

Electron- and hole-hopping amplitudes in a diatomic molecule. III. p orbitals

J. E. Hirsch

*Department of Physics, University of California, San Diego
La Jolla, California 92093-0319*

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The dependence of electronic hopping amplitude between neighboring atoms on the charge occupation of the orbitals is studied here for the case of p orbitals. Three different orientations of the orbitals at the two atoms are considered: σ , π , and π' , corresponding to an angle between the orbitals and the line connecting the atoms of 0° , 90° , and 45° , respectively. The Mulliken approximation is found to hold accurately for the π arrangement but not for the σ and π' arrangements; as a consequence in the latter cases the hopping amplitudes are found to vary with charge occupation even if a single rigid orbital per atom is considered. When modification of atomic orbitals with charge occupation is allowed for and intraatomic radial correlations are considered, the hopping amplitude is found to vary with charge occupation in all three cases, becoming increasingly smaller as more electrons are added. The dependence of our results on the ionic charge Z , and possible implications for the understanding of superconductivity in high- T_c oxides and fullerenes are discussed.

I. INTRODUCTION

This is the third in a series of papers where we study the dependence of electronic hopping amplitude between neighboring atoms on the charge occupation of the atoms. In Refs. 1 and 2 (hereafter referred to as I and II) this question was studied for the case of $1s$ orbitals, in the Hartree approximation (I) and with inclusion of radial correlations (II). Here we consider the same question for the case of $2p$ orbitals.

It was found in I and II that in a range of parameters of physical interest the hopping amplitude for electrons decreases as the atomic charge occupation (number of electrons in the atom) increases. This finding could be relevant to the understanding of superconductivity, as discussed in I and references therein. It contradicts the expectation³⁻⁵ that hopping amplitudes should increase as the atomic charge occupation increases, due to the orbital expansion that occurs when an electron is added to an atom which leads to increased overlap between orbitals at neighboring sites. Reasons for the failure of this expectation are discussed in I and II. It also contradicts the common assumption that no significant dependence of electronic hopping amplitude with charge occupation exists, as embodied in the conventional single-band Hubbard⁶ and related models.

It is important to extend our study to p orbitals, as it is conceivable that the above described behavior could be specific to $1s$ orbitals. We will find that this is not the case. Also, p orbitals are relevant to superconductors of great current interest: oxygen $2p$ orbitals in high- T_c oxides and carbon $2p\pi$ orbitals in fullerenes are believed to play a significant role in conduction. More generally, p orbitals are involved in metallic conductivity in a wide range of substances.

We consider here diatomic molecules with atomic $2p$ Slater orbitals, given by

$$a_\alpha(r) = \left(\frac{\alpha^5}{\pi}\right)^{1/2} r \cos\theta e^{-\alpha r_a}, \quad (1)$$

with r_a the coordinate relative to atom a . For a single electron in such an orbital in the presence of ionic charge Z the lowest energy state occurs for

$$\alpha = Z/2. \quad (2)$$

Two electrons in such an orbital experience a repulsion given by (we use atomic units with energy measured in Rydbergs)

$$U_0 = \int d^3r d^3r' a_\alpha^2(r) a_\alpha^2(r') \frac{2}{|r-r'|} = \frac{501}{640} \alpha, \quad (3)$$

which will be lowered if the orbital exponent α decreases. The single-particle energy, however,

$$\epsilon = \alpha^2 - \alpha Z \quad (4)$$

increases in that case, and the energy is minimized for an orbital exponent

$$\bar{\alpha} = \frac{Z}{2} - \frac{501}{2560}. \quad (5)$$

We can do even better by allowing for radial correlations between the two electrons in the atom through the Eckart wave function⁷

$$\Psi(r_1, r_2) = \frac{a_1(r_1)a_2(r_2) + a_2(r_1)a_1(r_2)}{[2(1+S_{12}^2)]^{1/2}}, \quad (6)$$

$$S_{12} = (a_1, a_2), \quad (7)$$

with a_i the Slater orbital Eq. (1) with orbital exponent α_i . The energy is minimized by choosing rather different values for α_1 and α_2 . For $Z = 2$, the result is $\alpha_1 = 1.0642$,

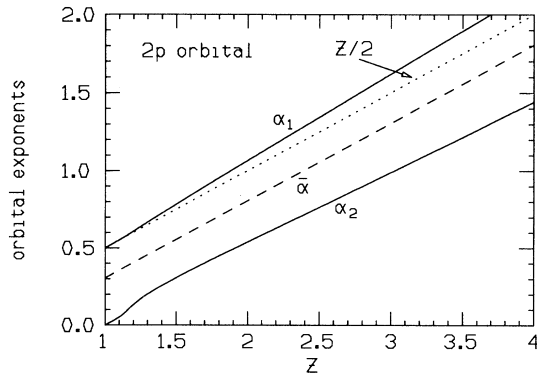


FIG. 1. Orbital exponents for a single electron in a p orbital ($Z/2$, dotted line) and for two electrons within the Hartree approximation ($\bar{\alpha}$, dashed line) and allowing for radial correlations (α_1 and α_2 , solid lines), versus ionic charge Z .

$\alpha_2 = 0.5381$. The energy in this case is $E = -1.322$, lower than the one with a single exponent $\bar{\alpha}$, $E = -1.294$ (as well as the one with $\alpha = Z/2$, $E = -1.217$).

Figure 1 shows the orbital exponents for the three cases discussed above as a function of ionic charge Z . The behavior is remarkably similar to what was found in the case of s orbitals:² when allowing for radial correlations, one of the exponents remains very close to the one appropriate to the single electron ($Z/2$ in this case) and the other one is substantially reduced. The effective repulsion between the two electrons in the orbital,

$$U_{\text{at}} = E(2) + E(0) - 2E(1) \quad (8)$$

[with $E(n)$ the energy of the atom with n electrons], is reduced as the two-electron wave function is modified to lower the energy. Figure 2 shows U_{at} versus ionic charge Z for the three cases.

