Precise Tight-binding Description of the Band Structure of MgB$_2$

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We present a careful recasting of first-principles band structure calculations for MgB$_2$ in a non-orthogonal sp-tight-binding (TB) basis. Our TB results almost exactly reproduce our full potential linearized augmented plane wave results for the energy bands, the densities of states and the total energies. Our procedure generates transferable Slater-Koster parameters which should be useful for other studies of this important material.

The recent discovery of superconductivity in MgB$_2$ has created great interest in the study of this material, both to understand the mechanism of superconductivity and to explore other properties of MgB$_2$ and related materials. Intensive research has been carried out both by experimentalists and theorists. There have been several studies of the electronic structure of MgB$_2$ including total energy, band structure and phonon spectra calculations as well as evaluations of the electron-phonon coupling, which seems to have emerged as the prime candidate for explaining the superconducting behavior.

In this paper we present a highly accurate tight-binding (TB) description of the band structure and total energy of MgB$_2$. While there have been TB interpretations of the electronic structure of MgB$_2$ in the literature, a realistic recasting of the details of the first-principles electronic structure calculations is lacking. Our approach follows the NRL-TB methodology, which is based on deriving a non-orthogonal TB Hamiltonian by fitting to both the total energy and energy band results of a first-principles full-potential Linearized Augmented Plane Wave (LAPW) calculation using the Hedin-Lundqvist parametrization of the Local Density Approximation (LDA). We first performed detailed LAPW calculations for MgB$_2$ in its ground state (AlB$_2$) structure, varying c and a, thus determining the LDA equilibrium volume. It was necessary to perform 17 independent LAPW calculations over a large range of volumes and c/a ratios. Our LAPW equilibrium parameters are c = 6.55 a.u. and a = 5.75 a.u., as compared to the experimental values of c = 6.66 a.u. and a = 5.83 a.u. As is usually the case the LDA underestimates the experimental values, here by about 1.5%.

All the above results, i.e., 17 values of the total energy and the energy bands for 76 k-points in the irreducible hexagonal Brillouin zone, were used as a database to determine the parameters of our tight-binding Hamiltonian. According to the NRL-TB scheme the on-site parameters depend on the density of the neighboring atoms and the hopping integrals have a polynomial dependence that extends to at least the third nearest-neighbor distance. Our basis included the s and p orbitals on both Mg and B in a non-orthogonal two-center representation. A wave-function analysis of our LAPW results shows that the bands up to the Fermi level, $\varepsilon_F$, are strongly dominated by the B p states with very little contribution from the Mg ions. It turns out, however, that an accurate TB fit including only the B orbitals is impossible, and therefore the Mg s and p orbitals were included in the fit. Furthermore, to obtain a highly accurate fit it was essential to block diagonalize the Hamiltonian at the high symmetry points $\Gamma$, A, L, K and H. We find that at a given set of lattice parameters (c,a) we can perfectly reproduce the energy bands of MgB$_2$. A comparison is shown in Fig. 1, where the solid and broken lines represent the LAPW and TB bands, respectively, at the LDA values of the equilibrium lattice parameters. The TB bands are in excellent agreement with the LAPW bands, including the two-dimensional B-$\sigma$ band in the $\Gamma \rightarrow A$ direction just above $\varepsilon_F$, which has been identified as hole band controlling superconductivity. The RMS fitting error is 2 mRy for the total energy, and close to 10 mRy for the first five bands. Beyond the fifth band our fit is not as accurate, as the Mg d-bands, which are not included in our Hamiltonian, come into play. The values of our TB parameters are given in Table 1 following the notation of Bernstein et al. In this table we also show, for the convenience of the reader, the actual Slater-Koster pa-
The B amount to multiplying the decomposed values by 2.37.

