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Two-site Hubbard molecule with a spinless electron-positron pair

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We determine the eigenvalues of the two-site Hubbard molecule with one electron and one positron to describe the characteristics of electron-positron interactions in solids. While the effect of hopping is, in general, opposite to the effect of on-site interaction, we find a complex scenario for the electron-positron pair with a non-vanishing potential drop. We give analytical solutions and discuss the combined effects of the model parameters. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4769741>]

I. INTRODUCTION

Electron-positron interactions in solids are particularly interesting for spectroscopy, since the two γ photons from the annihilation are not collinear due to the electron crystal momentum.¹ This discovery has triggered the development of experimental techniques to produce a moderated narrow energy range beam of positrons,^{2–4} making positrons a good probe for studying materials. The most important application is the investigation of defects, mainly vacancies and dislocations,^{4–6} particularly at the surface. For a full review, see Ref. 7 and the references therein. The positronic states in such defects are localized and show longer annihilation time as compared to defect-free crystals. Their interaction with the electrons in the solid is enhanced.

Many theoretical studies aim at supplying a tool to accurately interpret spectroscopic data,⁸ such as the angular correlation of the positron annihilation radiation. A frequently used formalism, yielding the dispersion of the positron, is the two component density functional theory,^{9–11} which, however, has limits in dealing with strongly correlated systems as well as excited states. A more recent study on the angular correlation of the positron annihilation radiation¹² has shown that neither the local density approximation (LDA) nor the generalized gradient approximation (GGA) accurately reproduces the experimental spectra. Self-energy corrections (GW approximation) can partially address this problem but discrepancies persist. Only an analytical approach can overcome these problems. In this respect, lattice models are very powerful for small systems, but the solutions also help in understanding more complicated systems and are useful for improving approximations made in *ab initio* calculations. Recently, transport properties¹³ as well as the performance of the GW approximation have been studied in this context.¹⁴

Among the lattice models, the Hubbard model is popular due to the simple form of its Hamiltonian. Though a general solution is not known, there are cases where the problem can be tackled analytically, for example, for small molecules. The repulsive two-site Hubbard model without potential

drop has been investigated in Refs. 14–16. In addition, the two-site Hubbard-Holstein model, which describes the coupling of a two-site Hubbard molecule to optical phonons, has been studied.^{17,18} The attractive Hubbard model has been discussed in some detail in Ref. 19. However, a solution for a two-site molecule with a potential drop is missing so far. In the present paper, we bridge this gap to study the characteristics of the electron-positron interaction. Note that the potential drop, which describes the chemical environment and is typically comparable to the on-site interaction, is in general different for electrons and positrons.

II. SYSTEM SETUP

We consider a system of two sites with two energy levels containing two kinds of particles, electrons (e) and positrons (p), which interact only when localized on the same site. This assumption is justified by the fact that the mutual interaction is screened by the surrounding valence electrons (or eventually holes) if the particles are not on the same site. We impose the interaction to be the same for both sites, since it only depends on the charge. Moreover, since annihilation occurs between electron and positron with antiparallel spin, we can neglect the spin in our model, and thus refer to the Hamiltonian

$$\mathcal{H} = - \sum_{\alpha=e,p} t_{\alpha} (c_{1\alpha}^{\dagger} c_{2\alpha} + c_{2\alpha}^{\dagger} c_{1\alpha}) + \sum_i W_{ie} c_{ie}^{\dagger} c_{ie} - \sum_i W_{ip} c_{ip}^{\dagger} c_{ip} - U \sum_i c_{ie}^{\dagger} c_{ie} c_{ip}^{\dagger} c_{ip}, \quad (1)$$

where U denotes the on-site interaction, W the potential drop, and t the hopping. Our model conserves the particle number and therefore is already block-diagonal for subsystems with fixed occupancy. We aim to find the eigenvalues of $\mathcal{H}$ in the subspace of double occupancy, spanned by the states $|ep\rangle|0\rangle$, $|0\rangle|ep\rangle$, $|e\rangle|p\rangle$, and $|p\rangle|e\rangle$. The ordering of the fermionic creation operators is defined by the following rules: Site 1 is written to the right of site 2 and the electron to the right of the positron for the same site. For example, we have $|pe\rangle = e_2^{\dagger} p_1^{\dagger} |vac\rangle$. The matrix representation of $\mathcal{H}$ in our subspace is

