



## Effect of the size of the quantum region in a hybrid embedded-cluster scheme for zeolite systems

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### ABSTRACT

Recently we presented an improved scheme for constructing the border region within the covEPE hybrid quantum mechanics/molecular mechanics (QM/MM) embedded cluster approach for zeolites and covalent oxides in the framework of the elastic polarizable environment method. In the present study we explored how size and shape of the embedded QM cluster affect the results for structural features, energies, and characteristic vibrational frequencies of two model systems, adsorption complexes of H<sub>2</sub>O and Rh<sub>6</sub> in faujasite frameworks that contain Brønsted acid sites. Comparison of calculated characteristics of different QM cluster models suggests that the local structure and vibrational frequencies of acid sites in adsorbate-free zeolite are well reproduced with all embedded QM clusters, which contain from 5T to 14T atoms. A proper description of systems with an H<sub>2</sub>O adsorbate requires larger QM clusters, with at least 8T atoms, whereas vibrational frequencies of OH groups participating in hydrogen bonds demand even larger quantum clusters, preferably with 12T or 14T atoms. The structure of the metal particle in adsorbed rhodium species is well reproduced with all QM clusters scrutinized, from 12T atoms. Larger QM models, with 18T or 24T atoms, are recommended when one aims at a high accuracy of Rh–O and Rh–H distances and characteristic energies.

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### 1. Introduction

Hybrid quantum mechanics/molecular mechanics (QM/MM) methods are chosen for their computational efficiency and accuracy, when one wants to model large systems, from complexes and biomolecules [1] to inorganic materials [2,3]. Key features of these methods are the size of the embedded QM cluster and the treatment of the border between the QM and MM partitions of the system. Assuming convergence of the results with increasing size of the QM partition, computational economy will select the smallest QM cluster that yields essentially the same results as larger clusters. Therefore, successful practical application of a specific QM/MM scheme requires one to understand how the method performs when one varies the size of the QM cluster. Of course, such convergence may depend to some extent on the problem under study, e.g. on the size of the adsorbate investigated or the properties modeled.

Probing energy characteristics of acidic zeolites, Sierka and Sauer [4] studied this type of convergence for the hybrid QM–Pot method, which invokes a subtraction scheme on the basis of separate QM and MM calculations [4,5]. They found calculated deprotonation energies of bridging OH groups of zeolites (with FAU and MFI structure) to vary by only 6 kJ/mol between models containing QM clusters with 2T (2 tetrahedral framework atoms) and 28T atoms. Also, the calculated chemisorption energy of ammonia on bridging hydroxyls of FAU-type zeolite was essentially constant (within 1 kJ/mol) for model systems with 3T, 5T and 9T QM clusters. Thiel and co-workers [6] showed that specific spectral parameters, such as <sup>51</sup>V NMR chemical shifts in a vanadium-containing enzyme, can be correctly described with a hybrid QM/MM model. Employing four model systems with QM clusters increasing from 19 to 94 atoms, they demonstrated that the NMR chemical shift can be predicted even with a small QM region, provided that the electrostatic effect of the environment is included at least via an array of suitable atomic charges.

Recently we proposed the hybrid density functional/molecular mechanics (DF/MM) method covEPE (covalent elastic polarizable environment) [7–9] for modeling covalently bonded silica-based

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materials by embedding clusters in an elastic polarizable environment. Directional bonds in the border region are saturated by special oxygen centers that are described by charged halogen-like pseudo potentials that form only one covalent bond to the QM region. These pseudo potentials were adjusted [9] to minimize distortions of the electronic structure of the QM region due to the MM treatment of the environment. In previous works we found the covEPE scheme suitable for modeling electronic and geometric properties of separated active sites of various zeolites (CHA, FAU, MFI), including pure silicalite as well as zeolites doped with Al and Ti atoms at framework positions [7–11]. In the present work we studied for two types of model systems how size and shape of the embedded QM cluster of the covEPE method affect structural features, energies, and characteristic vibrational frequencies. For this purpose, we considered adsorption complexes of H<sub>2</sub>O and Rh<sub>6</sub> species in cavities of FAU zeolite. In the first case, two hydrogen bonds of the adsorbate, with the bridging OH group of the zeolite and a basic oxygen center, determine the location of the guest species; therefore, it is important to account adequately for mechanical as well as electrostatic aspects of the interaction between the adsorption complex and the surrounding zeolite framework [12]. The second set of test systems addresses small metal particles which are important active catalytic sites in zeolite cavities [13,14]. The bonding of such metal species to a zeolite framework and the hydrogenation of such metal particles due to their interaction with acidic hydroxyl groups of the support are central issues in this context [11].

