SPIN-SPLIT STATES IN AROMATIC MOLECULES

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A state where spin currents exist in the absence of external fields has recently been proposed to describe the low-temperature phase of Chromium. It is proposed here that such a state may also describe the ground of aromatic molecules. It is argued that this point of view provides a more natural explanation for the large diamagnetic susceptibilities and NMR shifts observed in these molecules than the conventional viewpoint. Our model suggests a new memory mechanism.

1. Introduction

Chromium[1] and aromatic organic molecules[2] share the property of being relatively inert. In this paper we suggest that this may be a manifestation of a more fundamental property that they may have in common: that both types of systems possess spin currents in the ground state. The existing experimental evidence in favor of such a state for Chromium termed a "spin-split state" in Ref. 3, was discussed in Ref. 4. If such a state indeed exists in Chromium, one is naturally led to search for other realizations of this state. Aromatic molecules suggest themselves as natural candidates.

The question of the existence of ring currents in planar aromatic molecules has been of long-standing interest to both chemists and physicists since first proposed by Pauling.[5] Such currents appear to be necessary to explain the large diamagnetic anisotropy observed in these molecules,[2] as well as the observed NMR frequency shifts at nearby atoms.[6] It has also been argued that these induced currents may bear some relationship to the supercurrents in superconductors.[7,8] However, there exists an important difference between the behaviour of superconductors and of aromatic molecules in the conventional picture: in the latter, the currents are thought to be induced by the applied magnetic field and to vanish when the field is removed, while in superconductors it is clearly possible to maintain a persistent current after the external magnetic field is removed.

In this paper we suggest a picture of aromatic molecules where ring currents already exist in the absence of applied fields. These currents do not carry charge but only spin in the laboratory frame (i.e. the frame where the nuclei are at rest) when no external magnetic field is present. However, a charge current can be thought of as pre-existing in a rotating reference frame. An applied magnetic field merely modifies these pre-existing currents and gives rise to a charge current in the laboratory frame. We argue that this point of view provides a more natural explanation for the existence of induced ring currents in aromatic molecules than the conventional viewpoint. Furthermore, our model appears to provide a more natural explanation of a certain feature of the optical spectrum of benzene than the conventional picture.

In the next section we review the conventional view of aromatic molecules and discuss why we believe it is unlikely to be correct, and in Sect. 3 we discuss the proposed spin-split picture of aromatic molecules. Most of the discussion centers on the case of benzene as the archetypical example. We conclude in Sec. 4 with a discussion of the implications of our model, in particular as a possible memory mechanism.

2. The Conventional Picture

The properties of aromatic molecules of interest here are generally ascribed to the π orbitals oriented perpendicular to the plane of the molecule.[2] A simple Hamiltonian to describe the π electrons in an N-site ring may be taken to be:

$$H = -t \sum_{\substack{\langle ij \rangle \\ \sigma}} (c_{i\sigma}^+ c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j \tag{1}$$

where $c_{i\sigma}^+$ creates an electron in the π_z orbital φ_i centered at site i, which we assume has been orthogonalized with respect to the π_z orbitals on neighboring sites. t is the resonance integral and U and V are on-site and nearest-neighbor Coulomb repulsions. Each atom contributes one electron to these orbitals so that the band described by the Hamiltonian Eq. (1) is half-filled.

Detailed studies of aromatic molecules where Coulomb interactions between π electrons are taken into account have been recently carried out within a generalized valence bond framework.[9] However, these studies have not shed any light on the question of induced ring currents so far. Instead, this aspect is generally treated within the simple Hückel theory[10] that neglects electron-electron interactions. The single particle eigenstates are given by

$$\psi_k = \frac{1}{\sqrt{N}} \sum_i e^{ik \cdot R_i} \varphi_i \tag{2a}$$

$$k = \frac{2\pi}{Na} r, \qquad -\frac{N}{2} + 1 \leq r \leq \frac{N}{2} \tag{2b}$$

where $N = 4n + 2$ is the number of atoms in the ring and a the interatomic distance ($a = 1.4$ Å for benzene). The single particle energies are given by

$$\varepsilon_k = -2t \cos ka \tag{3}$$

and in the ground state, the states with

$$|r| \leq n \tag{4}$$

are occupied.