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FIG. 1. Energy eigenvalues versus on-site interaction for zero potential drop (column 1) and finite potential drop (columns 2 to 4). The value of $W_{2e} - W_{2p}$ is 0.1 and the energies are expressed in units of t_p .

$$\begin{pmatrix} -U + W_{1e} - W_{1p} & 0 & -t_p & t_e \\ 0 & -U + W_{2e} - W_{2p} & -t_e & t_p \\ -t_p & -t_e & W_{1e} - W_{2p} & 0 \\ t_e & t_p & 0 & W_{2e} - W_{1p} \end{pmatrix}. \quad (2)$$

The energy eigenvalues ϵ are determined by exact diagonalization and will be functions in the six-dimensional parameter space given by U , $W_{1e} - W_{1p}$, W_{2e} , W_{2p} , t_e , and t_p .

In the following, we express all parameters with respect to t_p . In a solid the positrons thermalize, acquiring the same energy as the free-electron system: $t_e \approx t_p$. We will also study the interplay of positrons with localised electrons (d or f electrons), for which we have $t_p > t_e$, and the opposite case where localized positrons (for example, trapped in a defect) interact with nearly free electrons, $t_p < t_e$. Since we want to study a potential drop for the electronic system, we set the potential of one site to zero, $W_{1e} = 0$, and vary the value of W_{2e} . Concerning the positronic subsystem, we assume that if no potential is present for the electron no potential is present for the positron either. A local potential which attracts the positron repels the electron and in most cases the interaction

strength will be similar, $W_{2p} \approx W_{2e}$. However, we will also discuss cases when they are rather different.

For limiting cases when some of the parameters vanish, a full analytical solution can be given. In the general case, the eigenvalue problem is solved in terms of an equation system by elimination of coefficients. The results obtained will be analyzed and the asymptotic behavior explored and evaluated by series expansions. We address the eigenvectors in order to discuss the ionicity of the states.

III. RESULTS AND DISCUSSION

A. Effects of the on-site interaction U

First, we discuss the spectrum of the energy eigenvalues as a function of the on-site interaction U . In the following,

TABLE I. Asymptotics of the energy eigenvalues as functions of U , W_{2e} , and t_e .

