Non-iterative method for constructing accurate antibonding orbitals

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While bonding molecular orbitals exhibit constructive interference relative to atomic orbitals, antibonding orbitals show destructive interference. When full localization of occupied orbitals into bonds is possible, bonding and antibonding orbitals exist in 1:1 correspondence with each other. Antibonding orbitals play an important role in chemistry because they are frontier orbitals that determine orbital interactions, as well as much of the response of the bonding orbital to perturbations. In this work, we present an efficient method to construct antibonding orbitals by finding the orbital that yields the maximum correlation orbital using second-order perturbation theory and compare it with other techniques with increasing the size of the basis set. We show how these orbitals are accurate and meaningful in electronic structure, basis set independent, and are useful to improve valence bond methods, construct efficient active space, and work as good guesses for excited states. Those can also be used to construct an effective minimal basis, which can be used for molecular properties and analysis such as population analysis. We examine an interesting chemical example of BeHCl in which the minimal basis is not very well defined with the other traditional methods.