In the presence of an external magnetic field the phase of the molecular orbitals is modified. As shown by London,[7] this may be taken into account by including a field dependent phase factor in the resonance integral, which becomes

$$t_{ij} = t \exp\left\{i\,\frac{e\phi}{N\hbar c}(i - j)\right\} \tag{5}$$

with ϕ the magnetic flux through the ring. The perturbed energies are now

$$\varepsilon_k = -2t \cos\left(ka + \frac{e\phi}{N\hbar c}\right) \tag{6}$$

which results in a net current as the velocity of the electrons, $1/\hbar\,\partial\varepsilon_k/\partial k$, is no longer zero on the average. It is given by

$$I = \frac{4e^2}{N^2\hbar^2 c}\,\frac{t}{\sin(\pi/N)}\,\phi \tag{7}$$

and such a current can account for observed values of diamagnetic susceptibilities and NMR shifts with values of t ranging from 0.5 to 0.7 eV.[11]

However, we believe that in the presence of Coulomb interactions this simple picture cannot be sustained. The difficulty is that the interaction U will tend to localize the electrons by suppressing double occupancy of the sites. It has been shown rigorously that a one-dimensional half-filled chain described by Eq. (1) with $V = 0$ (Hubbard model) becomes insulating for *any* non-zero U.[12] For large U the system is described by localized spins coupled antiferromagnetically rather than by Hückel's band electrons. We argue that such a system will generically not develop ring currents in the presence of an external magnetic field.

We obtain a quantitative estimate of this effect for the case of benzene ($N = 6$) by diagonalizing the Hamiltonian Eq. (1) exactly and computing the ring current in the ground state in the presence of an applied field. Figure 1 shows the current versus U for two cases, $V = 0$ and $V = 0.6U$. The semi-empirical estimates for these parameters for benzene are $U = 11.4$ eV and $V = 7.2$ eV,[13] and the resonance integral[2] has been estimated at $t = 0.78$ eV (in fact, estimated values have ranged between 0.4 eV and 1.3 eV).[2] The current obtained for these parameters is 1/140 of the value of the non-interacting case. Using the purely
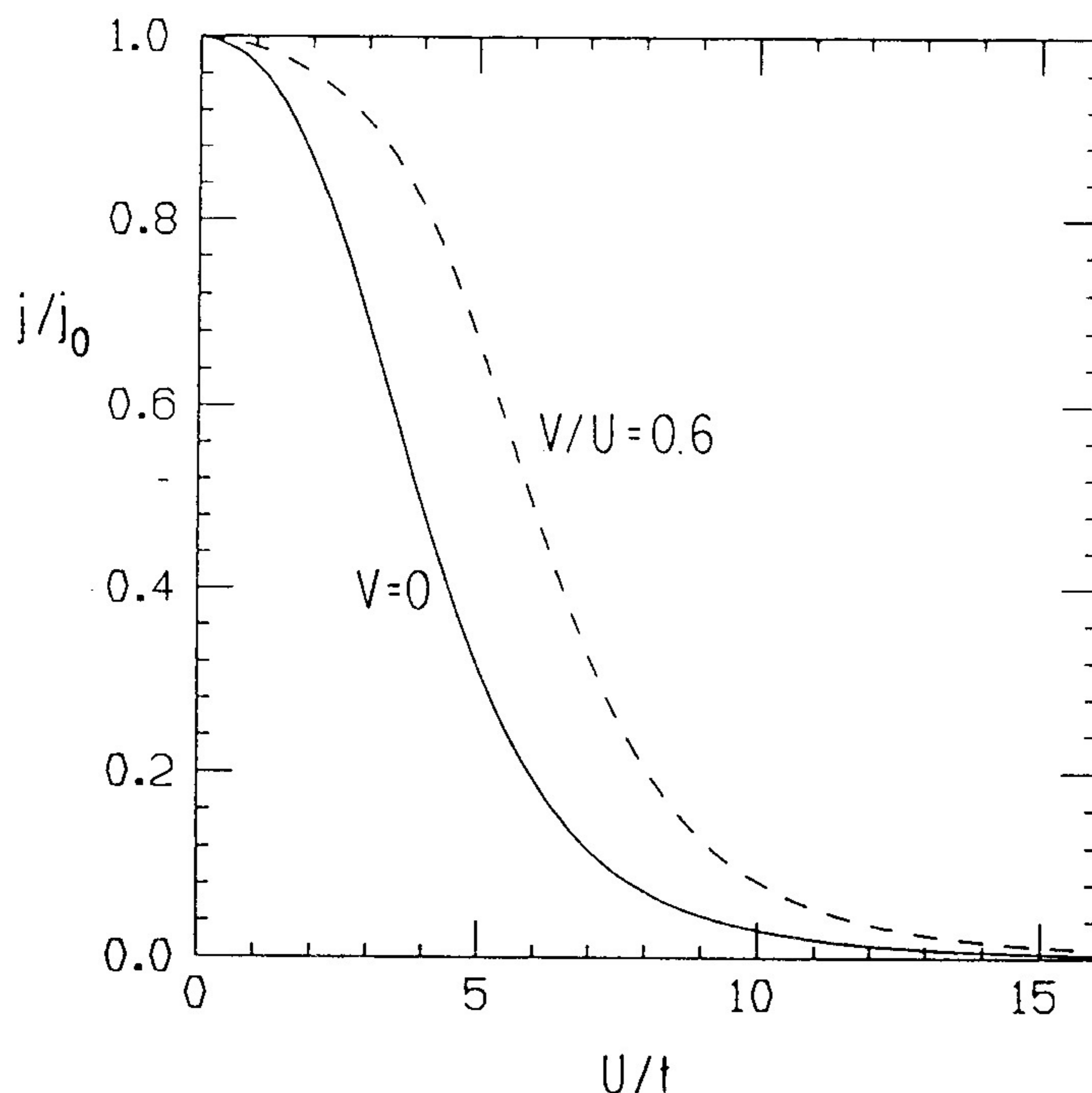
Fig. 1. Expectation value of the current induced in a benzene ring in the presence of a magnetic field versus on-site repulsion U. The current is normalized to its value in the absence of Coulomb repulsions, and U and V are measured in units of t. The full line corresponds to $V = 0$, the dashed line to $V/U = 0.6$.

