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Vacancy states in rock-salt ionic compounds

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A cluster–Bethe-lattice calculation of the electronic density of states of a vacancy in the rock-salt structure is presented. A simple one-orbital Hamiltonian is used. Occurrence and symmetry of localized states are discussed and compared with simple cluster calculations.

I. INTRODUCTION

The study of crystal imperfections is a problem which has challenged solid state experimentalists and theorists for the last couple of decades.[1,2] The atomic vacancy is probably the simplest type of imperfection, and it gives rise to interesting physical effects, such as color centers in ionic crystals,[3,4] and the strong dependence of the electric conductivity of VO on vanadium and oxygen vacancy concentrations.[5,6]

A standard theoretical treatment of the vacancy problem is the molecular approach,[7,8] in which the vacancy is considered as a large molecule formed by the missing atom and its nearest neighbors, and the vacancy states are assumed to be linear combinations of the atomic orbitals in the molecule. The molecular approach is capable of providing information about excitation energies of F centers,[4] but it is obviously not adequate to relate vacancy states to extended band states in the crystal.

A more rigorous approach to the vacancy problem consists of dividing the crystal into two parts: The (spherical) region around the vacancy is considered to be a vacuum, and the remainder of the solid is considered as a perfect crystal, with corrections in the potential due to the vacancy. The solution is obtained by solving two types of Schrödinger equations, one inside and another outside the vacancy region, and by matching the solutions at the boundary.[4] This leads to lengthy and complex calculations; the results for F-center excitation energies are in reasonable agreement with experiment.[4]

More recently, vacancy states in Si were investigated by Louie *et al.*, using a self-consistent pseudopotential method.[9] This was the first realistic calculation on semiconductor vacancies; the density-of-states diagram includes extended as well as vacancy levels, and the charge density around the vacant site is plotted. The method is, however, numerically involved, and requires the use of powerful computers.

In this paper we present a calculation for vacancies in rock-salt compounds, using the recently developed cluster–Bethe-lattice method.[10-12] This type of method has the limitations of the so-called LCAO (linear combination of atomic orbitals). It is, on the other hand, very well suited to this kind of problem because it treats part of the system (the vicinity of the vacancy) exactly, and in this respect, it is similar to the molecular approach; the effects of the rest of the crystal are simulated by attaching a Bethe lattice to each surface atom of the cluster, so that the connectivity and coordination number of the system are preserved throughout. In this way, vacancy and bulk states are treated simultaneously in a very simple mathematical way.

In Sec. II, we present a simple calculation for an isolated cluster of six atoms, with complete and general intraatomic and interatomic interactions. The eigenfunctions and eigenvalues of the system are easily obtained by group theory. The results of this section are useful in the interpretation of other results later in the paper. Since this calculation is not directly related to the rest of the calculation, we have explicitly labeled the parameters in a completely different way to avoid confusion.

In Sec. III, we get the local density of states at several atomic sites for a heteropolar fcc Bethe lattice with a vacancy, i.e., one atom with fewer than normal nearest neighbors. Finally, in Sec. IV, we present the cluster–Bethe-lattice calculation for an eighteen-atom cluster, surrounding a vacant site. In Secs. III and IV, we use a simple one orbital per site Hamiltonian[11]:

$$H=\sum_i U_i\,|i\rangle\langle i|+V\sum_{\substack{i,i'\\ \text{nearest}\\ \text{neighbors}}}|i\rangle\langle i'|\ , \qquad (1)$$

where $|i\rangle$ is an s-like orbital on site i, V is the hopping integral between nearest neighbors, and only nearest-neighbor interactions are taken into account. The origin of energies is taken in such a way that *for the perfect crystal* $U_i=+U$ on positive-ion sites and $U_i=-U$ on negative-ion sites. The effect of a vacancy on its nearest neighbors is to lower by one its coordination number, and also to change the local value of U_i there. The main contribution for this change is the Coulomb correction due to a charged-particle vacancy; in the case of a negative vacancy (which simulates a positive impurity), this correction is negative (attractive) and equals

$$-U_v^1 = -(ne^2/\epsilon a) , \qquad (2)$$

where n is the number of extra charges in each ion, ϵ is the applicable dielectric constant, and a is the nearest-neighbor distance. There is a second contribution U_v^2 which is due to the self-consistent change in the charge density at the site in question; this effect is of the opposite sign of U_v^1 and tends to cancel it partially. It can in principle be incorporated by using in (2) a self-consistent dielectric function ϵ. With the effect taken into account, for a positive ion nearest to a negative vacancy, $U_i = U - U_v$; and similarly, for a negative ion nearest to a positive vacancy, $U_i = -(U - U_v)$. No corrections are made for the other U_i's in our nearest-neighbor approximation.

