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Ferromagnetic spin interactions between benzene anions: Molecular-orbital analysis and the Hubbard model

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As a model for ferromagnetism in an organic system, the spin interactions between two benzene-radical anions have been considered. *Ab initio* molecular-orbital calculations for the energies of this dimer show that the ground state is a triplet for all separations of the benzene molecules, indicating a ferromagnetic interaction between spins on adjacent molecules. Furthermore, a three-parameter Hubbard model gives a quantitative fit to the energies of the 12 low-lying states.

In insulating materials the occurrence of ferromagnetic interactions between spins is relatively rare, compared with the predominance of antiferromagnetic interactions. Furthermore, the known cases of ferromagnetism always involve spins of either d or f electrons, which presumably play an essential role in the mechanism of this interaction. The idea of being able to synthesize an organic ferromagnet having only p electrons is, therefore controversial and challenging. A number of model systems have been proposed,[1-6] most of which involve orbital degeneracy for a radical subunit with Hund's rule leading to a high-spin ground state; this is also true for Van Vleck's model[7] for inorganic ferromagnetism. According to one proposal for organic ferromagnetism,[6] a stack of organic radicals which have a degenerate open shell will exhibit ferromagnetic interactions. The simplest model system having the essential features of this proposal is the dianion of the benzene dimer, which has the necessary orbital degeneracy and two unpaired spins. For a realistic model system, there has not been a rigorous theoretical electronic structure study which would justify a proposed mechanism for ferromagnetic interactions in an organic system. In this paper, we report the first such study for the model of the dianion of the benzene dimer.

We consider the dianion states of a dimer composed of two eclipsed (face-to-face) benzene molecules at a separation d between them. The states of interest are those that can be formed from all possible distributions of two electrons into the doubly degenerate e_{2u} anion orbitals of the two benzene molecules. The core electrons of neutral benzene are kept in fully occupied closed shells. These distributions lead to ten singlet and six triplet states for the dianion dimer. The relative energies of these states provide a direct test of the effects of Hund's rule. We have obtained these relative energies from all electron configuration interaction (CI) wave functions over the complete configuration space described above. The orbitals used for the CI are the self-consistent field (SCF) orbitals, suitably orthogonalized, of the isolated benzene monomer anion. Orbitals optimized for the dimer have also been used but, because of the weak chemical interaction between monomers, the CI results with these orbitals are essentially the same as those with monomer orbitals. The choice of the monomer orbitals for the CI allows a more direct interpretation of the physical significance of the interaction of the various structures.

As the separation d between the benzenes is varied near the van der Waals separation (~ 3.17 Å), there are large shifts in the energies of all the states due to the Pauli and Coulomb repulsions. Since we are not interested in these effects here, we choose as our zero of energy the energy of the ^3E state which, by symmetry, is represented by a single configuration, as we shall see below, and is not affected by the CI mixing.

The CI energies are shown in Fig. 1 as a function of the separation d between the benzene molecules. We concentrate first on the energies for large separation, $d \gtrsim 6$ Å. There are six lowest states, with zero energy, composed of purely B^- and B^- configurations formed from two benzene anions. These six configurations contain[8] two each of ^3A and ^1A as well as one each of ^3E and ^1E states. (Note that we count the doubly degenerate E states only once.) The singlet and triplet energies of these states are degenerate since, for such large d, there is no interaction between spins on adjacent benzene anions.

The six excited states are composed, for $d \gtrsim 6$ Å, of purely B^{2-} and B^0 configurations formed from a neutral benzene and a dianion with two states[8] each of ^3A, ^1E, and ^1A. The symmetries of the states of the B^{2-} and B^0 group arise because neutral benzene is a totally symmetric

