Electron- and hole-hopping amplitudes in a diatomic molecule.
II. Effect of radial correlations

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We continue our study of electron- and hole-hopping amplitudes in diatomic molecules. Here, we go beyond the Hartree approximation and use two different orbital exponents for the two-electron atom. It is found that the difference in hopping amplitudes between electrons and holes (Δt) is enhanced when the effect of radial correlations is taken into account. A tight-binding model with two orbitals per site is used to represent the results of the first principles calculation and gain insight into the physical origin of the quantity Δt.

I. INTRODUCTION

We continue here our study of the hopping amplitude of electrons in diatomic molecular ions with one, two, and three electrons (H_2^+, H_2, and H_2^- for the case where the nuclear charge $Z = 1$), denoted by t_0, t_1, and t_2, respectively. The motivation for this study and its possible relevance to superconductivity was discussed in Ref. 1 (hereafter referred to as I).

In I we used as wave function for the atom with two electrons

$$\psi(r_1, r_2) = \bar{a}(r_1)\bar{a}(r_2), \qquad (1a)$$

$$\bar{a}(r) = \frac{\bar{\alpha}^{3/2}}{\pi^{1/2}}e^{-\bar{\alpha}r_a}, \qquad (1b)$$

with r_a the electron position relative to the nucleus a. If one takes for $\bar{\alpha}$ the value appropiate to the one-electron atom

$$\bar{\alpha} = Z \qquad (2)$$

the hopping amplitudes are found to be very close in magnitude and to satisfy the relation

$$t_0 < t_1 < t_2 \qquad (3)$$

over a large range of interatomic separation R. However, if instead one takes the value of $\bar{\alpha}$ obtained from minimization of the two-electron atom energy

$$\bar{\alpha} = Z - 5/16 \qquad (4)$$

the ordering

$$t_0 > t_1 > t_2 \qquad (5)$$

is found to hold over a large range of R, with appreciable differences in the magnitudes of the hopping amplitudes. The ordering Eq. (5) is required within the model of hole superconductivity.[2] The same behavior is found if

the orbital exponents are optimized for each interatomic separation.

A more realistic description of the two-electron ion is achieved by allowing for radial correlations between the electrons. We use here the Eckart wave function[3]

$$a_{H^-} = \frac{a_1(r_1)a_2(r_2) + a_2(r_1)a_1(r_2)}{[2(1 + S_{H^-})]^{1/2}} \qquad (6)$$

with

$$a_i(r) = \frac{\alpha_i^{3/2}}{\pi^{1/2}}e^{-\alpha_i r_a}, \qquad (7)$$

$$S_{H^-} = (a_1, a_2)^2 \qquad (8)$$

and the exponents α_1, α_2 determined so as to minimize the electronic energy. Table I gives the orbital exponents and energies for the cases $Z = 1$ (H^-) and $Z = 2$ (He). It can be seen that allowing for radial correlations significantly improves on the value of the energy. Furthermore, H^- is unbound with the Hartree wave-function Eq. (1a) (its energy is larger than -1 Ry) while it becomes bound with the wave-function Eq. (6). Note that the larger orbital exponent, α_1, is close to Z, while α_2 is significantly smaller, indicating the importance of orbital correlation effects. It is natural to expect these effects to affect other molecular properties that depend on details of the wave function such as hopping amplitudes.

Since we will be interested in variable nuclear charge Z we plot in Fig. 1 the orbital exponents as a function of Z,

TABLE I. Energy (in Ry) of two-electron atom for $Z = 1$ (H^-) and $Z = 2$ (He) for the Hartree wave function Eq. (1a) [$E(\bar{\alpha})$] and the Eckart wave function Eq. (6) [$E(\alpha_1, \alpha_2)$]. The values of the exponents are chosen so as to minimize the energy with the given wave function. The experimental value of the energy ($E_{\exp}$) is also given.

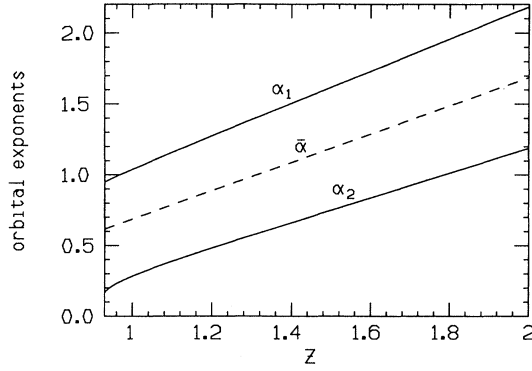| Z	$\bar{\alpha}$	$E(\bar{\alpha})$	α_1	α_2	$E(\alpha_1, \alpha_2)$	$E_{\exp}$
1	0.6875	-0.9453	1.0392	0.2832	-1.0266	-1.0554
2	1.6875	-5.6953	2.1832	1.1885	-5.7513	-5.808

