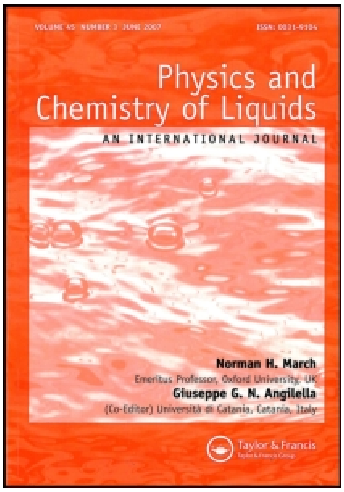

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Letter

Spin-polarized electron (hole) liquids: are π-electrons in metal–benzene sandwiches or injected carriers in C-doped BN nanotube candidates?

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In view of current interest in the emerging field of spin-tronics, we consider here two possible chemically oriented approaches to achieve spin-polarized electron (or hole) liquids. These are by way of (i) metal–benzene sandwiches and (ii) injected carriers in C-doped BN nanotubes. In area (i), the crystal field theory in cylindrical symmetry is employed to discuss in general terms the possible existence of a π-electron spin-polarized liquid, the main sandwich considered being $Mn_n(C_6H_6)_{n+1}$ for $n = 1, 2$. As to area (ii) discussed very recently numerically using spin-density functional theory by Guo *et al.* [*Solid State Commun.*, **137**, 246 (2006)], we emphasize the relevance of the local moment criterion derived some decades ago by Stoddart and March [*Ann. Phys.* (*NY*), **64**, 174 (1971)]. It is stressed that the strength of the (spin-independent) potential due to the C impurities times the Hilbert transform of the band density of states of the nanotube enters the criterion for local moment formation.

Keywords: Spin-polarized electron liquids; Metal–benzene sandwiches; Local moment criterion

1. Background

Spin-tronics is presently a very active area which involves processes that can both probe and manipulate the electronic spin degrees of freedom [1]. Therefore, materials containing electron liquids with a substantial degree of spin polarization are of current interest, and one area explored already in considerable detail by physicists is that of half-metallic ferromagnets, going back at least to the work of de Groot *et al.* [2]. For a more recent review, the reader is referred to Pickett & Moodero [3] or Dederichs & Golankis [4]. Heusler alloys, such as Co_2MnZ, where Z can be either Si or Ge, are specific examples of such 'half metals'.

However, it seems worthwhile to give attention also to more chemical assemblies, in seeking alternative ways of generating spin-polarized electron (hole) liquids to that

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afforded by the half-metallic alloys already cited. Therefore, in this letter, we consider two further areas, namely (i) metal–benzene sandwiches and (ii) injected carriers in C-doped BN nanotubes. Some computations for these two cases have already appeared [5–7] and will be noted. With this background, we turn immediately to discuss the application of crystal filed theory to classify the energy level spectra of specific metal–benzene sandwiches.

2. Cylindrically symmetric crystal field description of metal–benzene sandwiches

To begin, consider a 3d transition metal atom M or ion, which therefore has an Ar-like closed shell configuration supplemented by $4s^p3d^n$ electrons. This is now subjected to a crystal field due to benzene (or perhaps cyclopentadienide) ligands, particularly of their 6π-electrons, understanding that the metals are aligned along a line with the benzenes between them such that the benzene planes are oriented normal to this line. These ligands have a 6-fold symmetry about the axial line, but may be treated as approximating a circular ligand (as in the chemical network model), and such as that which has been successfully utilized before [8] in the similar context of ferrocene. Then for M sandwiched between two such ligands a cylindrical $\mathcal{D}_{\infty\mathrm{h}}$-symmetry crystal field arises

$$V_{\mathrm{CF}} = a_0 Y_{00} + a_2 Y_{20} + a_{40} Y_{40} \tag{1}$$

with the a_{lm} being coefficients to the spherical harmonics Y_{lm}. This permits the orbital states of M to be classified, as shown in figure 1, by the cylinder-symmetry quantum number $m(=0, \pm 1, \pm 2, \ldots)$. There the d-level of the isolated atom M (or ion) indicated on the left is split up into three levels $m=0$, $|m|=1$, and $|m|=2$, which then are further shifted through interaction of these crystal field orbitals and and ligad (C_6H_6) π-ortibals. The 4s level should in fact appear at different places relative to the 3d orbitals, shifting upward slightly as one proceeds left to right across the period