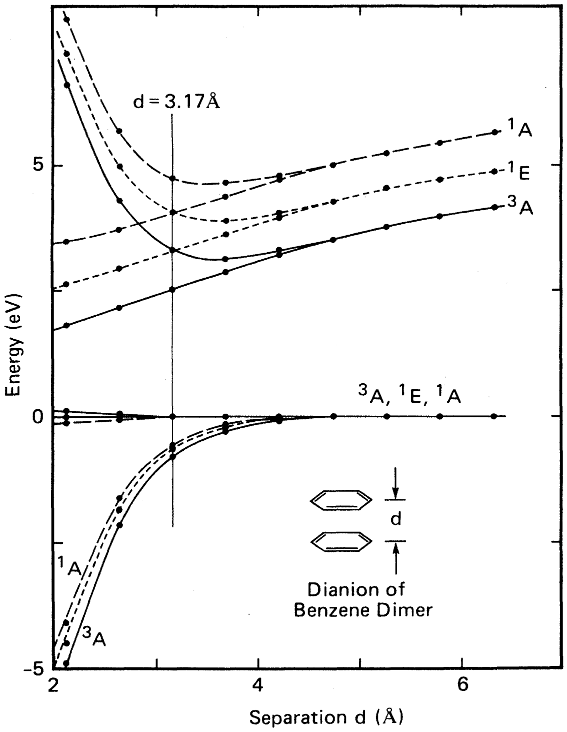

FIG. 1. Energies of the dianion of the eclipsed benzene dimer showing strong configuration interaction when the separation is < 4 Å, which results in a triplet ground state.

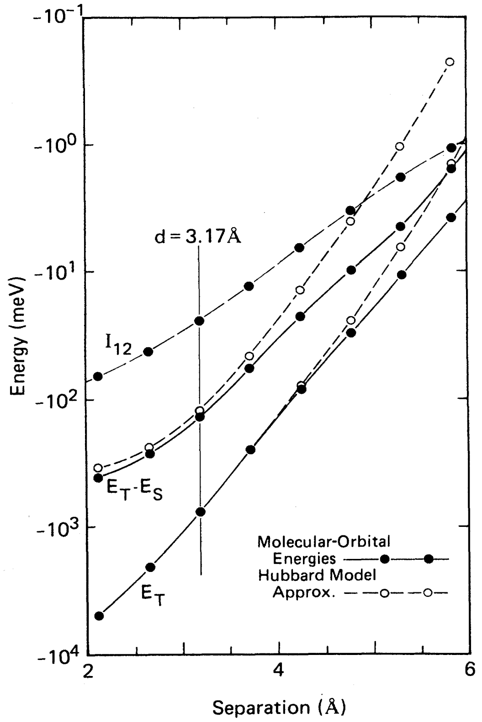

FIG. 2. Energy of lowest triplet state E_T showing strong stabilization at short distances caused by configuration interaction. The energy difference $E_T - E_S$ between the lowest triplet and lowest singlet is a measure of the strength of the ferromagnetic interaction. These are compared with the Hubbard model approximation which neglects two-center integrals, such as I_{12}.

singlet and the dianion has ^3A, ^1E, and ^1A states. The relative energies of the dianion states of the benzene monomer ^3A, ^1E, and ^1A, as given by Hund's rule, are $U_0 - K_0$, $U_0 + K_0$, and $U_0 + 3K_0$, respectively, where U_0 is an on-site Coulomb repulsion integral and K_0 is the on-site exchange integral. Using the SCF e_{2u} orbital of the benzene anion, we find values[9] of $U_0 = 6.746$ and $2K_0 = 0.738$ eV. For the dimer, the diagonal energies of the B^{2-} and B^0 states are given by the use of an effective Coulomb repulsion $U = U_0 - V_{12}$, where V_{12} is an intermolecular Coulomb repulsion integral between the monoanions. Thus, the diagonal energies of the B^{2-} and B^0 configurations are $U - K_0$, $U + K_0$, and $U + 3K_0$ for ^3A, ^1E, and ^1A, respectively. As for the isolated dianion, the ^3A state of the dimer is Hund's rule stabilized with respect to the lowest singlet ^1E by the on-site exchange, $2K_0$.

As the separation between the benzene molecules decreases and approaches the van der Waals separation, the molecules begin to overlap and interact, removing some of the degeneracies. As seen in Fig. 1, the interaction between the lowest triplet configuration B^- and B^- and the excited triplet configurations B^{2-} and B^0 significantly decreases the energy E_T of the lowest triplet. This decrease is plotted in Fig. 2. The same effect is seen for the singlets; but, because the energy separation between the B^- and B^- and B^{2-} and B^0 singlet configurations is larger (by $\sim 2K_0$), the decrease for the lowest singlet is less than that for the triplet. Thus, the singlet-triplet degeneracy of the ground state is removed by the configuration interaction; the calculation shows that the triplet lies lowest for all values of the separation studied ($d > 2$ Å). The difference in energy $E_T - E_S$ between triplet and singlet is also shown in Fig. 2 and is seen to increase exponentially for closer separations. This result may be interpreted as a ferromagnetic exchange interaction between the two benzene molecules. For $d = 3.17$ Å, the triplet-singlet splitting is 140 meV or 1625 K, corresponding to a very large ferromagnetic coupling indeed.