FIG. 1. Orbital exponents that minimize the energy of the two-electron atom as a function of the effective ionic charge Z. α_1 and α_2 are the exponents corresponding to the two orbitals in the wave function Eq. (6), and $\bar{\alpha} = Z - 5/16$ is the exponent of a single Slater orbital occupied by two electrons.
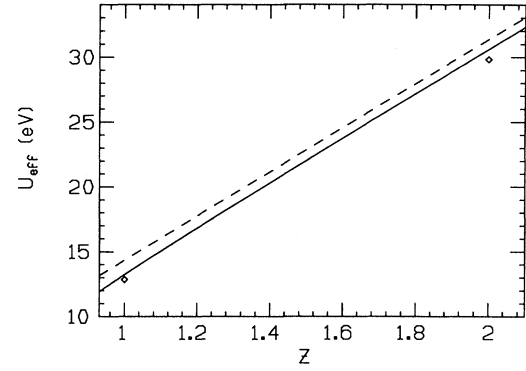
FIG. 2. Effective on-site repulsion for two electrons with the wave function Eq. (6) (solid line) and with the Hartree wave function with a single Slater orbital with exponent $\bar{\alpha} = Z - 5/16$ (dashed line). The experimental values of U_{eff} for $Z = 1$ and $Z = 2$ are shown by the squares.

which are seen to be approximately linear. A minimum in the electronic energy with the wave-function Eq. (6) and positive α_1, α_2 could only be found for $Z \geq 0.93$. In Fig. 2 we show the effective on-site repulsion

$$U_{\text{eff}} = E(2) + E(0) - 2E(1) \tag{9}$$

with $E(n)$ the atomic energy with n electrons, versus Z. The values of $E(1)$ are exact $(-Z^2$ Ry) so that a lower energy for the two-electron atom translates into a lower value for U_{eff}. Figure 2 also shows the experimental values of U_{eff} for $Z = 1$ and $Z = 2$, 12.852 eV and 29.824 eV, respectively; the values obtained from Eq.(9) are 13.24 eV and 30.60 eV, respectively.

It is certainly possible to construct wave functions for the simple diatomic molecules considered here that are much more accurate than the ones we use, and thus one may question the usefulness of the approach discussed here. Our purpose in using this step-wise approach is to gain an understanding of the physical origin of the difference in hopping amplitudes in the different molecular ions. This should allow us, for example, to estimate the importance of these effects in a variety of other situations without the need to perform a full configuration interaction calculation with a large basis set for each case.

In the next section we give some details of the calculation, and in Sec. III we present numerical results. In Sec. IV we interpret our results by using a tight-binding

model with two orbitals per site. We conclude in Sec. V with a discussion.

II. CALCULATION OF HOPPING AMPLITUDES

We follow the approach described in I. The Hamiltonian for three electrons in the diatomic molecule is

$$H_3 = h_1 + h_2 + h_3 + h_{12} + h_{23} + h_{31}, \tag{10}$$

$$h_i = -\nabla^2 - \frac{2Z}{r_{ia}} - \frac{2Z}{r_{ib}}, \tag{11}$$

$$h_{ij} = \frac{2}{r_{ij}}. \tag{12}$$

The bonding and antibonding wave functions are taken to be

$$\Psi_{\substack{b \\ a}}(r_1, r_2, r_3) = \frac{a_{\text{H}^-}(r_1, r_2)b(r_3) \pm a(r_1)b_{\text{H}^-}(r_2, r_3)}{[2(1 \pm S_{\text{H}_2^-})]^{1/2}} \tag{13}$$

with a_{H^-} and b_{H^-} the two-electron wave functions Eq. (6) for the two atoms, and a and b the single-electron wave functions, of the form Eq. (7) with $\alpha = Z$. The overlap $S_{\text{H}_2^-}$ is given by

$$S_{\text{H}_2^-} = \frac{(a_1, a)(a_2, b_1)(b, b_2) + (a_1, a)(a_2, b_2)(b, b_1) + (a_2, a)(a_1, b_1)(b, b_2) + (a_2, a)(a_1, b_2)(b, b_1)}{2(1 + S_{\text{H}^-})}. \tag{14}$$

The hopping amplitude for an electron in the three-electron molecule is then obtained from the difference in expectation values of the Hamiltonian with the two states Eq. (13) as

$$t_2 = \frac{-(a_{\text{H}^-}b, H_3, ab_{\text{H}^-}) + S_{\text{H}_2^-}(a_{\text{H}^-}b, H_3, a_{\text{H}^-}b)}{1 - S_{\text{H}_2^-}^2}. \tag{15}$$

It is straightforward to calculate the matrix elements of

H_3 needed in Eq. (15); some further calculational details are given in the Appendix.