We consider three different arrangements of the p orbitals in the molecule, as shown in Fig. 3. The π arrangement is relevant for example for the $2p\pi$ electrons in C_{60} . It would also be relevant to high- T_c oxides if conduction

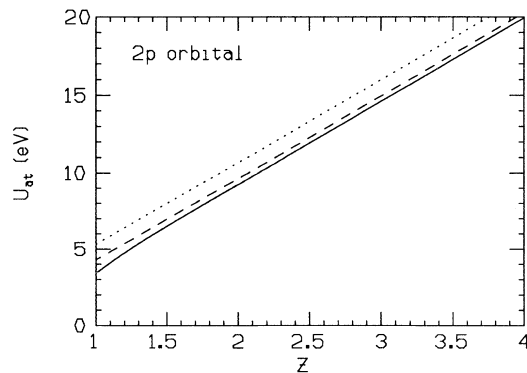


FIG. 2. Effective repulsion [Eq. (8)] for two electrons in a p orbital with no orbital relaxation (dotted line), within the Hartree approximation (dashed line), and allowing for radial correlations (solid line).

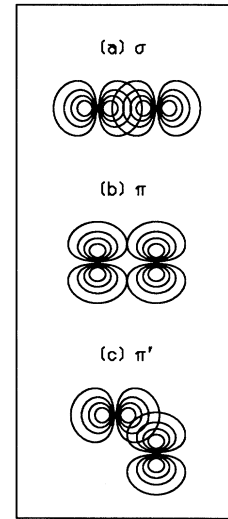


FIG. 3. Three different arrangements of the p orbitals at neighboring atoms. We plot contours where the wave function has an amplitude of 0.2, 0.4, 0.6, and 0.8 of its maximum value.

in the planes occurred through carriers in the oxygen p_z orbitals, which is however unlikely. The π' arrangement is relevant to high- T_c oxides if conduction occurs in the planes through the O orbitals that are perpendicular to the Cu-O bonds (usually termed “oxygen $p\pi$ ” orbitals also), as suggested by some authors.⁸ Finally, the σ arrangement would be relevant to high- T_c oxides if a rotation of oxygen planar p orbitals occurred so that they point along the line connecting two oxygens, as suggested by Abrikosov and Fal'covskii.⁹

II. CALCULATION

We use the method discussed in I and II to calculate the hopping amplitudes for the cases of one, two, and three electrons in the molecule. Because the Hamiltonian matrix elements become rather complicated for Slater p orbitals¹⁰ we use a Gaussian representation instead.¹¹ Each Slater orbital is represented as a sum of Gaussian functions:

$$a_\alpha(r) = \sum_{k=1}^K d_k g_{2p}(\alpha^2 \alpha_k, r_a), \quad (9a)$$

with

$$g_{2p}(\alpha_k, r) = \left(\frac{128\alpha^5}{\pi^3} \right)^{1/4} r \cos\theta e^{-\alpha_k r^2}. \quad (9b)$$

We used the coefficients d_k and exponents α_k given by Hehre *et al.*¹² with $K = 6$, which give an accurate representation of the Slater orbitals. Formulas for overlaps and the Hamiltonian matrix element between Gaussian orbitals are given by Saunders.¹³ Comparison of all Hamil-

tonian matrix elements and overlaps with the ones obtained by Kopineck¹⁴ and Kotani *et al.*¹⁵ using Slater orbitals for the σ and π orientations yielded agreement to better than 0.1% for interatomic distances between 1 and 7 atomic units [see Fig. 4(a) for an example]. As a further check on our program, we repeated the calculations of I and II using the Gaussian representation of $1s$ functions given by Hehre *et al.* (with $K = 6$) and found excellent agreement for interatomic distances up to 10 atomic units.

A general matrix element of the Coulomb interaction between electrons is given by

$$(ab|1/r|cd) = \int dv_1 dv_2 a(r_1)b(r_2) \frac{2}{|r_1 - r_2|} c(r_1)d(r_2). \quad (10)$$

In Fig. 4 we plot the hybrid matrix element

$$\Delta t^0 = (aa|1/r|ab) \quad (11)$$

(a and b are Slater orbitals centered at the two atoms, with orbital exponent $\alpha = Z/2$) versus interatomic distance, as well as the quantity $S(U + V)/2$, with

$$S = (a, b), \quad (12a)$$

$$U = (aa|1/r|aa), \quad (12b)$$

$$V = (ab|1/r|ab). \quad (12c)$$

It can be seen that the hybrid matrix element is rather large for intermediate interatomic distances (relevant to solids). The Mulliken approximation¹⁶

$$\Delta t^0 \sim \frac{S}{2}(U + V) \quad (13)$$

is seen to hold rather accurately for the π arrangement but not for the σ and π' arrangements. As shown in I if the orbitals do not change with electronic occupation the difference in hopping amplitudes for the different cases is

$$\Delta t = t_1 - t_2 = t_0 - t_1 = \frac{\Delta t^0 - \frac{S}{2}(U + V)}{1 - S^2}. \quad (14)$$

Here, t_i is the hopping amplitude for an electron when there are i other electrons at the orbitals involved. Therefore, we expect a positive Δt even for fixed orbitals for the arrangements σ and π' . This is in contrast to the results for the case of $1s$ orbitals^{1,2} where the Mulliken approximation was accurately satisfied, similarly to the case of π orbitals here. We do not have a simple explanation for why the Mulliken approximation holds accurately in some cases and not in others.

Figure 5 shows the hopping amplitudes for the three cases assuming fixed orbital exponents for all orbitals, $\alpha = Z/2$. As expected, we find an appreciable difference in hopping amplitudes for the cases of σ and π' orbitals at intermediate separations.