$U \rightarrow +\infty$
$\epsilon_{1/2} = -U + \frac{1}{2}(W_{2e} - W_{2p} \mp W_{2e} - W_{2p}) - (t_e^2 + t_p^2)U^{-1} \mp \frac{4t_e^2 t_p^2 - (t_e^2 W_{2e} - t_p^2 W_{2p})(W_{2e} - W_{2p})}{ W_{2e} - W_{2p} } U^{-2} + \mathcal{O}[U^{-3}]$
$\epsilon_{3/4} = +\frac{1}{2}(W_{2e} - W_{2p} \mp W_{2e} + W_{2p}) + (t_e^2 + t_p^2)U^{-1} \mp \frac{4t_e^2 t_p^2 - (t_e^2 W_{2e} + t_p^2 W_{2p})(W_{2e} + W_{2p})}{ W_{2e} + W_{2p} } U^{-2} + \mathcal{O}[U^{-3}]$
$U \sim 0$
$\epsilon_{1/2} = \frac{1}{2}\left(W_{2e} - W_{2p} - \sqrt{4t_e^2 + W_{2e}^2} \mp \sqrt{4t_p^2 + W_{2p}^2}\right) - \frac{1}{2}\left(1 \mp \frac{W_{2e}W_{2p}}{\sqrt{(4t_e^2 + W_{2e}^2)(4t_p^2 + W_{2p}^2)}}\right)U + \mathcal{O}[U^2]$
$\epsilon_{3/4} = \frac{1}{2}\left(W_{2e} - W_{2p} + \sqrt{4t_e^2 + W_{2e}^2} \mp \sqrt{4t_p^2 + W_{2p}^2}\right) - \frac{1}{2}\left(1 \pm \frac{W_{2e}W_{2p}}{\sqrt{(4t_e^2 + W_{2e}^2)(4t_p^2 + W_{2p}^2)}}\right)U + \mathcal{O}[U^2]$
$W_{2e} \rightarrow +\infty$
$\epsilon_{1/2} = -\frac{1}{2}\left(U + W_{2p} \pm \sqrt{4t_p^2 + (U - W_{2p})^2}\right) - t_e^2 W_{2e}^{-1} \pm \frac{t_e^2 U(U - W_{2p})}{\sqrt{4t_p^2 + (U - W_{2p})^2}} W_{2e}^{-2} + \mathcal{O}[W_{2e}^{-3}]$
$\epsilon_{3/4} = W_{2e} - \frac{1}{2}\left(U + W_{2p} \pm \sqrt{4t_p^2 + (U + W_{2p})^2}\right) + t_e^2 W_{2e}^{-1} \pm \frac{t_e^2 U(U - W_{2p})}{\sqrt{4t_p^2 + (U - W_{2p})^2}} W_{2e}^{-2} + \mathcal{O}[W_{2e}^{-3}]$
$W_{2e} \sim 0$
$\epsilon_{1/2} = -\frac{1}{2}\left(U + W_{2p} + \sqrt{4t_e^2 + 4t_p^2 + W_{2p}^2 + U^2 \pm 2\sqrt{4t_e^2(4t_p^2 + W_{2p}^2) + W_{2p}^2 U^2}}\right) \pm \left(\frac{1}{2} \pm \frac{UW_{2p}}{\sqrt{4t_e^2(4t_p^2 + W_{2p}^2) + W_{2p}^2 U^2}}\right)W_{2e} + \mathcal{O}[W_{2e}^2]$
$\epsilon_{3/4} = -\frac{1}{2}\left(U + W_{2p} - \sqrt{4t_e^2 + 4t_p^2 + W_{2p}^2 + U^2 \pm 2\sqrt{4t_e^2(4t_p^2 + W_{2p}^2) + W_{2p}^2 U^2}}\right) \mp \left(\frac{1}{2} \mp \frac{UW_{2p}}{\sqrt{4t_e^2(4t_p^2 + W_{2p}^2) + W_{2p}^2 U^2}}\right)W_{2e} + \mathcal{O}[W_{2e}^2]$
$t_e \rightarrow +\infty$
$\epsilon_{1/2} = -t_e + \frac{1}{2}\left(-U + W_{2e} - W_{2p} \mp \sqrt{4t_p^2 + W_{2p}^2}\right) - \left(\frac{U^2 + W_{2e}^2}{8} \mp \frac{UW_{2e}W_{2p}}{4\sqrt{4t_p^2 + W_{2p}^2}}\right)t_e^{-1} \pm U^2 t_p^2 \frac{4t_p^2 - W_{2e}^2 + W_{2p}^2}{4(4t_p^2 + W_{2p}^2)^{3/2}} t_e^{-2} + \mathcal{O}[t_e^{-3}]$
$\epsilon_{3/4} = +t_e + \frac{1}{2}\left(-U + W_{2e} - W_{2p} \mp \sqrt{4t_p^2 + W_{2p}^2}\right) + \left(\frac{U^2 + W_{2e}^2}{8} \mp \frac{UW_{2e}W_{2p}}{4\sqrt{4t_p^2 + W_{2p}^2}}\right)t_e^{-1} \pm U^2 t_p^2 \frac{4t_p^2 - W_{2e}^2 + W_{2p}^2}{4(4t_p^2 + W_{2p}^2)^{3/2}} t_e^{-2} + \mathcal{O}[t_e^{-3}]$
$t_e \sim 0$
$\epsilon_{1/3} = -\frac{1}{2}\left(U + W_{2p} \pm \sqrt{4t_p^2 + (U - W_{2p})^2}\right) + \mathcal{O}[t_e^2]$
$\epsilon_{2/4} = W_{2e} - \frac{1}{2}\left(U + W_{2p} \pm \sqrt{4t_p^2 + (U + W_{2p})^2}\right) + \mathcal{O}[t_e^2]$