theoretical estimates[13] $U = 16.9$ eV, $V = 9$ eV yields a ring current 1/45 of the Hückel value. These values are far too low to account for the experimental observations.

There exists in fact one situation where we have found appreciable induced currents in the presence of large Coulomb interactions U and V. This occurs if the parameters are close to the line $U/2V = 1$. Figure 2 shows this effect for the case of benzene, for $U/t = 14$. This occurs because $U \sim 2V$ is the boundary between two distinct phases, an antiferromagnetic state and a charge-density-wave state.[14] Despite the fact that these two phases are insulating, relatively large mobility can result if one is very close to this transition, as seen in Fig. 2. Although this possibility cannot be ruled out we believe it is rather unlikely to apply generically to aromatic molecules as it requires considerable fine-tuning of parameters.

We conclude from these considerations that if no currents exists in aromatic molecules in the absence of external fields the electrons are likely to be localized in the ground state rather than itinerant as in the Hückel picture. This conclusion is in agreement with the detailed valence-bond calculations.[9] If this is the case our results suggest that no substantial currents would be generated when an external magnetic field is turned on.
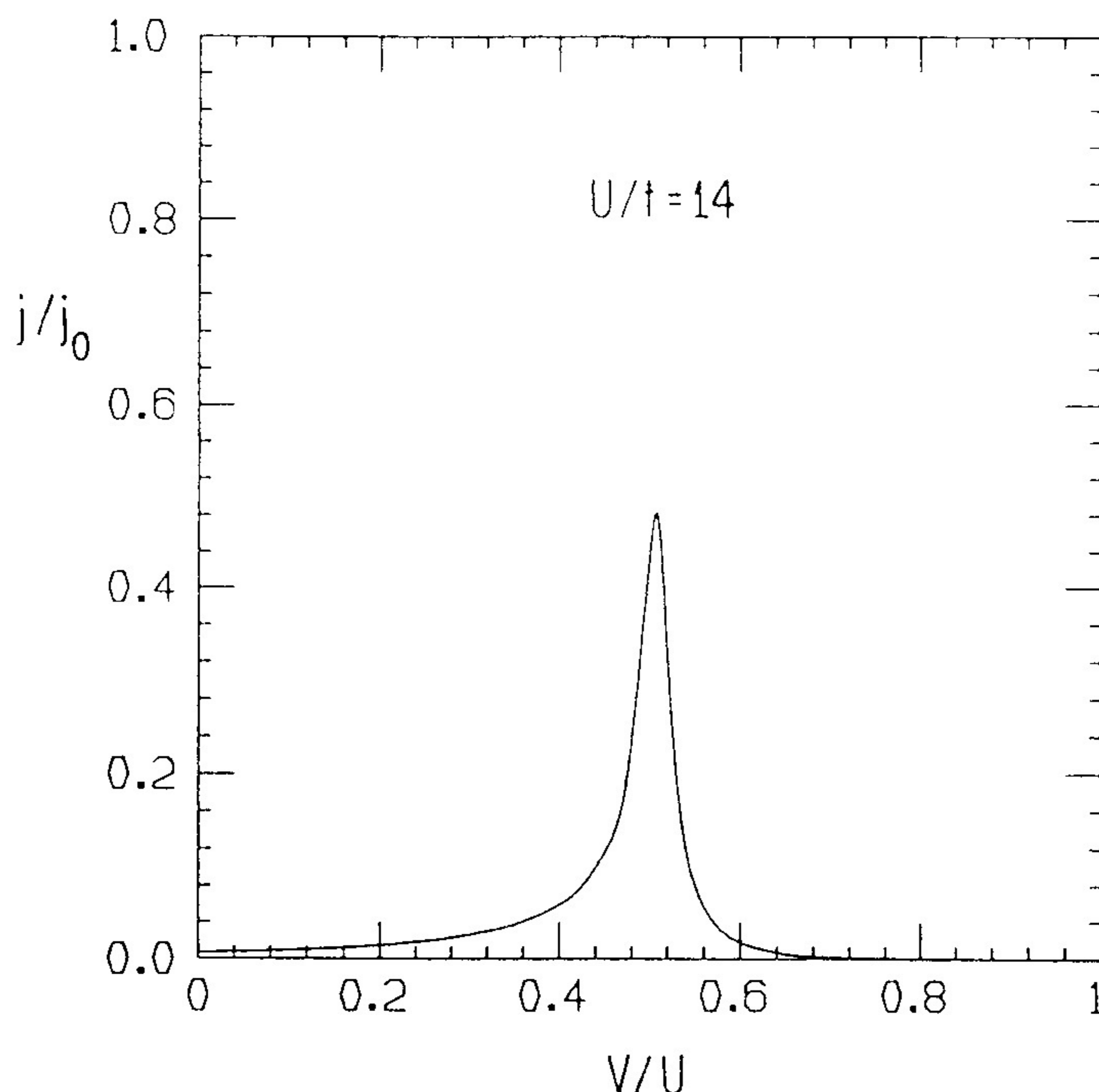