Similarly, for the case of two electrons in the molecule the Hamiltonian is

$$H_2 = h_1 + h_2 + h_{12}. \tag{16}$$

As in I, we obtain the hopping amplitude t_1 from the splitting of energies of the configurations

$$\Psi_{\substack{b\\a}}(r_1, r_2) = \frac{a_{H^-}(r_1, r_2) \pm a(r_1)b(r_2)}{[2(1 \pm S_{H_2})]^{1/2}}, \tag{17}$$

$$S_{H_2} = \frac{(a_1, a_2)(a_2, b) + (a_2, a)(a_1, b)}{[2(1 + S_{H^-})]^{1/2}} \tag{18}$$

as

$$t_1 = \frac{-(a_{H^-}, H_2, ab) + S_{H_2}\frac{(a_{H^-}, H_2, a_{H^-}) + (ab, H, ab)}{2}}{1 - S_{H_2}^2}. \tag{19}$$

Finally, for the one-electron case the hopping amplitude is

$$t_0 = \frac{-(a, h, b) + S_{ab}(a, h, a)}{1 - S_{ab}^2}, \tag{20}$$

$$S_{ab} = (a, b). \tag{21}$$

All hopping amplitudes reduce to the ones calculated in I if we take $\alpha_1 = \alpha_2 = \bar{\alpha}$.

III. RESULTS

The qualitative behavior obtained for the hopping amplitudes is similar to what was found in I. Figure 3 shows the hopping amplitudes for the case $Z = 1$. The difference in hopping amplitudes is larger than when no radial correlations are included (Fig. 3 of I). Figure 4 shows comparison of $\Delta t = t_1 - t_2$, the quantity relevant for superconductivity, with the results of I: Δt is substantially larger here and it remains positive for large interatomic
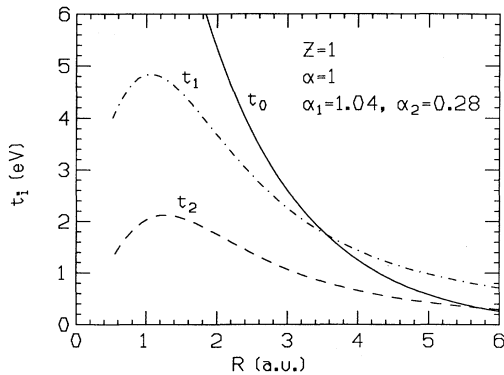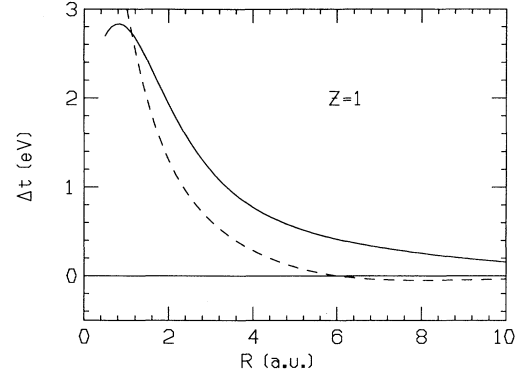

FIG. 4. Comparison of $\Delta t = t_1 - t_2$ with and without radial correlations (full and dashed lines, respectively) for $Z = 1$.

distances, in contrast with the results in the absence of radial correlations but in agreement with the "empirical estimate" of Ref. 4.

We examine next the effect of varying the nuclear charge Z. As mentioned in the previous section, no minimum of the two-electron atomic energy can be found for Z less than 0.93. This presumably indicates that the negative ion becomes unstable in vacuum, and could be remedied by including an external potential that simulates the atomic enviroment in a solid. Figures 5, 6, and 7 show the hopping amplitudes for $Z = 0.93$, $Z = 1.25$, and $Z = 2$, respectively. As in I the difference in hopping amplitudes decreases as Z increases, but $\Delta t = t_1 - t_2$ is found to be larger than in the absence of radial correlations, and positive in a larger range of interatomic distances. In fact, we find here that $t_1 > t_2$ for any interatomic distance for Z smaller than 1.75. In contrast, in I Δt became negative at $R \sim 6$ for $Z = 1$, and for smaller R when Z was larger.

We also examined here the effect of optimizing the orbital exponents separately for each interatomic separation. It was found difficult to obtain convergence for low values of Z, and in fact for $Z = 1$ no solution was found for R values smaller than 5.5. For $Z = 1.25$ the calcula-

FIG. 3. Hopping amplitudes for $Z = 1$ vs interatomic distance.
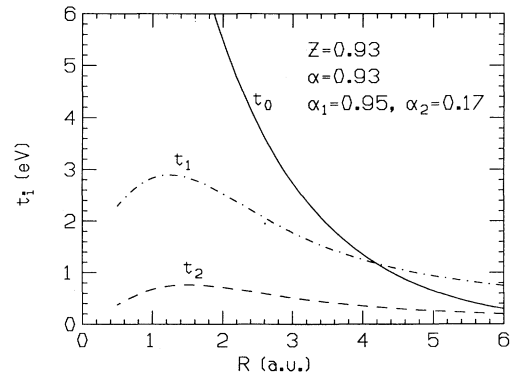

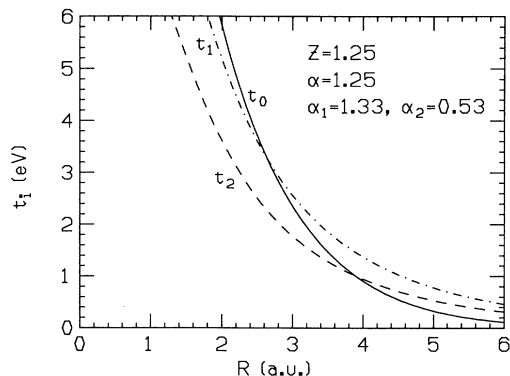FIG. 5. Hopping amplitudes for $Z = 0.93$ vs interatomic distance.