we label the eigenvalues ϵ_1 , ϵ_2 , ϵ_3 , and ϵ_4 from the lowest to the highest. For $W_{2e} = W_{2p} = 0$, we obtain analytically

$$\epsilon = \frac{-U \pm \sqrt{4(t_e \pm t_p)^2 + U^2}}{2}. \quad (3)$$

The eigenvalues for zero potential drop are plotted in Fig. 1 as a function of U , with the following values of the hopping parameter t_e from top to bottom: 0, $t_p/2$, t_p , and $2t_p$. Each graph shows four curves, one for each eigenvalue. For $t_e = 0$, the four equations split into two independent couples, with solutions

$$\epsilon_{1/3} = -\frac{U + W_{2p} \pm \sqrt{(U - W_{2p})^2 + 4t_p^2}}{2}$$

$$\epsilon_{2/4} = W_{2e} - \frac{U + W_{2p} \pm \sqrt{(U + W_{2p})^2 + 4t_p^2}}{2}, \quad (4)$$

where the first couple belongs to the subspace spanned by $|ep\rangle|0\rangle$ and $|e\rangle|p\rangle$. The physical reason is that without electronic hopping the electron will stay either in one or in the other site, while the positronic cloud covers both sites. For high on-site interaction, the eigenvalues also tend to group in the mentioned couples, which is in agreement with the fact that hopping and on-site interaction have an opposite effect.

FIG. 2. Eigenvalues versus potential drop. The plots in the first row show the results for $W_{2e} - W_{2p} = 0.1$, while in the second row we have $W_{2p} = 0.9$ (vertical dashed line).

However, the effect of t_e is less trivial. For $t_e = 1$, at $U = 0$, ϵ_2 and ϵ_3 are degenerate, while for $t_e \neq 1$ the gap between these eigenvalues around zero is larger, see also below. In general, we can separate the eigenvalues in positive and negative pairs. The asymptotic behavior is either $\epsilon \rightarrow 0$ or $\epsilon \rightarrow -U$. For $t_e = t_p$, we have exactly $\epsilon_2 = -U$ and $\epsilon_3 = 0$, which are degenerate for vanishing on-site interaction. Larger t_e shifts the onset of the asymptotic behavior to higher U . Accordingly, the splitting for small interaction becomes stronger.

Turning to a finite potential drop, we investigate the spectra for small, intermediate, and high W_{2e} . In Fig. 1, the potential drop increases from left to right, with $W_{2e} = 0.2t_p$ in the left column, $W_{2e} = t_p$ in the middle column, and $W_{2e} = 5t_p$ in the right column. The electron hopping t_e increases from top to bottom. The eigenvalues are still grouped in lower and higher couples, as long as the potential drop is within the range of the hopping energy (left and middle columns). For large W_{2e} , we rather are confronted with three groups (ϵ_1 , ϵ_2 and ϵ_3 , ϵ_4) as only ϵ_2 and ϵ_3 approach zero for small U . All eigenvalues depend on the potential drop, even in the case $t_e = t_p$ (in which there is no eigenvalue $\epsilon = -U$). In addition ϵ_2 and ϵ_3 have a small gap for weak on-site interaction, for any value of the potential drop. The effect of the electronic hopping is comparable to the behavior without potential drop, see Fig. 1, i.e., increasing t_e separates the eigenvalues for small interaction. The effect of the potential drop W_{2e} is to enhance the separation of the eigenvalues even for high U .