III. RESULTS

We next present the results obtained for the hopping amplitudes when the atomic wave function for two electrons is of the Eckart form Eq. (6), with exponents optimized for the isolated atom. We have not attempted to optimize the exponents separately for each interatomic separation; for the cases studied in I and II, such opti-

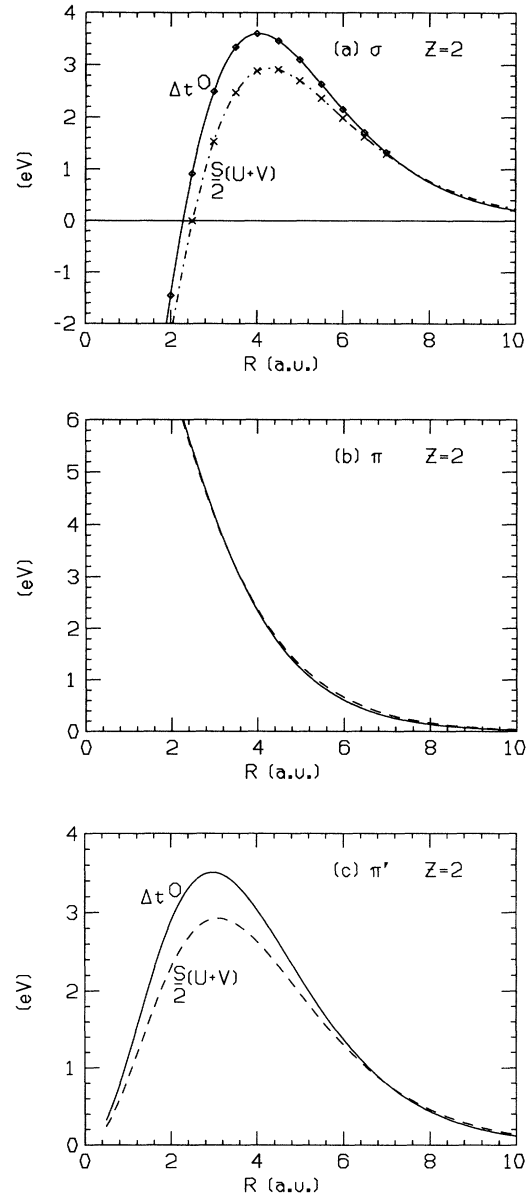


FIG. 4. Comparison of bare hybrid matrix element Δt^0 [Eq. (11)] (solid lines) with the form given by the Mulliken approximation Eq. (13) (dashed lines) for (a) σ , (b) π , and (c) π' arrangements (see Fig. 3). R denotes the distance between the two atoms. $Z = 2$. In (a) we also show results for Δt^0 (open squares) and $S(U + V)/2$ (crosses) using the Slater orbital integral expressions (Ref. 14) to illustrate the accuracy of the Gaussian representation.

mization did not have a large effect except at small interatomic distances. Results for the case of the Hartree atomic wave function, with exponent given by Eq. (5), will not be presented; it is generally found that they are in between those found with the more accurate Eckart wave function and with the fixed exponents $\alpha_i = Z/2$.

Figure 6 shows hopping amplitudes versus interatomic distance for $Z = 2$ and the three arrangements considered. In all cases, it can be seen that the hopping amplitude for a single hole (t_2) is smaller than for two holes (t_1), which is the situation favorable to hole

superconductivity.¹⁷ Surprisingly, we find that for the σ arrangement the parameter $\Delta t = t_1 - t_2$ is *reduced* when modification of the atomic orbital is allowed [compare Figs. 5(a) and 6(a)] at intermediate interatomic distances, contrary to what was found for the case of s orbitals.^{1,2} For the π and π' arrangements instead modification of the atomic wave function can be seen to enhance Δt , similarly to what occurred in the case of s orbitals.

Next we consider the effect of changing the ionic charge Z . Figures 7, 8, and 9 show the effect of varying Z in the σ , π , and π' arrangements respectively. In all cases the hopping amplitudes, and in particular the single-hole hopping amplitude t_2 , become substantially smaller as Z

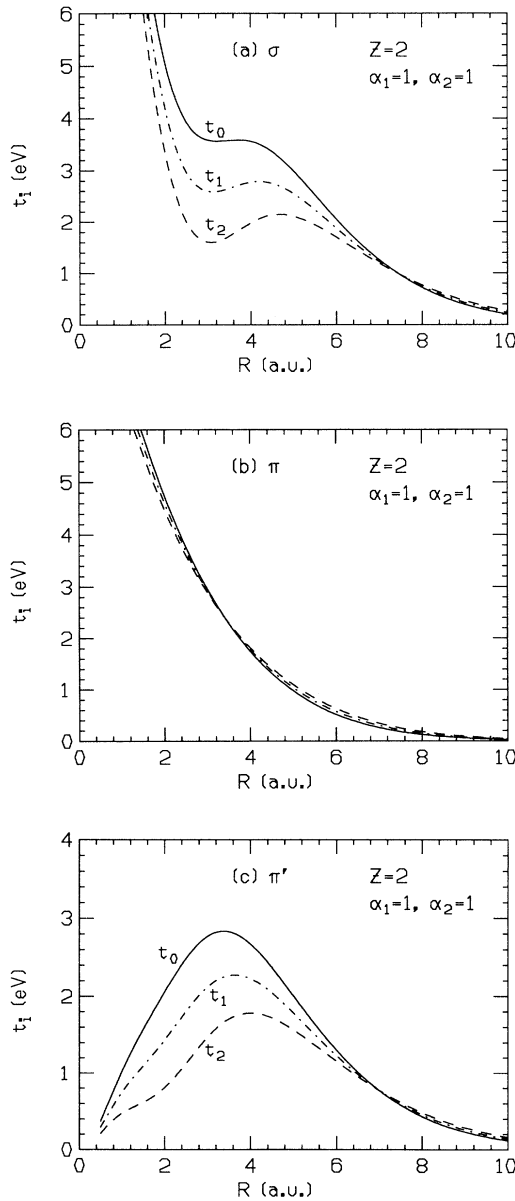


FIG. 5. Hopping amplitudes t_i for an electron when there are i other electrons in the orbitals versus interatomic distance, for $Z = 2$ and fixed orbital exponents $\alpha_1 = \alpha_2 = Z/2$. (a) σ , (b) π , and (c) π' arrangements. In this and the following figures, the solid, dash-dotted, and dashed lines correspond to t_0 , t_1 , and t_2 respectively.