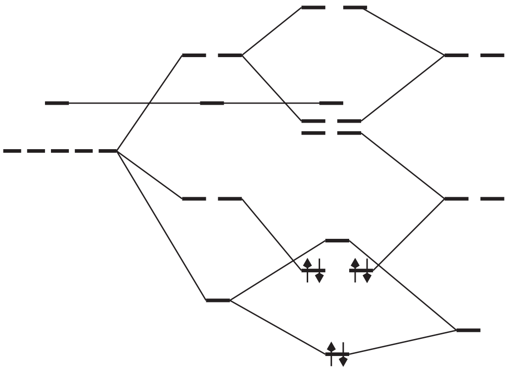

Figure 1. Schematic orbital energy level diagram for isolated atom (on the left), then (next) the atom in a crystal field, while benzene appears (on the far right), and finally (between the atom crystal field and benzene levels) the estimated levels for the complex is shown.

(in concert with the idea that for the first two elements K and Ca of the period that the 4s is lower in energy than the 3d levels). In this figure we have indicated the results per single metal center and a single benzene (or cyclopentadienide) ligand, understanding that when there is a chain of more centers and benzenes these levels are repeated as monomer-counting multiples of the degeneracies indicated in the figure, and that these repeating degeneracies are further slightly split due to the coupling between the monomers – ultimately for a long chain to give bands centered on the indicated levels.

Granted the surmised orbital energy level pattern of figure 1, the manner of its occupancy for different transition metals M may be considered. The occupancy of the orbitals due to the ligand electrons are indicated in the diagram (there being 6 electrons per benzene or cyclopentadienide). The additional $p+n$ valence electrons per transition metal then are to be placed into the next higher orbitals. For $p+n \geq 2$, the next lowest level identified as of symmetry $m=0$ and is anticipated to derive primarily from the transition metal; this orbital being well separated from the higher one should be doubly occupied. Next, the remaining $p+n-2$ valence electrons would begin filling the group of 5 nearly degenerate orbitals maintaining as little pairing as possible if we are to imagine that the electron repulsion dominates over these slight splittings, whence also we imagine that Hund's rule applies. Here for $n+p-2=5$ or 8, then one has first $m=\pm 2$ doubly degenerated level occupied by two parallel spin electrons, which are to be spin-aligned with notable density on both the benzene and metal. For electron counts $p+n-2 \geq 10$ the 5 near-degenerate orbitals would all be double occupied and any remaining electrons would be assigned to the higher $m=\pm 2$ level, localized on the metal and leading to a high-spin Hund's rule coupling.

With the indicated deportments of electrons in mind, we now consider the cases of Mn and V as the transition element. For neutral manganese (M = Mn) with $4s^2 3d^2$ one has a high-spin possibility with delocalization onto the benezene ligands (as well as the metal centers) over the length of the chain, this being consistent with the calculations of Mahida *et al.* [5]. For the case of neutral vanadium (M = V) with $4s^2 3d^3$ there is a high-spin (S = 3/2) prediction for the V atoms, though the spin density is localized primarily on the metal, whence it is anticipated that there is weak exchange coupling between the metal centers, and the material should appear largely paramagnetic. Such a negligible spin polarization of the benzene is in agreement with the computations of Atodiresei [6] for Nb (in the next period beneath V).

3. Spin-polarized electron liquid in C-doped BN nanotubes and the Stoddart–March criterion for local moment formation

Turning to area (ii) concerning doped BN nanotubes, we emphasize the relevance of the Stoddart–March (SM) criterion for local moment formation [9], set out some decades ago, in their early treatment of spin-density functional theory. They started out from a non-magnetic impurity in a periodic lattice. SM uncovered was, that depending on the nature of the spin-independent potential $V(r)$, the possibility under conditions they specified precisely for an instability to arise from the scattering of Bloch waves off the impurity potential, in which a local moment could form.

