

# Surface effect on the electronic structure and optical properties of Cu in CdSe Quantum Dots



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## Introduction

Cu-doping in colloidal semiconductor quantum dots (QDs) modifies the photoluminescence (PL) properties [1]. The corresponding Cu PL peaks exhibit large Stokes shifts (200 meV) and large full width at half maximum (FWHM) linewidths (500 meV). The source of this inhomogeneities were ascribed to either electron-phonon coupling [2] or to site-dependent symmetries of local bonding [3]. In this work, we investigate using both DFT calculations and experimental measurements the influence of the position of copper dopants in CdSe QDs on their electronic structure, the absorption and PL spectra, and PL lifetimes.

## Methods

Properties of Cu ion in bulk and QDs CdSe with zinc blende structure are analyzed by GGA+U calculations using QUANTUM-ESPRESSO code [4,5]. The correct value of both the bulk band gap, 1.75 eV, and that of 1.8 nm QD, 3.4 eV are obtained when  $+U(\text{Cd}) = 5\text{eV}$  and  $+U(\text{Se}) = 3.2\text{eV}$ .  $+U(\text{Cu}) = 2\text{eV}$  are applied [6].

$\text{Cd}_{43}\text{H}_{78}\text{Se}_{43}$  QD with diameter  $\sim 1.8\text{ nm}$  is employed, where H are pseudo hydrogens. Vacuum layer amounts to  $\sim 1.5\text{ nm}$ .

We computed the excited state energies employing the constrained delta-self consistent field ( $\Delta$ -SCF) method.

The QDs were synthesized using a one-pot method [7, 8]. The PL signal was excited using a Hamamatsu C8898 pulsed laser (400 nm, 100 ps pulse).

## Results

### A. Electronic structure Cu in CdSe QDs

Cu-impurity states are localized on d(Cu) and p(Se) orbitals of the nearest Se atoms (Fig.1). The calculated density of states (DOS) are plotted in Fig. 1 b, c.

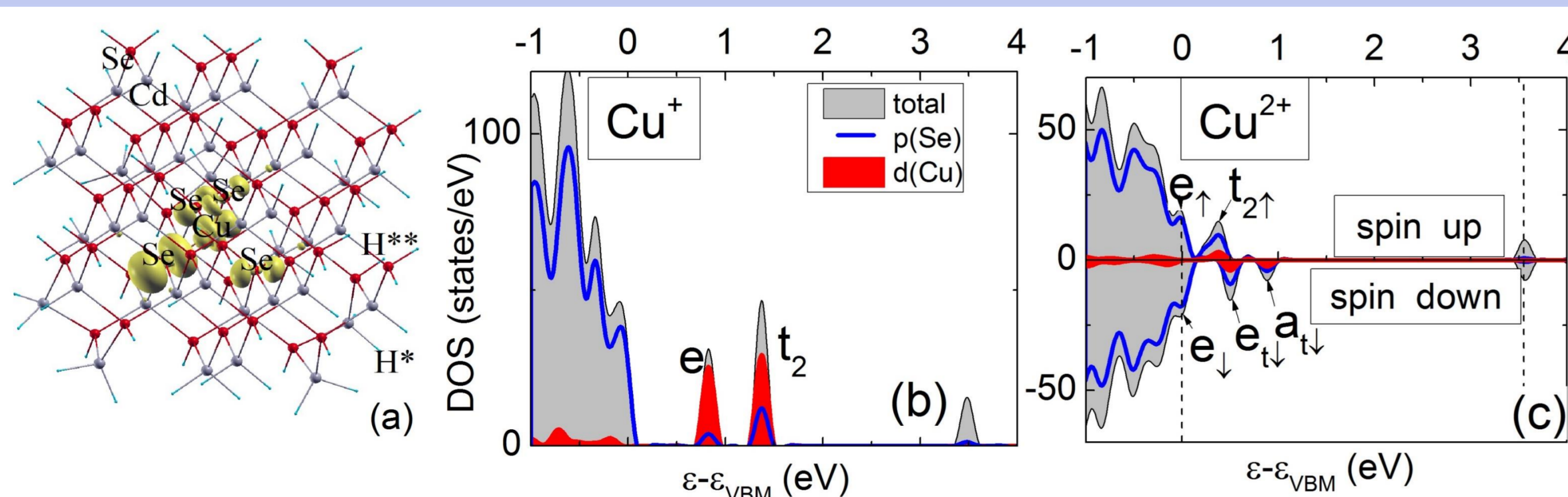


Fig. 1 (a) Spin density distribution of Cu<sup>2+</sup>-doped CdSe QD. DOS Cu<sup>1+</sup>-doped and (b) Cu<sup>2+</sup>-doped CdSe QDs with the impurities at the QD center.

### B. The impact of dopant location on electronic structure

The intra-gap Cu states move up towards the CBM as the impurity is moved further away from the center (Fig.2a,b). The shifts in energies are accompanied by shortening of the average Cu-Se bond lengths (Fig. 2c) and the enhancement of the contribution of the 3d(Cu) orbitals to the Cu impurity states (Fig. 2d). The spin-density distribution of Cu<sup>2+</sup> depends on the position of Cu relative to the center of QD (Figs. 2 e-g).