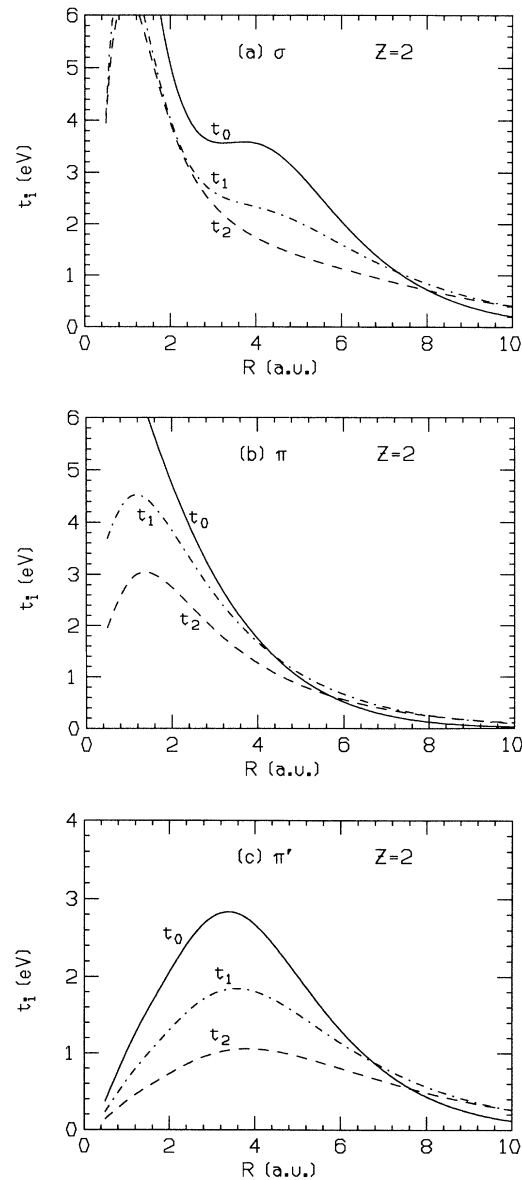


FIG. 6. Hopping amplitudes versus interatomic distance for the three arrangements considered and $Z = 2$. In this and the following figures the orbital exponents used are the optimal atomic ones with the Eckart wave function.

decreases at small and intermediate R . The single-hole hopping amplitude t_2 only becomes larger than t_1 for the largest Z at large R . The behavior of the hopping amplitudes in the σ case, Fig. 7, is rather anomalous as the difference Δt decreases substantially as the ionic charge decreases. In the other cases, Δt remains large and in particular becomes much larger than t_2 as the ionic charge decreases, which favors hole superconductivity,¹⁷ similarly to what was found in the case of s orbitals.^{1,2}

It is interesting to note that the hopping amplitudes in the π' geometry are not simply given by a linear combination of the hopping amplitudes in the σ and π geometries, as might have been expected. This is because the orbitals at the different atoms are not orthogonal. To illustrate this point Fig. 9(b) shows the average of σ and π hop-

ping amplitudes as dotted lines. Although they join the hopping amplitudes in the π' geometry at large R , they are generally larger at small R . Thus, estimating the hopping amplitudes in the π' geometry from the average of hopping amplitudes in the σ and π geometries would overestimate the hoppings, particularly t_2 , and underestimate the value of $\Delta t = t_1 - t_2$ over a wide range of R . This range however decreases as the ionic charge Z increases.

It was assumed in our work on hole superconductivity¹⁷ that the ratio $\Delta t/t_2$ was approximately independent of interatomic distance. To test this, we plot in Fig. 10 this ratio for the three arrangements and various values of Z . It can be seen that the assumption is not satisfied in the case of σ orbitals but holds rather

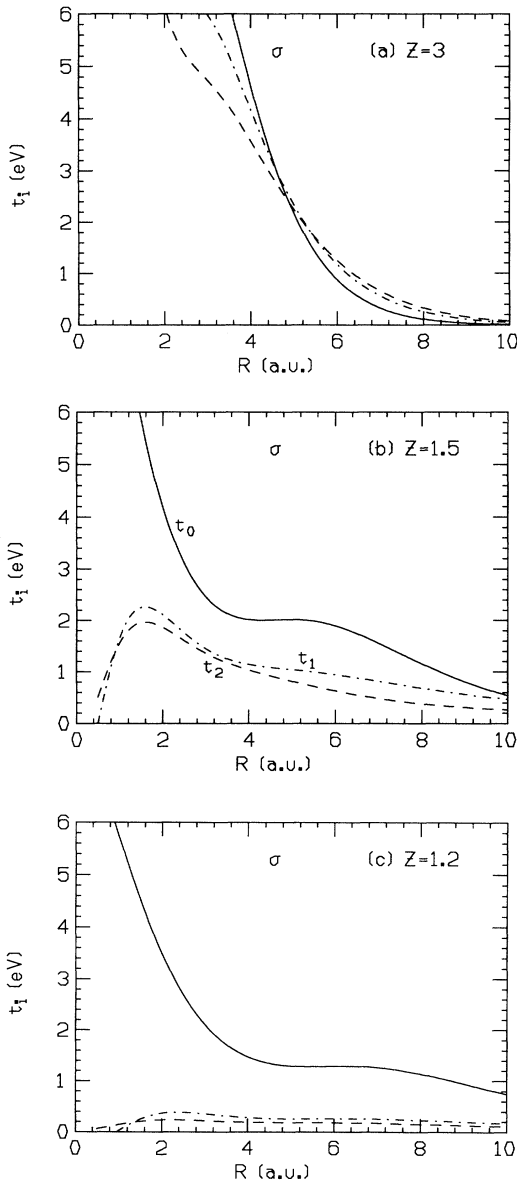


FIG. 7. Hopping amplitudes versus interatomic distance for $p\sigma$ orbitals for three different values of the ionic charge.

