Reply to "Comment on 'Critique of the tight-binding method: Ideal vacancy and surface states'"

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We show that the Comment by Vergés contains several misconceptions concerning our article on the tight-binding (orbital-removal) method as applied to the calculations of ideal vacancy and surface states, which invalidate his conclusions.

The preceding Comment by Vergés contains several misconceptions concerning our article,[1] hereafter referred to as I, which invalidate his conclusions.

First of all, he claims that we attribute the failure of the tight-binding (orbital-removal) method to the fact that in this method "the self-consistent readjustment of the charge in the proximity of the defect, and therefore the subsequent potential variation, is not taken into account." This is not the case. As stated in I (in the abstract, introduction, and discussed in detail in Sec. V), the orbital-removal method fails because it is not equivalent to removing the potential of the removed atom, i.e., the Hamiltonian matrix elements $\langle\phi_i|H^0|\phi_j\rangle$ (i,j not localized on the removed atom) are left unchanged as if the potential of the removed atom (which is part of H^0) were still present.

Second, the main point of Vergés's Comment is the demonstration that vacancy-induced gap states could be obtained by using a different finite set of Wannier functions as a basis set from the ones which we employed. This is similar to the material presented in Sec. IV of I where we show that one can obtain vacancy-induced gap states by this method, but the results depend on the basis employed.[2,3] Moreover, we have shown in Sec. III of I that as the basis is allowed to approach completeness, the vacancy-induced gap states will disappear (the energy levels will move into the bands).

Moreover, the use of Wannier functions as proposed by Vergés clearly leads to incorrect results when applied to the Kronig-Penney one-dimensional model. In this case the band structure is simple (i.e., nonoverlapping) and the Wannier functions for each band can be chosen to be localized about the attractive δ function sites. Then if the Wannier functions are chosen as a basis and the orbital-removal method is employed, it follows as shown in Sec. II a of I that there are no vacancy-induced gap states. But as is well known (and noted by us in Sec. II a) there *are* vacancy-induced gap states in the Kronig-Penney model.[4] Since the arguments advanced to justify the tight-binding (orbital-removal) method[5] are equally applicable to crystals of arbitrary number of atoms per unit cell, one is forced to conclude that a method which incorrectly gives no states in a simple (i.e., one atom per unit cell) one-dimensional model cannot be relied upon to give correct results in three-dimensional problems with possibly several atoms per unit cell.

Furthermore, contrary to Vergés's statement that our "amazing results remain unexplained," the reasons for the failure of the orbital-removal method have been thoroughly discussed in Sec. V of I. There we show that employing the method in a two-atom problem leads to the result that the potential of the removed atom continues to contribute because the matrix elements H^0_{ij} (i,j not on the removed atom) remain unchanged in this method, and that as the basis set is enlarged, the calculated eigenvalues approach the exact eigenvalues of the two-atom potential even though only one atom is left. These results are generalized to the case of a crystal and explain why the vacancy gap states must merge into the bands as the basis set becomes complete. In addition we show in Sec. V that if in the two-atom problem the change in potential is included in the Koster-Slater method, the exact result is obtained for the energy eigenvalue of a particle moving in the potential of the remaining isolated atom. This demonstrates that the incorrectness of the orbital-removal method does not stem from some peculiarity of the two-atom problem, but arises because the change in potential has not been properly treated.

A simpler way of seeing that the tight-binding (orbital-removal) method cannot lead to any reliable information about the vacancy state is to note that in this method the Hamiltonian matrix from which the eigenvalues and eigenvectors of the vacancy state are derived is identical to the Hamiltonian matrix that would be obtained if the orbitals on the central atom were removed from the basis set and no other changes were made in the Hamiltonian matrix.[5,6] However, the general principles of quantum mechanics tell us that employing a smaller basis set cannot lead to any new information about the physical system, i.e., such a procedure can only lead to an approximation to what the larger basis set would yield.

Consequently, any gap states deduced from such an incomplete basis must be spurious since they do not appear when the full basis set is employed.

It is therefore apparent that if vacancy- or surface-induced-gap-state-energy eigenvalues are to be calculated employing the orbital-removal method, the changes in the Hamiltonian matrix between the orbitals on the remaining atoms must be taken into consideration as discussed in Sec. VII of I. Moreover, even if this consideration is made, it should be noted that removal of a set of orbitals in the expansion of a wave function is equivalent to assuming that the wave function is orthogonal to this set. However, if the true vacancy state is not orthogonal to the orbitals on the removed atom, then the application of the orbital-removal method, even though the Hamiltonian matrix elements are modified to include the change in potential produced by the removal of an atom, is not justified.[7,8] In such a case, if a tight-binding formalism is employed, a full Koster-Slater treatment is required that includes the orbitals of the atom to be removed in the basis set.[8]

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[1]J. B. Krieger and P. M. Laufer, Phys. Rev. B 23, 4063 (1981).
[2]S. Das Sarma and A. Madhukar, Solid State Commun. 38, 183 (1981).
[3]M. Lannoo (private communication).
[4]A. Haug, *Theoretical Solid State Physics* (Pergamon, New York, 1972), Vol. 2, p. 158.
[5]J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978).
[6]J. Pollmann and S. T. Pantelides, Phys. Rev. B 18, 5524 (1978).
[7]R. E. Pena and D. C. Mattis, J. Phys. C 14, 647 (1981).
[8]J. B. Krieger and P. M. Laufer, J. Vac. Sci. Technol. 19, 307 (1981).