

## Interlayer states in graphite and in alkali-metal-graphite intercalation compounds

N. A. W. Holzwarth

*Department of Physics, Wake Forest University,  
Winston-Salem, North Carolina 27109*

Steven G. Louie

*Department of Physics, University of California,  
Berkeley, California 94720*

Sohrab Rabii

*Moore School of Electrical Engineering, University of Pennsylvania,  
Philadelphia, Pennsylvania 19104*

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The character of the first unoccupied band in the graphite intercalation compound  $\text{LiC}_6$  is examined. Based on a framework of interacting nonorthogonal states, an analysis of previous band-structure results shows that this band can be interpreted as a hybrid of Li 2s and graphite interlayer states.

In a recent Letter<sup>1</sup> and in several recent conference publications,<sup>2</sup> Posternak and co-workers (PBFWW) have discussed the role of "interlayer states" in graphite and in graphite intercalation compounds. These interlayer states comprise the first unoccupied  $\sigma$  band in both graphite and in  $\text{LiC}_6$ , having an energy minimum at  $\vec{k}=0$  with  $\Gamma_1^+$  symmetry. The existence of the interlayer bands, their approximate energies with respect to the Fermi levels, and their dispersion with respect to  $\vec{k}$  have been independently corroborated by several calculations<sup>1-8</sup> as well as by several experiments.<sup>9,10</sup>

The issue addressed by PBFWW concerns the qualitative description of the interlayer band in  $\text{LiC}_6$ . Specifically, PBFWW stress that the interlayer band in  $\text{LiC}_6$  is best described as arising from the interlayer band in pure graphite orthogonalized to the Li 1s core states. They take the position that "the occurrence of this band is not correlated to the presence of the Li atoms."<sup>1</sup>

By contrast, in several previous papers,<sup>3,4,7,8</sup> including in our work on the electronic structure of  $\text{LiC}_6$ ,<sup>3,4</sup> the same band has been associated with the unoccupied Li 2s states and termed a Li s-like or "metal" band. This point of view is a logical consequence of the notion<sup>11</sup> that the formation of alkali-metal-graphite intercalation compounds involves the charge transfer of the metal valence electrons to the graphite  $\pi$  bands. In a simple one-electron description of this mechanism, since they are unoccupied, the valence alkali-metal states in the intercalation compound must be energetically located above the Fermi level of the compound. Furthermore, from a consideration of the energetics of the charge-transfer process<sup>12</sup> such as the ionization potential of the alkali-metal atoms modified by the presence of a graphite lattice, one would expect the valence alkali-metal state in the intercalation compound to be located not more than a few electron volts above the Fermi level of the compound. These simple arguments are consistent with the results of detailed calculations of the electronic structure of  $\text{LiC}_6$ , if one associates the unoccupied "interlayer" band in  $\text{LiC}_6$  with significant contributions from the valence alkali-metal states. In modified Korringa-Kohn-Rostoker (KKR) calculations<sup>3</sup> as well as in self-consistent mixed basis pseu-

dopotential calculations,<sup>4</sup> such an identification was suggested by the fact that the eigenvectors for this band, especially near  $\vec{k}=0$ , have substantial amplitude multiplying the Li 2s basis functions. However, even in the early descriptions<sup>3</sup> of this band, it was known to be strongly hybridized with the unoccupied graphite  $\sigma$  band (i.e., the graphite interlayer band). If one accepts the hybrid point of view, the issue then becomes a quantitative question of the degree of hybridization.

Unfortunately, because of the spatially extended nature of both the Li 2s states and the pure graphite interlayer states and especially because of their large overlap with each other, it is very difficult to assess the degree of hybridization. However, despite the ill-defined nature of this issue, it is possible to discuss some reasonable measures of the degree of hybridization and to relate them to the analysis of some experimental results reported in the literature as well as the analysis of our own calculational results for the band structure of  $\text{LiC}_6$ .

Firstly, the photoyield experiments of Eberhardt, McGovern, Plummer, and Fischer<sup>9</sup> measured the absorption of photons due to transitions from a Li 1s initial state to unoccupied final states. Because the initial state is localized on the Li sites, the matrix element tends to weight the absorption yield toward transitions with final states having reasonable amplitudes on Li sites. Furthermore, the atomic portion of the selection rules for the dipole absorption process tend to favor final states of Li 2p character. Since the Li 2p states usually lie higher in energy than the Li 2s states, the absorption yield peak found near 2 eV above  $E_F$  indicates an upper limit for the experimental "location" of states having Li 2s character.

