

*Comment on*  
**HOW DO HARTREE–FOCK AND DFT–LDA  
(DENSITY FUNCTIONAL THEORY IN LOCAL DENSITY  
APPROXIMATION FOR EXCHANGE AND CORRELATION) COMPARE?**

A year or so ago it became apparent that some results of Hartree–Fock (HF)<sup>1</sup> and DFT–LDA<sup>2</sup> calculations, both on GaAs, differed in important regards by a factor of about three. The issue was the difference between the equilibrium energies of the stable tetrahedral ZnS structure and the denser metastable NaCl one, as well as the transition pressure between them. The energy minima came at very much the same volumes in the two calculations, but the energy scales simply differed by a factor of about three.

Since then, the matter has been investigated and cleared up with interesting conclusions. Incidentally the DFT–LDA total energy calculations, which were quite old, were repeated and confirmed with small deviations<sup>3</sup>.

Various approximations to add the correlation energy to the HF calculations have been tested<sup>4</sup>. They include: plain Hartree–Fock (HF); Hartree–Fock with an added correlation correction obtained by integrating the Perdew functional of the HF self–consistent electron density (HF+C); Hartree–Fock with a LDA correction (Dirac functional for the exchange and Ceperley–Alder functional as parametrized by Perdew and Zunger for correlation) with the self–consistent HF electron density (HF–LDA). The corresponding results concerning the equilibrium energy difference between the ZnS and the NaCl geometries are summarized in the following table, together with the DFT–LDA datum.

	HF	HF+C	HF–LDA	DFT–LDA
$E_{NaCl}^{eq} - E_{ZnS}^{eq} (eV/cell)$	2.26	1.67	0.81	0.67

To cut a long story short, there are two main conclusions. Firstly the experimental transition pressure agrees more or less with the DFT–LDA result. Secondly the HF calculations also agree with the DFT–LDA results if one adds the correlation energy using the LDA approximation applied as a retrofit to the electron density obtained from HF. We may thus conclude that it is the approximation used to deal with correlation that deeply affects quantities as the equilibrium energy differences between different crystalline phases.

The DFT-LDA and HF+C results for the ZnS and NaCl structures of GaAs have been used as distinct input data sets to fit two suitable Tight-Binding (TB) potentials for Molecular Dynamics simulations. The corresponding total energy curves, together with a comparison between the MD results for liquid GaAs obtained with the two TB parametrizations may be found in Ref.5.

C.Molteni and V.Heine  
Cavendish Laboratory, Cambridge (UK)

<sup>1</sup> C.Molteni, L.Miglio, L.Colombo and M.Causà, *Il Vuoto* **4**, 94 (1992)

<sup>2</sup> S.Froyen and M.Cohen, *Phys.Rev.* **B 43**, 447 (1982)

<sup>3</sup> S.de Gironcoli, private communication (1993)

<sup>4</sup> M.Causà, private communication (1993); M.Causà and A.Zupan, *Chem.Phys.Lett.* **220**, 145 (1994); M.Causà and A.Zupan, *Int.Journ.Quant.Chem.*, in press (1994)

<sup>5</sup> C.Molteni, L.Colombo and L.Miglio, *J.Phys.:Condens.Matter* **6**, 5243 (1994); C.Molteni, L.Colombo and L.Miglio, *J.Phys.:Condens.Matter* **6**, 5255 (1994)