

Electron- and hole-hopping amplitudes in a diatomic molecule

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We calculate the hopping amplitudes for an electron and for a hole added to the molecule H_2 . We use a linear combination of atomic orbitals approach and the Hartree approximation. The hopping amplitudes for electrons and holes are found to be different, reflecting the fundamental electron-hole asymmetry of condensed matter. The physical origin of this result is discussed. We study the dependence of hopping amplitudes on internuclear distance and on the nuclear charge Z ($Z = 1$ for H_2) and discuss the possible implication of our results to the understanding of superconductivity in solids.

I. INTRODUCTION

The kinetic energy for electrons in a band can be written in a Wannier representation as¹

$$H_{\text{kin}} = - \sum_{i,j} t_{ij}^{\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}) \quad (1a)$$

where $c_{i\sigma}^{\dagger}$ creates an electron of spin σ in Wannier state i . It is commonly assumed that the hopping amplitude t_{ij}^{σ} is a c number. However, it is plausible to postulate that t_{ij}^{σ} may vary with the electronic charge density in the system. The most important variation of t_{ij}^{σ} is likely

to originate in the charge occupation of sites i and j , and we may write

$$t_{ij}^{\sigma} = t_0 \delta_{n_i+n_j,1} + t_1 \delta_{n_i+n_j,2} + t_2 \delta_{n_i+n_j,3} \quad (1b)$$

with δ a Kronecker δ function. t_0 gives the hopping amplitude for an electron when there are no other electrons in the Wannier states at sites i and j , while t_1 and t_2 give the hopping amplitudes for an electron of spin σ when there is one and two other electrons of opposite spin at the two sites involved respectively. In operator form, the hopping amplitude Eq. (1b) can be written as

$$t_{ij}^{\sigma} = t_0(1 - n_{i,-\sigma})(1 - n_{j,-\sigma}) + t_1(n_{i,-\sigma} + n_{j,-\sigma} - 2n_{i,-\sigma}n_{j,-\sigma}) + t_2n_{i,-\sigma}n_{j,-\sigma}. \quad (1c)$$

For $t_0 \neq t_2$ this hopping amplitude is not electron-hole symmetric.

The variation of hopping amplitude with local charge occupation has been proposed as a possible mechanism for superconductivity.² In a dilute system of either electron or hole carriers, the kinetic energy Eq. (1) will lead to pairing of carriers if the difference $(t_1 - t_0)$ or $(t_1 - t_2)$ is sufficiently large (and positive), respectively. The reason is that carriers would be able to lower their kinetic energy by pairing over and above the cost in Coulomb energy arising from repulsive interactions between them.

For the particular case of

$$t_0 - t_1 = t_1 - t_2 \equiv \Delta t \quad (2)$$

Eq. (1c) reduces to

$$t_{ij}^{\sigma} = t_0 - \Delta t(n_{i,-\sigma} + n_{j,-\sigma}) \quad (3a)$$

or in terms of hole operators $n_{i\sigma}^h \equiv 1 - n_{i\sigma}$,

$$t_{ij}^{\sigma,h} = t_2 + \Delta t(n_{i,-\sigma}^h + n_{j,-\sigma}^h). \quad (3b)$$

The parameter Δt gives the difference in hopping ampli-

tudes between a single isolated carrier and that of a carrier in the presence of another carrier. One may also use the forms Eqs. (3a) and (3b) to describe a dilute system of electrons and holes, respectively, even if the condition Eq. (2) does not hold, since configurations with three carriers at the two sites involved will be improbable due to Coulomb repulsion. Then, Δt would be given by the first form

$$\Delta t = t_0 - t_1 \quad (4a)$$

or by the second form

$$\Delta t = t_1 - t_2 \quad (4b)$$

of Eq. (2), respectively. Another definition of Δt may be

$$\Delta t = \frac{t_0 - t_2}{2} \quad (4c)$$

which would be exact for both electrons and holes if Eq. (2) holds, and approximate otherwise.

It has been proposed that the ordering

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

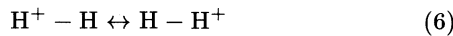
holds quite generally in real systems.³ In that case, the parameter Δt defined by either form of Eq. (4) would be positive, implying that holes are heavier than electrons. The kinetic energy Eq. (1) can then lead to pairing of holes but not of electrons. Various properties of high- T_c oxide superconductors appear to be describable by a Hamiltonian with kinetic energy Eq. (1) with an appreciable Δt .²⁻⁴

There is, however, no consensus on either the magnitude nor even the sign of the parameter Δt in real systems. In fact, it has also been proposed that Δt may be generally negative⁵ (implying that holes are lighter than electrons), as well as that it may be generally of negligible magnitude.⁶ The purpose of this paper is to address this fundamental question by calculating Δt from first principles for a simple diatomic molecule.

This paper is organized as follows. Section II defines the problem to be studied and reviews the calculation of the hopping amplitude in H_2^+ as well as some simple arguments regarding the expected behavior of the parameter Δt . In Secs. III and IV, we outline the procedure used for calculation of the hopping amplitudes in H_2^- and H_2 , respectively. In Sec. V we present results for the hopping amplitudes in the various cases and the parameter Δt , as function of interatomic distance and effective ionic charge. Section VI examines the effect of optimizing the orbital exponents used in the calculations, and compares our results with results of previous work. In Sec. VII we discuss the possible implications of our results for superconductivity, and conclude with a summary and discussion in Sec. VIII.

II. HOPPING IN A DIATOMIC MOLECULE

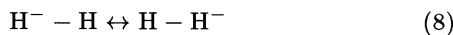
We follow the reasoning of Ref. 7 and consider a diatomic molecule of hydrogenlike atoms. For a single electron resonating between two protons



the hopping amplitude can be obtained from the difference between its lowest energy states of even and odd symmetry, $^2\Sigma_g^+$ and $^2\Sigma_u^+$ in spectroscopic notation:

$$t_0 = \frac{E(^2\Sigma_u^+) - E(^2\Sigma_g^+)}{2}. \quad (7)$$

These energies are known exactly from the solution of the hydrogen molecular ion problem.⁸ Similarly, we may think of the hydrogen negative molecular ion, H_2^- , as a single hole resonating between two H^- ions:



and obtain the hopping amplitude for the hole from the difference between the two lowest energy states of H_2^- , $^2\Sigma_u^+$ (H_2^-), $^2\Sigma_g^+$ (H_2^-):

$$t_2 = \frac{E[^2\Sigma_g^+(H_2^-)] - E[^2\Sigma_u^+(H_2^-)]}{2}. \quad (9)$$

These energies are not known exactly but have been calculated before.^{9,10} In Ref. 7 we estimated the parameter Δt from Eq. (4c) and the known energy values of these states.

Here we use a linear combination of atomic orbitals (LCAO) approach to calculate these hopping amplitudes approximately. For H_2^+ the procedure is straightforward. We define atomic orbitals $a(r)$ and $b(r)$ centered around the two atoms and construct the even and odd linear combinations for the bonding and antibonding states:

$$\phi_b(r) = \frac{a(r) + b(r)}{[2(1 + S_{ab})]^{1/2}}, \quad (10a)$$

$$\phi_a(r) = \frac{a(r) - b(r)}{[2(1 - S_{ab})]^{1/2}} \quad (10b)$$

with S_{ab} the overlap of the wave functions at the two centers:

$$S_{ab} = (a, b). \quad (11)$$

The bonding- and antibonding-state energies are given by

$$\varepsilon_b = \frac{(a, h, a) + (a, h, b)}{1 + S_{ab}}, \quad (12a)$$

$$\varepsilon_a = \frac{(a, h, a) - (a, h, b)}{1 - S_{ab}} \quad (12b)$$

with h the single-electron Hamiltonian. We associate the bonding and antibonding states with the states $^2\Sigma_g^+$ and $^2\Sigma_u^+$ mentioned and obtain the hopping amplitude

$$t_0 = \frac{\varepsilon_a - \varepsilon_b}{2} \quad (13a)$$

as

$$t_0 = \frac{-(a, h, b) + S_{ab}(a, h, a)}{1 - S_{ab}^2}. \quad (13b)$$

We will follow closely the notation and conventions in Slater.⁸ The single-particle Hamiltonian is, in atomic units (with energy measured in Rydbergs)

$$h = -\nabla^2 - \frac{2Z}{r_a} - \frac{2Z}{r_b} \quad (14)$$

(the nuclear charge $Z = 1$ for hydrogen, but we will allow for a more general case). The atomic wave functions are given by Slater orbitals

$$a(r) = \frac{\alpha^{3/2}}{\pi^{1/2}} e^{-\alpha r_a} \quad (15)$$

with r_a the coordinate relative to atom a , and α the orbital exponent. For a single electron in the atom $\alpha = Z$ is appropriate as it yields the exact atomic eigenstate. For the molecular ion, lower energies can be obtained by adjusting the value of the orbital exponent at each internuclear separation to minimize the energies.⁸ Figure 1 shows the hopping amplitude t_0 obtained from Eq. (13)