FIG. 6. Hopping amplitudes for $Z = 1.25$ vs interatomic distance.

tion did converge down to $R = 1.75$, and Fig. 8 shows the orbital exponents obtained for each state. For the molecule with two and three electrons the exponents α_1 and α_2 approach the atomic values 1.331 and 0.527 as R goes to infinity, while the exponent α approaches 1.25 in all cases. Figure 9 shows the hopping amplitudes obtained for this case with optimal exponents. The results start to differ appreciably with those found with atomic exponents (Fig. 6) for R less than 3; the improved calculation (with optimized exponents) yields larger values for the parameter $\Delta t = t_1 - t_2$ at short distances and slightly smaller ones at large distances.

The variation of Δt with distance for various values of Z is shown in Fig. 10. The results are similar to those found in I, but the values of Δt found here are appreciably larger, particularly for large interatomic separation.

In Fig. 11 we show comparison of our results for $(t_0 - t_2)/2$ for $Z = 2$ with the results of Gupta and Matsen.[5] The agreement with that calculation is somewhat improved compared with the results of I for small interatomic distances. In Fig. 12 we compare our results for $Z = 1$ with those of Eliezer, Taylor, and Williams[6]
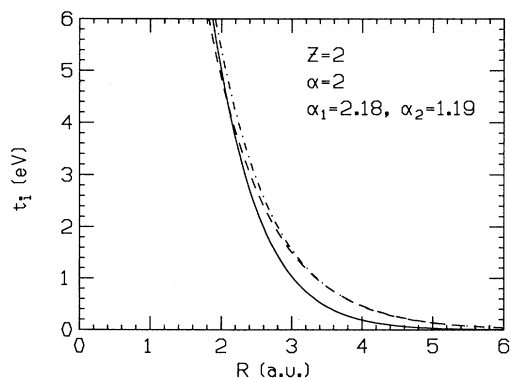
and Chen and Peacher.[7] Again the agreement is improved compared with the results of I, as expected.

In summary, we have found that inclusion of radial correlations further enhances the behavior found in I: the hopping amplitude for holes is smaller than that for electrons in a large range of interatomic separation, and the effect becomes more important for smaller effective ionic charge.
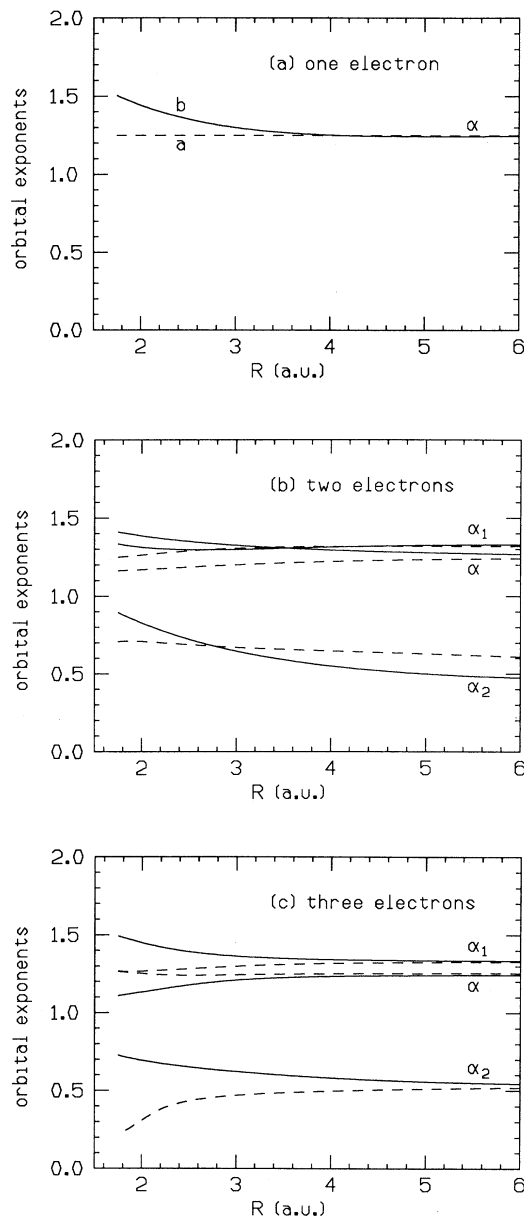

FIG. 8. Orbital exponents optimized for each interatomic separation to minimize the energy of bonding (full lines) and antibonding (dashed lines) states for $Z = 1.25$ and (a) one, (b) two, and (c) three electrons in the molecule. The limiting values for large R are the atomic values $\alpha_1 = 1.331$, $\alpha_2 = 0.527$, $\alpha = 1.25$.