Secondly, Fauster, Himpsel, Fischer, and Plummer<sup>10</sup> have recently measured the unoccupied interlayer bands in both graphite and  $\text{LiC}_6$  by means of inverse photoemission experiments, determining the positions of these bands with respect to their corresponding Fermi levels. Their results for  $\text{LiC}_6$  are compatible with the photoyield results mentioned above. By comparing the results for graphite and  $\text{LiC}_6$  and from a knowledge of the raising of the Fermi level in  $\text{LiC}_6$  due to charge transfer, Fauster *et al.*<sup>10</sup> inferred that

the interlayer band in  $\text{LiC}_6$  is shifted by approximately 1 eV to lower energy with respect to that of graphite. This 1-eV shift is interpreted as an indication of hybridization. Within the experimental error these results are consistent with our self-consistent mixed basis pseudopotential calculations for graphite<sup>5</sup> and  $\text{LiC}_6$  (Ref. 4) which determine the shift to be 1.6 eV.

Thirdly, we have analyzed the results of our calculations<sup>4</sup> in terms of a volumetric measure of the degree of hybridization.<sup>13</sup> We evaluated partial densities of states (PDOS) for  $\text{LiC}_6$  and for a reference graphite compound ( $\text{LiC}_6$  with the Li atoms removed) by weighting each state by its charge within spheres of radius 3.1 bohr about each Li site. This is shown in comparison with the total DOS in Fig. 1. We find a significant contribution to the total and partial Li DOS in the region of the interlayer state at approximately 23 eV about the bottom of the lowest  $\sigma$  band. Of course, in addition to contributing to the interlayer state, Li contributions are found throughout the spectrum.

Finally, we have analyzed our calculations<sup>4</sup> in terms of an orbital measure of the degree of hybridization. First consider a highly simplified model which exhibits an idealized physical situation. The most simple model would correspond to representing the wave function of the  $\text{LiC}_6$  interlayer state as a sum of a Li 2s linear combination of atomic orbitals (LCAO) wave function ( $\phi_s$ ) and a graphite inter-

layer state wave function ( $\phi_g$ ):

$$\Psi(\vec{k}, \vec{r}) = A(\vec{k})\phi_s(\vec{k}, \vec{r}) + B(\vec{k})\phi_g(\vec{k}, \vec{r}) \quad (1)$$

The secular equation for the coefficients  $A$  and  $B$  can be represented as

$$\begin{pmatrix} \epsilon_s & -V \\ -V & \epsilon_g \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \quad (2)$$

Here  $\epsilon_s(\vec{k})$ ,  $\epsilon_g(\vec{k})$ ,  $V(\vec{k})$ , and  $S(\vec{k})$  denote, respectively, the Li 2s LCAO band energy, the graphite interlayer band energy, the interaction matrix element, and the overlap matrix element. The quantity of interest is a measure of the Li 2s character in an eigenfunction  $\Psi$ , which we can take as the Mulliken population.<sup>14</sup>

$$Q_s = \langle A(\vec{k})\phi_s(\vec{k}, \vec{r}) | \Psi(\vec{k}, \vec{r}) \rangle \quad (3)$$

While this Mulliken population is not unique—depending both on the Li 2s LCAO function  $\phi_s(\vec{k}, \vec{r})$  as well as on the other members of the nonorthogonal basis set—we believe that it can provide a reasonable qualitative measure of the hybridization of Li 2s wave functions in the eigenstates  $\text{LiC}_6$  for this very simple model as well as for the realistic band structure which we will discuss in a moment.

If the overlap matrix element  $S(\vec{k})$  of Eq. (2) were zero, the hybridized spectrum of the intercalation compound  $E(\vec{k})$  would be given by

$$E_{\pm} = \frac{\epsilon_s + \epsilon_g}{2} \pm \left[ \left( \frac{\epsilon_s - \epsilon_g}{2} \right)^2 + V^2 \right]^{1/2} \quad [\text{for } S(\vec{k}) = 0] \quad (4)$$

In this case, the spectrum of the compound would consist of two energy levels symmetrically located with respect to the mean of  $\epsilon_s$  and  $\epsilon_g$ . The experimental evidence<sup>10</sup> suggests that  $\epsilon_g - E_- \approx 1$  eV. The upper hybrid level  $E_+$  has not been experimentally identified, but the data<sup>9,10</sup> suggest that  $E_+ - E_- > 7$  eV. These experimental results are consistent with the simplified model (4) only if  $\epsilon_s - \epsilon_g > 5$  eV (which is an unphysically large value), and the corresponding Li 2s Mulliken population would be relatively small:  $Q_s \leq 14\%$ .