The asymptotic values in Table I give quantitative relations between the eigenvalues and the model parameters.

The gap between ϵ_1 and ϵ_2 depends in first order on $W_{2e} - W_{2p}$, while the gap between ϵ_3 and ϵ_4 is proportional to $W_{2e} + W_{2p}$, and the gap between ϵ_2 and ϵ_3 is proportional to $U - W_{2e}$. For $t_e = t_p$, the gap between ϵ_2 and ϵ_3 at $U = 0$ is small as long as W_{2p} is close to W_{2e} . In case $W_{2p} = W_{2e}$ it is in fact zero, for all values of the potential drop, see Fig. 2. In the limit $U \rightarrow -\infty$, the eigenvalues ϵ_1 and ϵ_2 take the negative values of ϵ_4 and ϵ_3 for $U \rightarrow \infty$, respectively, and vice-versa. For $W_{2e} \rightarrow -\infty$, we obtain the same values as for $W_{2e} \rightarrow +\infty$.

B. Effects of the potential drop W_{2e}

The dependence on the electronic potential drop is studied for the other parameters set to representative values of $t_e = 0.5$ and $U = 0, 1$, and 4 . For $U = 0$, we can obtain the solutions explicitly, finding the zero order terms of the expansion given in Table I. Let us first refer to the first row of Fig. 2. While the lowest and highest eigenvalues depend linearly on $\mp W_{2e}$, the other two tend to $-U$ with a reduced gap. The graphs show that ϵ_1 and ϵ_4 as well as ϵ_2 and ϵ_3 are almost symmetric. There is a perfect symmetry for $U = 0$. While ϵ_2 does not depend on the potential drop, except for very small W , we find a crossover in case of ϵ_3 . For a large potential drop ϵ_2 and ϵ_3 tend to $-U$, see Fig. 1, while for a small potential drop ϵ_2 and ϵ_3 are proportional to $-W_{2e}$ for $W_{2e} > 0$ and $W_{2e} < 0$, respectively. The gap between ϵ_2 and ϵ_3 at $W_{2e} = 0$ grows linearly with U for large U , see Fig. 1, while the other two gaps decrease. We can infer that the on-site interaction lowers the eigenvalues ϵ_1 and ϵ_2 and the potential drop further lowers ϵ_1 and ϵ_3 . If $W_{2e} \gg U$, we find

FIG. 3. Eigenvalues versus electronic hopping. We note the degeneracy at $t_e = 0$ for $W = 0$ and the asymmetry of the upper couple with respect to the lower, particularly visible in the case $U = 4$.

the same three groups as in Fig. 1 for large W_{2e} , namely ϵ_1 , ϵ_2 and ϵ_3 ($W_{2e} - U$ above ϵ_1), ϵ_4 ($W_{2e} + U$ above $\epsilon_{2/3}$).

From the lower row of Fig. 2, we can get insights into the effect of the potential drop. We find that although the eigenvalues behave monotonically, the gaps between them do not. For sufficiently high W_{2e} , a gap opens, between ϵ_2 and ϵ_3 , where the onset depends on the on-site interaction. This is due to the fact that for a constant, positronic potential drop W_{2e} prevents electrons, but not positrons, from a site change. Such a situation may arise if the system is insulating due to antiferromagnetism. According to Fig. 1, the on-site interaction also reduces the gap $\epsilon_2 - \epsilon_1$ at $W_{2e} = W_{2p}$, which is the only point where it even could become zero.

