\substack{i,j,k,l \\ \sigma,\sigma',\sigma'',\sigma'''}} U_{i\sigma,j\sigma',l\sigma''',k\sigma''} d^+_{i\sigma} d^+_{j\sigma'} d_{k\sigma''} d_{l\sigma'''} \\
& + E_s \sum_{\sigma} s^+_\sigma s_\sigma + U_H n^s_\uparrow n^s_\downarrow + U_{\mathbf{R}} \sum_{m,\sigma,\sigma'} n^d_{m\sigma} n^s_{\sigma'} \\
& + \sum_{m,\sigma} t_m(\mathbf{R})(d^+_{m\sigma} s_\sigma + s^+_\sigma d_{m\sigma}) + V(\mid \mathbf{R} \mid) \sum_{m,\sigma} d^+_{m\sigma} d_{m\sigma}. \qquad (1)
\end{aligned}
$$

The first two terms are the Hamiltonian for interacting holes on the Ni atom alone, similarly the third and fourth terms refer to interacting holes on hydrogen, the fifth term contains the intersite hole–hole repulsion and the sixth term means the single hole hopping between nickel and the projectile 1s orbitals. The seventh term denotes the nuclear interaction.

We consider five different Ni $3d$ orbitals and one hydrogen 1s orbital. These 12 spin-orbitals are occupied by 9 electrons or, alternately, by 3 holes. By allowing for three hole configurations $3d^1 \otimes 1s^2$, $3d^2 \otimes 1s^1$ and $3d^3 \otimes 1s^0$ corresponding to $Ni^0 + H^+$, $Ni^+ + H^0$, and $Ni^{++} + H^-$, we take into account zero-, one- and two-electron capture, respectively. The choice of the $3d^1$ configuration for the neutral ground state of the Ni atom is in agreement with recent calculations[7]. For statistical reasons, there exist 220 possibilities to distribute 9 electrons or 3 holes in 12 spin-orbitals, thus the Fock space contains 220 states. As the "good" quantum numbers L_z and S_z are conserved in head-on collisions we classify the basis set with respect to L, L_z and S_z applying Russel-Saunders (or $L \cdot S$) coupling. The predicted terms are ^2D for the $3d^1$ configuration, ^1S, ^3P, ^1D, ^3F, and ^1G for the $3d^2$ configuration, ^2P, ^4P, ^2D (twofold), ^2F, ^4F, ^2G and ^2H for the $3d^3$ configuration, ^1S for the $1s^0$ and $1s^2$ configurations and ^2S for the $1s^1$ configuration. The number of physically relevant states is considerably reduced by conservation laws and symmetries. Thus only 52 states are left. Note that the calculation of these three-hole states by applying the Clebsch-Gordan algebra requires that the antisymmetrization be performed for the orbital and spin functions as a whole. These steps will be described elsewhere[8].

The parameters of the Hamiltonian are taken from spectroscopic tables for Ni, H and NiH. It has to be pointed out that in head-on collisions the z-component of the angular momentum is conserved and equal to zero in s-d hopping processes. Thus, only $t_0(\mathbf{R})$ is different from zero.

Setting up the second quantized Hamiltonian H_{ij} in the basis of 220 states and then transforming it to the smaller basis set is mainly a question of bookkeeping except for the treatment of the nickel on-site Coulomb interaction:

To set-up the most general atomic Hamiltonian allowed by symmetry (for the Ni atom) we have to go beyond the approach by Kleinman and Mednick[9] and by Oleś and Stollhoff[10] who take into account only those terms where two *pairs* of indices are equal. Instead, we allow for general contributions containing *four different* indices. For details of this calcu-

lation we refer again to a forthcoming publication[8]. As a by-product of this calculation and in contrast to earlier work[9,10], we get the correct degeneracies of the spectroscopic terms of the nickel atom.
The calculation of the projectile trajectory is the familiar classical mechanics problem (for head-on collisions without angular momentum)

$$t(R) = \int_{\overline{R}}^{R} \frac{dR'}{\sqrt{\frac{2}{m}(E_{kin,\perp} - V(R'))}}, \tag{2}$$

$$\text{with } V(R') = \frac{2(28\overline{U}(R') - 2\pi \int_0^{R'} dR''(R'' \mid \psi(R'') \mid^2 (\mid R' + R'' \mid - \mid R' - R'' \mid)))}{R'} \tag{3}$$

consisting of self-consistent Hartree-Fock potential and outermost electron correction. $\overline{U}(R)$ and $\psi(R)$ are taken from *ab initio* calculations[11].
For the trajectory, there are two underlying assumptions: i) The classical description of the ionic motion is adequate. This assumption is supported by calculations for electron stimulated desorption of hydrogen[4]. ii) The Born-Oppenheimer decoupling of electronic and ionic degrees of freedom in the Schrödinger equation is justified in view of the small electron-proton mass ratio and the relatively small velocities of the projectile in the vicinity of the distance of closest approach where most of the electronic hopping processes occur.
Assuming i) and ii) we formulate the time dependent Schrödinger equation for the real and imaginary parts of the 52 basis states. As the Hamiltonian commutes with the quantum numbers L_z and S_z the 104 (real) equations of motion decouple in systems of 18, 18, 22, 22 and 24 coupled differential equations (for all times). These differential equations are solved numerically along the projectile trajectory on the femtosecond timescale and the important and experimentally accessible physical properties of the system such as particle position, occupation numbers of the various states, spin-polarization, etc. are monitored as a function of time.

