What can multireference spin-orbit calculations tell us about Ni+CO spin crossover reaction?

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The interaction between CO molecule and transition metal surfaces has interested chemists in two aspects: 1. due to practical applications in CO_2 reduction catalytic reactions and 2. due to basic interest in the nature of bonding given by the Dewar-Chart-Duncanson model[1,2] of σ donation and π back donation. To understand the basic building block, the interaction between a single TM atom and CO has been extensively studied using various quantum chemistry methods. Of the 3d TM atoms, the reaction between CO and Ni atom is interesting because the lowest energy pathway involves a spin crossover: Ni(triplet $3d^9 4s^1$) + CO(singlet) → NiCO(singlet $^1\Sigma^+$), where a triplet spin state reactant ends up as a singlet product. Furthermore, because the Ni atom has ten valence electrons, there are many low-lying electronic states which make this association reaction very complex. In many of the previous calculations, density functional theory (DFT) methods with minimum energy pathway (MEP) were utilized. In this MEP method, one connects the lowest energy spin state at each relative geometry and defines an effective potential energy curve that has varying spin states along the way. Then spin-orbit interaction is evaluated at the crossing points of two varying spin-state potential energy curves. In the present calculation, we will perform spin-orbit interaction calculation along the whole association process and compare it with the MEP curves.
Multireference configuration interaction (MRCI) using the orbitals from11 state average complete active space of 16 electron 12 orbital active space were used to calculate the adiabatic potential energy curve along the colinear Ni+CO association. At each geometry, we diagonalized the spin-orbit coupling matrix element using these MRCI wavefunctions. When we compared the binding energy of NiCO, we found that the MEP DFT methods using hybrid functionals gave energies consistent with the MRCI results. On the other hand, generalized gradient approximation gave 1 eV over binding. So energetically, MEP hybrid DFT can give good results; however, we found that Ni(triplet $3d^9 4s^1$) + CO(singlet) → NiCO(singlet $^1\Sigma^+$), involves the spin-orbit coupling interaction of the $^3\Pi_0$ state (Ni occupation: $3d_{z^2}^2 3d_{xz}^2 3d_{yz}^1 3d_{xy}^2 3d_{x^2-y^2}^2 4s^1$) and the open shell $^1\Sigma^+$ state (Ni occupation: $3d_{z^2}^1 3d_{xz}^2 3d_{yz}^2 3d_{xy}^2 3d_{x^2-y^2}^2 4s^1$). This was different from the MPE picture, which involved the $^3\Sigma^+$ state connecting to the $^1\Sigma^+$ state. Since there is no spin-orbit coupling among these states, the MEP gives good energies but with the wrong physics.

References:

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