Fig. 2.   Same as Fig. 1 for fixed U as function of V/U. An appreciable current can be induced only in a narrow range around $V/U = 0.5$ where the transition between spin-density wave and charge-density wave states occurs.

3.   The Spin-Split Picture

A Coulomb interaction term not included in Eq. (1) leads to a tendency for the electrons of opposite spin to move in directions opposite to each other.[3] This Coulomb "exchange" matrix element is defined by

$$J = \int d^3r d^3r' \, \phi_i^*(r)\phi_j(r) \, \frac{e^2}{|r - r'|} \, \phi_j^*(r')\phi_i(r') \tag{8}$$

and is always positive. It gives rise to an interaction term in the Hamiltonian

$$H_J = J \sum_{\langle ij \rangle} c_{i\sigma}^+ c_{j\sigma} c_{j\sigma'}^+ c_{i\sigma'} \tag{9}$$

and in particular it can be seen that it provides a way for electrons to delocalize by exchanging their position thus avoiding the on-site repulsion U. It was shown in Ref. 3 that this interaction can stabilize a state in a metal where up and down spin electrons occupy slightly different regions of the Brillouin zone. In the

simplest treatment the wavefunction is written as

$$|\psi\rangle = \prod_{k\varepsilon A} c^{+}_{k\uparrow} c^{+}_{-k\downarrow} |0\rangle \tag{10}$$

where the set A is not invariant under inversion. That is, if a state $k\varepsilon A$, it does not follow that the state $(-k)$ does.