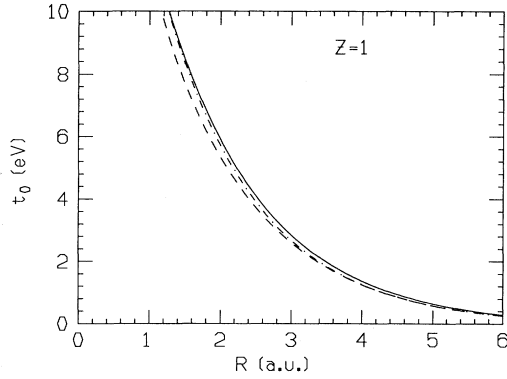


FIG. 1. Hopping amplitude in H_2^+ vs interatomic distances. Solid line: exact results; dashed line: LCAO results with $\alpha = Z$; dash-dotted line: LCAO results with α optimized in bonding and antibonding states.

and from the exact eigenenergies.¹¹ It can be seen that the LCAO results slightly underestimate t_0 , although the error becomes smaller when using optimized exponents. The disagreement is presumably due to the fact that the LCAO bonding wave function underestimates the true bond charge density, and could be remedied by using non-spherical atomic orbitals that “lean” towards the other atom. Nevertheless, the agreement found in Fig. 1 is reasonable and sufficient for our purposes.

The calculation of the hopping amplitudes in H_2^- and H_2 will be discussed in the next sections. First we need to consider the wave function for the hydrogen negative ion, H^- . We use a simple Hartree wave function for the two electrons

$$\Psi(r_1, r_2) = \bar{a}(r_1)\bar{a}(r_2) \quad (16)$$

with

$$\bar{a}(r) = \frac{\bar{\alpha}^{3/2}}{\pi^{1/2}} e^{-\bar{\alpha}r_a} \quad (17)$$

a Slater orbital, and determine its exponent $\bar{\alpha}$ by minimization of the expectation value of the atomic Hamiltonian with the electron-electron interaction

$$h_{12} = \frac{2}{r_{12}} \quad (18)$$

using the wave function Eq. (16). The result is well known: the atomic energy as function of $\bar{\alpha}$ is given by

$$E(\bar{\alpha}) = 2\bar{\alpha}^2 - 4Z\bar{\alpha} + \frac{5}{4}\bar{\alpha} \quad (19a)$$

and is minimized by

$$\bar{\alpha} = Z - 5/16 \quad (19b)$$

expressing the physical fact that the wave function “expands” due to the electron-electron interaction. This physical effect will be crucial in what follows.

Before going on to the calculation of the hopping amplitude in H_2^- , we believe it is useful to review the various

arguments that have been given in the past regarding the relative size of the various hopping amplitudes.

A. Orbital expansion

It has been argued that the orbital expansion as more electrons are added to an atom [Eq. (19)] should give rise to an increasing hopping amplitude, i.e., $t_2 > t_1 > t_0$.⁵ Indeed, the overlap of two Slater orbitals centered at the two atoms

$$S_{ab} = \int d\mathbf{r} a(r)b(r) = e^{-\alpha R} \left(1 + \alpha R + \frac{(\alpha R)^2}{3} \right) \quad (20)$$

(R = interatomic distance) will increase as α decreases. However, the situation is less clear for the hopping amplitudes. For example, from Eq. (13) one finds that decreasing α in the exponent of the wave function increases t_0 at large R but decreases it at smaller R , due to a cancellation that occurs between the two terms in the numerator.

B. Reduction in effective atomic charge

If we neglect the wave-function overlap in Eq. (13) and furthermore assume that the atomic orbitals are eigenstates of the atomic Hamiltonian the hopping t_0 can be written as

$$t_0 = -(a, u_a, b) \quad (21)$$

with

$$u_a = -\frac{2Z}{r_a} \quad (22)$$

the atomic potential at site a . The form Eq. (21) suggests that when electrons are added to the molecule the “effective” ionic charge Z decreases leading to a decrease of the atomic potential u_a and hence the hopping amplitude Eq. (21), hence $t_2 < t_1 < t_0$.¹²

C. Coulomb matrix element

The term Δt appears in the Hamiltonian as a “hopping interaction”:

$$V_h = \sum_{i,j} \Delta t (n_{i,-\sigma} + n_{j,-\sigma}) (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) \quad (23)$$

and as such may be associated with a matrix element of the Coulomb interaction between electrons:¹

$$\Delta t^0 = (aa, h_{12}, ab) = \int d\mathbf{r}_1 d\mathbf{r}_2 a^2(r_1) a(r_2) b(r_2) \frac{2}{r_{12}} \quad (24)$$

[we use the superscript zero to distinguish this matrix element from the definition Eq. (4)]. It is clear that this “hybrid” matrix element is positive if the orbitals have s symmetry. More generally it can be argued³ that the

sign of Δt as given by Eq. (24) is always opposite to the sign of the single electron hopping t_0 , independent of the symmetry of the orbital, leading thus always to the same physics, holes being heavier than electrons, i.e., $t_2 < t_1 < t_0$.

However, it has been pointed out⁶ that the expression Eq. (24) should be used with orthogonal (Wannier) orbitals rather than with atomic orbitals. This is a non-negligible correction and it is found that Δt from Eq. (24) becomes then vanishingly small. The reason is as follows: the form Eq. (24) is closely related to the degree of overlap of the site wave functions. To lowest order, we can orthogonalize the atomic orbitals as

$$a^\perp = a - \frac{S_{ab}}{2}b, \quad (25a)$$

$$b^\perp = b - \frac{S_{ab}}{2}a. \quad (25b)$$

Equation (24) then yields to lowest order in S_{ab}

$$\Delta t^\perp = (a^\perp a^\perp, h_{12}, a^\perp b^\perp) = \Delta t^0 - \frac{S_{ab}}{2}(U + V) \quad (26)$$

with

$$U = (aa, h_{12}, aa), \quad (27a)$$

$$V = (ab, h_{12}, ab), \quad (27b)$$

the on-site and nearest-neighbor Coulomb repulsions. Within the Mulliken approximation¹³ for the overlap charge distribution the form Eq. (26) exactly vanishes; in reality small deviations from the Mulliken approximation do occur but direct calculation¹³ shows Eq. (26) to be negligibly small at all internuclear distances.

D. Orbital relaxation

When an electron is removed from the ion H^- the second electron reverts from an orbital exponent $\bar{\alpha} = (Z - 5/16)$ to $\alpha = Z$. The overlap between the electronic wave functions with orbital exponents α and $\bar{\alpha}$ is

$$S_{a\bar{a}} = (\bar{a}, a) = \frac{8(\alpha\bar{\alpha})^{3/2}}{(\alpha + \bar{\alpha})^3}. \quad (28)$$

Since the orbital relaxation process is much faster than

the hopping process, one is in the antiadiabatic regime and may expect the hoppings in H_2 and H_2^- to be

$$t_1 = S_{a\bar{a}}t_0, \quad (29a)$$

$$t_2 = S_{a\bar{a}}^2t_0, \quad (29b)$$

i.e., smaller than t_0 , leading to a positive Δt . For $Z = 1$, Eq. (29) yields $t_2 = 0.90t_0$.

It can be seen that these simple arguments lead to contradictory expectations: Secs. IIB and IID suggest $\Delta t > 0$, Sec. IIA suggests $\Delta t < 0$, and IIC suggests $\Delta t \sim 0$. Thus, it is necessary to do a more detailed calculation to settle this question even qualitatively.

