Ab initio Hartree-Fock with electronic correlation study of the electronic properties of MgB$_2$

Armando Reyes-Serrato$^*$ and Donald H. Galván
Centro de Ciencias de la Materia Condensada de la UNAM
Apartado Postal 2681, Ensenada, Baja California, 22800 México.
(March 22, 2022)

Abstract

We performed all-electron ab initio self-consistent field Hartree-Fock linear combination of atomic orbital, in which electronic correlation using density functional were included to perform electronic calculations in MgB$_2$ new superconductor. Superconductivity in this compound was correlated with existence of $p_{x,y}$ band holes at $\Gamma$ point.
I. INTRODUCTION

MgB$_2$ has attracted lots of attention of the international scientific community due that it shows a superconducting transition of the order of 39 K. Furthermore, its unitary cell (three atoms per unit cell), is simple enough that provides a tool to understand the mechanism proposed for this material to behave like a BCS type of superconductor i.e. electron-phonon interaction.

Early theoretical studies of the electronic structure, using other methods of calculations like OPW and tight-binding, have shown similar behavior to graphite, from the point of view of band theory. Transition metal diborides (TMD), as expected, show a more complex structure due to the consideration of d-states.

Recently, an electronic structure calculation on MgB$_2$ shows that some states of boron are responsible for the metallic behavior of this compound. Furthermore, phonon frequencies and electron-phonon coupling (at the most symmetric point of the Brillouin zone) lead these authors to conclude to phonon based superconductivity.

II. COMPUTATIONAL DETAILS

The calculations reported in the present work had been carried out using CRYSTAL98 ab initio Self-consistent-field (SCF) Hartree-Fock linear combination of atomic orbital computer program which provide solution to crystalline system of any space group. Electronic correlation using density functional (DFT) has been included as a correction to the total energy using the correlation function proposed by Perdew-Zunger (PZ). More details about the mathematical formulation of CRYSTAL98 have been described elsewhere and will be omitted here.

The crystal structure of MgB$_2$ is illustrated in Fig. 1. It has a hexagonal unit cell, with the primitive vectors $a = 3.086$ Å and $c = 3.504$ Å respectively. The space group for this compound is $P6/mmm$ (No. 191). From the figure is possible to notice that the boron atoms are arranged in layers, with the next layers of Mg interleaved between them. In order to form the unit cell two layers of magnesium and one of boron are needed along the c-axis in the hexagonal configuration. For the basis set for magnesium and boron, we selected 6-21G* and 6-21G basis set respectively, provided in Ref. (11). The selection of the basis set was obtained between a compromise between accuracy and computational resources.

III. RESULTS AND DISCUSSION

For this calculation, we used the experimental lattice parameters provided by Nagamatsu et al of $a = 3.086$ Å, $c = 3.524$ Å respectively. Band structure calculations for MgB2 are depicted in Fig. 2. In order to obtain the band structure for this compound, we used 133 $k$-points sampling the FBZ.

Our results are in good qualitative agreement with the results obtained by other theoretical methods, such as the results obtained by Kortus et al. who used a general potential LAPW code, whilst Satta et al. using local-density approximation to the density functional theory, and full-potential linearized augmented plane waves, obtained similar results.
Furthermore, Belaschenko\textsuperscript{13} calculated the electronic structure for this compound using Stuttgart LMTO-TB (ASA) to compute the energy bands with similar results.

We spanned the FBZ covering the three dimensional space going from $\Gamma$-M-K-$\Gamma$-A-L-H-A of $k_x = p/a, k_y = p/b, k_z = p/c$. The $\Gamma$-M-K-$\Gamma$ lines are in the basal plane, while the A-L-H-A are located on the top of the plane at $k_z$. The upper part of the valence band for MgB$_2$, composed of B 2p-states which form two peculiar set of bands of $\sigma(2p_{x,y})$ and $\pi(p_z)$ character, whose $k$ dependence changes considerably while spanning the three dimensional space. For B 2p$_{x,y}$ the most pronounced dispersion is along $\Gamma$-K. These bands are of quasi-two dimensional type and form an almost flat zone along $\Gamma$-A, which reflects the distribution of pp-$\sigma$-states in the B layers. These states provide a big contribution to the density of states close to the Fermi energy, providing the metallic properties to the borides.