II. ISOLATED OCTAHEDRAL CLUSTER

In this section we get the eigenfunctions and eigenvalues for the six-atom cluster in Fig. 1; the atoms are the nearest neighbors of a vacant site at the center. The Hamiltonian h of this problem is defined by its matrix elements between the basis functions $|i\rangle$: the six atomiclike s orbitals at the atomic sites. With orbitals numbered as in Fig. 1, the matrix elements are

$$\begin{aligned} &h_{11} = h_{22} = \cdots = h_{66} = \alpha , \\ &h_{13} = h_{14} = \cdots = h_{45} = \beta , \qquad (3) \\ &h_{12} = h_{34} = h_{56} = \gamma . \end{aligned}$$

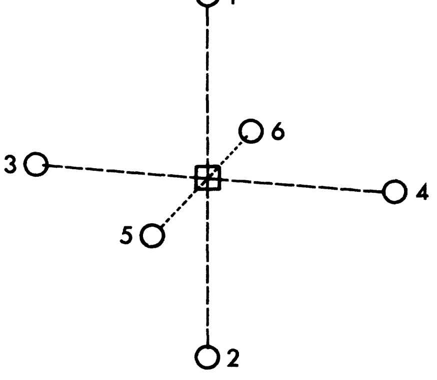

FIG. 1. Octahedral cluster with a central vacancy.

It should be noted that α is the equivalent of U in (1), while β and γ are interaction parameters similar to V in (1) but corresponding to second- and fourth-nearest neighbors. For $\beta = \gamma = 0$, the six functions are degenerate, but when intersite potentials are nonzero, they split into three levels: a singlet (Γ_1), a triplet (Γ_4), and a doublet (Γ_3). The normalized wave functions for these states are

$$\Gamma_1 \rightarrow (1/\sqrt{6})(1\ 1\ 1\ 1\ 1\ 1) , \qquad (4)$$

$$\Gamma_4 \rightarrow \begin{cases} (1/\sqrt{2})(1\ {-1}\ 0\ 0\ 0\ 0) , \\ (1/\sqrt{2})(0\ 0\ 1\ {-1}\ 0\ 0) , \\ (1/\sqrt{2})(0\ 0\ 0\ 0\ 1\ {-1}) , \end{cases} \qquad (5)$$

$$\Gamma_3 \rightarrow \begin{cases} (1/\sqrt{12})(2\ 2\ {-1}\ {-1}\ {-1}\ {-1}) , \\ (1/\sqrt{4})(0\ 0\ 1\ 1\ {-1}\ {-1}) , \end{cases} \qquad (6)$$

where the notation is

$$\Psi = (a_1\, a_2\, a_3\, a_4\, a_5\, a_6) = \sum_{i=1}^{6} a_i\, |i\rangle \qquad (7)$$

and the index i is as in Fig. 1.

The eigenvalues are easily obtained from (3)–(6):

$$\begin{aligned} &E(\Gamma_1) = \alpha + 4\beta + \gamma , \quad E(\Gamma_4) = \alpha - \gamma , \\ &E(\Gamma_3) = \alpha - 2\beta + \gamma . \end{aligned} \qquad (8)$$

Since usually $\gamma \ll \beta$, the ground state of the system is Γ_1 or Γ_3 according to whether β is negative or positive, respectively.

The two-electrons problem may also be solved exactly for this cluster,[13] but this is beyond our scope here.