III. HOPPING AMPLITUDE IN H_2^-

The Hamiltonian for three electrons moving between two charge centers is

$$H_3 = h_1 + h_2 + h_3 + h_{12} + h_{23} + h_{31} \quad (30)$$

with the single- and two-particle terms given by Eqs. (14) and (18), respectively. We construct the bonding and antibonding states simply from linear combinations of the two resonating states in Eq. (8). Schematically

$$\Psi = [(H^- - H) \pm (H - H^-)] \times \text{normalization}. \quad (31a)$$

For each configuration we use a simple product of the H^- wave function Eq. (16) and the single-electron atomic wave function for H. We have then explicitly

$$\Psi_a^b(r_1, r_2, r_3) = \frac{\bar{a}(r_1)\bar{a}(r_2)b(r_3) \pm a(r_1)\bar{b}(r_2)\bar{b}(r_3)}{[2(1 + S_{H_2^-})]^{1/2}}, \quad (31b)$$

$$S_{H_2^-} = (\bar{a}, a)(\bar{a}, b)(b, \bar{b}). \quad (32)$$

The energies of bonding and antibonding states are obtained by taking the expectation value of the Hamiltonian Eq. (30), and the hopping amplitude results as in Eq. (13):

$$t_2 = \frac{-(\bar{a}\bar{a}b, H_3, a\bar{b}\bar{b}) + S_{H_2^-}(\bar{a}\bar{a}b, H_3, \bar{a}\bar{a}b)}{1 - S_{H_2^-}^2}. \quad (33)$$

The required matrix elements are then

$$(\bar{a}\bar{a}b, H_3, a\bar{b}\bar{b}) = 2(\bar{a}, h, a)S_{a\bar{a}}S_{a\bar{b}} + (\bar{a}, h, \bar{b})S_{a\bar{a}}^2 + 2(\bar{a}\bar{a}, h_{12}, a\bar{b})S_{a\bar{a}} + (\bar{a}b, h_{12}, a\bar{b})S_{a\bar{b}}, \quad (34a)$$

$$(\bar{a}\bar{a}b, H_3, \bar{a}\bar{a}b) = 2(\bar{a}, h, \bar{a}) + (a, h, a) + (\bar{a}\bar{a}, h_{12}\bar{a}, \bar{a}) + 2(\bar{a}b, h_{12}, \bar{a}b) \quad (34b)$$

with the overlap matrix elements defined analogously to Eq. (28).

Evaluation of these matrix elements is discussed in the Appendix. Before giving numerical results it is interest-

ing to consider the hopping Eq. (33) for the case $\bar{\alpha} = \alpha$. We have then $S_{a\bar{a}} = 1$, and Eq. (34) reduces to

$$(aab, H_3, aab) = 3(a, h, a) + U + 2V, \quad (35a)$$

$$(aab, H_3, abb) = 2(a, h, a)S_{ab} + (a, h, b)S_{ab}V + 2\Delta t^0 \quad (35b)$$

and Eq. (33) yields

$$t_2 = \frac{-(a, h, b) + S_{ab}(a, h, a) + S_{ab}(U + V) - 2\Delta t^0}{1 - S_{ab}^2}. \quad (36)$$

Thus to the extent that the Mulliken approximation

$$\Delta t^0 \sim \frac{S_{ab}}{2}(U + V) \quad (37)$$

is valid, Eq. (36) reduces to the hopping t_0 in H_2^+ , Eq. (13b). From the Appendix, we find for small $\omega = \alpha R$

$$\Delta t^0 = \alpha \left[\frac{5}{4} - \frac{7}{24}\omega^2 + \frac{3}{32}\omega^4 + \dots \right] \quad (38)$$

and

$$\frac{S_{ab}}{2}(U + V) = \alpha \left[\frac{5}{4} - \frac{7}{24}\omega^2 + \frac{119}{720}\omega^4 + \dots \right] \quad (39)$$

so that the relation Eq. (37) holds through order ω^2 . This implies that for small interatomic distances any difference found between the hoppings t_0 and t_2 should be ascribed to the change in orbital exponent from α to $\bar{\alpha}$.

IV. HOPPING AMPLITUDE IN H_2

The Hamiltonian for two electrons is given by

$$H_2 = h_1 + h_2 + h_{12}. \quad (40)$$

It is of interest to obtain the hopping in this case, t_1 , to be able to evaluate the various forms of Δt in Eq. (4). Unfortunately this is conceptually not as straightforward as the cases of H_2^+ and H_2^- . In those cases the splitting of the lowest energy eigenstates of even and odd symmetry directly yielded the hopping amplitudes. Here, instead (as discussed, e.g., in Ref. 7), the lowest energy states in the various sectors also involve other interaction parameters such as U and V .

Rather than dealing with the lowest energy states, we adopt the following simplified procedure: we consider the resonance process analogous to Eqs. (6) and (8):

$$H^- - H^+ \leftrightarrow H - H \quad (41)$$

and construct the even and odd linear combinations as in Eq. (31):

$$\Psi_a^b(r_1, r_2) = \frac{\bar{a}(r_1)\bar{a}(r_2) \pm a(r_1)b(r_2)}{[2(1 + S_{H_2})]^{1/2}}, \quad (42)$$

$$S_{H_2} = (\bar{a}, a)(\bar{a}, b). \quad (43)$$

We do not expect the states Eq. (42) to be close to any of the eigenstates of H_2 . Nevertheless the difference in the expectation value of the Hamiltonian between those two states should approximate the desired hopping amplitude. We obtain

$$t_1 = \frac{-(\bar{a}\bar{a}, H, ab) + S_{H_2} \frac{(\bar{a}\bar{a}, H, \bar{a}\bar{a}) + (ab, H, ab)}{2}}{1 - S_{H_2}^2}. \quad (44)$$

For the case $\bar{\alpha} = \alpha$ Eq. (44) reduces to

$$t_1 = \frac{-(a, h, b) + S_{ab}(a, h, a) + \frac{S_{ab}}{2}(U + V) - \Delta t^0}{1 - S_{ab}^2} \quad (45)$$

so that we obtain $t_1 = t_0 = t_2$ if the Mulliken approximation holds. More generally, Eqs. (13b), (36), and (45) satisfy Eq. (2):

$$t_0 - t_1 = t_1 - t_2 = \frac{\Delta t^0 - \frac{S_{ab}}{2}(U + V)}{1 - S_{ab}^2} \quad (46)$$

if there is no change in the orbital exponent.

V. NUMERICAL RESULTS

Figure 2 shows results for the three hopping amplitudes assuming no change in the orbital exponents. In agreement with the foregoing discussions, t_0 , t_1 , and t_2 become equal for small interatomic spacing. For larger distances deviations from the Mulliken approximation do occur, and as Fig. 2 shows

$$t_0 < t_1 < t_2 \quad (47)$$

so that the parameter Δt is *negative* (in fact for small R , Δt is small and positive but this is not visible with the resolution of Fig. 2).

The situation changes drastically, however, when we allow for orbital relaxation, as shown in Fig. 3: the hole hopping amplitude t_2 is now substantially reduced with respect to both t_1 and t_0 at small and intermediate separations. In fact the relation $t_0 > t_1 > t_2$ holds at small distances while $t_0 < t_1 < t_2$ holds at sufficiently large distances and various other combinations in between. This suggests that the effect of increased hopping amplitude due to expanded orbital does indeed exist at sufficiently large separation, but that at smaller separations, the effects discussed in Sec. II related to orbital relaxation

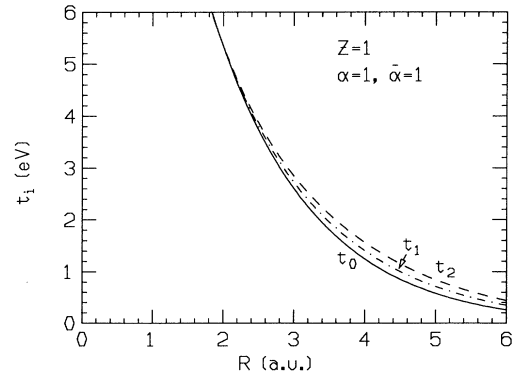


FIG. 2. Hopping amplitudes for $Z = 1$, assuming orbital exponents $\alpha = \bar{\alpha} = Z$. The full, dash-dotted and dashed lines correspond to the hopping amplitudes in H_2^+ , H_2 , and H_2^- , respectively, t_0 , t_1 , and t_2 .