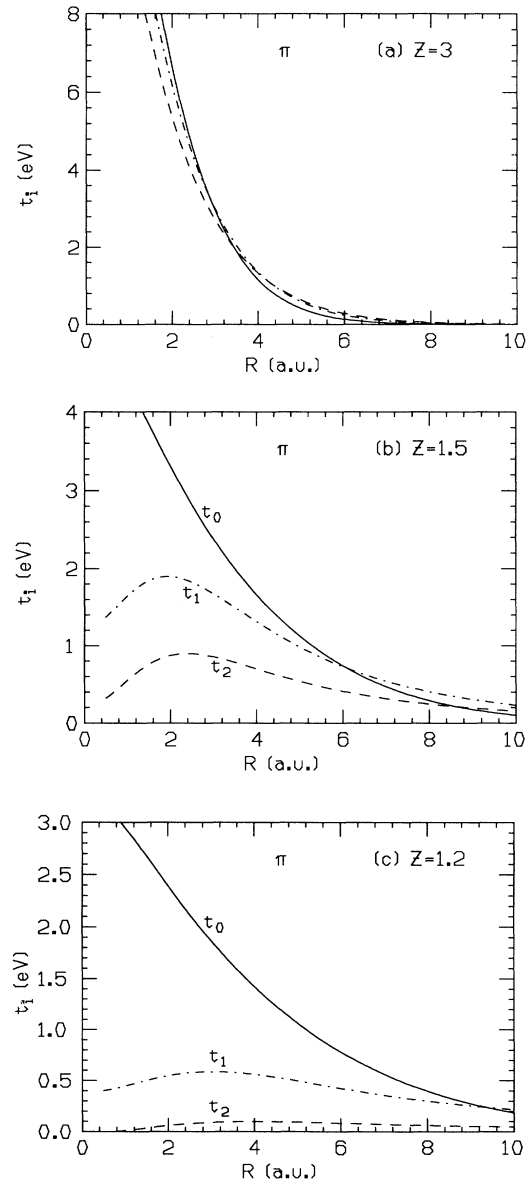


FIG. 8. Hopping amplitudes versus interatomic distance for $p\pi$ orbitals for three different values of the ionic charge.

well for the π and π' arrangements. In the latter two cases, the ratio $\Delta t/t_2$ becomes much larger than unity as Z decreases, while in the case of σ orbitals the ratio is always less than unity. It was assumed in our work on hole superconductivity that that ratio could become much larger than unity.

In Fig. 11 we show the variation of Δt and t_2 with ionic charge for fixed interatomic separation, $R = 5.25$ a.u. This corresponds to the planar oxygen-oxygen separation in high- T_c oxides. For the σ case Δt is always smaller

than t_2 , while for the π and π' cases it becomes larger at small values of Z . This together with the reduction in the on-site repulsion with decreasing Z (Fig. 2) favors superconductivity. For the π orientation we also show these quantities for interatomic distance $R = 2.65$ a.u., corresponding to the intercarbon distance in the standard C-C π bond, in Fig. 12. It can be seen that the value of Δt is rather substantial here for a wide range of ionic charge.

IV. SUPERCONDUCTIVITY IN HIGH- T_c OXIDES

In this section we examine whether the obtained values of Δt and t_2 in the π' arrangement can give rise to

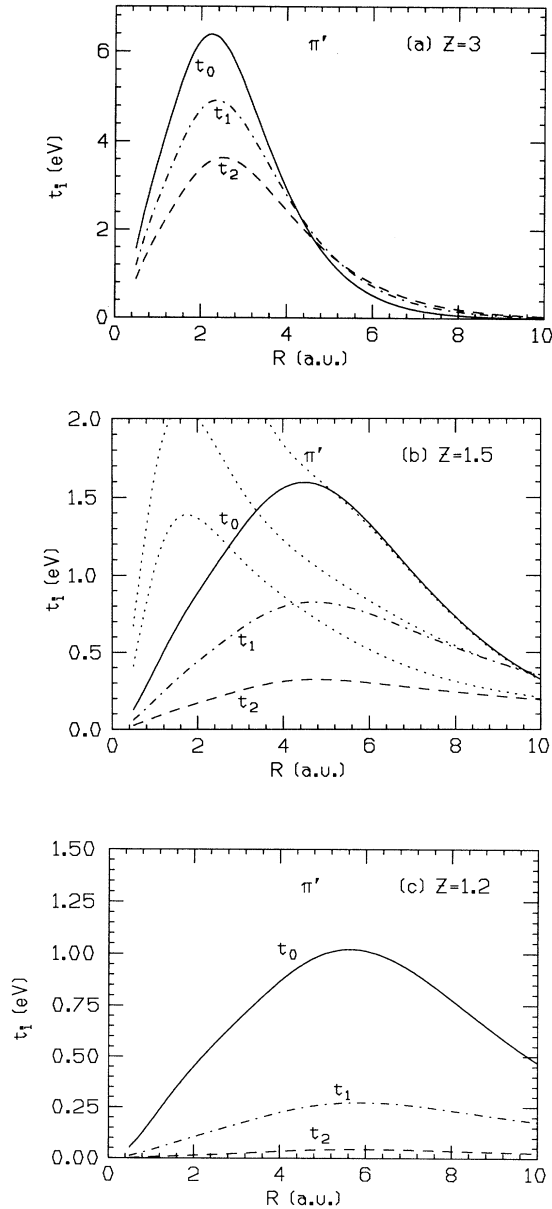


FIG. 9. Hopping amplitudes versus interatomic distance for $p\pi'$ orbitals for three different values of the ionic charge. The dotted lines in (b) show the average of the hopping amplitudes in the σ and π geometries [Figs. 7(b) and 8(b)]; they join the corresponding hopping amplitudes in the π' geometry for large R .