III. ROCK-SALT BETHE LATTICE

A Bethe lattice (or Cayley tree) is a topological construction consisting of an infinitely connected system of atoms of coordination m, such that every atom is equivalent and there are no rings of bonds in the system. Such a lattice is usually employed to replace a given infinite crystal structure. The coordination m is given by the local properties of the crystal, and for the rock-salt structure, $m = 6$. The heteropolar Bethe-lattice problem is discussed extensively by Yndurain and Joannopoulos.[11] The solution for the density of states is obtained in the Green's-function formalism, taking the matrix elements of Dyson's equation between the basis set $\{|i\rangle\}$. An infinite set of linear equations results, which can be solved exactly by the transfer function technique.[10]

The local density of states at a reference site 0 is obtained from the diagonal matrix element of the Green's function, $\langle 0|G|0\rangle$; there are two types of contributions to it. Continuous states are given by

$$n_0(E) = -(1/\pi)\,\mathrm{Im}\langle 0|G|0\rangle \ , \tag{9}$$

and sharp or δ-function states are given by the poles of $\langle 0|G|0\rangle$.

The diagonal matrix element of the Green's function for the rock-salt Bethe lattice is[11]

$$\langle 0|G^{+}|0\rangle = [E - U_0^{+} - z\phi^{+}(E)]^{-1} \ , \tag{10}$$

$$\langle 0|G^{-}|0\rangle = [E - U_0^{-} - z\phi^{-}(E)]^{-1} \ , \tag{11}$$

where the + (−) sign indicates a positive (negative) reference ion, U_0 is the diagonal matrix element of the Hamiltonian (1) at the reference site 0, and z is the number of nearest neighbors to the reference ion.

The field operators ϕ^{+} and ϕ^{-} simulate mathematically the effect of a heteropolar Bethe lattice, acting along *one bond* on a positive or negative ion, respectively, for the calculation of the Green's-function matrix elements. They are equivalent to the corresponding transfer functions[10] multiplied by the parameter V, and depend only on the properties of the Bethe lattice. In the case of the rock-salt structure, they are[11]

$$\phi^{+}(E) = \tfrac{1}{10}E_2 \pm [E_1E_2(E_1E_2 - 20V^2)]^{1/2}/10E_1 \ , \tag{12}$$

$$\phi^{-}(E) = \tfrac{1}{10}E_1 \pm [E_1E_2(E_1E_2 - 20V^2)]^{1/2}/10E_2 \ , \tag{13}$$

where

$$E_1 = E + U \quad \text{and} \quad E_2 = E - U \ . \tag{14}$$

The sign of the square root in the field operators (12) and (13) must be determined unambiguously for all energy values. It is easily shown that $\phi^{+}(E)$ and $\phi^{-}(E)$ must have the same sign; in the regions in which the density of states is a continuum, the sign to be chosen is the one that gives a positive density of states. In the other regions, the following conditions[14] determine the correct sign:

$$\lim_{E\to\pm\infty} |\phi^{\pm}(E)| \tag{15}$$

must be bounded, and

$$(m-1)\,|\phi^{+}(E)\,\phi^{-}(E)/V^2| \leq 1 \ , \tag{16}$$

where m is the coordination number. In the gap region, condition (15) is satisfied by the plus sign, and in the two regions outside the bands, the sign determined from (16) is negative.

In the perfect rock-salt Bethe lattice, $z = 6$ and $U^{\pm} = \pm U$ in (10) and (11), and the local density of states given by (9) is

$$n^{+}(E) = \frac{3}{\pi E_2}\,\frac{[E_1E_2(20V^2 - E_1E_2)]^{1/2}}{36V^2 - E_1E_2} , \tag{17}$$

$$n^{-}(E) = \frac{3}{\pi E_1}\,\frac{[E_1E_2(20V^2 - E_1E_2)]^{1/2}}{36V^2 - E_1E_2} , \tag{18}$$

where E_1 and E_2 are given in (14), and n^{+} (n^{-}) is the local density of states at a positive (negative) ion site, normalized to 1. The curves for $n^{+}(E)$ and $n^{-}(E)$ are plotted in Ref. 11, and consist of two bands with a gap between $E = \pm U$ and outer edges at $E = \pm(U^2 + 20V^2)^{1/2}$. From (17) and (18), $n^{+}(E)$ and $n^{-}(E)$ have square-root singularities at $E = +U$ and $E = -U$, and these represent *pure cation* and *pure anion* states, respectively.[11]