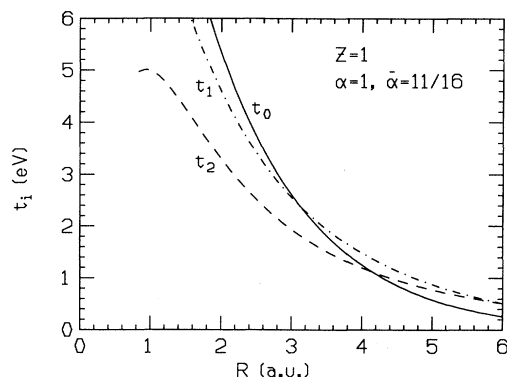


FIG. 3. Hopping amplitudes for $Z = 1$, using orbital exponents appropriate to the isolated atom: $\alpha = Z$, $\tilde{\alpha} = Z - 5/16$. The line convention is the same as in Fig. 2.

and reduction in effective atomic charge take over. Using orbital exponents to minimize the energies for each molecular ion separately yields very similar results, as shown in Fig. 4. This is further discussed in Sec. VI.

It is interesting to examine how these results are modified in the presence of different effective ionic charge Z . One would expect the importance of orbital relaxation to increase as the effective ionic charge decreases and the Slater exponents decrease. Indeed, as Fig. 5(a) shows, the difference in hopping amplitudes becomes more pronounced for $Z = 0.75$, and the ordering Eq. (47) that occurs in the absence of orbital relaxation is only achieved at even larger interatomic separation. As Z increases to 1.25 the difference in hopping amplitudes decreases, and for $Z = 2$, where the electrons are very tightly bound, the ordering Eq. (47) holds over a large range of interatomic distances as the effect of orbital relaxation has become negligible.

Figure 6 compares various estimates of the hopping interaction Δt for the case $Z = 1$. A similar graph was presented in Ref. 7, Fig. 2. There, the estimates were obtained from earlier quantum-chemical calculations for H_2^- , H_2 , and H_2^+ ; however, the values of t_1 for H_2 were ob-

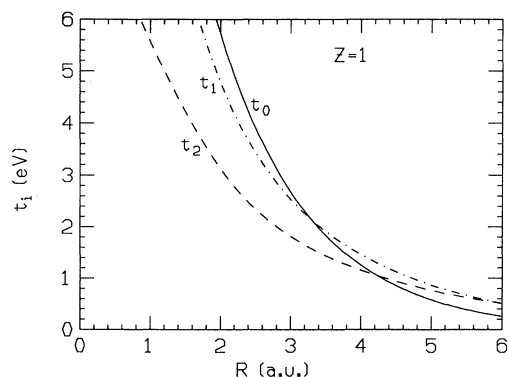


FIG. 4. Hopping amplitudes for $Z = 1$, using optimized orbital exponents for each molecular ion. Line convention is the same as in Fig. 2.

tained using certain assumptions which were to some extent unjustified. The qualitative behavior obtained here and in Ref. 7 is the same. Figure 6 also shows the values of the bare hybrid integral Eq. (24) (Δt^0) as well as the value of Δt that is obtained in the absence of orbital relaxation, termed Δt^\perp [as seen from Eq. (46) this is the same for all forms of Eq. (4)]. This quantity is related and closely similar in size to the value of Δt that would be obtained from the hybrid integral Eq. (24) by using orthogonalized single-particle orbitals (they are the

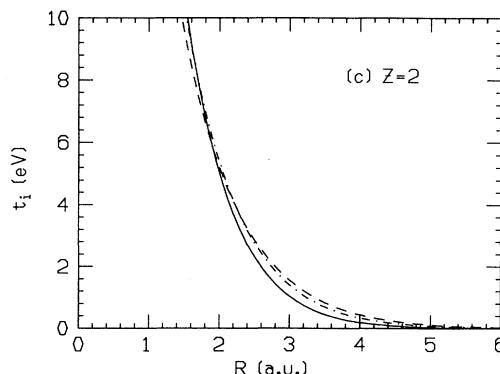
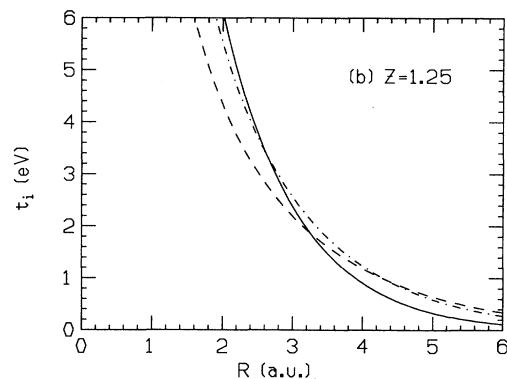
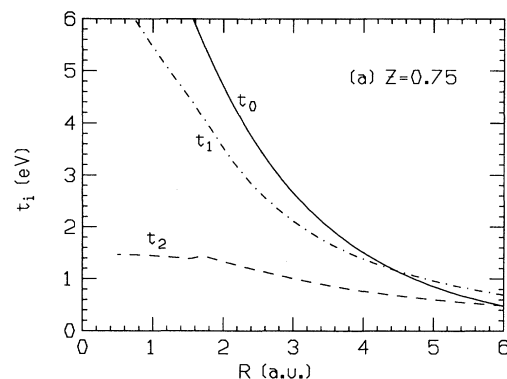


FIG. 5. Hopping amplitudes for (a) $Z = 0.75$, (b) $Z = 1.25$, and (c) $Z = 2$ (with optimized exponents). Line convention is the same as in Fig. 2.

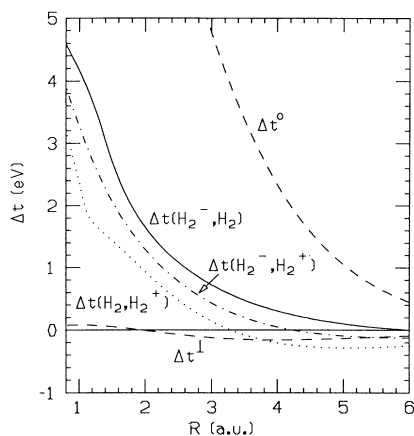


FIG. 6. Different estimates of the hopping interaction Δt , Eq. (4), for $Z = 1$. Full, dash-dotted, and dotted lines correspond, respectively, to results from our calculation for $(t_1 - t_2)$, $(t_0 - t_2)/2$, and $(t_0 - t_1)$, using optimized exponents. Upper dashed line is the bare hybrid matrix element Eq. (24) calculated using atomic orbitals; lower dashed line is the value of Δt obtained using orbital exponents $\alpha = \bar{\alpha} = Z$, which is closely related to the hybrid integral Eq. (24) using orthogonalized orbitals.

same to lowest order in S_{ab}); that procedure was used in evaluating Δt^\perp plotted in Fig. 2 of Ref. 7.

Having found that in the range of R where the differences in hopping amplitudes are appreciable the ordering Eq. (5) holds we conclude that this effect may lead to pairing of holes but not of electrons. Hence the form of Δt given by Eq. (4b) is the relevant one on which to focus. In Fig. 7 we plot this Δt versus R for various values of the effective nuclear charge Z , showing clearly how a reduced value of Z gives rise to larger values of Δt in a large range of internuclear separation.

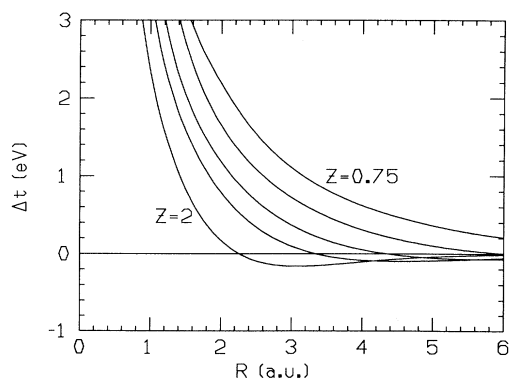


FIG. 7. Results for $\Delta t = t_1 - t_2$ (the form relevant to hole pairing) vs interatomic distance for various values of the effective ionic charge Z . $Z = 0.75, 1, 1.25, 1.5$, and 2 (increasing Δt values correspond to decreasing Z). Optimized orbital exponents were used.