C. Effects of the electronic hopping t_e

Turning to the dependence on t_e , we find that the spectra are fully symmetrical with respect to $t_e = 0$, see Fig. 3. In the previous discussions, we have already identified two special values of the hopping parameter: $t_e = 0$ and $t_e = t_p$. In between, the gaps $\epsilon_2 - \epsilon_1$ and $\epsilon_4 - \epsilon_3$ increase to a constant

value, while the gap $\epsilon_3 - \epsilon_2$ decreases (reaching its minimum at $t_e = t_p$) and increases constantly thereafter. The asymptotic values are $\pm t_e$, where the eigenvalues form couples separated by $\sqrt{4t_p^2 + W_{2p}^2}$. For $W_{2e} = 0$, we find a degeneracy at $t_e = 0$ and the eigenvalues are symmetric with respect to the axis $t_e = \pm U$, which is lost for $W_{2e} \neq 0$. We have already seen that the effect of U is not the same on the lower and upper couple, reflected by the fact that ϵ_3 tends to be monotonic for large U , unlike ϵ_2 . In the degenerate case $t_e = 0$, there are transitions between $|\epsilon_1\rangle$ and $|\epsilon_3\rangle$ as well as $|\epsilon_2\rangle$ and $|\epsilon_4\rangle$ only. For $t_e \rightarrow 0$, the derivatives tend to zero for $W_{2e} \neq 0$ and to ± 1 for $W_{2e} = 0$.

D. Analysis of the eigenstates

We project the eigenstates on the basis of double occupancy (Fock states): $\{|ep\rangle|0\rangle, |0\rangle|ep\rangle, |e\rangle|p\rangle, |p\rangle|e\rangle\}$. We shall deal with the limiting cases only, as they are sufficient to explain the effect of the parameters. The components of the eigenvectors in the above base are (for $|\epsilon_i\rangle = a_{i1}|ep\rangle|0\rangle + a_{i2}|0\rangle|ep\rangle + a_{i3}|e\rangle|p\rangle + a_{i4}|p\rangle|e\rangle$)

TABLE II. Components of the projection of the eigenstates onto the basis $\{|ep\rangle|0\rangle, |0\rangle|ep\rangle, |e\rangle|p\rangle, |p\rangle|e\rangle\}$ for zero potential drop. Since the two sites are equivalent, a_{i2}/a_{i1} and a_{i4}/a_{i3} are ± 1 . For $t_e = t_p$, the components of the second and third eigenvectors simplify to $(1/\sqrt{2}, -1/\sqrt{2}, 0, 0)$ and $(0, 0, -1/\sqrt{2}, 1/\sqrt{2})$, respectively.

	a_{i1}	a_{i2}	a_{i3}	a_{i4}
$ \epsilon_1\rangle$	$\frac{U + \sqrt{U^2 + 4(t_e + t_p)^2}}{N_1}$	$+\frac{U + \sqrt{U^2 + 4(t_e + t_p)^2}}{N_1}$	$+2\frac{t_e + t_p}{N_1}$	$+2\frac{t_e + t_p}{N_1}$
$ \epsilon_2\rangle$	$\frac{U + \sqrt{U^2 + 4(t_e - t_p)^2}}{N_2}$	$-\frac{U + \sqrt{U^2 + 4(t_e - t_p)^2}}{N_2}$	$-2\frac{t_e - t_p}{N_2}$	$+2\frac{t_e - t_p}{N_2}$
$ \epsilon_3\rangle$	$\frac{U + \sqrt{U^2 + 4(t_e - t_p)^2}}{N_3}$	$-\frac{U + \sqrt{U^2 + 4(t_e - t_p)^2}}{N_3}$	$-2\frac{t_e - t_p}{N_3}$	$+2\frac{t_e - t_p}{N_3}$
$ \epsilon_4\rangle$	$\frac{U + \sqrt{U^2 + 4(t_e + t_p)^2}}{N_4}$	$+\frac{U + \sqrt{U^2 + 4(t_e + t_p)^2}}{N_4}$	$+2\frac{t_e + t_p}{N_4}$	$+2\frac{t_e + t_p}{N_4}$
with $N_{1/2} = \sqrt{2((U + \sqrt{U^2 + 4(t_e \pm t_p)^2})^2 + 4(t_e \pm t_p)^2)}$ and $N_{3/4} = \sqrt{2((U - \sqrt{U^2 + 4(t_e \mp t_p)^2})^2 + 4(t_e \mp t_p)^2)}$