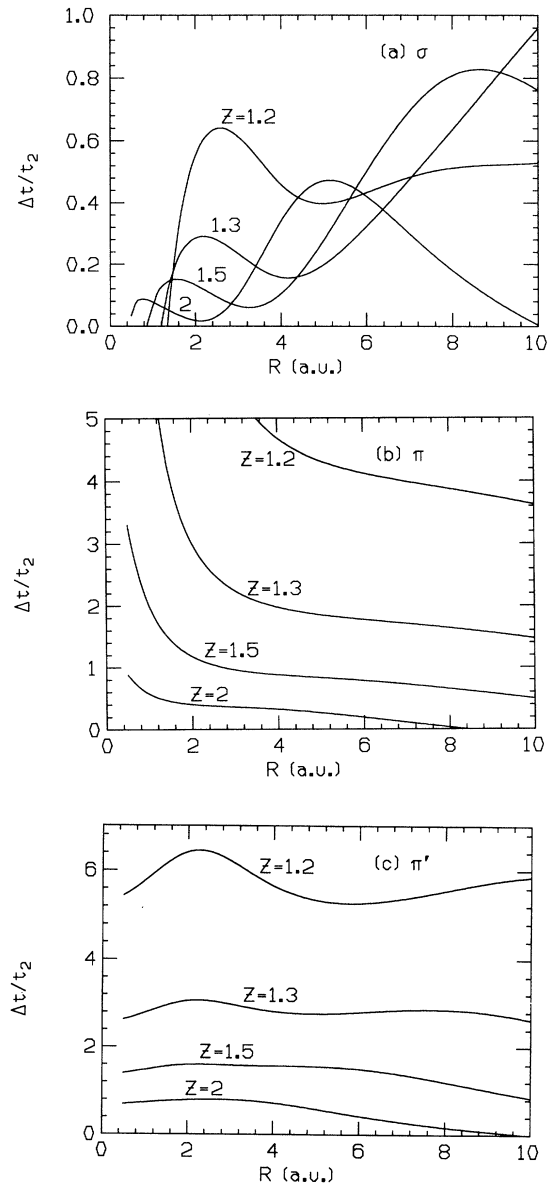


FIG. 10. Ratio $\Delta t/t_2$ versus interatomic distance for (a) σ , (b) π , and (c) π' arrangements for various values of the ionic charge.

superconductivity. We assume an interatomic distance $R = 5.25$ a.u., appropriate to the planar 0-0 distance in the cuprates, and use the weak coupling form of the T_c equation¹⁷ which is accurate except for very low hole density.

In the absence of nearest-neighbor Coulomb repulsion superconductivity is obtained in the entire range of ionic charge $1.1 < Z < 2$ using the atomic value of U (Fig. 2) and the values of t_2 and Δt calculated in the previous section, with a maximum T_c of 588 K at $Z = 1.5$. Although the oxygen-oxygen Coulomb repulsion has been estimated by some authors to be negligible,¹⁸ a nonzero value should be included in our calculation as it has a large effect in suppressing T_c . The maximum value of

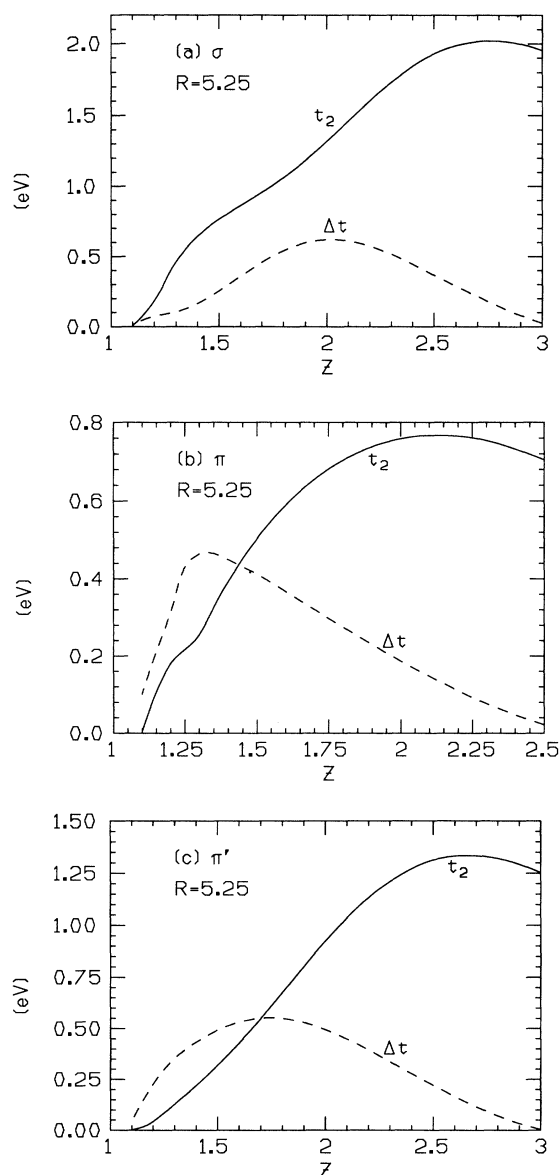


FIG. 11. Hole hopping amplitude t_2 and $\Delta t = t_1 - t_2$ versus ionic charge for the various arrangements and interatomic distance $R = 5.25$ a.u.

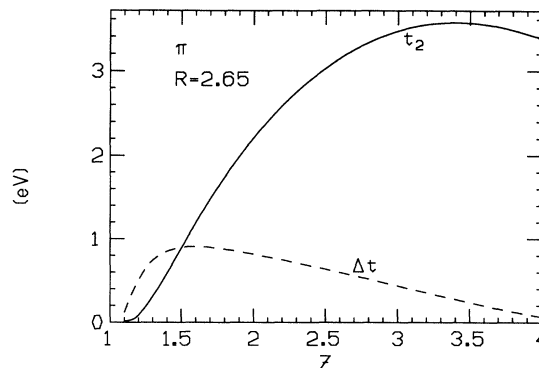


FIG. 12. Hole hopping amplitude t_2 and Δt versus ionic charge for the π arrangement and interatomic distance $R = 2.65$ a.u.

nearest-neighbor repulsion that still allows for superconductivity in our model is given by¹⁹

$$V_{\max} = 2t_2 \left[\frac{(1 + \frac{\Delta t}{t_2})^2}{1 + \frac{U}{2zt_2}} - 1 \right] \quad (15)$$

(z is the number of nearest neighbors, 4 in the present case). Using the atomic values of U and the calculated values of t_2 and Δt the maximum nearest-neighbor repulsion allowed is shown in Fig. 13 (solid line). We also show the maximum V allowed under the assumption that the intraatomic repulsion in the solid state has been reduced to 3/4 of its atomic value.