VI. EFFECT OF OPTIMIZING α AND COMPARISON WITH PREVIOUS WORK

As discussed earlier the appropriate values for the orbital exponents in the limit of large internuclear separation are $\alpha = Z$, $\bar{\alpha} = Z - 5/16$. As the distance between nuclei decreases, lower energy values can be obtained by adjusting the orbital exponents at each internuclear separation. For example, for H_2^+ the optimal value of the exponent α for the bonding state goes smoothly from $\alpha = 1$ to $\alpha = 2$ (appropriate to He^+) as R decreases from infinity to zero.

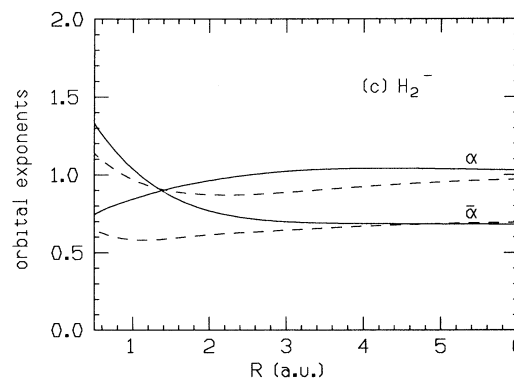
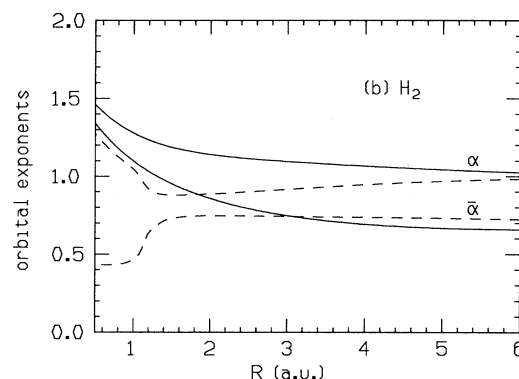
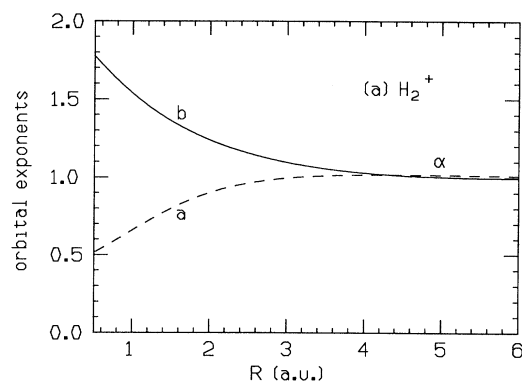


FIG. 8. Optimized values for orbital exponents, obtained from minimizing energies of bonding (full lines) and antibonding (dashed lines) states, for (a) H_2^+ , (b) H_2 , and (c) H_2^- . For (b) and (c) the curves for α and $\bar{\alpha}$ approach the limits Z and $Z - 5/16$, respectively.

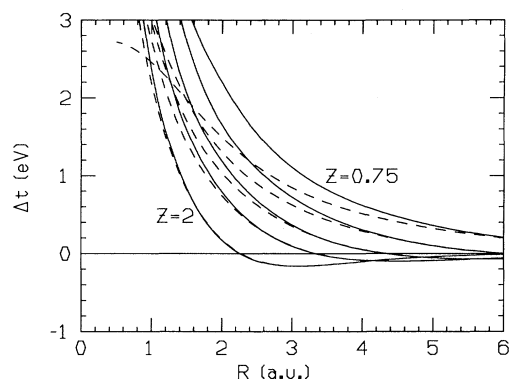


FIG. 9. Comparison of results for $\Delta t = t_1 - t_2$ using optimized (full lines) and atomic (dashed lines) orbital exponents for various values of Z . $Z = 0.75, 1, 1.25, 1.5$, and 2 . For large R the results of both procedures coincide.

The values of α and $\bar{\alpha}$ for bonding and antibonding states for each molecular ion obtained from minimization of the energies are shown in Fig. 8 for $Z = 1$. The variation found is rather large, but although it translates into an appreciable lowering of the energies of bonding and antibonding states separately it has remarkably a small effect on the hopping amplitudes. As already seen in Fig. 1, for H_2^+ optimization of α only slightly improves the agreement of t_0 with the exact results. Figure 9 shows comparison of $\Delta t = t_1 - t_2$ obtained with optimized exponents and with atomic exponents for various values of Z . The qualitative behavior is the same and it is only for small Z and small internuclear distance that quantitative differences become appreciable. We conclude that evaluation of Δt using the orbital exponents appropriate to the isolated atom in the various charge states does capture the essential physics of the problem. That physics is lost, however, as seen earlier, if the atomic orbital exponent is not allowed to change with atomic charge occupation. We note also that evaluation of Δt using the atomic orbital exponents underestimates its magnitude compared to the presumably more accurate calculation using opti-

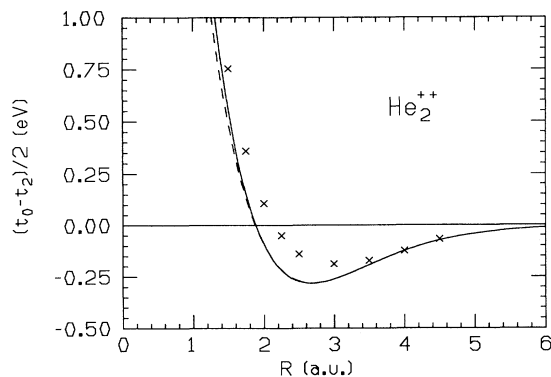


FIG. 10. Comparison of results for $(t_0 - t_2)/2$ for $Z = 2$ with results from Gupta and Matsen (Ref. 14) (crosses). The full and dashed lines give our results with optimized and atomic exponents, respectively.

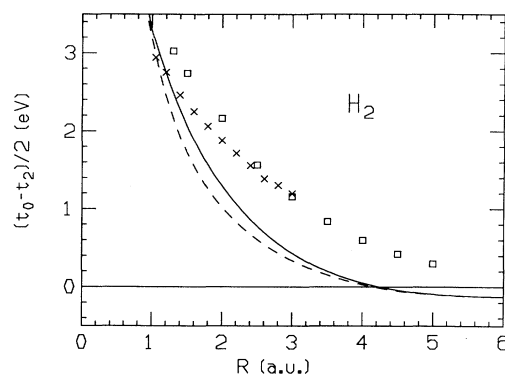


FIG. 11. Comparison of results for $(t_0 - t_2)/2$ for $Z = 1$ with results from Eliezer, Taylor, and Williams (Ref. 9) (crosses) and Chen and Peacher (Ref. 10) (squares). The full and dashed lines give our results with optimized and atomic exponents, respectively.

mized orbital exponents.

It is also of interest to compare the results obtained here with results of other calculations. For $Z = 2$, the energies of the ion He_2^{+++} are known exactly [the values of $E(R)$ for energy versus distance in H_2^+ correspond to $Z^2 E(R/Z)$ in He_2^{+++}], and for He_2^+ have been calculated by several workers using rather more complicated wave functions than the ones used here. We use the numerical results given by Gupta and Matsen¹⁴ (GM) for comparison. Our calculated energies are found to differ from those of GM by a few percent (typically 2% or less). Remarkably, our hopping amplitude t_2 is also found to differ by only a few percent from the GM values, despite the fact that it is smaller than the energies by about two orders of magnitude (meaning that the errors in bonding and antibonding energies are highly correlated). Comparison of $\Delta t = (t_0 - t_2)/2$ obtained from our wave functions and from the GM wave function for He_2^+ together with the exact results for He_2^{+++} , is shown in Fig. 10. It can be seen that the behavior obtained is very similar and that our calculation of Δt somewhat underestimates the results of the presumably more accurate calculations.

Similarly, Fig. 11 shows comparison of our results for $(t_0 - t_2)/2$ for the case $Z = 1$ with results from the calculations of Eliezer, Taylor, and Williams⁹ and of Chen and Peacher¹⁰ for H_2^- and the exact results for H_2^+ . Here the discrepancy is somewhat larger, but it should be noted that there are also some differences between the results of Refs. 9 and 10. The qualitative behavior obtained, however, is the same in the three cases, and it should be noted that again our results for Δt are smaller than those obtained by other methods. We conclude from these comparisons that our finding that Δt is positive and of appreciable magnitude for small R and Z is on firm ground. We are not aware of existing results for other Z values with which to compare our results.