FIG. 4. Occupation of the eigenstates versus U , for zero potential drop and $t_e \neq t_p$ (left) or $t_e = t_p$ (middle) as well as for finite potential drop and $t_e = 0$ (right). Eigenstates belonging to the two separate subspaces are indicated by circles and crosses in the rightmost graph. The crossover of $|a_{ij}|^2$ happens for $U \neq 0$.

$$\begin{aligned}
 a_{i1} &= (\epsilon_i - W_{2e})(\epsilon_i + U - W_{2e} + W_{2p})(\epsilon_i + W_{2p}) \\
 &\quad - t_e^2(\epsilon_i - W_{2e}) - t_p^2(\epsilon_i + W_{2p}), \\
 a_{i2} &= t_e t_p (2\epsilon_i - W_{2e} + W_{2p}), \\
 a_{i3} &= -t_e \left((\epsilon_i + U - W_{2e} + W_{2p})(\epsilon_i + W_{2p}) - (t_e^2 - t_p^2) \right), \\
 a_{i4} &= -t_p \left((\epsilon_i + U - W_{2e} + W_{2p})(\epsilon_i - W_{2e}) + (t_e^2 - t_p^2) \right).
 \end{aligned} \quad (5)$$

For a zero potential drop, the two sites have the same energy. Hence, the projections of the eigenstates onto $|ep\rangle|0\rangle$ and $|0\rangle|ep\rangle$ differ only by a sign (the same for $|e\rangle|p\rangle$ and $|p\rangle|e\rangle$) for every eigenvalue, see Table II. Figure 4 shows the module squares needed for calculating the occupation characteristics of the ground state $|\epsilon_1\rangle$ and the first excited state $|\epsilon_2\rangle$, as a function of U . The occupations of $|\epsilon_3\rangle$ and $|\epsilon_4\rangle$ can be obtained with the relations $|a_{11}|^2 = |a_{43}|^2$, $|a_{21}|^2 = |a_{33}|^2$, $|a_{31}|^2 = |a_{23}|^2$, and $|a_{41}|^2 = |a_{13}|^2$. The first two eigenvectors have the majority of contribution from states with a doubly occupied site for $U > 0$ and from states with a singly occupied site for $U < 0$. However in $|\epsilon_1\rangle$, this contribution is slightly reduced as compared to $|\epsilon_2\rangle$. The same applies to $|\epsilon_4\rangle$ as compared to $|\epsilon_3\rangle$. The extreme case occurs for $t_e = t_p$, where $|\epsilon_2\rangle$ is composed only of states with a doubly occupied site. Hence, it has a more localized electron-positron cloud.

For zero electronic hopping, see the rightmost graph in Fig. 4, we have two independent subspaces spanned by the first/third and second/fourth basis states, respectively. The projections of the eigenstates onto the double occupancy basis are reported in Table III and crosses are plotted in Fig. 4. We note that in the subspace spanned by the first and third basis states the occupations of these states are equal for $U = W_{2p}$, while in the subspace spanned by the second and fourth basis states equality happens for $U = -W_{2p}$. When U exceeds these values, we have a crossover of the occupations. Hence, the ground state of the former subspace has an antibonding character for small U , and viceversa for large U . The ground state of the latter subspace has always a bonding character (for $U > 0$). The occupation of $|ep\rangle|0\rangle$ is less than that of $|e\rangle|p\rangle$ due to the preference of the positron to the second site, in the presence of a potential step.

