Stable Covalent Bonding Between Two Closed-Shell Atomic Orbitals

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Interactions between two fully occupied atomic orbitals are conventionally expected to be repulsive because both the bonding and antibonding molecular orbitals are occupied, resulting in zero bond order[1]. Here, we demonstrate that proximity to a metallic substrate can qualitatively alter this picture and stabilize a covalent interaction between two atoms with closed-shell valence orbitals. Using scanning tunnelling microscopy, atom manipulation, inelastic electron tunnelling spectroscopy, and first-principles calculations, we investigate Ho dimers manually assembled on two monolayers of MgO on Ag(100). Individual Ho atoms possess fully occupied, atomic-like 6s orbitals and show no spin excitations within the investigated energy range[2][3]. In contrast, Ho dimers exhibit intense spin-flip excitations between approximately 60 and 130 meV. The spatial distribution and energy of these excitations, combined with electronic-structure calculations and a tight-binding model, identify an unpaired electron in an antibonding molecular orbital derived predominantly from the Ho 6s states. We show that formation of this state results from partial depopulation of the antibonding orbital through coupling to the metallic substrate. The resulting imbalance between bonding- and antibonding-state occupations produces a net attractive covalent interaction despite the closed-shell character of the isolated atoms. Furthermore, changing the adsorption-site coordination modifies atom–substrate hybridization and systematically tunes the spin-flip excitation energy. These results reveal a substrate-enabled mechanism for covalent bond stabilization between surface adsorbates and illustrate how interfaces can fundamentally modify chemical bonding at the atomic scale.

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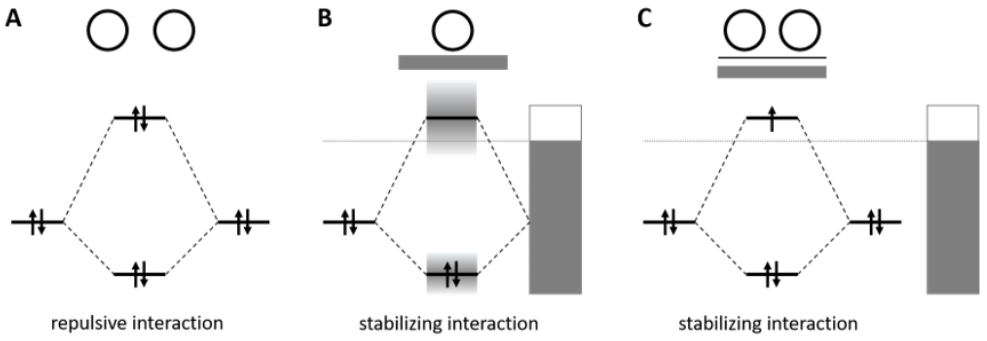

Figure 1. Covalent interactions between fully occupied orbitals. A) Schematic representation of covalent interaction between two atoms with fully filled atomic orbitals. The net interaction in an isolated system is repulsive. B) Interaction of a filled molecular orbital with a filled band of a metal surface. Antibonding states are depopulated as they reach above the Fermi level (indicated by the dashed grey line) resulting in a net-bonding interaction. C) Covalent interaction between two atoms with filled atomic orbitals, bound at a thin insulating film on a metal surface. The antibonding molecular orbital is depopulated as it rises towards the Fermi level stabilizing the adsorbate-adsorbate bond. The emergence of this mechanism is demonstrated on the example of two Ho atoms interacting on 2ML MgO/Ag(100).