The values of interatomic repulsion thus obtained are admittedly small (less than 1 eV) but consistent with various estimates of this quantity in high- T_c oxides.^{18,20} The bare value of V for two point charges at this distance is 5.2 eV, and the Coulomb matrix element with the actual wave functions Eq. (12c) ranges between $V = 4.8$ eV and 6.0 eV for Z between 1 and 2. Reduction to values below those shown in Fig. 13 thus requires a dielectric constant ϵ of 10 or larger. This is however not unrealistic given for example that the dielectric constant in the

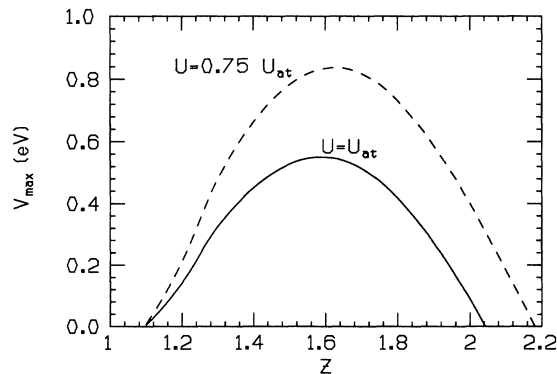


FIG. 13. Maximum nearest-neighbor repulsion in the presence of which superconductivity can occur in the dilute hole concentration regime for intraatomic repulsion given by the atomic value Eq. (3) (solid line) and 3/4 of that value (dashed line). $R = 5.25$ a.u., π' geometry.

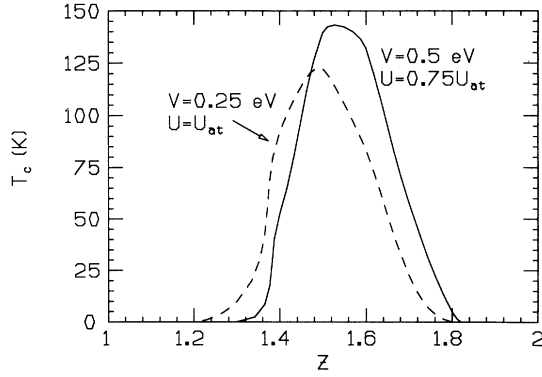


FIG. 14. Maximum T_c versus effective ionic charge for $U = U_{at}$, $V = 0.25$ eV (dashed line) and for $U = 0.75U_{at}$, $V = 0.5$ eV (solid line). $R = 5.25$ a.u., π' geometry.

insulating state of $\text{La}_2\text{CuO}_{4+y}$ has been estimated to be around 35.²¹

In fact, to obtain a large T_c the nearest-neighbor repulsion needs to be substantially below the upper limit given by Eq. (15). To illustrate the Z dependence we plot in Fig. 14 the maximum T_c obtained for nearest-neighbor repulsion $V = 0.25$ and 0.5 eV and intraatomic repulsion given by the atomic value and $3/4$ the atomic value respectively. It can be seen that the optimal situation occurs in a range of effective ionic charge around $Z = 1.5$. The carrier concentration dependence of T_c for a few parameter values is shown in Fig. 15.

Next we consider the effect of pressure on T_c . For definiteness we take the case $Z = 1.5$, $U = 5$ eV (77% of the atomic value), and $V = 0.5$ eV. Figure 16 shows the effect of hydrostatic pressure in the planes: On reducing R from 5.25 to 5.20 atomic units t_2 changes from 0.3184 to 0.3192 eV and Δt from 0.4922 to 0.4940 eV; the maximum T_c increases by 7.3 K. Assuming a change in lattice constant of²² $d \ln a/dP = -0.0032/\text{GPa}$ this

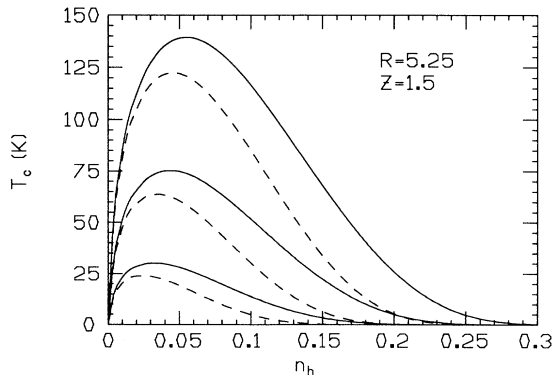


FIG. 15. T_c versus hole concentration (number of holes per oxygen) for $Z = 1.5$, $R = 5.25$ a.u. for various values of on-site and nearest-neighbor repulsion and the calculated values of Δt and t_2 : $\Delta t = 0.492$ eV, $t_2 = 0.318$ eV. Solid lines: $U = 0.75U_{at} = 4.86$ eV, and $V = 0.5, 0.55$ eV, and 0.6 eV in order of decreasing T_c . Dashed lines: $U = U_{at} = 6.49$ eV and $V = 0.25, 0.3$, and 0.35 eV in order of decreasing T_c .

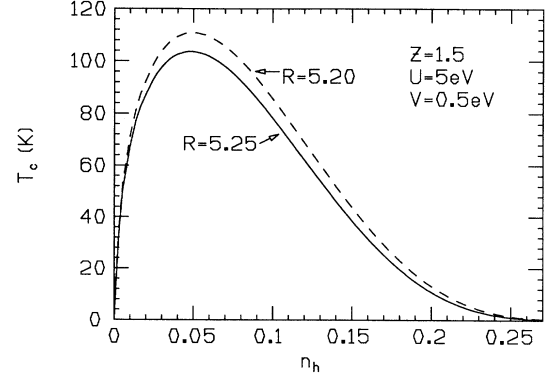


FIG. 16. Effect of pressure on T_c : T_c versus hole concentration for parameters given in the figure and Δt and t_2 obtained from the first-principles calculation (see text).

implies $dT_c/dP = 2.4$ K/GPa, which is consistent with various measurements of the effect of pressure on T_c .²³

Finally the question of what the appropriate value of Z is needs to be addressed. It corresponds to the charge “seen” by the first electron added to an oxygen atom, and nominally it would be zero since O is neutral. However, it is larger than zero due to incomplete screening. One may think that a reasonable way to estimate Z would be to use Slater’s rules:²⁴ subtract from the nuclear charge 0.85 for the screening of each $1s$ electron and 0.35 for the screening of each $2s$ or $2p$ electron. This leads to an effective ionic charge of

$$Z = 4.20 \quad (16)$$

for an electron in O^- . If this value was indeed the appropriate one to use, the results discussed above indicate that this mechanism certainly would not cause nor even contribute to superconductivity in high- T_c oxides.

