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Towards mapping atomic orbitals in the TEM

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Directly imaging orbitals is possible using a scanning tunneling microscope (STM) [1]. However, this is an intrinsically surface-sensitive technique. As such, it is used mainly for investigating adsorbents or surfaces but cannot be used for studying, e.g., defects in the bulk, grain boundaries, interfaces, etc.

In this work, we propose a way to visualize atomic orbitals — or rather the transition probabilities between an occupied and an unoccupied (antibonding) state — by means of transmission electron microscopy (TEM), electron energy loss spectrometry (EELS), and particularly energy-filtered TEM (EFTEM). With modern TEMs, chemical analyses using EFTEM can readily achieve atomic resolution [2]. Thus, the logical next step is to investigate the possibilities of boosting the resolution to sub-atomic distances in last-generation aberration corrected instruments.

To that end, we performed simulations of EFTEM images, including both elastic and inelastic scattering effects. The central quantity for these simulations is the mixed dynamic form factor (MDFF)[3-4]. It can be used to describe inelastic scattering in a density matrix formalism, which has the advantage of not only modeling single wave functions, but also the correlations between different states and the entanglement between probe and target states.

To simplify the MDFF, we show how it can be interpreted as a quadratic form, regardless of the transition orders investigated. Consequently, the whole theory of quadratic forms can be applied to the MDFF. In particular, a principal axis transformation can be used to diagonalize it. This corresponds to a description in a symmetry-adapted basis which is chosen such that all correlation effects between different states vanish. This facilitates the numerical simulations, but also greatly helps in the physical interpretation of both the underlying physics and the resulting images. Figure. 1 shows an example of transitions that are correlated in a spherical harmonics basis, but clearly show p character in the symmetry-adapted new basis system.

The theoretical framework of diagonalizing the MDFF is applied to a number of systems. Examples include energy-loss magnetic chiral dichroism (EMCD) or the imaging of defects in graphene. Of particular interest is rutile TiO_2 which exhibits a tetragonal distortion giving rise to an e_g–t_{2g} splitting. These are perfect conditions to image transitions between orbitals. Figure. 2 shows a simulated EFTEM image under typical illumination conditions for two different energies. The two images show a 90° rotation consistent with the excitation of p_x and p_y type transitions expected in those energy regions.

Another interesting application is the mapping of asymmetries due to the presence of defects in the crystal structure. As an example, we calculated the electronic properties for graphene with two vacancies and then simulated an EFTEM map of the C K-edge. As expected, we find that the effect of the vacancy is to induce an asymmetry in the p_y orbital of the nearest neigbour carbon atoms, leaving those atoms in an environment similar to pure graphene essentially unaffected.

From these simulations, it is clear that mapping transitions between orbitals can be achieved in the near future. This will give rise to many exciting new possibilities, including the direct imaging of the electronic properties of grain boundaries, defects, or interfaces.

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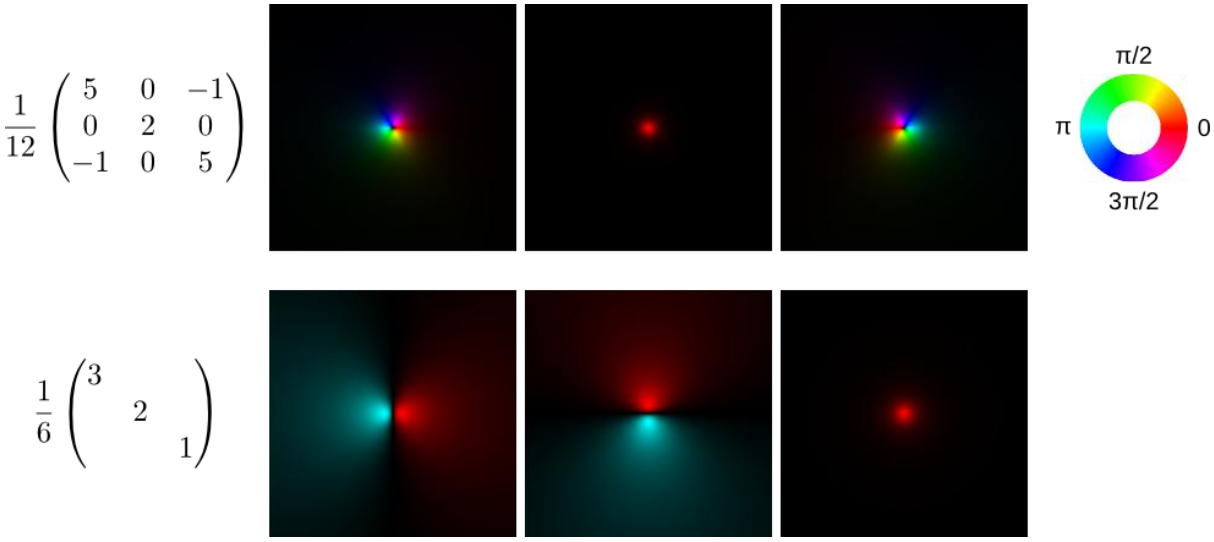

Figure 1. Example of dipole-allowed transitions that are correlated in a spherical harmonics basis (top), but become independent in the symmetry-adapted new basis (bottom). The matrices show the relevant subset of the MDFF matrix while the images show the real space wavefunctions of the basis states. The amplitude is given by the brightness, while the phase is color-coded according to the color wheel on the right.

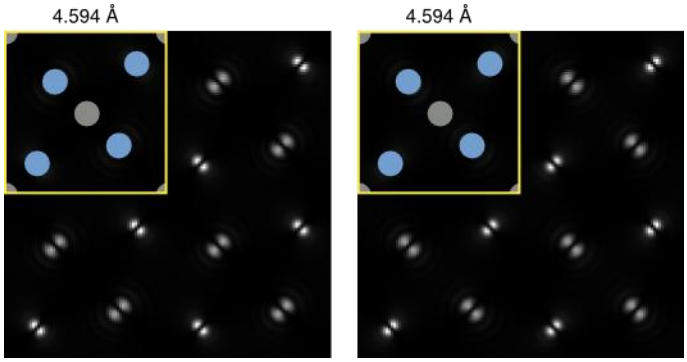

Figure 2. Simulated high-resolution EFTEM images for the O K-edge in a one unitcell thick rutile sample oriented along the [001] zone axis under ideal imaging conditions. The left image shows the situation 4 eV above the edge onset, the right image shows the situation 7 eV above the edge onset. The inset shows the projected unit cell with oxygen atoms in blue and titanium atoms in gray.