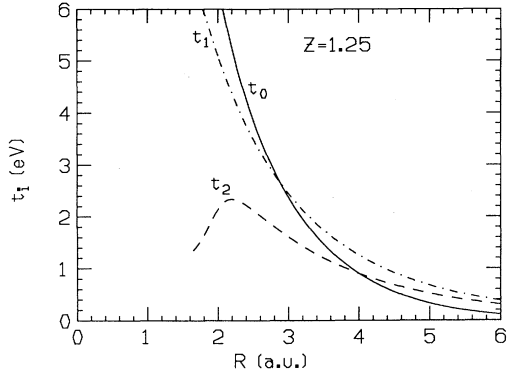FIG. 7. Hopping amplitudes for $Z = 2$ vs interatomic distance.

FIG. 9. Hopping amplitudes for $Z = 1.25$ with optimized orbital exponents vs interatomic distance.
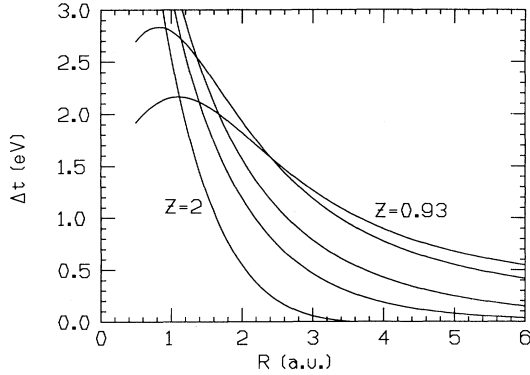

FIG. 10. Results for $\Delta t = t_1 - t_2$ vs interatomic distance for various values of the effective ionic charge Z. $Z = 0.93$, 1, 1.25, 1.5, and 2 (increasing Δt values correspond to decreasing Z at large R). Atomic orbital exponents were used.
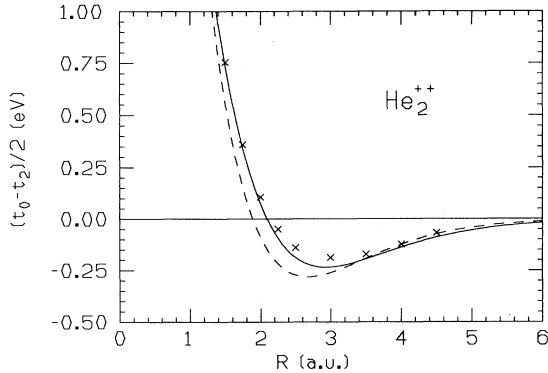

FIG. 11. Comparison of results for $(t_0 - t_2)/2$ for $Z = 2$ with results from Gupta and Matsen (Ref. 4) (crosses). The dashed line gives the results using the Hartree wave function of I.
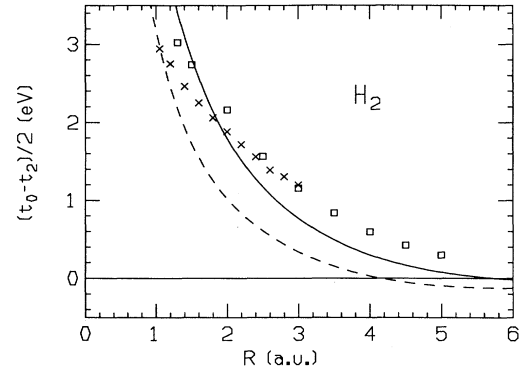

FIG. 12. Comparison of results for $(t_0 - t_2)/2$ for $Z = 1$ with results from Eliezer, Taylor, and Williams (Ref. 6) (crosses) and Chen and Peacher (Ref. 7) (squares) with radial correlations (full line) and without (dashed line). (Atomic exponents were used in both cases.)

IV. EFFECTIVE TIGHT-BINDING MODEL

An effective single-band tight-binding model that approximately describes the lowest energy state of each atom with zero, one, and two electrons is given by

$$H = -\sum_{ij\sigma} t_{ij}^{\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma} + \text{H.c.})$$
$$+ U_{\text{eff}}\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j \qquad (22\text{a})$$

with

$$t_{ij}^{\sigma} = t_0(1 - n_{i,-\sigma})(1 - n_{j,-\sigma})$$
$$+ t_1(n_{i,-\sigma} + n_{j,-\sigma} - 2n_{i,-\sigma}n_{j,-\sigma})$$
$$+ t_2 n_{i,-\sigma}n_{j,-\sigma}. \qquad (22\text{b})$$

The hopping amplitudes t_0, t_1, and t_2 are obtained as described earlier. The on-site repulsion U_{eff} is obtained from the difference in atomic energies Eq. (9). The nearest-neighbor repulsion V is approximately given by the nearest-neighbor Coulomb integral [Eq. (27b) of I]; more accurately, an "empirical" value for V can be found from the difference in energy of two excited states of the diatomic molecule with two electrons, as discussed in Ref. 4. Equation (22a) omits nearest-neighbor terms describing exchange and pair hopping (denoted by J in Ref. 4) as we do not expect them to be important for superconductivity.