It is of interest to see if these results can be described by a Hubbard model with a Hamiltonian similar to those used previously.[10-12] For the dianion of the benzene dimer, the appropriate[13] Hubbard Hamiltonian is

$$\begin{aligned} H = {} & U \sum_{i,s,s'} n_{i,A,s} n_{i,B,s'} + (U+2K) \sum_{i,\lambda} n_{i,\lambda,\uparrow} n_{i,\lambda,\downarrow} \\ & - K \left(\sum_{i,s,s'} d^\dagger_{i,A,s} d_{i,A,s'} d^\dagger_{i,B,s'} d_{i,B,s} + \sum_{i,\lambda=\lambda'} d^\dagger_{i,\lambda,\uparrow} d_{i,\lambda',\uparrow} d^\dagger_{i,\lambda,\downarrow} d_{i,\lambda',\downarrow} \right) - t \sum_{\lambda,s} (d^\dagger_{2,\lambda,s} d_{1,\lambda,s} + \text{H.c.}) , \end{aligned} \quad (1)$$

where U is the effective repulsion between two electrons on the same site, K is the on-site exchange, and t is the one-electron transfer integral between two sites. For the annihilation, creation, and number operators (d, $d^\dagger$, and n), the i,λ,s indices indicate the site i, degenerate component λ ($\lambda = A,B$), and spin ($s = \uparrow,\downarrow$).

Recognizing the physical significance of U, K, and t, we can readily relate them to specific integrals over the e_{2u} orbitals localized on each benzene molecule. Here, we use the SCF orbitals of the isolated benzene anion as we did for our CI calculation. However, the orbitals of the two different benzene molecules, denoted a and b, must be orthogonalized before the integrals are meaningful since the Hubbard formalism implicitly assumes an orthogonalized basis. In order to retain the equivalent character of the a and b orbitals, we have used a procedure based on Löwdin's symmetric orthogonalization.[14] We denote the components of the orbitals localized on sites a or b by a_A and a_B or b_A and b_B. The general two-electron integral, which may involve up to four orbitals, is

$$I(i,j,k,l) = \int \varphi_i^*(1)\varphi_j(1)(1/r_{12})\varphi_k^*(2)\varphi_l(2)dv_1dv_2 . \tag{2}$$

Thus, the on-site Coulomb U_0 and exchange K_0 integrals are

$$U_0 = I(a_A,a_A;a_B,a_B) = I(b_A,b_A;b_B,b_B) ,$$

$$K_0 = I(a_A,a_B;a_A,a_B) = I(b_A,b_B;b_A,b_B) .$$

There are two possible off-site Coulomb integrals: $V(A,A) = I(a_A,a_A;b_A,b_A)$ and $V(A,B) = I(a_A,a_A;b_B,b_B)$; we find that these two integrals are almost identical and denote their average by V_{12}. In Eq. (1), we use $U = U_0 - V_{12}$ and $K = K_0$. For the transfer integral of Eq. (1), the screening due to the closed shells of neutral benzene must be taken into account. Thus for t, we use

$$t = t_{12} = t(a_A,b_A) = t(a_B,b_B)$$
$$= \int a_B(1)(h + J_{\text{core}} - K_{\text{core}})b_B(1)dv_1 , \tag{3}$$

where h is the usual kinetic energy and nuclear attraction operator and J_{core} and K_{core} are Coulomb and exchange operators[9] for the core electrons.

The integrals U_0, K_0, V_{12}, and t_{12} are plotted in Fig. 3. The on-site integrals are practically constant at their values for an isolated benzene molecule while the off-site Coulomb interaction varies roughly as $1/d$. As expected, t_{12} varies approximately exponentially with d because the integral depends on the overlap of the charge distributions of orbitals localized on sites a and b. While Eq. (3) gives the only nonzero two-site transfer integral, there are a large number of nonzero two-site, two-electron integrals in addition to those used for V_{12}. However, these integrals are very small compared to U_0, K_0, and V_{12}. These integrals are neglected in the Hubbard Hamiltonian, Eq. (1); one of the larger of them is denoted I_{12}, $I_{12} = I(a_A,a_B;b_A,b_B)$, and is plotted in Fig. 3.