In order to investigate the vacancy states, we calculate the local density of states at a reference atom with five instead of six attached Bethe lattices, i.e., $z = 5$ in (10) or (11). As discussed at the end of Sec. I, a Coulomb correction ($\pm U_v$) must be added to the potential at the ions nearest to a vacancy. Considering a negative ion vacancy, and consequently a positive reference ion,[15] $U_0^{+} = U - U_v$, and from (9) and (10), the continuum local density of states is

$$n_0^{+}(E) = \frac{1}{\pi}\,\frac{[E_1E_2(20V^2 - E_1E_2)]^{1/2}}{|2E_1(E_2U_v + U_v^2) + 10E_2V^2|} , \tag{19}$$

and consists of two bands in the same regions described above. If U_v is nonzero, the Green's-function element $\langle 0|G|0\rangle$ is not analytic; it has one or two poles depending on the value of U_v.

Let

$$P_{1,2} = -(U_v^2 + 5V^2) \pm [(U_v^2 + 5V^2)^2 - 4U_vU(U_v^2 - UU_v - 5V^2)]^{1/2}/2U_v , \tag{20}$$

where P_1 has a positive and P_2 a negative sign before the radical, and

$$U_v^{\text{crit}} = \tfrac{1}{2}[U + (U^2 + 20V^2)^{1/2}] \ . \tag{21}$$

For $U_v < U_v^{\text{crit}}$, only P_1 is a pole of $\langle 0|G|0\rangle$, and there is a δ function in the density of states at $E = P_1$. In the limit $U_v = 0$, this state merges into the band, and the singularity at $E = U$, discussed previously, appears. There is no singularity at $E = U$ for $U_v > 0$.

If $U_v = U_v^{\text{crit}}$, then $P_1 = 0$ and $P_2 = -(U^2 + 20V^2)^{1/2}$, i.e., P_2 is exactly at the lower edge of the bands.

For $U_v > U_v^{\text{crit}}$, both P_1 and P_2 are poles of (19), and there are two δ-function states due to the vacancy. In the limit $U_v \to \infty$, $P_1 \to -U$, i.e., P_1 tends to merge into the lower band, and $P_2 \to -\infty$.

This result is depicted in Fig. 2 for $U = 2$ and $V = 1$, so that from (21) $U_v^{\text{crit}} \cong 3.45$. In Fig. 2(a), $U_v = 0$, and no localized vacancy state appears. In Figs. 2(b) and 2(c), $U_v < U_v^{\text{crit}}$, and a vacancy state

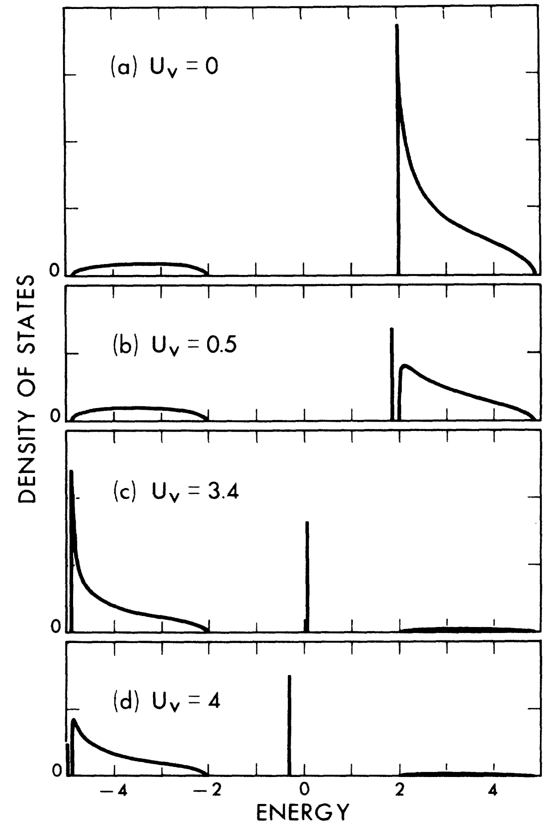

FIG. 2. Local density of states at the nearest neighbor to a negative vacancy in a rock-salt Bethe lattice for $U = 2$ and $V = 1$ as a function of U_v. The vertical lines represent δ-function states, and the height is proportional to its weight.

splits off the bottom of the upper band. In Fig. 2(d), $U_v > U_v^{\text{crit}}$, and an extra vacancy state splits off the lower band.