## 2. Computational details

### 2.1. Method

Embedded cluster calculations were carried out with the hybrid DF/MM method covEPE [7–9], which was developed especially for modeling zeolites and other covalently bonded silica-based materials. As the main characteristics of the covEPE embedded-cluster scheme have previously been described in detail [7–11], we summarize here only main features:

- At variance with most other QM/MM schemes (ONIOM, QM-pot, etc.) [1,5], the covEPE method does not use H atoms to cap dangling bonds of the QM cluster, but invokes specially adjusted charged monovalent oxygen pseudoatoms, O\*, with seven valence electrons. To ensure proper polarization of O\* centers, described with a flexible basis set, we chose to endow Si atoms in the MM region, which bind to O\*(QM) centers at the QM/MM boundary, with a repulsive pseudopotential (without an orbital basis set); we refer to those centers as Si<sup>PP\*</sup>. In this way, one is able to avoid distortions of the wave functions as they occur in link-atom schemes where H atoms do not adequately represent the electronic environment of the border atoms.
- The QM and MM methods applied to represent the system are carefully chosen to provide similar structural descriptions for silicalite and aluminosilicate systems. This is accomplished by a special polarizable force field for the MM environment, which was parameterized on the basis of DF calculations with ionic charges that are consistent with the electrostatic potential produced in reference DF systems.
- The covEPE method completely and explicitly includes mechanical and electrostatic interactions between the QM cluster and its MM environment. It thus allows completely unconstrained optimizations of all structural degrees of freedom, not only within the QM and MM partitions, but also across the QM/MM border region between the two subsystems. Oxygen centers of the MM framework are also permitted to be polarized in a

shell-model fashion in response to changes of the charge distribution in the QM cluster; hence, the designation “elastic polarizable environment” for the embedding method.

- The covEPE method affords an energy expression which ensures full variationality; in addition, a correction scheme is applied similar to that of the EPE method for ionic solids [2].

Our approach for determining effective-core pseudopotentials is similar to that used to derive optimal neutral capping atoms (no electrostatic embedding) [2] or charged Si capping pseudoatoms (to account for electrostatic embedding effects) [3].

The calculations were carried out with the latest parameterization of the covEPE scheme [15] as implemented in the density functional program PARAGAUSS [16,17]. The MM part of all systems was described with a force field developed for modeling silica and protonated aluminosilicates [7,8]. The charge of the whole QM/MM system is balanced by assigning incremental point charge  $\Delta q_{pp}$  to O\* border pseudoatoms; these increments of  $-0.3 e$  are half of the charge assigned to oxygen centers in the MM region. These centers are parameterized to have an effective charge of  $-0.6 e$  [9]. The other centers at the QM/MM border, Si<sup>PP\*</sup> cations, which do not have a QM charge contribution, have the same effective charge,  $1.2 e$ , as their MM analogues Si(MM).

For electronic structure calculations we employed the linear combination of Gaussian-type orbitals fitting-functions density functional method (LCGTO-FF-DF) [18] with the gradient-corrected exchange–correlation functional BP suggested by Becke (exchange) and Perdew (correlation) [19]. The all-electron calculations on systems containing Rh were carried out at the scalar relativistic level as obtained in the Douglas–Kroll–Hess approach to the Dirac–Kohn–Sham equation where electronic and positronic degrees of freedom are decoupled to second order [20,21]. We pre-optimized structures with the recently proposed economic atomic Douglas–Kroll–Hess variant [22]. For comparison, we also report the results for the structure of one of the largest models optimized at the non-relativistic level (see Section 3.2).

The Kohn–Sham molecular orbitals of the QM partition were represented with Gaussian-type basis sets, contracted in generalized fashion: (6s1p) → [4s1p] for H [23,24], (9s5p1d) → [5s4p1d] for C and O [23,24], (5s5p1d) → [4s3p1d] for O\* boundary atoms [9], (12s9p2d) → [6s4p2d] for Al and Si [23,24]. The polarization *d*-exponents of Al (0.2881, 1.0084) and Si (0.50, 2.05) were taken from Ref. [25]. The basis set for Rh was derived by augmenting a set of quality (17s12p8d) [26] by two *s*- (0.01303, 0.2253), three *p*- (0.03666, 0.09165, 0.2291), and two *d*-exponents (0.04588, 0.1147); this set was contracted to [8s6p4d] using atomic Kohn–Sham eigenvectors from scalar-relativistic calculations. In the non-relativistic calculations for systems with an Rh<sub>6</sub> cluster, we used the same primitive basis set, but contracted it with eigenvectors from a non-relativistic calculation on Rh.

In the LCGTO-DF-FF method, one calculates the Hartree contribution to the electron–electron interaction by representing the electronic density with an auxiliary Gaussian-type basis set [18]. The exponents of this basis were determined by suitably scaling the exponents of the orbital basis. In addition, on each atom, “polarization” functions of *p*- and *d*-type were added as five-member geometric series with a factor 2.5, starting at 0.1 au (*p*-exponents) or 0.2 au (*d*-exponents). Only *p*-type polarization functions were used for H atoms.

As in previous studies [11,27,28], we applied C<sub>3</sub> symmetry constraints to reduce the computational effort when modeling faujasite-supported Rh<sub>6</sub> and Rh<sub>6</sub>H<sub>3</sub> species. All other calculations were carried out without any symmetry restrictions. Adsorption energies,  $E_{\text{ads}}$ , were corrected for the basis set superposition error (BSSE) with the counterpoise scheme [29] at the equilibrium

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