

**Galvão *et al.* Reply:** In the previous Comment<sup>1</sup> the authors focus on two main issues which must arise from a misunderstanding of our methods and results.<sup>2</sup> The first regards the theoretical approaches we adopted, which the authors claim “fail to reproduce the . . . lack of electron-hole symmetry” in the band structure of the reduced compound. The second refers to comparison with some of the available experimental results. We argue that we do obtain electron-hole asymmetry, and that our results agree with recent experimental data.

Concerning the first issue our results clearly exhibit an asymmetrical density of states (DOS) (for all forms, Figs. 2 to 4 in Ref. 2). For the reduced form of leuco-emeraldine we obtain in the first conduction states a band crossing between an extremely localized, flat band and a wider band, so that for  $\mathbf{k} \sim 0$  the bottom of the conduction band is given by the wide band, and for  $\mathbf{k}$  towards the zone edge it is given by the flat band. We remark, however, that the ordering of virtual levels cannot be given accurately by either the method we are using or the method quoted in the Comment.<sup>3</sup> The parametrization we use distinguishes different oxidation states for nitrogen, and incorporates corrections to the self-energy of neighboring carbon sites; the effect of geometrical relaxations is thus qualitatively taken into account. This parametrization has been successfully applied to compounds of quinoid character.<sup>4</sup>

The interpretation of the rise of the conductivity in polyanilines in terms of ordered metallic polaron lattices is controversial (Refs. 4–6 in Ref. 2). Vanishing magnetic susceptibility in a highly conducting state has been interpreted as evidence for a mostly “bipolaron”-like structure.<sup>5</sup> Still, we must stress that in Ref. 2 we do not *induce* the formation of large clusters to obtain “compositionally disordered polymers.” For the 50%-oxidized compound emeraldine (composition  $1 - y = 0.5$ , where  $y$  is the fraction of quinoid-imine groups) we work *within* the very small *probabilistic* occurrence of clusters (< 5%).

Turning to the experimental evidence quoted in the Comment,<sup>1</sup> the authors suggest that in the 50%-oxidized compound no clustering would be detected, implying compositional order. This is inferred from NMR experiments<sup>6</sup> (Ref. 3 in the Comment) on two samples: one is solid phase  $1 - y > 0.5$ , and the other is solution phase  $1 - y < 0.5$ . We certainly expect significantly higher clustering of majority units. Indeed, clearly resolved clustering peaks are seen for the solution-phase sample for benzenoid-amine units; unresolved peaks are seen for the solid-phase sample in the imine region. It is doubtful if minority-unit clustering could be detected, since (i) the ratio “cluster”/“normal” signals should be small, and (ii) the clustering peak splitting is less than the linewidth of the amine peak in the solid-phase sample. Unfortunately, precise determination of  $y$  seems difficult; no measurements were performed, apparently, for the composition  $y = 0.5$ . Thus, we cannot accept that there is ac-

tual evidence of compositional order in emeraldine chains.

On the other hand, our results are in very good agreement with recent experimental data (Refs. 4–6 in Ref. 2). Measurements<sup>7</sup> of electron-spin resonance and optical absorption (UV, visible, near ir, and x-ray photoemission) on polyaniline films in different oxidation states led recently to the conclusion that “. . . the conduction mechanism in polyaniline is that of variable range, interchain and intrachain hopping between localized charge sites on the polymer backbone.” The behavior of the valence-band DOS with electrochemical treatment is very well predicted in our results. For two samples of similar oxidation states, the one which has higher value for the DOS at the Fermi energy (corresponding in our model to a Fermi energy deeper in the valence band, and hence more distant from the states that would form the “conduction band” of emeraldine) also has higher energy for the first transition. It is worth mentioning that this transition is sharp, indicating a transition between energy levels, and of high intensity, which led the authors to suggest a transition between valence band and gap level. This suggestion is, of course, in perfect agreement with our model.

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<sup>1</sup>J. L. Brédas, A. J. Epstein, and A. G. MacDiarmid, preceding Comment, *Phys. Rev. Lett.* **65**, 526 (1990).

<sup>2</sup>D. S. Galvão, D. A. dos Santos, B. Laks, C. P. de Melo, and M. J. Caldas, *Phys. Rev. Lett.* **63**, 786 (1989).

<sup>3</sup>It is well known that Hartree-Fock calculations at mean-field level cannot predict virtual energies [see, for instance, R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, New York, 1969)]; even within density-function formalisms the “band-gap problem” cannot be completely solved [see R. W. Godby, M. Schluter, and L. J. Sham, *Phys. Rev. B* **37**, 10159 (1988)].

<sup>4</sup>D. S. Galvão and M. J. Caldas, *J. Chem. Phys.* **88**, 4088 (1988); **92**, 2630 (1990).

<sup>5</sup>E. M. Genies and M. Lapowski, *J. Electroanal. Chem.* **220**, 67 (1987).

<sup>6</sup>A. F. Richter, A. Ray, K. V. Ramanathan, S. K. Manohar, G. T. Furst, S. J. Opella, A. G. MacDiarmid, and A. J. Epstein, *Synth. Metals* **29**, E243 (1989).

<sup>7</sup>A. P. Monkman, D. Bloor, G. C. Stevens, and P. Wilson, *Synth. Metals* **29**, E277 (1989).