We propose Eq. (10) as a simple description of the ground state of aromatic molecules instead of the Hückel state. For the case of benzene this state is shown in Fig. 3. More generally, the occupied single-particle states will be defined by

$$k = \frac{2\pi}{Na} r \tag{11a}$$

$$-n_1 \le r \le n_2 \tag{11b}$$

with $n_1 \ne n_2$. In such a state a spin current exists in the absence of external fields. When the magnetic field is turned on the wave vectors shift as described by Eq. (5) and a charge current results similarly as for the Hückel case.

It is easy to see that the interaction Eq. (9) favors the spin-split state over an unsplit one. Consider the case of benzene ($N = 6$) for simplicity. The ground state wave function in the uncorrelated (Hückel) state is given by Eq. (10) with

$$A_H = \left\{ 0, -\frac{\pi}{3}, \frac{\pi}{3} \right\} \tag{12a}$$

and in the spin-split state by

$$A_S = \left\{ 0, \frac{\pi}{3}, \frac{2\pi}{3} \right\} . \tag{12b}$$

The expectation value of the Hamiltonian in these states is

$$E_H = -8t + \frac{4}{3} J \tag{13a}$$

for the uncorrelated state and

$$E_S = -4t - \frac{2}{3} J \tag{13b}$$

for the spin-split state. We have omitted the contributions from the interactions U and V which are the same for both states. Thus, J lowers the energy in the spin-split state while it raises it in the uncorrelated state. By comparing Eqs. (13a) and (13b) we find that the spin-split state is favored over the uncorrelated state
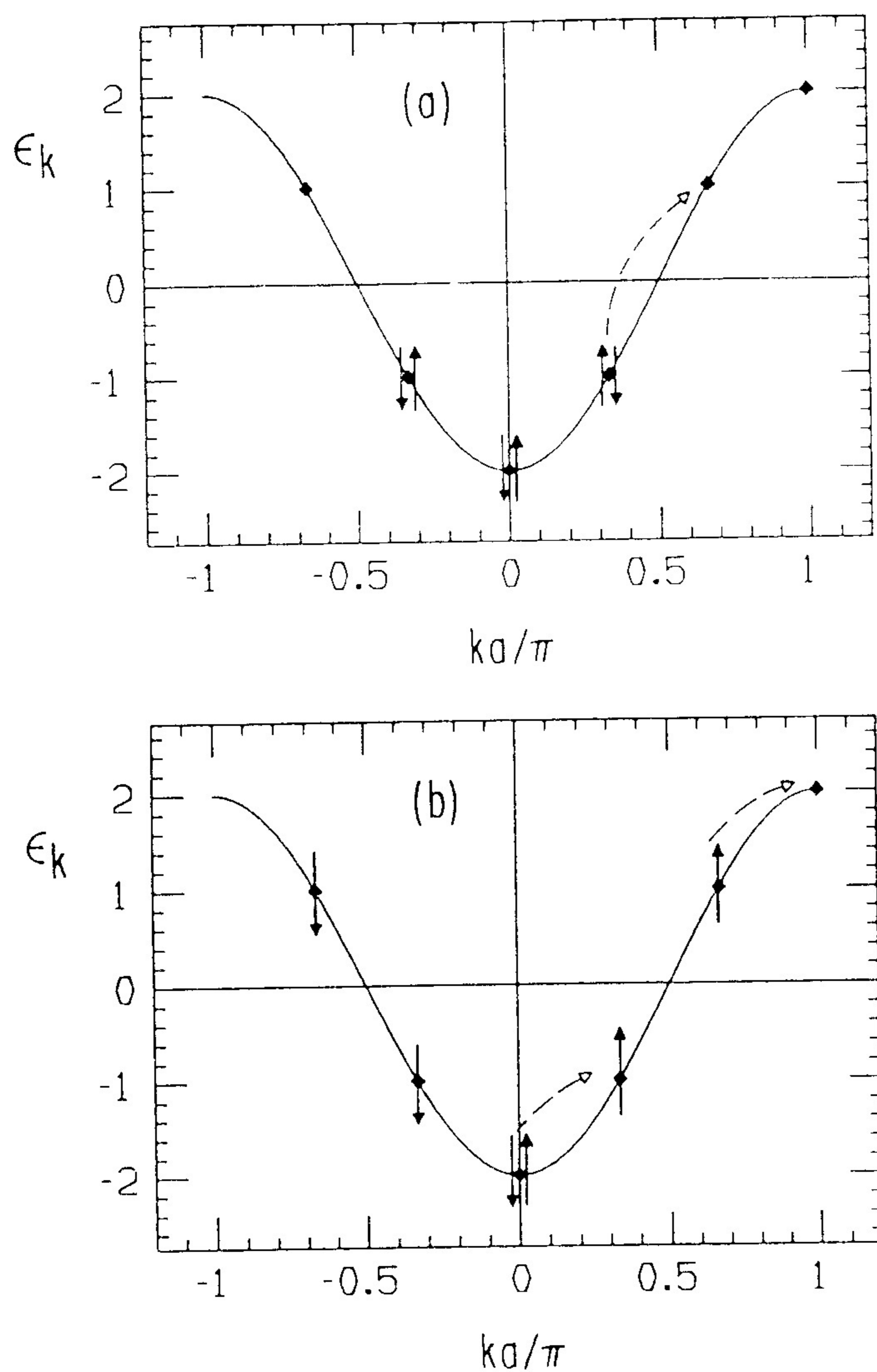
Fig. 3. (a) Conventional Hückel picture and (b) spin-split picture of the ground state of benzene. The dashed lines indicate allowed optical transitions (see text).