VII. CONSEQUENCES FOR SUPERCONDUCTIVITY

The results of the previous sections indicate that in a lattice of H^- ions with a few holes the kinetic energy of

the holes will be lowered by pairing of holes. However, the tendency to pairing will be opposed by the potential energy, the usual Coulomb repulsion between holes. It is of interest to estimate the parameter region of R and Z where pairing may occur. Assuming only short-range repulsions U and V [Eq. (27)], the condition on the parameter to give rise to pairing and superconductivity in the dilute hole concentration regime is found to be²⁻⁴

$$\Delta t > \frac{\sqrt{(1+gU)(1+gzV)} - 1}{2zg} \quad (48)$$

with z the number of nearest neighbors to a site and

$$g = \frac{1}{2zt_2} \quad (49)$$

the average single-particle density of states. We use for Δt the value obtained from comparison of H_2^- and H_2 ($\Delta t = t_1 - t_2$) and for the nearest-neighbor repulsion V the value obtained from the Coulomb integral Eq. (27). This value is shown in Fig. 12 for various nuclear charges. As discussed in Ref. 7, an empirical value can be obtained for V from calculated energies of H_2 , which is somewhat smaller than the one obtained from Eq. (27). However, we will use the latter values as we can easily obtain them for arbitrary values of Z . For the interatomic repulsion U , we use the value obtained from the Slater orbital with exponent $\bar{\alpha}$ which is $5/4\bar{\alpha}$.

The values of V shown in Fig. 12 are substantially larger than values commonly estimated to be appropriate for solids. This is because screening is expected to play an important role in reducing the nearest-neighbor (and further) electron repulsion. We will assume a simple Thomas-Fermi form

$$V_{sc}(R) = V(R)e^{-\lambda R} \quad (50)$$

and consider various values of λ . Within Thomas-Fermi theory $\lambda^2 = 4\pi e^2 g(\epsilon_F)$, with $g(\epsilon_F)$ the density of states at the Fermi energy, so that the screening length ($1/\lambda$) decreases for high density of states.

Using Eq. (48) (with V replaced by V_{sc}) we obtain the phase diagram shown in Fig. 13. We show the phase boundaries for $\lambda = 1$ (for comparison recall that in Cu

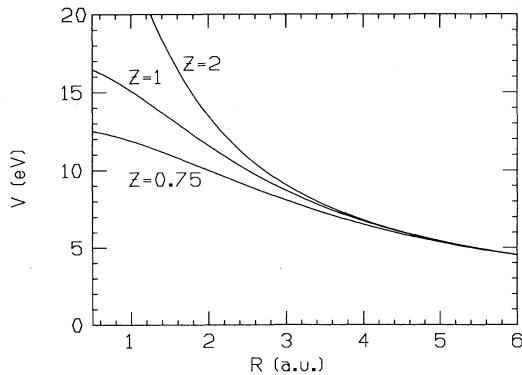


FIG. 12. Nearest-neighbor repulsion V from Eq. (27b) for various values of Z .

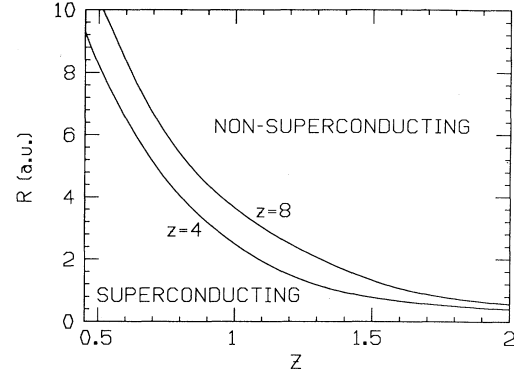


FIG. 13. Phase diagram from Eq. (48) using $\Delta t = t_1 - t_2$ (computed with nonoptimized exponents), U and V from the matrix elements of the Coulomb interaction, Eq. (27), and screening constant $\lambda = 1$. The phase boundaries between superconducting and nonsuperconducting regions for coordination numbers $z = 4$ and 8 are shown.

$\lambda = 0.96$, corresponding to a screening length of 0.55 \AA) for coordination numbers $z = 8$ and 4 . As the effective ionic charge increases the interatomic distance required for superconductivity decreases, as the value of Δt becomes smaller. Also as the coordination number decreases, the required interatomic distance decreases. The cases $z = 8$ and 4 correspond to the number of oxygen nearest neighbors to an oxygen in the cubic perovskites such as $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and to a planar oxygen in high- T_c oxides, respectively; in those cases also the interoxygen distance is found to decrease as the coordination number decreases (from 3.05 \AA to 2.75 \AA).

The effect of varying screening parameter λ is shown in Fig. 14. In the absence of screening superconductivity is found to occur only for rather small interatomic distances. In the high- T_c oxides, however, the screening length should be rather small due to the high density of states and the large polarizability of the ions involved. In fact, estimates of the oxygen-oxygen nearest-neighbor

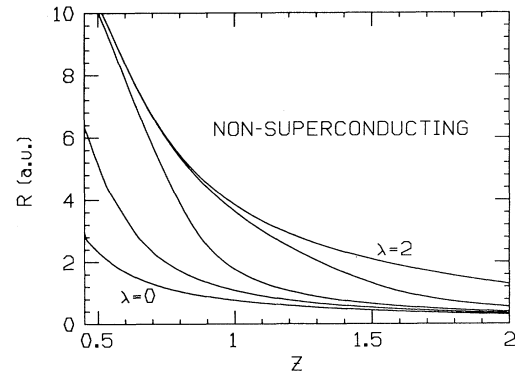


FIG. 14. Same as Fig. 13, with coordination number $z = 8$, and various values of the screening constant λ . For given Z the curves with increasing ordinate correspond to $\lambda = 0, 0.25, 0.5, 1$, and 2 . Superconductivity is expected in the parameter region below the corresponding curve for each λ .

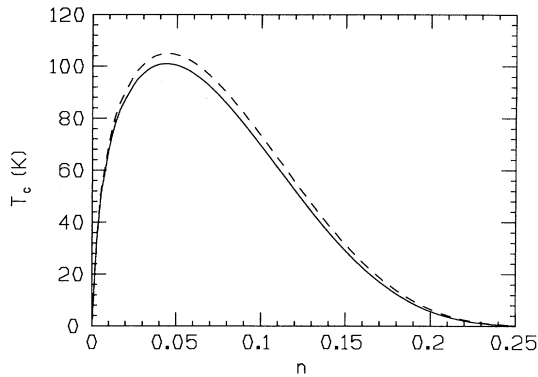


FIG. 15. Critical temperature (obtained from solution of the BCS equation) vs number of holes per site n for parameters obtained from the present calculation for $Z = 0.6$, $\lambda = 1$. Full line: $R = 5.25$ a.u.; dashed line: $R = 5.24$ a.u.

repulsion¹⁵ have consistently yielded values under 1 eV.

Finally we show in Fig. 15 as an example the critical temperature obtained from solution of the BCS equation for $\lambda = 1$, $Z = 0.6$, coordination number $z = 4$, and interatomic distance as found for the planar oxygen-oxygen distance in high- T_c oxides (2.75 Å). As discussed earlier⁴ the behavior resembles experimental observations.¹⁶ By slightly changing the interatomic distance we can examine the effect of pressure in the planes. The dominant effect of reducing the interatomic distance is to increase the magnitude of Δt . The changes in T_c seen in Fig. 15 are of similar magnitude as seen experimentally in some high- T_c oxides.¹⁷

VIII. SUMMARY AND DISCUSSION

We have computed hopping amplitudes for electrons in the molecular ions H_2^+ and H_2^- , and in the molecule H_2 . The cases of H_2^- and H_2^+ may be thought of as obtained from the “half-filled band” H_2 case by adding an electron and a hole, respectively. Alternatively, they may be thought of as a single hole in a full band and a single electron in an empty band, respectively. Within the models commonly used for condensed matter systems, such as the Hubbard model, a single electron and a single hole added to a half-filled band or to empty and full bands, would have the same effective mass. Thus one may have expected the hopping amplitudes in H_2^- and H_2^+ to be similar. We have found by direct calculation that this is not the case.

Our findings are summarized in the following:

(1) Quite generally the single hole (case of H_2^-) has a smaller hopping amplitude (t_2) than the single-electron hopping amplitude (t_0 , case of H_2^+) for small and intermediate nuclear separation, and the opposite is true for large internuclear separation.

