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Wu, Zhang, and Pantelides Reply:

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Wu, Zhang, and Pantelides respond:

The Comment by Chen and Pasquarello [1] contrasts the new theory of charged point defects that we introduced in a recent paper [2] with the conventional approach. The Comment asserts that “it is unclear how this revised method is conceptually superior” and presents numerical calculations claiming to show that the two methods are numerically equivalent. In Ref. [2] we made the case that the conventional approach entails ad hoc numerical procedures while the new theory is derived rigorously from statistical mechanics and entails no ad hoc numerical procedures, but we shall offer further clarification of the main points. We will then demonstrate that the two approaches are not numerically equivalent both in principle and in practice. In contrast, only calculations based on the new theory can claim fundamentally rigorous results *when supercell calculations are converged or properly extrapolated*. Unconverged results based on any method are not reliable.

The conventional approach assumes at the outset that one or more electrons are removed from or added to the supercell, which results in a defect potential with a Coulomb tail. The definition of formation energy includes the energy of electrons at the Fermi energy, which is assumed to be independently fixed. *Ad hoc* numerical procedures are introduced to remove the divergence introduced by the Coulomb potentials and to deal with Coulomb interactions between supercells. In contrast, the theory of Ref. 2 recognizes that, physically, defects only exchange electrons with the energy bands (or other defects, e.g., dopant impurities) and employs rigorous statistical mechanics to derive expressions for both the formation energy *and* the Fermi energy. The resulting neutral supercells have no issues with Coulomb potentials. It is not correct to assert that, in the conventional approach, the hypothetical electrons at the Fermi level mimic the role of the band electrons in the new theory because no such electrons are included in the definition of the electron density in the supercell. They are only invoked to remove the divergence in the Coulomb potentials. Thus, the two approaches are not conceptually equivalent. In fact, Deng and Wei [3] have argued that the conventional approach can be claimed to be equivalent to the new theory only if the latter were modified to place the carriers in *perfect-crystal* energy bands instead of the energy bands in the presence of the defect. Such a modification, however, is untenable. Overall, *there is no justifiable reason or advantage to replace the physical electrons with hypothetical electrons*. Unconverged calculations, on the other hand, are unreliable no matter how they are carried out.

Since the mathematical definitions of charged-defect formation energies are fundamentally different in the two approaches, one cannot claim that the two approaches are numerically equivalent. In particular, the electron densities of the physical carriers that neutralize the charged defect in the new method are totally absent in the self-consistent-field iterations in the conventional approach, no matter how large the supercell. The differences are manifest in the examples given in Refs. 2 and 3 and in the Comment by Chen and Pasquarello [1]. In the latter, in the case of MgO, the formation-energy curves fitted to finite supercell sizes extrapolate to *different* values. Differences are also present in the values reported for ZnO. As emphasized in Ref. [2], the differences in lattice relaxations are even more substantial. The existence of numerical differences confirms that the two approaches are neither conceptually nor numerically equivalent, contrary to the assertion by Chen and Pasquarello [1]. It should then be recognized that the definition given in Ref. 2 is the only fundamentally rigorous definition of charged-defect formation energies, while the conventional approach can only claim to mimic that definition by envisioning hypothetical carriers at the Fermi energy [1,3] with numerical consequences that cannot be known *a priori*. It is of course necessary to converge with respect to supercell size or properly extrapolate the results – unconverged calculations are not reliable.

In closing, we note that the case mentioned in the last two sentences of Ref. 1 is treated correctly in Ref. 2. The Fermi level is never pinned at the band edges.

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1. Chen and Pasquerello, preceding Comment.
2. Y.-N. Wu, X.-G. Zhang, and S. T. Pantelides, Phys. Rev. Lett. 119, 105501 (2017).
3. H.-X. Deng and S. H. Wei, Comment, Phys. Rev. Lett. 119, LKK1130 (2017).