In order to understand the nature of these δ-function states, we calculate their weight in the local density of states at the first four neighbors to the negative vacancy.

The weight of a pole at $E = P$, at any particular ionic site i, is easily obtained in the Green's-function formalism:

$$W_i(P) = \text{res}_{E=P}\langle i|G|i\rangle \; . \tag{22}$$

Expression (22) is normalized so that the integrated density of states at each site is 1. The weights at the first four neighbors to a vacancy for $U = 2$, $V = 1$, and for several values of U_v are given in Table I. There, the weight at each point is multiplied by the number of sites equivalent to it with respect to the vacancy in the rock-salt Bethe lattice. It is interesting to observe the change in the nature of the vacancy states as U_v varies. For small U_v, the state at P_1 is relatively extended (only 73% contained within the first four layers of neighbors around the vacancy for $U_v = 0.5$), and oscillates as it decays into the bulk so that its contribution from *positive* ion states (first, third, ..., neighbors) is bigger than from the negative ones. For U_v around U_v^{crit}, the state in the gap, P_1, becomes much more localized (96% within the first four layers for $U_v = 3.5$), and decays monotonically into the bulk, most of its weight being at site 0. The state outside the gap P_2 is very extended for U_v just above U_v^{crit} (12% within the first four layers for $U_v = 3.5$), and oscillates as it decays in such a way that the contribution from the negative ion states (second, fourth, sixth, ..., neighbors) is bigger than that from the positive ones. For big U_v, the state outside the gap tends to become completely localized at the first neighbor to the vacancy; the state in the gap tends to be localized at the second neighbor, and also becomes oscillatory as it approaches the inner band edge and in the limit merges into the continuum.

IV. CLUSTER-BETHE-LATTICE VACANCY CALCULATION

We present in this section the results obtained in the cluster–Bethe-lattice approximation for the 18-atom cluster with a central vacancy shown in Fig. 3. The matrix elements of the Green's function relative to the reference atom 0 satisfy the following set of linear equations[11]:

$$\begin{aligned}
&(E - U + U_v)\langle 0|G|0\rangle = 1 + 4V\langle 1|G|0\rangle + \phi^+\langle 0|G|0\rangle ,\\
&(E + U)\langle 1|G|0\rangle = V\langle 0|G|0\rangle + V\langle 2|G|0\rangle\\
&\qquad + 4\phi^-\langle 1|G|0\rangle ,\\
&(E - U + U_v)\langle 2|G|0\rangle = V\langle 1|G|0\rangle + 2V\langle 3|G|0\rangle\\
&\qquad + V\langle 4|G|0\rangle + \phi^+\langle 2|G|0\rangle ,\\
&(E + U)\langle 3|G|0\rangle = 2V\langle 2|G|0\rangle + 4\phi^-\langle 3|G|0\rangle ,\\
&(E + U)\langle 4|G|0\rangle = V\langle 2|G|0\rangle + V\langle 5|G|0\rangle\\
&\qquad + 4\phi^-\langle 4|G|0\rangle ,\\
&(E - U + U_v)\langle 5|G|0\rangle = 4V\langle 4|G|0\rangle + \phi^+\langle 5|G|0\rangle ,
\end{aligned} \tag{23}$$

where ϕ^+ and ϕ^- are given in (10) and (11).

The solution of (23) for the diagonal element of the reference atom is

$$\langle 0|G|0\rangle = \frac{E''}{V}\,\frac{5 - (E'E'' - 5)^2}{(E'E'' - 2)(E'E'' - 4)(E'E'' - 8)} \; , \tag{24}$$

where

$$\begin{aligned}
E' &= (1/V)(\phi^+ - E + U - U_v) \; ,\\
E'' &= (1/V)(4\phi^- - E - U) \; .
\end{aligned} \tag{25}$$

The imaginary part of (24) is nonzero in the two regions $(-(U^2 + 20V^2)^{1/2}, -U)$ and $(U, (U^2$

TABLE I. Position and weight of the poles P_1 and P_2 at the first four neighbors to a negative vacancy in the rock-salt Bethe lattice.