A minimal tight-binding model with hopping amplitudes that are constant rather than functions of electronic occupation needs to have at least two orbitals per site, to allow for the modification of the electronic wave functions when there are two electrons at the site. A simple Hamiltonian of this kind that approximately describes the physics discussed in the previous sections is given by

$$H = \sum_i H_i + \sum_{\langle ij\rangle} H_{ij}, \qquad (23\text{a})$$

$$H_i = U_1 n_{i1\uparrow} n_{i1\downarrow} + U_2 n_{i2\uparrow} n_{i2\downarrow} + V_{12} n_{i1} n_{i2} + \epsilon n_{i2}, \quad (23\text{b})$$

$$H_{ij} = \sum_{l,l'=1,2} t_{ll'} (c_{il\sigma}^\dagger c_{jl'\sigma} + \text{H.c.}). \quad (23\text{c})$$

For an estimate of the parameters in this Hamiltonian we take as orbitals 1 and 2 the Slater orbitals with exponents α_1 and α_2 discussed in the previous sections. This is strictly speaking not correct because these orbitals are neither orthogonal nor eigenstates of the single-particle atomic Hamiltonian. Nevertheless we believe this procedure is reasonable to obtain a qualitative understanding. As observed earlier the exponent α_1 is very close to the exponent $\alpha = Z$ corresponding to the single-electron eigenstate, and we will ignore the difference here (i.e., take $\alpha_1 = Z$). As an example we consider the case $Z = 1$. The parameters are

$$U_1 = (a_1 a_1, h_{12}, a_1 a_1) = 17 \text{ eV}, \quad (24\text{a})$$

$$U_2 = (a_2 a_2, h_{12}, a_2 a_2) = 4.76 \text{ eV}, \quad (24\text{b})$$

$$V_{12} = (a_1 a_2, h_{12}, a_1 a_2) = 6.97 \text{ eV}, \quad (24\text{c})$$

$$\epsilon = (a_2, h, a_2) - (a_1, h, a_1) = 7.05 \text{ eV}. \quad (24\text{d})$$

Note that the relations

$$V_{12} + \epsilon < U_1, \quad (25\text{a})$$

$$V_{12} + \epsilon < U_2 + 2\epsilon \quad (25\text{b})$$

hold, implying that two electrons will occupy each one of the orbitals rather than both the same orbital, as described by the wave function Eq. (6).

A somewhat better description of the single atom is obtained by orthogonalizing the two Slater orbitals Eq. (7). Furthermore, in principle one should also include intra-atomic off-diagonal matrix elements of the Coulomb interaction. However, including these effects does not seem to clarify the physics and will not be pursued here.

The parameters $t_{ll'}$ in Eq. (23c) give the hopping amplitude for a single electron between orbitals l and l' at the two atoms. We estimate these parameters from the relation Eq. (20) for a single electron in the molecule, generalized to the case where the orbitals at the two atoms can be different, as

$$t_{ll'} = \frac{-(a_l, h_{ll'}, b_{l'}) + S_{a_l, b_{l'}} \frac{(a_l, h_{ll'}, a_l) + (b_{l'}, h_{ll'}, b_{l'})}{2}}{1 - S_{a_l, b_{l'}}^2}, \quad (26\text{a})$$

$$S_{a_l, b_{l'}} = (a_l, b_{l'}) \quad (26\text{b})$$

and as a single-particle Hamiltonian we use Eq. (11) with ionic charges given by the orbital exponents

$$h_{ll'} = -\nabla^2 - \frac{2\alpha_l}{r_{ia}} - \frac{2\alpha_{l'}}{r_{ib}}. \quad (26\text{c})$$

Finally, to map the two-orbital Hamiltonian Eq. (23) onto the effective single-band model Eq. (22) we project onto the lowest atomic eigenstates for each electronic occupation. If $|\sigma, \sigma'\rangle$ is the atomic state with an electron of spin σ in state 1 and one of spin σ' in state 2, the relevant atomic states are given by

$$|\tilde{0}\rangle = |0, 0\rangle, \quad (27\text{a})$$

$$|\tilde{\uparrow}\rangle = |\uparrow, 0\rangle, \quad (27\text{b})$$

$$|\tilde{\downarrow}\rangle = |\downarrow, 0\rangle, \quad (27\text{c})$$

$$|\widetilde{\uparrow\downarrow}\rangle = \frac{|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle}{\sqrt{2}} \quad (27\text{d})$$

and we obtain for the effective hopping amplitudes of the single-band Hamiltonian

$$t_0 = t_{00}, \quad (28\text{a})$$

$$t_1 = \frac{t_{01}}{\sqrt{2}}, \quad (28\text{b})$$

$$t_2 = \frac{t_{11}}{2} \quad (28\text{c})$$

and for the effective on-site repulsion, using the relation Eq. (9)

$$U_{\text{eff}} = V_{12} + \epsilon. \quad (29)$$

For $Z = 1$, Eqs. (29) and (24) yield $U_{\text{eff}} = 14.02$ eV, which is not too far from the value obtained in Sec. I, $U_{\text{eff}} = 13.24$ eV (the difference arises from the neglect of nonorthogonality of the orbitals and intra-atomic off-diagonal Coulomb matrix elements). The values of the effective hoppings obtained from Eqs. (26) and (28) are shown in Fig. 13. They resemble the results obtained in the previous section, although at short distances the hopping amplitudes t_1 and t_2 are significantly smaller here. The error arises presumably due to the fact that at short distances the approximation of treating one electron as moving in the effective field arising from the ions screened by the other electrons, as assumed in Eq. (26), breaks down. In Fig. 14 we compare the hopping amplitudes at larger distances. It can be seen that the agreement is remarkably good. For smaller Z the comparison is found to be even better, and it becomes slightly worse for larger Z.

