Supplementary Information: The nature of bonding and electronic properties of graphene with iridium adatoms

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The diagonalization algorithm in VASP, Davidson block iteration scheme, produced discontinuous potential energy curve and even diverged at some distances using standard settings in VASP, due to the multi-reference nature of the system (see manusript). We attempted to improve the convergence and we increased the width of the smearing σ, which determines how the partial occupancies are set for each orbital. Partial occupancies can stabilize a self-consistent cycle that otherwise would oscillate instead of converge, when there are several orbitals close to the Fermi level.[1] We employed Gaussian and Fermi-Dirac broadening of partial occupancies, which should in principle yield the same result. The results are displayed in Fig. 1b. The smearing of 0.5 eV stabilized the self-consistent cycle and provided continuous potential energy curve. However, the absolute values of the total energy lie above the total energies in Fig. 1a, and, in particular, the total energies obtained with Gaussian and Fermi-Dirac broadening differ by a large amount of the energy. This behaviour illustrates the problems occurring when finite-temperature density functional theory is applied to such systems. First, one should be aware that the free energy $F = E - TS$ is the variational quantity in finite-temperature calculation instead of the total energy E. The electronic entropy term TS will of course favour degenerate solutions of the Kohn-Sham problem. This is exactly what happens in Figure 1b; large broadening leads to degenerate partial occupancy of iridium d-states, whereas the calculation depicted in Figure 1a correctly uses only the low-lying levels.

Second, in order to obtain the energies from finite temperature calculation, it is necessary to extrapolate the results from finite smearing to $T \to 0$ results. Grotheer and Fahnle[2] rigorously showed that $(F(\sigma) + E(\sigma))/2 = E_0 + O[\sigma^4]$. The T^4 dependence of the correction of the ground-state energy E_0 allows to use relatively large broadening σ. The energies extrapolated from Fermi-Dirac and Gaussian broadening of 0.5 eV coincide near equilibrium distances, however disagree at distance larger than 3 Å. Broad Fermi-Dirac smearing caused too large occupancy in the spin-down part of the eigenvalue spectrum, resulting in unphysical net magnetic moment of 1.8 μ for the Ir atom isolated by 7 Å from benzene (the quartet state of Ir should have 3 μ). Therefore, narrow enough broadening should be used in order to minimize artificial degeneracy of states near the Fermi level.

We finally obtained convergent and continuous potential energy curve by setting the value of σ to 0.01 eV and by switching to all bands simultaneous diagonalization instead of iterative approach in blocked Davidson algorithm. The simultaneous diagonalization of all bands was considerably slower, but prevented oscillatory convergence of self-consistent cycle in the critical distance region between 3 and 5 Å. Resulting potential energy curves do not depend on the broadening used and are displayed in Figure 1c.

References

1 M. Springborg, R. C. Albers and K. Schmidt, *Phys. Rev. B*, 1998, **57**, 1427.
2 O. Grothheer and M. Fahnle, *Phys. Rev. B*, 1998, **58**, 13459.

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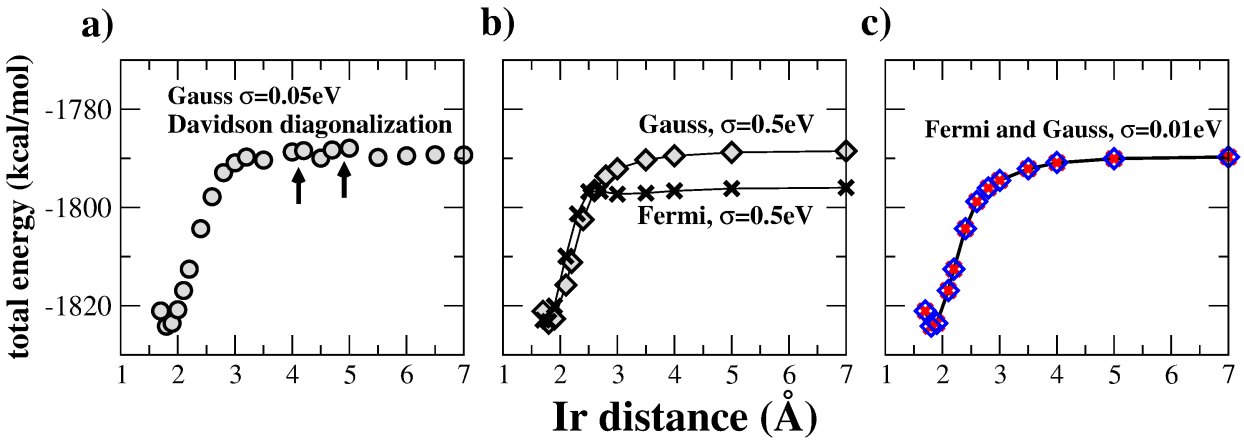

Fig. 1 The interaction energy of the Ir-benzene complex as a function of Ir distance calculated by traditional PBE functional using various diagonalization and smearing schemes: a) iterative diagonalization algorithm in connection with rather narrow smearing width of 0.05 eV leads to oscillatory convergence at distances between 3 Å and 5 Å, b) broad smearing of 0.5 eV causes unphysical lowering of the total energy owing to forced degeneracy of Ir $d-$states, c) converged total energies are provided by all bands simultaneous diagonalization.