(2) The hopping amplitude for an electron in H_2 (t_1) is intermediate between the two other cases both at small and large internuclear distances. For small distances, the

difference between the hopping amplitudes in H_2^- and H_2 (which is the relevant one for possible pairing of holes) is larger than that between H_2 and H_2^+ .

(3) As the effective ionic charge Z is reduced the difference in hopping amplitudes increases and the range in internuclear separation where the ordering $t_0 > t_1 > t_2$ holds grows. For large Z (e.g., the case of He^{+n} , $Z = 2$) the hopping amplitudes become very similar and the ordering $t_0 < t_1 < t_2$ holds except at very small internuclear distances.

(4) The orbital relaxation process that occurs when an electron is removed from a doubly occupied orbital is central to give rise to the ordering $t_0 > t_1 > t_2$ and large differences in hopping amplitudes at small distances. If no orbital relaxation is allowed, the hopping amplitudes are found to be very similar and the ordering $t_0 < t_1 < t_2$ holds over all relevant internuclear distances.

(5) Optimization of the orbital exponents for each molecular ion separately does not change qualitatively the results obtained by using the orbital exponents appropriate for the isolated atoms. It does, however, further increase the difference between the hopping amplitude in H_2^- and the other cases.

(6) Calculation of the difference in hopping amplitudes by computing the parameter Δt from the hybrid matrix element of the Coulomb interaction with orthogonal orbitals yields qualitatively incorrect results, which are close to the results obtained for the difference in hopping amplitudes without allowing for orbital relaxation. Estimation of the difference in hopping amplitudes from the hybrid matrix element calculated with atomic orbitals yields the correct sign and qualitative interatomic distance dependence but overestimates the magnitude.

Many important questions have been left open in this study. We have used the self-consistent field approximation and ignored possible correlation effects; these could be taken into account within a configurational interaction approach. We do not expect these effects to qualitatively change the results found here, but this is clearly a topic for further study. Another direction for future study is to investigate these effects for orbitals with higher angular momentum, e.g., the p orbitals in O^{-n} ions. We see no reason to expect the behavior in that case not to be qualitatively similar to the one found here. Also, the effect of screening in a solid-state environment is an important open question. While for the case of ordinary density-density Coulomb repulsion the effect of metallic screening is well understood, it is not clear how screening would affect the parameter Δt , which arises from a combination of kinematic and interaction effects.

Furthermore, we have not addressed here the question of the stability of the ionic species involved. For example, our calculation yields that for $Z = 0.9$ the ground state of the molecular ion with three electrons has higher energy than the one with two electrons for $R < 3$ a.u., which implies that the ion with three electrons would be unstable in vacuum. For smaller Z the instability occurs for larger R . Similar results were found in Refs. 9 and 10. However, in a solid-state environment the unstable negative ions could be stabilized by the electrostatic potential of neighboring ions (e.g., like O^{2-} in high- T_c oxides), so

that the results obtained here would still be applicable.

Despite the many open questions, we believe that the results found here are a manifestation of a general property of condensed matter, the *absence* of electron-hole symmetry. We have found it to be quantitatively important in what is perhaps the simplest condensed matter system, and there is no argument known to us that would suggest that it is less important in more complicated systems. Thus in studies of condensed matter systems using Hubbard-like models we believe it is important to allow for the fact that the electron hopping amplitude is likely to decrease as the local electronic charge density increases, as modeled by the hopping interaction Δt .

Concerning superconductivity, the results found here together with our earlier studies of pairing in Hamiltonians with the hopping interaction Δt (Refs. 2–4) suggest that superconductivity will be favored, everything else being equal, by having hole rather than electron states at the Fermi energy. Interestingly, as already pointed out by Chapnik many years ago,¹⁸ superconductivity in solids appears to be correlated with a positive value of the Hall coefficient, indicating hole conduction.

If one assumes that superconductivity may occur in nature solely due to the difference in hopping amplitudes discussed here, the phase diagrams shown in Sec. VII are of interest. They show that as the effective nuclear charge decreases the range of internuclear separation where superconductivity may occur increases. Thus a solid of inert gas atoms with a few holes would not superconduct unless it is compressed to extremely small internuclear separation. The conflicting requirements of negatively charged ions (small Z) in as densely packed a structure as possible (small R) are found to be conducive to superconductivity, as well as of course the ability to introduce a small number of holes into the system. Such dense packing of negatively charged anions could be achieved in certain ionic structures, where the positive ions would only play the role of holding the negative ions close together. As seen from Fig. 13, two dimensionality would be favored over three dimensionality only insofar as it might allow for a more densely packed negative ion array.

In conclusion, we note that if the results found in this paper had been opposite, that is, if the ordering $t_0 < t_1 < t_2$ would have been found to hold with large differences in the hopping amplitudes, it would not have been very good news for superconductivity. Although one may write down a model with $t_0 < t_1$ that will predict superconductivity for low electron concentration, such a model would not be physical. The reason is that it can be shown by general arguments¹⁹ that two electrons in an empty band, in the absence of other degrees of freedom (such as phonons or electrons in other bands), cannot possibly pair, simply due to the inherently repulsive nature of the Coulomb interaction. In other words, the magnitude of the parameters could never be such as to satisfy Eq. (48) [with $\Delta t = t_1 - t_0$, $g = 1/(2zt_0)$]. This argument, however, does not hold for two holes in a full band, as the dynamics of all the electrons in the band now play a role. Pairing of two holes in a full band is *in principle* possible in the presence of only Coulomb in-

teraction between electrons and ions and no motion of the ionic degrees of freedom. The results of this paper suggest that it may also be possible in practice.

ACKNOWLEDGMENT

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APPENDIX

We list here the matrix elements needed for the calculation of the hopping amplitudes, so that the interested reader can easily reproduce and extend the results given in the text. We define

$$\omega = \alpha R, \quad (\text{A1a})$$

$$\bar{\omega} = \bar{\alpha} R, \quad (\text{A1b})$$

$$\tilde{\omega} = \frac{\omega + \bar{\omega}}{2}, \quad (\text{A1c})$$

$$\hat{\omega} = \frac{\omega - \bar{\omega}}{2}, \quad (\text{A1d})$$

$$\tilde{\alpha} = \frac{\alpha + \bar{\alpha}}{2}, \quad (\text{A1e})$$

$$\alpha_g = (\alpha \tilde{\alpha})^{1/2}. \quad (\text{A1f})$$

Some expressions are rather lengthy and rather than writing them out we leave them expressed in terms of the following functions:

$$L_n(\omega) = \int_1^\infty d\lambda \lambda^n e^{-\omega\lambda}, \quad (\text{A2a})$$

$$M_n(\omega) = \int_{-1}^1 d\mu \mu^n e^{\omega\mu}, \quad (\text{A2b})$$

given by

$$L_0(\omega) = e^{-\omega}/\omega, \quad (\text{A3a})$$

$$L_1(\omega) = e^{-\omega}(1 + \omega)/\omega^2, \quad (\text{A3b})$$

$$L_2(\omega) = e^{-\omega}(2 + 2\omega + \omega^2)/\omega^3, \quad (\text{A3c})$$

$$M_0(\omega) = (e^\omega - e^{-\omega})/\omega, \quad (\text{A3d})$$

$$M_1(\omega) = [e^{-\omega} - e^\omega + \omega(e^{-\omega} + e^\omega)]/\omega^2, \quad (\text{A3e})$$

$$M_2(\omega) = [(2 + \omega^2)(e^\omega - e^{-\omega}) - 2\omega(e^\omega + e^{-\omega})]/\omega^3. \quad (\text{A3f})$$

1. Overlaps

$$(a, \bar{a}) = (\alpha_g/\tilde{\alpha})^3, \quad (\text{A4a})$$

$$(a, b) = e^{-\omega}(1 + \omega + \omega^2/3), \quad (\text{A4b})$$

$$(\bar{a}, b) = \frac{(\omega\bar{\omega})^{3/2}}{4} [L_2(\tilde{\omega})M_0(\hat{\omega}) - L_0(\tilde{\omega})M_2(\hat{\omega})]. \quad (\text{A4c})$$