It is convenient here to refer to the recent summary given by Howard *et al.* [10] of non-linear scattering theory. They follow SM by specifying the scattering potential $V(\vec{r})$

introduced above through its average between Wannier functions, say $w_n(\vec{r} - \vec{R}_i)$, on band n and centered on lattice sites $\vec{R}_i$. Explicitly the assumption is

$$\int w_n(\vec{r} - \vec{R}_i)V(\vec{r})w_m(\vec{r} - \vec{R}_i)d\vec{r} = V_{nn}\delta_{mn}\delta(\vec{R}_j - \vec{R}_0) \tag{2}$$

where the impurity is placed at the site $\vec{R}_0$. Then, because the presence of δ_{mn} in equation (2) shows that the impurity potential does not couple different energy bands. The perturbed wave function $\psi_{\vec{k}}(\vec{r})$, with corresponding Bloch wave function $\phi_{\vec{k}}(\vec{r})$, may be expanded in the Lippmann–Schwinger integral equation, equivalent to Schrödinger's equation, as

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}_t} u_{\vec{k}}(\vec{R}_i)w_n(\vec{r} - \vec{R}_i) \tag{3}$$

Then by purely mathematical manipulation, it can be shown that $u_{\vec{k}}(\vec{R}_0)$ is determined by the density of states $n(E)$ in the band n remaining as

$$u_{\vec{k}}(\vec{R}_0) = \frac{\exp(i\vec{k} \cdot \vec{R}_0)}{1 - V_{nn}F(E) + i\pi V_{nn}n(E)} \tag{4}$$

The main message of the SM local moment formation is that the criterion for this to occur is (in essence see [9] for complete quantitative details) that the real part of the denominator shall vanish, where $F(E)$ is the Hilbert transform of the one-band density of states $n(E)$ of the unperturbed lattice

$$F(E) = \mathcal{P}\int \frac{n(s)}{E - s}ds \tag{5}$$

where $\mathcal{P}$ denotes the principal value.

The numerical spin-density functional study of Guo *et al.* [7] indicates that the SM local moment formation occurs in their approximation, though in Fuo *et al.*'s work the injected carriers were holes. However, this explains the spin-density in the local region of the substitutional C. But their finding that there is delocalized polarization throughout the C nanotube requires transcending the SM one-body potential approach. Whether delocalized polarization can occur would appear to depend on electron correlation for the injected electron (or hole) density. As Bloch initially indicated without considering the electron–electron correlation, but later Ceperley [11] indicated that electron correlation was accounted by QMC, it is anticipated that at sufficiently low density, a homogeneous electron (or hole) liquid can become spin-polarized.

It might be imagined that a possible mechanism for macro-spin polarization is *via* the Nagaoka [12] scheme, for an infinite-U Hubbard model. But this is not so directly relevant to BN, in that to a first approximation (for the π electrons) the N atoms are doubly occupied while the B atoms are unoccupied, so that corresponding to Nagaoka's ideas for the present circumstances, the proper choice for the restricted space with three states per site would entertain empty, spin-↑, and spin-↓ on the B sites, but spin-↑, spin-↓, and double occupied ⥮ on the N sites. Then the introduction of an extra electron (or hole) or two would still leave the bulk of the sites in the 0-order description singlet paired (largely and the N atoms) so that there would be no macro-spin polarization. Evidently any macro-spin polarization would entail being well away from the circumstance where the Nagaoka-like three (orbital) states per site approximation is reasonable.

4. Conclusions

To summarize, we argue that in Mn–benzene sandwiches [5], spin polarization of the π-electrons of benzene is quite feasible, but not yet conclusively established. Other 'almost' cylindrically symmetric molecules like cyclopentadienide also deserve more quantitative study in the area, both experimentally and theoretically. In the second area discussed here, injected currents into C-doped BN nanotubes [7] can perhaps become spin polarized due to the local moment formation resting on the SM criterion [9] involving the Hilbert transform of the energy band density of states. But in such SM-like work, one can expect spin-polarized carriers to occur near the C substitutional impurities in BN nanotubes.

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