Thus the difference in the hopping amplitudes t_0, t_1, and t_2 is seen to arise from several additive effects. On one hand, the hoppings $t_{ll'}$ get reduced by overlap matrix elements [Eq. (28)] as more electrons are added, due to the rearrangement of the wave function that occurs when an electron leaves a doubly occupied site or enters a singly occupied one. On the other hand the "bare" hoppings $t_{ll'}$ are not all equal, and here again the difference is due to two effects. On one hand the fact that
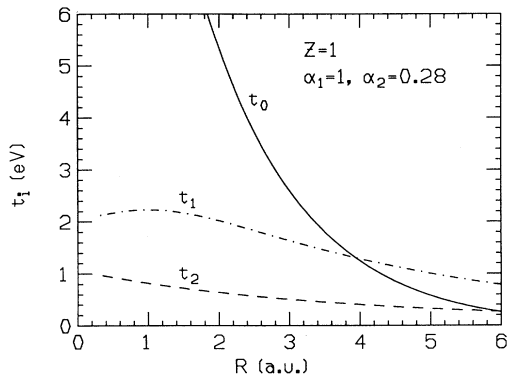
FIG. 13. Hopping amplitudes for effective tight-binding model obtained from Eqs. (26) and (28) with $Z = 1$ and orbital exponents $\alpha_1 = 1$, $\alpha_2 = 0.28$, vs interatomic distance.
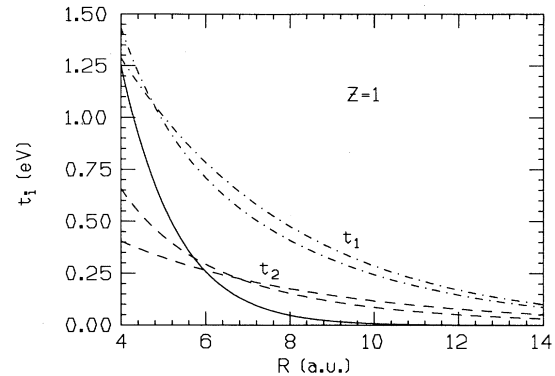

FIG. 14. Comparison of hopping amplitudes for effective tight-binding model and those from the first-principles calculation for larger distances. $Z = 1$. For t_0 (full line) the results of both calculations are identical, as $\alpha_1 = Z$. For t_1 (dash-dotted lines) and t_2 (dashed lines) the results of the effective tight-binding model are smaller than those of the first-principles calculation at the lowest R, and the curves cross for larger R.

the wave function is more extended for a smaller orbital exponent leads to $t_{00} < t_{01}, t_{11}$ at large distances; on the other hand, the fact that the effective ionic potential [Eq. (26c)] is smaller for smaller α due to the screening of the other electron leads to $t_{00} > t_{01} > t_{11}$ at shorter distances. The combination of all these effects is seen to lead to the ordering $t_0 > t_1 > t_2$ at short and intermediate distances, with the crossover distance to other orderings a decreasing function of the ionic charge Z.

V. DISCUSSION

Continuing our study of the dependence of electronic hopping amplitude between two atoms on the number of electrons in the atom we have considered here the effect of radial correlations. Allowing for radial correlations is seen to improve on the estimate of the ground-state energy of the atom with two electrons and to substantially change the wave function: one electron occupies an orbital with exponent α_1 very close to the atomic charge Z, while the second one occupies an orbital with exponent α_2 that is substantially smaller, i.e., an orbital that is substantially more extended in space.

It was found that inclusion of radial correlations significantly enhances the qualitative behavior found in I: the hopping amplitude for electrons decreases as the number of electrons increases, i.e., $t_0 > t_1 > t_2$ in a large range of interatomic distances. In contrast to the results in I, here the ordering $t_1 > t_2$ (relevant to hole superconductivity) was found to hold for arbitrarily large distances for not too large Z ($Z < 1.75$). Furthermore, the single-hole-hopping amplitude t_2 was found here to be appreciably reduced compared to the results in I. Optimization of the exponents for each interatomic separation was found not to have a large effect (as in I) except at rather small distances.

The results in this paper and in I indicate that a Hubbard model with a single orbital per site[8] is inadequate to describe the physics of correlations of electrons in metals,

except perhaps for cases of low electronic band occupation, where the probability of two electrons occupying the same atom is small. The key point is that when two electrons occupy the same atom a new degree of freedom opens up: in the qualitative picture underlying the results of this paper, the second electron tends to occupy a high-energy orbital that is substantially more diffuse than the first one. This is simply due to the fact that the intra-atomic Coulomb repulsion between electrons is larger than the spacing between atomic energy levels. In the end it is still possible to map the low-energy physics onto an effective single-band tight-binding Hamiltonian, provided the hopping amplitude for an electron is allowed to depend on the electronic charge occupation of the two sites involved in the hopping process. Alternatively, a "minimal" tight-binding model with hopping amplitudes that are constants needs to include at least two orbitals per site, as given by Eq. (23).