if the condition

$$J > 2t \tag{14}$$

is satisfied. For benzene, the first principles estimate for J yields $J = 0.92$ eV, and the estimates for t were discussed earlier. Given the uncertainties in the estimation of these parameters we believe that it is possible that the condition Eq. (14) could be satisfied.

Returning to the general case Eq. (11), the current due to spin σ in the presence of magnetic flux ϕ is given by

$$I_\sigma = \frac{2te}{N\hbar \sin \frac{\pi}{N}} \left[\sin \frac{\pi}{N}(n_2 - n_1)\sigma + \frac{e\phi}{N\hbar c} \cos \frac{\pi}{N}(n_2 - n_1) \right] . \tag{15}$$

The net spin current is given by

$$I_s = I_\uparrow - I_\downarrow \tag{16}$$

and the net charge current by

$$I_c = I_\uparrow + I_\downarrow . \tag{17}$$

It can be seen that the spin current is not affected by the presence of an external magnetic field. The charge current is reduced with respect to the Hückel case by a factor that depends on the degree of spin splitting:

$$I_c = \frac{4e^2}{N^2\hbar^2 c} \frac{t \cos \frac{\pi}{N}(n_2 - n_1)}{\sin \frac{\pi}{N}} \phi . \tag{18}$$

In particular, for the case of benzene (Fig. 3b) $n_1 = 0$, $n_2 = 2$ and Eq. (18) is 1/2 of Eq. (7). However, the total kinetic energy of the electrons is correspondingly reduced, as it is given by

$$E_{kin} = -4t \frac{\cos \frac{\pi}{N}(n_2 - n_1)}{\sin \frac{\pi}{N}} . \tag{19}$$

Thus the relationship found in Ref. 11 between ring currents and resonance energies is preserved, and equally good agreement with experiments as reported in Ref. 11 would be found by renormalizing the value of t used.

Our Hamiltonian Eq. (1), as well as the interaction Eq. (9), are spin-rotationally invariant, while the spin-split state clearly defines a direction in spin space. We argue that a natural spin quantization direction is set by the direction perpendicular to the plane of the molecule, and that spin-orbit coupling will stabilize the spin-split state with the electron spin being either parallel or antiparallel to the direction of the orbital angular momentum of the spin current depending on the environment. A low-lying excited state of the system will then correspond to a state where the relative orientation of spin and orbital angular momentum is reversed.