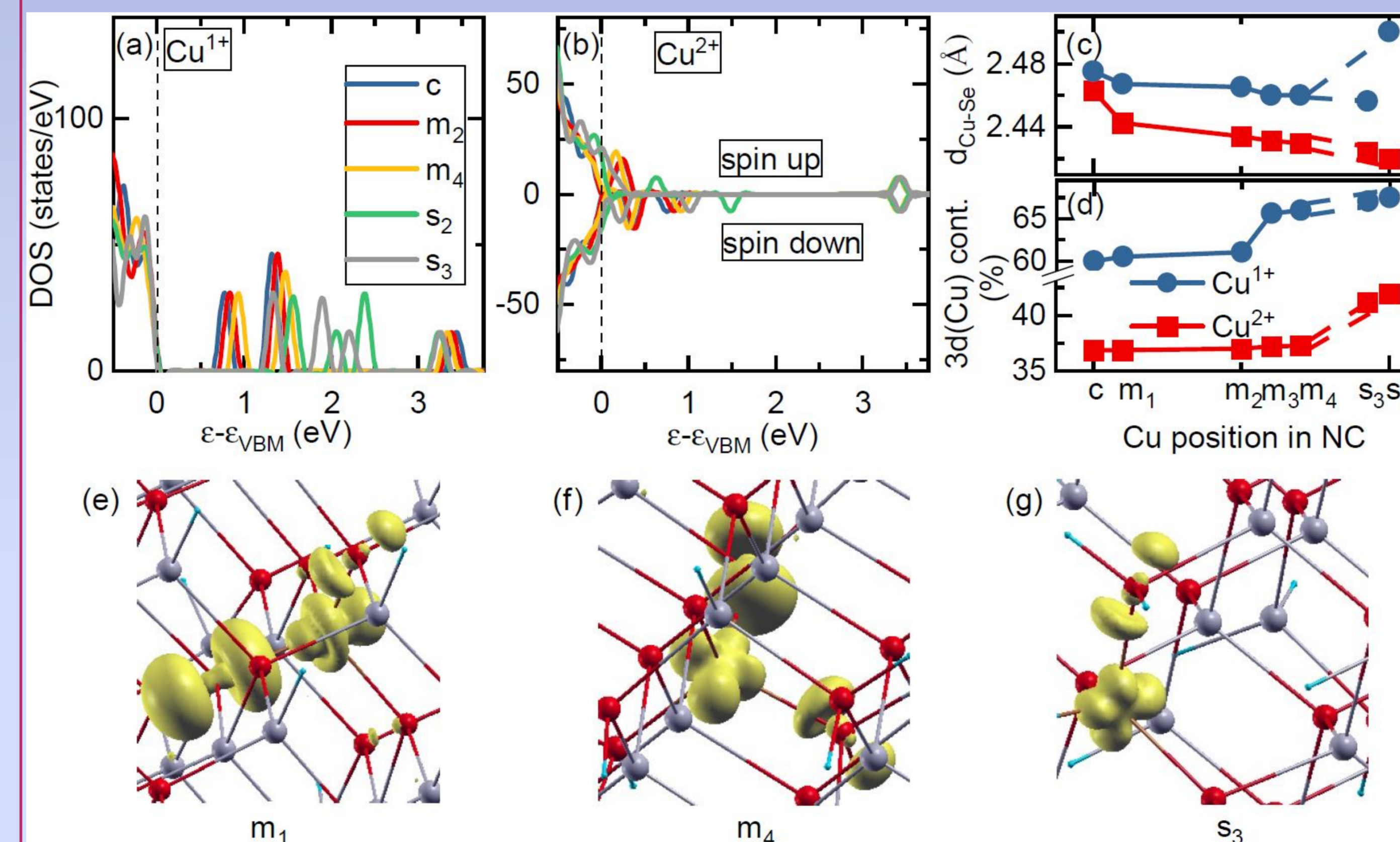


Fig. 2 Site dependence on the DOSs for Cu<sup>1+</sup> (a) and Cu<sup>2+</sup>(b). (c) shows the average Cu-Se bond lengths, (d) 3d(Cu) orbital contribution to the impurity ground state. (e)-(g) spin density distributions of Cu<sup>2+</sup>.

### C. The impact of dopant location on charge transfer optical transitions

The charge transfer optical transition  $\text{Cu}^{2+} + e_{\text{CBM}} \rightarrow \text{Cu}^{1+}$  was examined. Impurities incorporated closer to the surface give rise to PL transitions at lower energies, with lower probabilities, and larger Stokes shifts than impurities at the QD center. PL transition probability ( $P$ ) was calculated as [9]:

$$P = \frac{e^2 E_{\text{PL}}}{3\pi\epsilon_0 m^2 \hbar^2 c^3} |\langle \Psi_{a_{11}} | \hat{p} | \Psi_{\text{CBM}} \rangle|^2 \quad \text{where} \quad \langle \Psi_{a_{11}} | \hat{p} | \Psi_{\text{CBM}} \rangle = \sum_{\vec{G}} \vec{G} C_{a_{11}}^*(\vec{G}) C_{\text{CBM}}(\vec{G})$$

[6,10].