On the other hand, B p$_z$ like bands are responsible to the weak pp-$\pi$ interactions. These bands are considered to be a three dimensional like type, which have maximum dispersion along $\Gamma$-A. Furthermore, Mg s, p and B s states are admixed with B 2p bands close to the bottom of the valence band, as well as in the conduction band. Hence the electronic properties of MgB$_2$ are associated with metallic 2p-states of B atoms located in planar nets, which determines the DOS close to the Fermi level.

For the total and projected density of states (PDOS) for B and Mg, see Fig. 3. Concentrating on those states close to the Fermi level, which presumably are responsible for the superconductor behavior of the material, as we mentioned before in the energy band discussion, the main contributions comes from p-$\sigma$ bonding and p$_z$ having $\pi$ bonding and anti bonding character on the basal and top planes, respectively. Which one of these two bands is responsible for the superconductor behavior is unclear so far.

In summary, we have shown energy bands, as well as total and projected density of states for the medium temperature superconductor MgB$_2$. From these analysis, we were able to infer the most important contributions from each atom to the superconductor behavior for the compound. So far, this study is not conclusive, but continues in order to provide other important physical properties such as charge density profiles and Mulliken population analysis.

ACKNOWLEDGMENTS

Both of us acknowledge DGSCA-UNAM and CoNaCyT for providing financial support.
REFERENCES

* Author to whom correspondence should be addressed: Centro de Ciencias de la Materia Condensada UNAM, P. O. Box 439036, San Ysidro, CA 92143 USA.
1 J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature, 40, 63 (2001).
2 S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Cndfield, Phys. Rev. Lett., 86, 1877 (2001).
3 J. Bardeen, L. N. Cooper, and J. R. Schriffer, Phys. Rev., 108, 1175 (1957).
4 I. I. Tupitsyn, I. I. Lyakovskaya, M. S. Nakhmanson, and A. S. Sukhikh, Sov. Phys. Solid State, 16, 2015 (1975).
5 D. R. Armstrong, A. Breeze, and P. G. Perkins, J. Chem. Soc. Faraday Trans. I, 173, 952 (1977).
6 J. Kartuz, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, (cond-mat/0101440).
7 V.R. Saunders, R. Dovesi, C. Roetti, M. Causá, N.M. Harrison, R. Orlando, and C.M. Zicovich-Wilson, CRYSTAL98 User’s Manual, University of Torino, Torino (1998).
8 J. P. Perdew, and A. Zunger, Phys. Rev. B 23, 5048 (1981).
9 C. Pisani, R. Dovesi, and C. Roetti, Hartree-Fock Ab initio Treatment of Crystalline Solids (Springer-Verlag, Berlin, 1988), vol. 48.
10 M. J. Jones, and R. Marsh, J. Am. Chem. Soc., 76, 1434 (1954).
11 R. Poirier, R. Kari, and I. G. Csizmandia, Handbook of Gaussian Basis Sets (Elsevier, New York, 1985), vol. 24.
12 G. Satta, G. Profeta, F. Bernardini, A. Continenza and S. Massida, (cond-mat/0102358)
13 K. D. Belashchenko, M. van Schilfgaarde, and V. P. Antropov, (cond-mat/0102290).
FIGURES

FIG. 1. Crystal structure of MgB$_2$. Large spheres represent magnesium and small spheres represent boron atoms.

FIG. 2. Crystal structure of MgB$_2$. Large spheres represent magnesium and small spheres represent boron atoms.

FIG. 3. Band structure calculations for MgB$_2$.

FIG. 4. Total density of states for MgB$_2$.

FIG. 5. Boron projected DOS for MgB$_2$.

FIG. 6. Magnesium projected DOS for MgB$_2$. 
Fig. 1(a) Reyes-Serrato (PRB)
Fig. 1(b) Reyes-Serrato (PRB)
Fig. 2 Reyes-Serrato (PRB)
Total DOS of MgB$_2$

Fig. 3(a) Reyes-Serrato (PRB)
Fig. 3(b) Reyes-Serrato (PRB)
Fig. 3(c) Reyes-Serrato (PRB)