On the other hand  $\phi_s$  and  $\phi_g$  are known to overlap appreciably. From our mixed basis pseudopotential calculation results,<sup>4,5</sup> we have evaluated  $S(\vec{k})$  and have found  $S(\vec{k}) \approx 0.6$  throughout most of the Brillouin zone. Therefore, it is important to consider the spectrum of the full generalized eigenvalue problem (2):

$$E_{\pm} = \frac{\epsilon_s + \epsilon_g + 2VS}{2(1 - S^2)} \pm \left[ \left( \frac{\epsilon_s + \epsilon_g + 2VS}{2(1 - S^2)} \right)^2 + \frac{V^2 - \epsilon_s\epsilon_g}{1 - S^2} \right]^{1/2} \quad (5)$$

In this case, the spectrum of the compound consists of two energy levels which are highly skewed with respect to the mean of  $\epsilon_s$  and  $\epsilon_g$ . Analysis of the experimental results,<sup>9,10</sup>  $\epsilon_g - E_- = 1$  eV and  $E_+ - E_- \approx 7$  eV, leads to the conclusion that  $\epsilon_s - \epsilon_g \approx 1$  eV and that  $Q_s^- \approx 40\%$ . These values are more consistent with the physical arguments<sup>11,12</sup> discussed above.

With slight generalization we can use this orbital partition to analyze the full wave functions  $\Psi_i(\vec{k}, \vec{r})$  of the  $i$ th band of our self-consistent calculations.<sup>4</sup> For this purpose, it is necessary to add to the terms of Eq. (1) a residual function

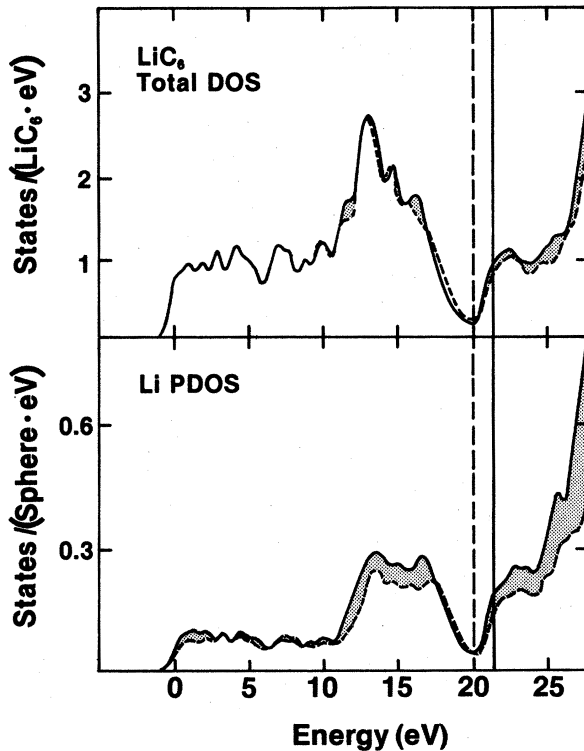


FIG. 1. Total density of states (top) and partial density of states (bottom) for  $\text{LiC}_6$  (full curve) and a reference graphite compound— $\text{LiC}_6$  with Li atoms removed—(dashed curve). Shading highlights the positive difference between the  $\text{LiC}_6$  and reference curves. The PDOS was determined by weighting each state by its charge within spheres of radius 3.1 bohr about each Li site. The zero of energy was taken at bottom of lowest  $\sigma$  band. Vertical lines denote locations of Fermi levels.

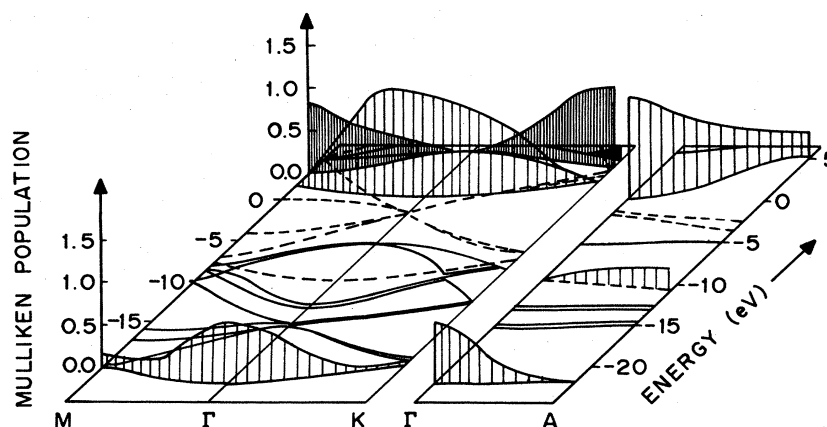


FIG. 2. Three-dimensional representation of the Mulliken population  $Q_s^i$  of the Li 2s LCAO functions (vertical direction) along various symmetry directions in the band structure of  $\text{LiC}_6$ . Zero of energy is taken as  $E_F$ . Bands are denoted with dashed lines for  $\pi$  bands and full lines for  $\sigma$  bands.

