COMPUTATIONAL STUDIES OF SELF-TRAPPED EXCITONS IN SILICA

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Abstract

A brief review of electronic structure calculations of the properties of self-trapped excitons (STEs) in silica is presented. The focus has been on crystalline systems because amorphous systems, such as fused silica, pose a significant technical challenge. The tremendous growth in speed of computer processors and available memory has led to a new generation of ab initio computer codes capable of carrying out extensive calculations. The capabilities of these codes have also grown with regards to the sophistication of both basis sets, for wave function based methods, and pseudopotentials, for density functional methods. In particular, these codes have made calculations of excited states more accessible. Calculations of varying degrees of sophistication are presented including preliminary studies of STEs at surfaces and in amorphous structures. Previous ab initio calculations have been repeated with larger basis sets and more accurate calculation methods. The new results agree nicely with experimental results, thus further legitimizing the original predictions. Recent results also predict the presence of multiple STEs that may have low energy connective paths between them.

1. Introduction

Since the establishment of the existence of self-trapped excitons in both glassy and crystalline silica [1], there have been theoretical efforts to understand the nature of the self-trapping exciton. Theoretical efforts have lagged several years behind experimental work, largely due to the complexity and computational intensity of the electronic structure calculations. The first effective theoretical effort to describe the structural response of the lattice network to a triplet electronic excitation was done in 1988 by Shluger, for a β-cristobalite cubic crystal structure using a semi-empirical electronic structure calculation in the intermediate neglect of differential orbital approximation (INDO) [2]. Following this work, in 1990 Fisher, Hayes and Stoneham carried out an all-electron Hartree-Fock calculation using clusters of silica in an α-quartz configuration [3], thus establishing a direct connection between theory and experiment. These calculations largely established...
that the intrinsic STE of α-quartz with an emission at 2.8 eV was due to an oxygen displacement with an apparent breaking of one of the SiO bonds.

It was not until later in the decade, after density functional theory (DFT) computer codes for periodic systems became widely available and an accepted methodology [4] that a new effort to study STEs in silica was initiated. Part of the motivation came from the desire to understand the nature of the STE in glassy (or fused) silica. As part of this effort, the Vienna ab initio simulation program (VASP) [5], a periodic DFT code, was tested for its ability to verify the existence of an STE state in α-quartz, with surprising results. Consequently, we sought to verify the DFT results using wave function ab initio methods on silica clusters that were extracted from the periodic bulk structure. To this end, a combination of high level theories and more accurate basis sets were used to determine the emission energies of the triplet to singlet transition.

2. The STE in α-Quartz: Periodic Density Functional Theory Calculations

The DFT calculations were carried out using VASP [5]. VASP is a plane wave DFT code based on local-density approximation (LDA) and generalized gradient corrections (GGC) using the Perdew-Wang 91 (PW91) functional. In addition, the ultrasoft Vanderbilt pseudopotential (USPP) and spin polarization were used. The energy cutoffs were 29 Ry for the wave functions and 68 Ry for the augmented electron density. The Brillouin zone of the cell was sampled only at the Γ point. The system consisted of 72 atoms made up of 24 silicon and 48 oxygen atoms in a periodic orthorhombic cell, i.e. standard periodic boundary conditions (PBC) are used. Optimization of the structures was carried out using an iterative conjugate gradient minimization scheme.

The STE state in α-quartz was first calculated using a silica cluster configured to approximate the crystalline structure as much as possible [3]. The STE in a periodic system was expected to behave in a similar way. However, this is not what was found in a DFT-PW91 calculation [6]. If a triplet excitation is introduced in the perfect crystal configuration the excited electron and hole are observed to distribute themselves uniformly. The size of the periodic system is small, consisting of 72 atoms, and thus this infinite delocalization of the exciton is likely an artifact of the calculation. In a real system such a delocalization is expected to be over a small region of the bulk material. To find a self-trapped state, an oxygen atom was displaced to mimic the initial cluster result and then allowed to relax. This approach lead to a very different STE structure, one that mainly involves a Si-displaced structure instead of a O-displaced structure. Alternatively, other near neighbors were also displaced in an initial configuration and allowed to relax. Consequently, two STE states were found [6], neither of which has a configuration that looks like that found by Fisher et. al. [3].

In the cluster calculation, the initial triplet excitation is at a higher energy than the final relaxed STE state. In the DFT calculation, the initial triplet excitation of the perfect crystal (the delocalized state) is at a lower energy than any of the STE states thus far found. There is an implication that there exists a barrier between the delocalized and localized (self-trapped) states. The low energy delocalized triplet state is, however, most likely an artifact of the PW91 functional. There are issues regarding the ability of DFT to give the correct triplet to singlet transition energies based on the fact that DFT is known to give incorrect band gap energies. The band gap determined for SiO₂ is 6.1 eV, consistent