Time resolved PL study revealed that the PL decay rate increases with photon energy. These results support the conclusions of DFT calculations.

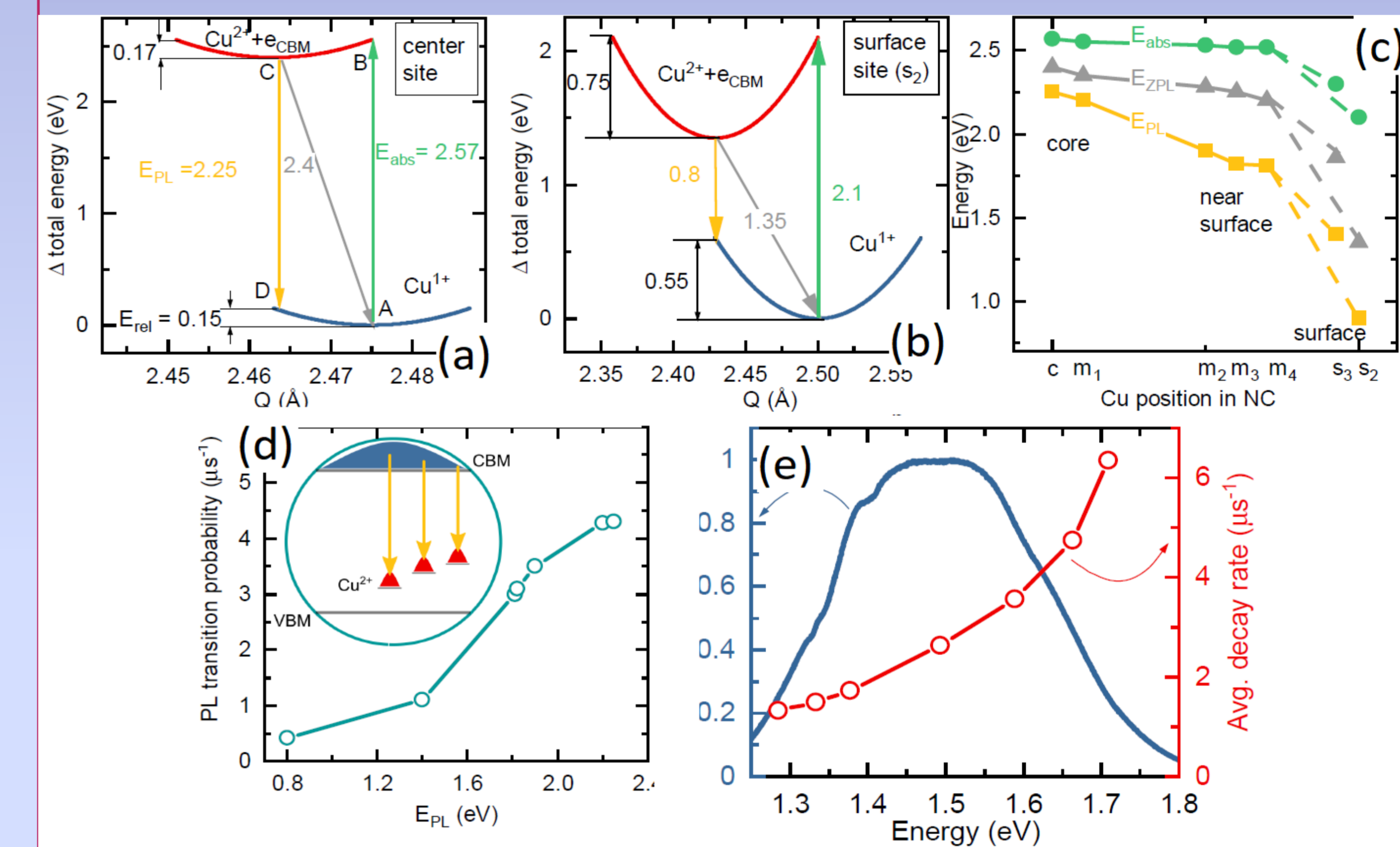


Fig. 3 (a), (b) Calculated CC diagrams for a Cu impurity. (c) The site dependence on the absorption and PL peak energies, and the zero phonon line energy, (d)  $P$  as a function of PL energy. (e) Line: the PL spectrum of Cu-doped CdSe QDs. Points: average PL decay rates plotted as a function of the photon energy.

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## Conclusion

We identify an additional source of heterogeneity in optical properties of Cu-doped CdSe QDs. Depending on the placement of the Cu dopant within the QD, the PL and absorption energies as well as transition probabilities change. The proximity to the QD surface plays the key role: charge transfer transitions involving dopants closer to the surface exhibit lower energies and lower probabilities than transitions involving dopants closer to center.

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