For $U \rightarrow \infty$, we compute the ratios a_{12}/a_{11} , a_{13}/a_{11} , and a_{14}/a_{11} , from the general formulas as given previously. Considering only the zero order terms, we obtain for $t_e = t_p$ and $W_{2e} = W_{2p} = t_p$ the results $a_{12}/a_{11} = -1$ and $a_{13}/a_{11} = a_{14}/a_{11} = 0$, for every value of the potential drop. If the two potential drops are different, we have

$$\lim_{U \rightarrow \infty} \frac{a_{12}}{a_{11}} = \lim_{U \rightarrow \infty} \frac{a_{13}}{a_{11}} = \lim_{U \rightarrow \infty} \frac{a_{14}}{a_{11}} = 0, \quad (6)$$

TABLE III. Components of the projections of the eigenstates onto the basis $\{|ep\rangle|0\rangle, |0\rangle|ep\rangle, |e\rangle|p\rangle, |p\rangle|e\rangle\}$ for $t_e = 0$.

	a_{i1}	a_{i2}	a_{i3}	a_{i4}
$ \epsilon_1\rangle$	$\frac{U - W_{2p} + \sqrt{(U - W_{2p})^2 + 4t_p^2}}{M_1}$	0	$\frac{2t_p}{M_1}$	0
$ \epsilon_2\rangle$	0	$\frac{U + W_{2p} - \sqrt{(U + W_{2p})^2 + 4t_p^2}}{M_2}$	0	$-\frac{2t_p}{M_2}$
$ \epsilon_3\rangle$	$\frac{U - W_{2p} - \sqrt{(U - W_{2p})^2 + 4t_p^2}}{M_3}$	0	$\frac{2t_p}{M_3}$	0
$ \epsilon_4\rangle$	0	$\frac{U + W_{2p} + \sqrt{(U + W_{2p})^2 + 4t_p^2}}{M_4}$	0	$-\frac{2t_p}{M_4}$
with $M_{1/3} = \sqrt{(U - W_{2p} \pm \sqrt{(U - W_{2p})^2 + 4t_p^2})^2 + 4t_p^2}$ and $M_{2/4} = \sqrt{(U + W_{2p} \pm \sqrt{(U + W_{2p})^2 + 4t_p^2})^2 + 4t_p^2}$				

with $|a_{14}|^2 > |a_{13}|^2$ for finite U so that the positronic cloud is more localized if only a single site is occupied (since $|a_{11}|^2$ is the leading term). For the first excited state, we have for $t_e = t_p$, the results $a_{22}/a_{21} = -1$, and $a_{23}/a_{21} = a_{24}/a_{21} = 0$. For $t_e = 0.5t_p$, the limits of the three ratios are all zero (as for the ground state) with $|a_{24}/a_{21}|^2 > |a_{23}/a_{21}|^2$.

IV. CONCLUSIONS

We have investigated the two-site Hubbard molecule with a spinless electron and positron pair. We use the Fock states to calculate the energy eigenvalues. Assuming physically realistic parameters, we have discussed the eigenvalues spectrum, giving reference to the asymptotic values and to the character of specific eigenstates. By projecting the eigenstates onto the double occupancy basis, we have evaluated the contributions of the different basis states to the ground and excited states. We argue that the interplay of the model parameters gives rise to a non-intuitive behavior, in particular with respect to non-monotonic dependence of energy gaps in specific parameter ranges and grouping of eigenvalues. The eigenstates can be very sensitive to small parameter changes. The quantitative description of defects is therefore complex when these parameters are in strong competition. Furthermore, neither the ground state nor the excited states of the electron-positron molecule are well described by local potentials. Since in spectroscopy experiments the positron is an invasive probe, interpretation of the results to investigate the host material is a complex task. In order to separate the intrinsic material properties from the alterations induced by the positron usually, a theoretical model based on two component density functional theory is employed. However, this method is not able to correctly describe the effects of

electronic correlations. Our results establish the required corrections of the density functional approach when the onsite interaction deviates from zero.

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