$R_i(\vec{k}, \vec{r})$ , since  $\phi_s$  and  $\phi_g$  do not form a complete set:

$$\Psi_i(\vec{k}, \vec{r}) = A_i(\vec{k})\phi_s(\vec{k}, \vec{r}) + B_i(\vec{k})\phi_g(\vec{k}, \vec{r}) + R_i(\vec{k}, \vec{r}) . \quad (6)$$

In our calculation the Li 2s LCAO function  $\phi_s(\vec{k}, \vec{r})$  was included in our actual basis set, so that the coefficient  $A_i(\vec{k})$  was determined variationally. The graphite interlayer wave function  $\phi_g(\vec{k}, \vec{r})$  was not explicitly included in the basis set so that we have no direct information about the coefficient  $B_i(\vec{k})$  or about the contribution of the residual function  $R_i(\vec{k}, \vec{r})$ . Nevertheless, the Li 2s Mulliken population can be evaluated according to Eq. (3). Due to the normalization of the wave function  $\Psi_i$ , information regarding the sum of the graphite and residual contributions can be obtained from the sum rule:

$$Q_s^i + Q_g^i + Q_k^i = 1 , \quad (7)$$

where

$$Q_g^i \equiv \langle B_i(\vec{k})\phi_g(\vec{k}, \vec{r}) | \Psi_i(\vec{k}, \vec{r}) \rangle$$

and

$$Q_k^i \equiv \langle R_i(\vec{k}, \vec{r}) | \Psi_i(\vec{k}, \vec{r}) \rangle .$$

We have reanalyzed our results<sup>4</sup> for the band structure of  $\text{LiC}_6$  in order to evaluate  $Q_s^i(k)$  throughout the spectrum as shown in Fig. 2. These results indicate that for the interlayer band of  $\text{LiC}_6$ ,  $Q_s^i$  has a value of 1.2 at  $\vec{k}=0$  ( $\Gamma$  point), decreases to 0 at the band edges in the  $\vec{k}=0$  plane due to interaction with higher energy  $\sigma$  bands, and decreases to 0.3 at the A point. We again see that Li contributions are significant throughout the spectrum of  $\text{LiC}_6$ . In particular,  $Q_s^i$  takes a value of 0.7 at the  $\Gamma$  point for the lowest-energy  $\sigma$  band and a value of 0.3 at the A point for the lowest-energy  $\pi$  band. A Mulliken population greater than 1.0 can occur for highly overlapping systems such as in the present case. Consequently, the exact value of  $Q_s^i$  is less significant than the fact that it is large for the interlayer band in comparison

with its value for different bands  $i$  at the same wave vector  $\vec{k}$ .

In conclusion, we have shown both in terms of a volumetric PDOS analysis and an orbital Mulliken population analysis that the interlayer state of  $\text{LiC}_6$  does contain an appreciable amount of Li 2s character. Upon closer examination, within the framework of these analyses, we find evidence of Li 2s character throughout the spectrum of  $\text{LiC}_6$ . Thus, the description of the interlayer state of  $\text{LiC}_6$  as a hybrid of Li 2s and graphite interlayer state contributions is necessarily a simplification of a more highly coupled set of states. However, within this simplification, if one examines the simple model of Eqs. (2) and (5) representing the physics of interacting nonorthogonal states, the hybrid nature of the  $\text{LiC}_6$  interlayer band is entirely compatible with the theoretical and experiment results for this system and, in particular, with the "preexistence" of the analogous interlayer band in pure graphite. Because the Li 2s LCAO and the graphite interlayer state are so similar in their spatial extent, other interpretations<sup>1</sup> are possible. However, we feel that the point of view that the occurrence of the  $\text{LiC}_6$  interlayer band is not correlated to the presence of Li atoms<sup>1</sup> is misleading. On the other hand, previous<sup>3,4,7,8</sup> shorthand terminology of this band as a "metal band" is perhaps an overstatement on the other extreme.

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