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Simple avoidance of Pauli repulsion error in the generalized hybrid orbital (GHO) method

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Introduction

We assess transformation matrices in the combined quantum mechanical and molecular mechanical (QM/MM) method based on generalized hybrid orbitals (GHO). In addition to the previous ones, we examine a restrained transformation matrix based on the assumption that all coefficients of the p -hybridized orbitals are uniform and each hybridized orbital points toward a vertex of a tetrahedron. It is clearly shown that the new implementation improves the accuracy of the GHO method reducing the error concerning the Pauli repulsion about auxiliary orbitals.

Method

A. The original GHO scheme^{1,2}

In the GHO method, a set of hybridized orbitals is constructed from the s - and p -valence orbitals at the boundary atom. The transformation matrix relating the hybrid and atomic orbitals is a product of rotation and hybridization matrices. Rotation matrix is built by using three unit vectors \mathbf{x} , \mathbf{y} , and \mathbf{z} obtained from the given geometry of the boundary and the neighboring MM atoms. \mathbf{x} is chosen to be perpendicular to the plane formed by three unit vectors in the directions from the boundary atom to the MM atoms. The vector \mathbf{y} and \mathbf{z} are constructed to be perpendicular to \mathbf{x} . The hybridization matrix offers four orthonormal hybrid orbitals and is determined from the amplitudes of the s - and p -components of the active orbital obtained from the direct cosine between \mathbf{x} and the unit vector from the boundary to one of the neighboring atoms.

B. Modified transformation by Eckard et al.³

Recently, Eckard and Exner modified the transformation matrix such that the active orbital points toward the QM atom connected to the boundary atom. \mathbf{x} is chosen to have the same direction from the boundary atom to the QM atom and the equation to get the amplitudes of s and p orbital components becomes

$$\frac{c_s^2}{c_p^2} = -\frac{\mathbf{x} \cdot \mathbf{m}_1 + \mathbf{x} \cdot \mathbf{m}_2 + \mathbf{x} \cdot \mathbf{m}_3}{3}$$

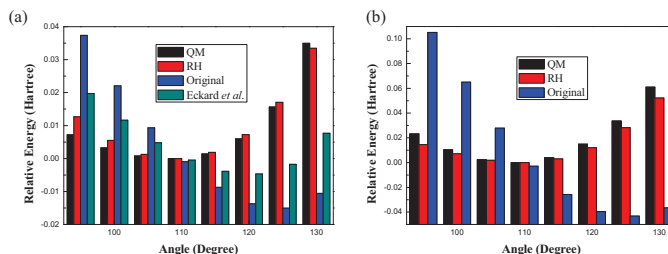
where \mathbf{m}_1 , \mathbf{m}_2 , and \mathbf{m}_3 are unit vectors from the boundary atom to each neighboring MM atoms.

C. Restrained hybridization⁴

In the GHO method, the Pauli repulsion forces over the GHO auxiliary orbitals are underestimated due to their partial occupations. This fact causes systematic errors in energy profile concerning the neighboring atoms, e.g. the optimized structure is largely deviated from the exact tetrahedron even for methane. Adjustment of the energy profile generally requires heavy parameterizations of non-bonded interactions. Nevertheless, there exists a simple alternative of using a restrained hybridization (RH) matrix with all the amplitudes of s orbital components fixed to the values in the ideal sp^3 hybridization limit, i.e. $c_s = \frac{1}{2}$.

Result and Discussion

For the simplest example, we check the energy profile of methane with the carbon atom as the boundary and three hydrogen atoms as neighboring MM atoms using the aug-cc-pVDZ basis set and OPLSAA force field. We examine the energy profiles by changing one and all of the QM-boundary-MM angles, respectively. The energy profiles of the original GHO hybridization are largely deviated from the full QM one. The error is reduced substantially by the present hybridization with restraint. The scheme of Eckard *et al.* also improves the performance for the anisotropic distortion of the geometry (a) while the method coincides with the original GHO for the simultaneous change of the angles (b)



We also investigate the optimized geometries of ethane and alanine dipeptide. In both the ethane and the alanine dipeptide, the original hybridization of GHO overestimates the bond angles including the boundary and QM atoms. RH clearly reduces the error in the optimized structure.

Molecule (basis)	Connectivity	QM	Original GHO	RH
Ethane (cc-pVDZ)	C – C – H	111.255	121.755 (10.500)	110.697 (-0.558)
Alanine dipep. (cc-pVDZ)	C – C – N	109.788	120.990 (11.202)	108.387 (-1.401)
	C – C – H	108.678	121.979 (13.301)	110.075 (1.397)
	C – C – C	111.438	119.388 (7.950)	108.155 (-3.283)

Reference

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