U_v	P_1	(+) W_0	(−) $5W_1$	(+) $25W_2$	(−) $125W_3$
0.5	1.86	0.47	0.012	0.24	0.006
1.0	1.58	0.62	0.004	0.21	0.014
3.0	0.27	0.62	0.20	0.11	0.04
3.5	−0.03	0.57	0.25	0.10	0.04
4	−0.30	0.52	0.30	0.09	0.05
10	−1.70	0.07	0.54	0.03	0.21
	P_2				
3.5	−4.899	0.026	0.04	0.016	0.037
4.0	−4.95	0.17	0.29	0.09	0.16
10	−8.8	0.88	0.11	0.006	0

$+20V^2)^{1/2})$, so that there are bands of extended states in these regions, similar to what was obtained for the Bethe lattice alone. The new and interesting information we get from considering a cluster around the vacancy is the δ-function states arising from the poles of $\langle 0|G|0\rangle$, i.e., the roots of

$$E'E''=2,\quad E'E''=4,\quad E'E''=8\,. \tag{26}$$

To *each* of the three equations in (26), a discussion similar to the one in Sec. III applies. For small values of U_v, one δ-function state splits off the bottom of the upper band ($E=U$), and as U_v increases, this state gets lower in energy, but remains always inside the gap. For U_v greater than a critical value (which is not the same for the three equations), a second δ-function state splits off the bottom of the lower band, and it gets lower in energy as U_v increases. The complete picture for the density of states consists of two bands, three δ-function states in the gap, and zero, one, two, or three δ-function states below the bands, depending on the value of U_v. The position of the poles for $U=2$ and $V=1$ is given for five arbitrary values of U_v in Table II.

The appearance of three types of poles is expected from the symmetry arguments presented in Sec. II, where we get six states in an octahedral cluster grouped into three levels: a singlet (Γ_1), a triplet (Γ_4), and a doublet (Γ_3). The present situation has the same cubic symmetry, and it is possible to identify each of the wave functions corresponding to the poles of (25) as a Γ_1, a Γ_4, or a Γ_3. This can be easily done using the nondiagonal matrix elements of the Green's function, which give the wave-function amplitude ratios at different sites.[16] From the wave functions (4)–(6), the identification of the poles given by (26) is trivial:

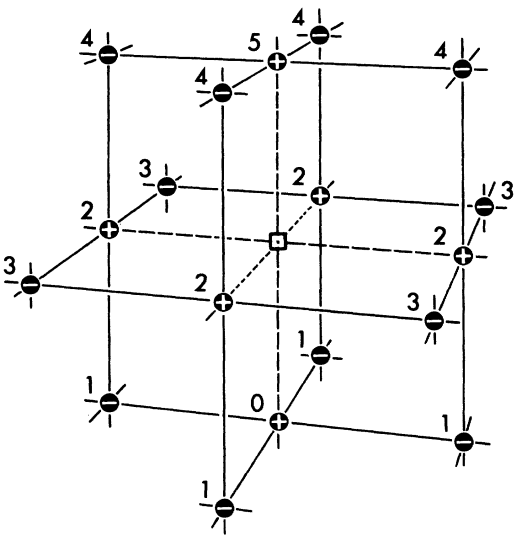

FIG. 3. Cluster of atoms in the rock-salt structure, with a central vacancy. The reference atom is labeled 0. All equivalent atoms are labeled with the same number. A Bethe lattice is connected to each dangling bond of the atoms.

TABLE II. Position and weight of poles (P) at the first two neighbors to a negative vacancy in the cluster-Bethe approximation.

U_v	Symmetry	P	W_0	W_1
0.1	Γ_3	1.986	0.086	0.78×10^{-4}
	Γ_4	1.994	0.054	0.42×10^{-4}
	Γ_1	1.998	0.006	0.03×10^{-4}
0.5	Γ_3	1.787	0.21	0.21×10^{-2}
	Γ_4	1.882	0.21	0.26×10^{-2}
	Γ_1	1.956	0.03	0.03×10^{-2}
3.5	Γ_3	−0.375	0.20	0.030
	Γ_4	0.032	0.28	0.055
	Γ_1	0.608	0.08	0.018
	Γ_1	−5.234	0.05	0.035
4.0	Γ_3	−0.663	0.18	0.038
	Γ_4	−0.239	0.26	0.066
	Γ_1	0.365	0.08	0.022
	Γ_4	−4.902	0.033	0.021
	Γ_1	−5.406	0.063	0.035
10	Γ_3	−1.841	0.031	0.06
	Γ_4	−1.658	0.037	0.12
	Γ_1	−1.276	0.021	0.05
	Γ_3	−8.496	0.31	0.008
	Γ_4	−8.785	0.44	0.027
	Γ_1	−9.302	0.14	0.012