3. Results and Discussion

Fig. 1 shows the sum of the occupation numbers of all the many-body states belonging to neutral hydrogen as a function of time for a fixed initial Ni state. These curves represent the probability of an incoming proton to be found as neutral hydrogen after the time t. The trajectory was chosen according to the situation of Rau's[1] first experiment (E_{kin} = 150 keV at 0.2° angle of incidence). For this trajectory the distance of closest approach (corresponding to time zero) is 1.25 Å and the elementary time step is 0.05 fsec. The most physical case is the full line of Fig. 1 for intermediate hopping which gives a neutral hydrogen yield of 22 % in very good agreement with Rau's experiment. In this case the hopping was taken to be exponential with parameters fitted to the optical spectrum of NiH but levelled off to a constant value for distances smaller than the interatomic equilibrium distance of nickel hydride (the charge density cannot grow any more inside the core). The hopping leading to the dashed curve in Fig. 1 grows exponentially even for very small internuclear distances and thus overestimates the charge transfer. It becomes clear that the smaller the hopping is the less quantum oscillations of the capture process

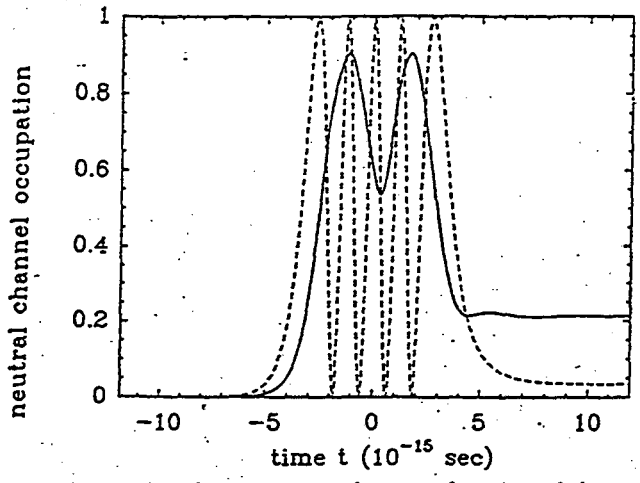

Fig. 1 Neutral hydrogen occupation as a function of time

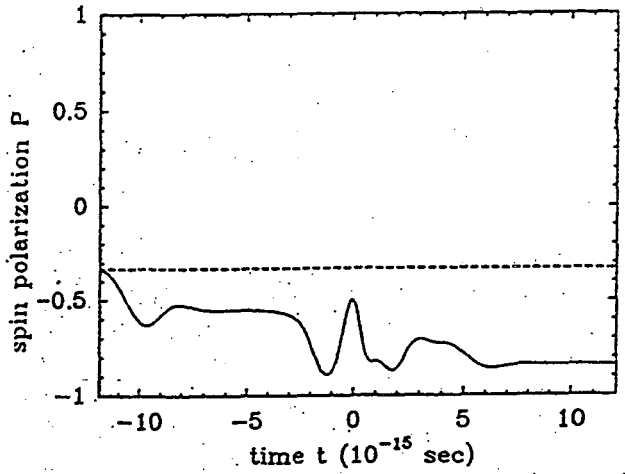

Fig. 2 Spin polarization as a function of time (see text).

occur. The two-electron capture probability (for the physical case) is about 0.33% and agrees well with recent theoretical and experimental data for $H^-/Al(111)$[3,12].
Concerning the spin polarization of the captured electrons, we find typical values between -60 % and -100 % (in good agreement with experiment). Fig. 2 shows the time dependence of the spin polarization which corresponds to the full line of Fig. 1 and ends up at -82 %. If we neglect hole-hole onsite correlations we always obtain a spin polarization of -33 % (dashed curve). Thus correlations enhance the absolute value of the spin polarizations. Furthermore the final value of the spin-polarization is immediately reached without correlations no matter how small the amount of transferred charge is whereas correlations act with some delay (the full curve also starts at -33 %). Thus the probing of magnetism as a phenomenon of correlated electrons requires significantly more time than the probing of single electron properties.
The resulting highly negative spin polarization (captured from a nickel atom of majority spin polarization!) also shows that electron capture is a complicated many-body process. But even without intraatomic correlations the capture of minority electrons is favored due to the angular momentum selection rules (Clebsch-Gordan coefficients). Thus it becomes clear that ECS i) neither simply probes the spin-polarization at the Fermi-level ii) nor has to reflect the capture of sp-electrons if negative spin-polarization is encountered[12]. There is only one exception where the spin polarization is for all times exactly +100% (with and without correlations): If the initial hole is in the $(3z^2\text{-}r^2)$-orbital the Pauli principle forbids any other spin polarization. This corresponds to a dangling bond surface.

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