Assuming the spin orientation is parallel or antiparallel to the orbital angular momentum it is easy to see that this will give rise to a dipolar charge distribution on the plane of the molecule in the laboratory frame, since a magnetic dipole **m** moving with velocity **v** gives rise to an electric dipole moment

$$-\mathbf{p} = \frac{\gamma}{2}\,\mathbf{m} \times \frac{\mathbf{v}}{c} \tag{20}$$

where the factor $\frac{1}{2}$ arises from Thomas precession, and $\gamma = 1/\sqrt{1 - v^2/c^2}$. For our purposes, $\gamma \sim 1$. Summing the contributions from all the electrons we obtain a dipolar density

$$P = \frac{te}{Nmc^2} \frac{\sin\frac{\pi}{N}(n_2 - n_1)}{\sin\frac{\pi}{N}} \tag{21}$$

along the ring. In particular, for the case of benzene,

$$P = \frac{et}{2\sqrt{3}mc^2}. \tag{22}$$

Figure 4 shows the dipolar charge distribution for the two possible spin-split states in an aromatic ring. In general, we expect case (a) to be lower in energy as it will be stabilized by electronic charge density in the bonds connecting to atoms outside the ring.
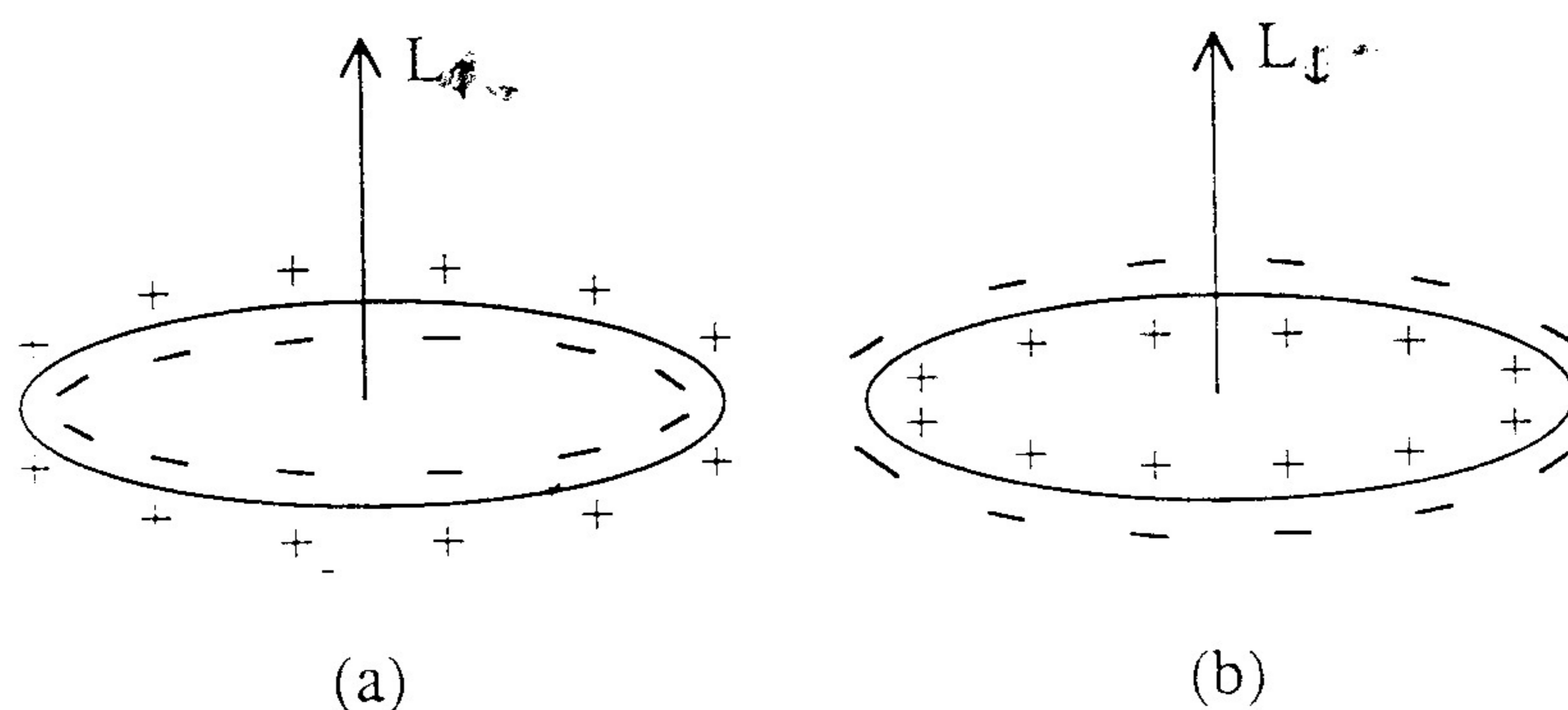