2. Single-particle matrix elements

a. Kinetic energy

$$(a, -\nabla^2, a) = \alpha^2, \quad (\text{A5a})$$

$$(a, -\nabla^2, b) = \alpha^2 e^{-\omega} (1 + \omega - \omega^2/3), \quad (\text{A5b})$$

$$(\bar{a}, -\nabla^2, a) = \alpha_g^5 / \bar{\alpha}^3, \quad (\text{A5c})$$

$$(\bar{a}, -\nabla^2, b) = \alpha^2 (\omega \bar{\omega})^{3/2} \left[\frac{1}{\omega} [L_1(\bar{\omega}) M_0(\hat{\omega}) + L_0(\bar{\omega}) M_1(\hat{\omega})] + \frac{1}{4} [-L_2(\bar{\omega}) M_0(\hat{\omega}) + L_0(\bar{\omega}) M_2(\hat{\omega})] \right]. \quad (\text{A5d})$$

b. Potential energy

$$\left(a, -\frac{2}{r_a}, a \right) = -2\alpha, \quad (\text{A6a})$$

$$\left(\bar{a}, -\frac{2}{r_a}, a \right) = -\frac{2\alpha_g^3}{\bar{\alpha}^2}, \quad (\text{A6b})$$

$$\left(a, -\frac{2}{r_b}, a \right) = \alpha \left[-\frac{2}{\omega} + e^{-2\omega} \left(2 + \frac{2}{\omega} \right) \right], \quad (\text{A6c})$$

$$\left(\bar{a}, -\frac{2}{r_b}, a \right) = \frac{2\alpha_g^3}{\bar{\alpha}^2} \left[-\frac{2}{\omega + \bar{\omega}} + e^{-(\omega + \bar{\omega})} \left(1 + \frac{2}{\omega + \bar{\omega}} \right) \right], \quad (\text{A6d})$$

$$\left(a, -\frac{2}{r_a}, b \right) = -\alpha e^{-\omega} (2 + 2\omega), \quad (\text{A6e})$$

$$\left(\bar{a}, -\frac{2}{r_a}, b \right) = -\alpha \frac{(\omega \bar{\omega})^{3/2}}{\omega} [L_1(\bar{\omega}) M_0(\hat{\omega}) - L_0(\bar{\omega}) M_1(\hat{\omega})], \quad (\text{A6f})$$

$$\left(\bar{a}, -\frac{2}{r_b}, b \right) = -\alpha \frac{(\omega \bar{\omega})^{3/2}}{\omega} [L_1(\bar{\omega}) M_0(\hat{\omega}) + L_0(\bar{\omega}) M_1(\hat{\omega})]. \quad (\text{A6g})$$

3. Two-particle matrix elements

$$(aa, h_{12}, aa) = \frac{5}{4}\alpha, \quad (\text{A7a})$$

$$(ab, h_{12}, ab) = \alpha \left[\frac{2}{\omega} - e^{-2\omega} \left(\frac{2}{\omega} + \frac{11}{4} + \frac{3}{2}\omega + \frac{1}{3}\omega^2 \right) \right], \quad (\text{A7b})$$

$$(aa, h_{12}, ab) = \alpha \left[e^{-\omega} \left(2\omega + \frac{1}{4} + \frac{5}{8\omega} \right) + e^{-3\omega} \left(-\frac{1}{4} - \frac{5}{8\omega} \right) \right], \quad (\text{A7c})$$

$$(\bar{a}b, h_{12}, \bar{a}b) = \frac{-2\bar{\alpha}}{\bar{\omega}(\bar{\omega} - \omega)^3(\bar{\omega} + \omega)^3} \left\{ (\omega^2 - \bar{\omega}^2)^3 + \bar{\omega}^4 e^{-2\omega} [\bar{\omega}^2(1 + \omega) - \omega^2(3 + \omega)] - \omega^4 e^{-2\bar{\omega}} [\bar{\omega}^2(1 + \bar{\omega}) - \bar{\omega}^2(3 + \bar{\omega})] \right\}, \quad (\text{A7d})$$

$$(\bar{a}b, h_{12}, a\bar{b}) = \frac{\alpha_g^6}{\bar{\alpha}^5} \left[\frac{2}{\bar{\omega}} - e^{-2\bar{\omega}} \left(\frac{2}{\bar{\omega}} + \frac{11}{4} + \frac{3}{2}\bar{\omega} + \frac{1}{3}\bar{\omega}^2 \right) \right], \quad (\text{A7e})$$

$$(\bar{a}\bar{a}, h_{12}, a\bar{b}) = \left(\frac{\alpha_g}{\bar{\alpha}} \right)^3 \bar{\alpha} \omega^2 \left[2L_1(\bar{\omega}) - M_0(-\bar{\omega})L_1(\bar{\omega} + \bar{\omega}) + M_1(-\bar{\omega})L_0(\bar{\omega} + \bar{\omega}) - \frac{\bar{\omega}}{2} [M_0(-\bar{\omega})L_2(\bar{\omega} + \bar{\omega}) - M_2(-\bar{\omega})L_0(\bar{\omega} + \bar{\omega})] \right], \quad (\text{A7f})$$

$$(\bar{a}\bar{a}, h_{12}, ab) = \frac{\alpha_g^4}{\bar{\alpha}^3} \omega \bar{\omega} \left[L_1(\bar{\omega}) M_0(\hat{\omega}) - L_0(\bar{\omega}) M_1(\hat{\omega}) - L_1(2\bar{\omega}) M_0(-\bar{\omega}) + L_0(2\bar{\omega}) M_1(-\bar{\omega}) - \frac{\bar{\omega}}{2} [L_2(2\bar{\omega}) M_0(-\bar{\omega}) - L_0(2\bar{\omega}) M_2(-\bar{\omega})] \right]. \quad (\text{A7g})$$

Other matrix elements needed are obtained from the ones given here by replacing ω by $\bar{\omega}$, α by $\bar{\alpha}$, or interchanging a 's and b 's.

- ¹ J. Hubbard, Proc. R. Soc. London Ser. A **276**, 238 (1963).
- ² J. E. Hirsch and F. Marsiglio, Phys. Rev. B **39**, 11515 (1989).
- ³ J. E. Hirsch, Physica C **158**, 326 (1989); Phys. Lett. A **138**, 83 (1989); Phys. Rev. B **43**, 11400 (1991).
- ⁴ F. Marsiglio and J. E. Hirsch, Phys. Rev. B **41**, 6435 (1990); Physica C **165**, 71 (1990); **171**, 554 (1990).
- ⁵ O. Gunnarson and N. E. Christensen, Phys. Rev. B **42**, 2363 (1990); I. O. Kulik, Fiz. Nizk. Temp. **16**, 602 (1990) [Sov. J. Low. Temp. Phys. **16**, 350 (1990)]; A. Zawadowski, Phys. Rev. B **39**, 4682 (1989).
- ⁶ M. S. Hybertsen, E. B. Stechel, and D. R. Jennison, Phys. Rev. B **41**, 11068 (1990); M. Schluter, *Third Annual Conference on Superconductivity and Applications*, Buffalo, NY, 1989 (Plenum, New York, 1990), p. 1.
- ⁷ J. E. Hirsch, Chem. Phys. Lett. **171**, 161 (1990).
- ⁸ J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963).
- ⁹ I. Eliezer, H. S. Taylor, and J. K. Williams, J. Chem. Phys. **47**, 2165 (1967).
- ¹⁰ J. C. Chen and J. L. Peacher, Phys. Rev. **167**, 30 (1968).
- ¹¹ D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. R. Soc. London **246**, 215 (1953).
- ¹² J. Zaanen, C. Westra, and G. Sawatzky, Phys. Rev. B **33**, 8060 (1986).
- ¹³ R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).
- ¹⁴ B. K. Gupta and F. A. Matsen, J. Chem. Phys. **47**, 4860 (1967).
- ¹⁵ E. B. Stechel and D. R. Jennison, Phys. Rev. B **38**, 4632 (1988); A. K. McMahan, R. M. Martin, and S. Satpathy, *ibid.* **38**, 6650 (1988); A. K. McMahan, J. F. Annett, and R. M. Martin, *ibid.* **42**, 6268 (1990).
- ¹⁶ J. B. Torrance *et al.*, Phys. Rev. B **40**, 8872 (1989).
- ¹⁷ J. Schilling and S. Klotz, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), Vol. III.
- ¹⁸ I. M. Chapnik, Dok. Akad. Nauk SSSR **141**, 70 (1962) [Sov. Phys. Dokl. **6**, 988 (1962)]; J. Phys. F **13**, 975 (1983).
- ¹⁹ V. J. Emery (private communication).