This tight-binding model with two orbitals per site was seen to describe the behavior of the hopping amplitudes reasonably well at not too short interatomic distances. Within this model the difference in hopping amplitudes with different number of electrons can be understood as arising from the combination of the following effects: the facts that the hopping amplitude for an electron depends on the "effective charge" of the atoms seen by that electron and on the spatial extent of its wave function, and the rearrangement of the electronic wave functions that occurs when an electron leaves a doubly occupied site or enters a singly occupied site.

As seen in this paper and in I, a lower effective ionic charge Z enhances the difference in hopping amplitudes. Additionally, as seen in Fig. 2, the effective on-site repulsion between two electrons decreases with decreasing ionic charge. These two effects are favorable to s-wave

superconductivity.[2]

The possibility of a Δt term in the low-energy effective Hamiltonian for high-T_c oxides has recently been considered by Martin.[9] This author finds in small-cluster calculations that the conducting holes reside in the planar O $p\sigma$ Cu $d_{x^2-y^2}$ orbitals, and that the parameter Δt is too small to be relevant for superconductivity. However, we believe that the relevant conducting holes may reside in the O $p\pi$ orbitals in the planes.[10,11] The calculations here suggest that the parameter Δt for holes conducting through these orbitals should be rather large and relevant to the superconductivity of these materials.

Whether the variation of hopping amplitude with charge occupation in metals may have observable effects other than superconductivity remains an interesting open question.

APPENDIX

Many of the matrix elements needed here, in particular all the overlap and single-particle matrix elements of the Hamiltonian, were given in the Appendix of I. We list here the general form of the two-particle matrix elements needed. The functions $L_i(\omega)$ and $M_i(\omega)$ were also given in the Appendix of I.

1. On-site Coulomb

$$(a_1, a_2, h_{12}, a_3, a_4) = 64(\alpha_1\alpha_2\alpha_3\alpha_4)^{3/2}\frac{(\alpha_1+\alpha_3)^2 + 3(\alpha_1+\alpha_3)(\alpha_2+\alpha_4) + (\alpha_2+\alpha_4)^2}{(\alpha_1+\alpha_3)^2(\alpha_2+\alpha_4)^2(\alpha_1+\alpha_2+\alpha_3+\alpha_4)^3}. \tag{A1}$$

2. Nearest-neighbor Coulomb

$$\begin{aligned}(a_1 b_2, h_{12}, a_3 b_4) = &\frac{(4\alpha_1\alpha_3)^{(3/2)}}{(\alpha 1 + \alpha_3)^3}(\alpha_2\alpha_4)^{1/2}\omega_2\omega_4 \\ &\times \{L_1(\omega_{24})M_0(\omega_{24}) - L_0(\omega_{24})M_1(\omega_{24}) - L_1(\omega_L)M_0(\omega_M) + L_0(\omega_L)M_1(\omega_M) \\ &- (\omega_1 + \omega_3)[L_2(\omega_l)M_0(\omega_M) - L_0(\omega_L)M_2(\omega_M)]/4\}.\end{aligned} \tag{A2}$$

3. Hybrid

$$\begin{aligned}(a_1 a_2, h_{12}, a_3 b_4) = &\frac{(4\alpha_1\alpha_3)^{(3/2)}}{(\alpha 1 + \alpha_3)^3}(\alpha_2\alpha_4)^{1/2}\omega_2\omega_4 \\ &\times \{L_1(\omega_{24})M_0(\omega_{42}) - L_0(\omega_{24})M_1(\omega_{42}) - L_1(\omega_L)M_0(\omega_{\bar{M}}) + L_0(\omega_L)M_1(\omega_{\bar{M}}) \\ &- (\omega_1 + \omega_3)[L_2(\omega_l)M_0(\omega_{\bar{M}}) - L_0(\omega_L)M_2(\omega_{\bar{M}})]/4\},\end{aligned} \tag{A3}$$

where

$$\omega_{24} = \frac{\omega_2 + \omega_4}{2}, \tag{A4a}$$

$$\omega_{42} = \frac{\omega_4 - \omega_2}{2}, \tag{A4b}$$

$$\omega_L = \frac{\omega_1 + \omega_2 + \omega_3 + \omega_4}{2}, \tag{A4c}$$

$$\omega_M = \frac{-\omega_1 + \omega_2 - \omega_3 + \omega_4}{2}, \tag{A4d}$$

$$\omega_{\bar{M}} = \frac{-\omega_1 - \omega_2 - \omega_3 + \omega_4}{2}. \tag{A4e}$$

The expressions for the matrix elements of the Hamiltonian with the two-electron atomic wave function Eq. (6) are straightforward to evaluate in terms of these matrix elements but lengthy, and will not be given here.

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