(a)   (b)

Fig. 4. Dipolar charge distribution produced by spin currents. (a) Spin parallel to orbital angular momentum. (b) spin antiparallel to orbital angular momentum. L_σ denotes the orbital angular momentum for spin σ, and only the one pointing up is shown in each case. In general, we expect (a) to be lower in energy.

We may think of the dipolar charge distribution shown in Fig. 4 as highly mobile as it is not associated with particular ions as the electronic charge density is. Thus it is easily set into motion by applied magnetic fields, with the negative

and positive component of the dipoles rotating in opposite directions. This provides a heuristic picture in support of our hypothesis that aromaticity will result if spin currents are present, while insulating behavior would result in their absence.

4. Discussion

We have suggested the possibility that aromaticity in organic molecules may result from the existence of spin ring currents in the ground state. While we do not have a quantitative theory that establishes this we have presented arguments in support of the view that the conventional picture of aromaticity is probably incorrect and that pre-existing spin currents would provide a more natural explanation of the phenomenon.

Another argument in favor of our picture is found in the optical absorption properties of benzene. Three bands are found in the ultraviolet at wavelengths 225, 205 and 183 nm.[15] The one at 255 nm is weak and has considerable fine structure, and thus is attributed to a forbidden transition involving coupling to vibrational degrees of freedom. The other two are strong, and their interpretation has been controversial. The difficulty within the conventional picture is that only one electronic transition is allowed between the ground states and excited states due to the selection rule that only one unit of angular momentum can change[15] (see Fig. 3a). Within the spin-split model instead two distinct allowed transitions exist (see Fig. 3b) which could provide a natural explanation for the two observed bands.

The dipolar charge distribution generated by the spin current gives rise to an electric field that decays very rapidly, as the fourth power of the distance to the center of the ring, and is directed radially in the plane of the ring. For a point x in the plane it is given approximately by

$$\varepsilon(x) \sim \frac{3pr}{x^4} \tag{23a}$$

with r the radius of the ring, x the distance to its center and p the integrated dipole moment along the ring ($p = NaP$). For benzene we obtain as an order-of-magnitude estimate at $x = 2r$

$$\varepsilon \sim 5\mu V/\text{Å} \tag{23b}$$

(assuming $t = 1$ eV). Although these quadrupolar fields should in principle be observable their small size and rapid decay with distance makes it a difficult task. Nevertheless, they could play an important role in highly organized biological matter where aromatic rings are ubiquitous.

In particular, an important consequence of our picture is that it implies the existence of two distinct low-lying states for aromatic molecules, as shown in Fig. 4. We expect the barrier for transition between both states to be large as the

transition involves changing the states of all the electrons involved in a highly correlated way. This will lend stability to be excited state, particularly so the larger the number of electrons (i.e. the size of the ring) involved. A change in the electrostatic potential in the vicinity of an aromatic ring would presumably induce transitions between these two states.

What we have just described suggests itself as an ideal memory storage mechanism. While it may be difficult to implement it in an actual computer, it would seem unlikely that nature had not taken advantage of it in biological organisms. Each aromatic ring would store one bit of information, and memories would be stored and retrieved by slight changes in the electrostatic potential in the nearby vicinity of the ring. The number of aromatic rings within a human brain is certainly sufficient to store the estimated amount of information over a lifetime.[16] "Long term" and "short term" memories[16] would naturally be associated with information stored in large and small aromatic rings, respectively.

Acknowledgments

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