$$E'E''=2\rightarrow\Gamma_3\,,\quad E'E''=4\rightarrow\Gamma_4,\quad E'E''=8\rightarrow\Gamma_1\,. \tag{27}$$

The local density of states for the second neighbor to a vacancy is obtained solving a system similar to (23). The position and weights of the poles at the first and second neighbor to a negative vacancy[15] for $U=2$ and $V=1$ are given in Table II for five different values of U_v. The following observations are worth making:

(i) For a fixed value of U_v, the relative weight of the poles is given by the degeneracy of the states, and also by how localized or extended they are. So for $U_v=0.1$, the triplet Γ_4 has a lower weight than the doublet Γ_3 because it is very near the bottom of the band, and is consequently more extended, as discussed in Sec. III.

(ii) The existence of three critical values of U_v may be confirmed. For small values of U_v, there are no δ-function states out of the gap. For $U_v=3.5$, the state Γ_3 is below the midpoint in the gap and a Γ_1 state splits off the lower band. Finally, for $U_v=10$, the three states in the gap are at $E<0$, and there are three states below the lower band.

(iii) The average of the position of the three poles, weighted according to the degeneracy of the corresponding state, gives within reasonable accuracy the position of the single pole for the Bethe lattice for the same values of the parameter (Table I).

(iv) Among the states in the gap, the lowest-energy one is of Γ_3 symmetry, and among those below the bands, the ground state is Γ_1. We may try to understand that qualitatively based on the simple cluster calculation of Sec. II, in which the results for the energy eigenvalues are given by (8). As we point out there, the ground state is Γ_1 or Γ_3 depending on the sign of β—the Hamiltonian matrix element between orbitals 1 and 3 in Fig. 1. For the cluster problem we are considering here, this matrix element between second neighbors is zero in first order, but we may take the second-order matrix element of the Hamiltonian sites 0 and 2 in Fig. 3, which interact via site 1 with hopping constant V, and call this an "effective β":

$$\beta_{\text{eff}}=V^2/(2U-U_v)\,. \tag{28}$$

For small values of U_v, β_{eff} is positive; according to (8) the states in order of *increasing* energy are Γ_3, Γ_4, and Γ_1, and this is the case in Table III for the states in the gap. For big values of U_v, β_{eff} is negative, and the order of the state gets inverted, the ground state is then Γ_1. From Table II, we observe that for large values of U_v the three states below the bands are in the expected energy order. The states in the gap however keep their relative position for all values of U_v, which is not in contradiction with the discussion above, since they tend to become localized at the 12 second-neighbor sites as U_v increases (see Table II, $U_v=10$), so that the arguments based on the simple cluster in Fig. 1 do not apply. The analogy holds only when the vacancy state is mainly localized at the six nearest neighbors to the vacancy, and in that case we may assume the only relevant parameter for the problem is β.

V. CONCLUSIONS

The results of our calculations show the viability of the cluster–Bethe-lattice method in studying the electronic structure of a vacancy. The calculations show sensible physical results and demonstrate the behavior of localized states, their symmetry and their dependence on the details of the potential in the vicinity of the vacancy.

The method has the following appealing features: (a) It is not restricted to a finite cluster and therefore is able to produce both localized and continuum states; (b)it can be improved by enlarging the cluster and/or including more atomic states in the Hamiltonian; (c) it is numerically simple and the calculation can be carried to a large extent analytically; (d) it permits easy symmetry identification of the bound states as well as complete analysis of the dependence of those states on the parameters of the potential.

In our actual results of Sec. IV, the states in the gap are physically significant. States splitting off the lower band at the low-energy end of the spectrum correspond to excessively large potentials U_v, completely outside the range of physical interest for the vacancy problem.

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