Adsorption of cobalt on graphene: a quantum chemical perspective

A.N. Rudenko¹, F.J. Keil¹, M.I. Katsnelson², and A.I. Lichtenstein³

¹Institute of Chemical Reaction Engineering, Hamburg University of Technology, Eißendorfer Str. 38, D-21073 Hamburg, Germany
²Institute for Molecules and Materials, Radboud University Nijmegen, Heijendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
³Institute of Theoretical Physics, University of Hamburg, Jungiusstraße 9, D-20355 Hamburg, Germany <u>rudenko@tu-harburg.de</u>

Magnetic properties of graphene attract considerable attention because of their potential use in spintronics. One of the natural ways to induce magnetic moment in a closed-shell system is to include magnetic impurities, such as transition metal (TM) atoms, to the system. Apart from being magnetic, TM adatoms deposited on graphene may also give rise to a variety of many-body effects [1], which stimulated considerable theoretical activity in the description of the TM/graphene systems in recent years.

In contrast to molecular closed-shell adsorbates or light monovalent impurities, theoretical investigation of TM adatoms on graphene is more challenging due to the presence of strong electron correlations. The results of the commonly used density functional theory (DFT) are controversial and strongly depend on the parametrization of the exchange-correlation functional. In order to take into account the effects of electron correlations in a more systematic way in this study, we apply the multiconfigurational complete active space self-consistent field formalism (CASSCF) to the investigation of the electronic structure and chemical bonding of the cobalt adatom supported on graphene.

In Fig. 1 we show potential energy curves obtained for different electronic configurations of cobalt on graphene. As can be seen, the electronic structure of cobalt undergoes several transitions upon adsorption, giving rise to two prominent minima located at the distances of 1.5 and 3.1 Å from the surface $(3d^9s^0 \text{ and } 3d^7s^2 \text{ configurations}, \text{ respectively})$. The hybridization between graphene and cobalt orbitals in the $3d^7s^2$ configuration is weak and the bonding is of the van der Waals-like type. As the occupation of the 4*s* orbital decreases, the 3*d* orbitals start to hybridize with the π orbitals of graphene, lowering the energy. Both minima are fairly close to each other and do not exceed 0.5 eV in absolute values. This is significantly smaller than the adsorption energy predicted by the DFT studies (1-2 eV) [2], but consistent with experimental observations of very fast surface diffusion of metal atoms on graphene [3].

As a next step, we analyze obtained results in terms of a mean-field model Hamiltonian, which involves the intraorbital and interorbital Coulomb interactions U and U' as well as the interorbital exchange coupling J at the 3d cobalt orbitals. The energies obtained at the CASSCF level for different electronic configurations of cobalt allow us to extract information on the magnitude of these parameters. We find that the exchange interaction varies only slightly as cobalt approaches the surface and bounded within 1.1 - 1.15 eV. In contrast, the interorbital Coulomb repulsion U changes significantly from ~6 eV in the dissociation limit to ~2.0 eV at the distance of 1.5 Å. In the intermediate region (the $3d^8s^1$ state) the U parameter varies between 3.0 and 4.5 eV.

Although obtained adsorption energy curve for cobalt on graphene is not trivial and involves several states of the adatom, the electronic configuration of cobalt can be reproduced for different distances within the LDA+*U* approach by varying the on-site Coulomb repulsion. Indeed, in the regime of small *U* our results, in respect to the cobalt state $(3d^9s^0)$, are similar to that obtained within the DFT using the standard LDA (GGA) functional [2,4]. On the other hand, the results of intermediate *U* $(3d^9s^1)$ are comparable with the GGA+*U* [5] or hybrid functional calculations [6]. Therefore, previously reported inconsistency between the GGA and GGA+*U* methods does not indicate a failure of one of these approaches, but only implies that they describe different adsorption regimes.

References

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Figures



Fig. 1. Potential energy curves obtained for different electronic configurations of cobalt on graphene. Solid line is the total adsorption energy curve. Zero energy corresponds to the energy of non-interacting graphene and a cobalt atom in its ground state $(3d^74s^2, S=3/2)$.