However, we may also estimate the effective Z in a different way. The binding energy for an electron in O^- (i.e., the electron affinity of O) is $E_b = -1.45$ eV.²⁵ If we define the effective ionic charge through the relation

$$E_b = -\frac{Z^2}{n^2} \text{Ry}, \quad (17)$$

with n the principal quantum number (2 in our case), we obtain a value

$$Z = 0.65, \quad (18)$$

i.e., very much smaller than Eq. (16). The range of values of Z needed to obtain superconductivity is in between these two estimates.

Why are these two values of Z so different? One may understand it through the different effects of inner and outer shielding, as discussed by Slater.²⁴ We can, however, also think about it in the following way: If we estimated the binding energy of an electron in O^- using the effective ionic charge Eq. (16) and the energy formula Eq. (17) we would obtain $E_b = -60$ eV, which is very far from the true value. The reason is that when an electron is removed from O^- all the other electrons change

their orbits as they become more bound: Their effective Z is increased by 0.35. That is, the binding energy should be estimated as

$$E_b = \left[-7 \frac{Z^2}{n^2} + 6 \frac{(Z + 0.35)^2}{n^2} \right] \text{ Ry}, \quad (19)$$

which leads for $Z = 4.20$ to $E_b = 2.5$ eV, not too far from the exact value [taking $Z = 4.46$ in Eq. (19) would yield the exact value]. In other words, the modification of the states of all other electrons with quantum number $n = 2$ is essential to understand the observed value of the binding energy. A similar effect is likely to occur for the hopping amplitudes.

A similar argument can be made based on the value of the effective intraatomic repulsion U_{at} . From the Slater value Eq. (16) for the effective ionic charge and Fig. 2 one would conclude that U_{at} is larger than 20 eV. This is however certainly not the case, and estimates of this quantity range between 5 and 10 eV and sometimes even smaller.^{18,20} From Fig. 2 this would indicate an effective Z between 1 and 2. Once again the reduction in U_{at} may be understood as arising from the modification of the orbitals of all the other electrons with $n = 2$.

In summary we conclude that taking into account the modification of the states of all electrons with $n = 2$ as well as correlations between those electrons and the electrons in the orbital under consideration will likely significantly reduce the effective Z from its maximum estimated value Eq. (16), possibly bringing it closer to the estimate Eq. (18). Unfortunately it does not seem possible to reliably estimate the amount of the reduction without a detailed calculation.

V. CONCLUSION

We have studied hopping amplitudes for one, two, and three electrons in p orbitals for various geometries and effective ionic charges. The qualitative trends found here, particularly for the π and π' geometries, are very similar to what was found in I and II for the case of $1s$ orbitals: The hopping amplitude for holes is smaller than the one for electrons (i.e., $\Delta t > 0$) if the ionic charge and interatomic distance is not too large. As the effective ionic charge decreases the range of interatomic distances where $\Delta t > 0$ increases; furthermore the hole-hopping amplitude t_2 decreases and the ratio of Δt and t_2 increases, which is the situation that favors hole superconductivity. For large effective ionic charge the hopping amplitude for electrons is found to be slightly smaller than the one for holes for not too small R ; however the difference in hopping amplitudes is so small that it does not seem plausible to assume that *electron* (as opposed to hole) pairing would be significantly enhanced through this mechanism.²⁶ It was also found, as in I and II, that the difference in hopping amplitudes increases as the calculation becomes more accurate, from assuming fixed atomic orbitals to allowing for change in the orbital

in the Hartree approximation to including radial correlations. The similarity of these findings for s and p orbitals leads us to conjecture that they may be rather general.

There were however some findings that were different than for the case of $1s$ orbitals: For the case of $p\sigma$ orbitals, lowering the ionic charge did not create more favorable conditions for hole superconductivity. In fact the difference in hopping amplitudes never became larger than the hole hopping amplitude. Within the point of view of Ref. (19) this finding suggests that conduction through $p\sigma$ orbital may generally not be conducive to superconductivity. Also for the π' geometry it was found that if the effective ionic charge becomes too small superconductivity is suppressed, in contrast to the results for $1s$ orbitals.

Another surprising finding was that the Mulliken approximation fared rather badly both for the cases of σ and π' geometries. In those cases an appreciable difference in hopping amplitudes exists at intermediate distances even when considering fixed atomic orbitals. There is however reason to believe, based on considerations involving the conductivity sum rule,²⁷ that the effect of orbital relaxation is essential in bringing about hole superconductivity.

In the π geometry at the short distances appropriate to the C-C π bond it was found that Δt is appreciable in a wide range of effective ionic charge. This indicates that it could play an important role in the superconductivity of fullerenes. This possibility has apparently recently been suggested by Campbell.²⁸

For the geometry appropriate to oxygen orbitals in high- T_c oxides, it was found that superconductivity could be explained solely due to the difference in hopping amplitudes if the effective ionic charge is in a range around $Z = 1.5$. Arguments were given to the effect that the effective Z is likely to be much smaller than the value given by Slater's rules ($Z = 4.20$), due to the fact that we did not take into account the other electrons in the $n = 2$ shell in the treatment in this paper. Because many observed properties of high- T_c oxides resemble those resulting from a model where superconductivity results due to the difference in hopping amplitudes^{17,29} we conjecture that indeed the appropriate value of Z within the framework of the present paper is in the above mentioned range. To obtain a reliable estimate of the magnitude of Δt in high- T_c oxides however would appear to require to take into account the modification of the orbitals of all electrons in the $n = 2$ oxygen shells in the hopping process. Future calculations should be able to shed further light on this point.

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