For the dimer, the Hubbard model, Eq. (1), can be solved analytically and the twelve energies are given in terms of U, K, and t in Table I. These expressions are evaluated using the molecular-orbital integrals for $d = 3.17$ Å and compared with the exact CI energies for this distance. The maximum error of the Hubbard model is for the highest singlet state; it is 119 meV or 2.5% of the exact CI energy. Even better agreement was obtained

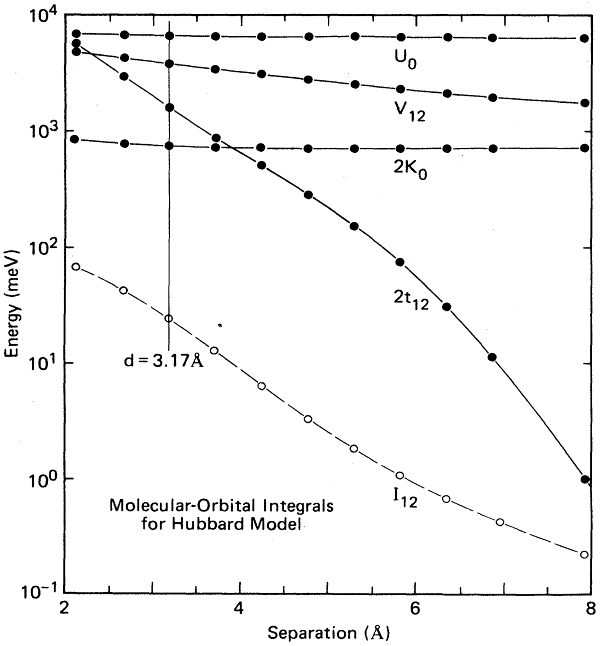

FIG. 3. The calculated values of the integrals U_0, V_{12}, $2K_0$, and $2t_{12}$ for use in the Hubbard model (with $U = U_0 - V_{12}$). The value of one of the neglected terms, I_{12}, is shown for comparison.

TABLE I. Comparison of calculation and model at $d = 3.17$ Å.

Hubbard model[a]		Molecular-orbital energies
	Triplets	
$-\Delta(U-K)$[b]	−791 meV	−776 meV
0[c]	0[c]	0[c]
0	0	39
$U-K$	2535	2545
$U-K+\Delta(U-K)$	3326	3342
	Singlets	
$-\Delta(U+K)$[c]	−664[c]	−636[c]
$-\Delta(U+3K)$	−568	−516
0	0	−39
$(U+K)$[c]	3297[c]	3299[c]
$[U+K+\Delta(U+K)]$[c]	3963[c]	4037[c]
$U+3K$	4064	4053
$U+3K+\Delta(U+3K)$	4632	4751

[a] Calculated for $2K = 764.3$ meV, $2t = 1622$ meV, and $U = U_0 - V_{12} = 6805.5 - 3892.3 = 2917.2$ meV.

[b] The function $\Delta(X) \equiv 1/2(\sqrt{X^2 + 16t^2} - X)$.

[c] Doubly degenerate E state.

when we determined U, K, and t from empirical fits to the exact energies. However, our use of the orbital integrals ensures that in this case the Hubbard parameters have physical meaning. The Hubbard model results for E_T and $E_T - E_S$ obtained with the orbital integrals for other benzene distances are plotted in Fig. 2. For 2 Å $\leq d \leq$ 4 Å, the Hubbard and exact CI results agree closely. Only for $d > 4$ Å, where E_T and $E_T - E_S$ become small and approach the values of the neglected two-electron integrals, see I_{12}, are the Hubbard and CI values significantly different.

In conclusion, it is shown that the interaction between spins in the dianion of the benzene dimer is ferromagnetic and can be strong. This calculation provides theoretical justification for the proposal[6] that a stack of organic radicals which have a degenerate open shell can exhibit ferromagnetic interactions. Furthermore, the calculation demonstrates that the energies of such a system can be quantitatively described by a Hubbard model using directly calculated (rather than empirical) parameters. Together, it is hoped that these results will encourage and support further experimental and theoretical work on organic ferromagnets[15-17] in order to go beyond the preliminary reports of two such materials.[6,18]

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