Additionally, we have omitted the Mg-like DOS, which is also small below $\varepsilon_F$. They are much smaller than the presence at the bottom of the valence band, from -0.8 Ry to -0.6 Ry on our scale. They are much smaller than the $s$-components of the DOS have their strongest presence at the bottom of the valence band, from -0.8 Ry to -0.6 Ry on our scale. They are much smaller than the $p$-like DOS, so we chose not to include them in Fig. 2. Additionally, we have omitted the Mg $p$-like DOS, which is also small below $\varepsilon_F$, although it becomes significant above $\varepsilon_F$. Our TB value of the total DOS at $\varepsilon_F$ is $N(\varepsilon_F) = 0.69$ states/eV, which is almost identical to that found from our direct LAPW calculation. This value of $N(\varepsilon_F)$ corresponds to the LDA equilibrium volume and is slightly smaller than the value of 0.71 states/eV reported by other workers. We infer a value of $\lambda$ = 0.65 which is consistent with the high superconducting transition temperature in MgB$_2$. It should also be noted that the B-$p$ states contribute 81% of the DOS at $\varepsilon_F$.

Our TB-Hamiltonian also provides an accurate description of the energetics of MgB$_2$, which is expected to be very useful for other theoretical studies. We have further tested our parameters by computing the TB equilibrium structure. We find an equilibrium of $c = 6.66$ a.u.

FIG. 2. The electronic density of states (DOS) of MgB$_2$ in the AlB$_2$ structure at the theoretical equilibrium volume, comparing the total DOS as determined by the full-potential LAPW method (upper solid line) and our tight-binding parametrization (upper dashed line), and the partial single-atom B-$p$ decomposition (lower lines). The LAPW result decomposition was determined inside the muffin-tin and then scaled by a factor of 2.37 (see text).

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TABLE I. Tight-binding parameters for MgB₂, generated following the methods of Mehler and Papaconstantopoulos and Bernstein et al. Also shown are the generated Slater-Koster tight-binding parameters for the nearest neighbors at the LDA equilibrium lattice constants, \( a = 5.75 \) a.u. and \( c = 6.53 \) a.u. On-site energies are generated from the “densities” of like atoms, that is, the Mg on-site parameters come from the density of Mg atoms and the B on-site parameters from the density of B atoms. \( F(R) \) is the cutoff function from equation (2) of Berstein et al., with \( R_c = 12.5 \) a.u. and \( L_c = 0.5 \) a.u. All energies are in Rydbergs, all distances in a.u.

### Mg-Mg Interactions

| \( \ell \) | \( \alpha \) | \( \beta \) | \( \gamma \) | \( \chi \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|-----------------|
| \( s \) | 0.20169 | -0.25368 | -0.04017 | 19.84215 | 0.03516 |
| \( p \) | 0.39868 | -0.22303 | 1.35834 | 53.36624 | 0.52322 |

**Hopping Terms:** \( H_{\ell\ell'}(R) = (a_{\ell\ell'} + b_{\ell\ell'}R + c_{\ell\ell'}R^2 + g_{\ell\ell'}R^4) \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( a \) | \( b \) | \( c \) | \( g \) | \( \sqrt{3a} \) |
|---------|--------|--------|--------|--------|--------|
| \( H(ssr) \) | 5715.697 | -310.863 | -182.0526 | 1.35579 | -0.05372 |
| \( H(spr) \) | 5704.286 | -5412.67 | -3874.05 | 1.84506 | -0.01250 |
| \( H(ppr) \) | 1920.935 | 498.3775 | -22.58129 | 1.12482 | 0.13720 |
| \( H(ppp) \) | 2000.513 | -739.8181 | 70.26517 | 1.13170 | 0.04414 |

**Overlap Terms:** \( S_{\ell\ell'}(R) = \left( \delta_{\ell\ell'} + t_{\ell\ell'}R + q_{\ell\ell'}R^2 + r_{\ell\ell'}R^3 \right) \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( t \) | \( q \) | \( r \) | \( \alpha \) | \( \beta \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|--------|-----------------|
| \( S(ssr) \) | 1.04886 | -1.27181 | 0.55328 | 1.01629 | 0.18512 |
| \( S(spr) \) | 0.41781 | 0.03630 | -0.00873 | 0.63936 | 0.19274 |
| \( S(ppp) \) | -24.36368 | 0.17541 | 0.41661 | 1.07340 | 0.07662 |
| \( S(ppr) \) | -68.95974 | 5.97517 | 2.55826 | 1.19338 | 0.00308 |

### B-B Interactions

| \( \ell \) | \( \alpha \) | \( \beta \) | \( \gamma \) | \( \chi \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|-----------------|
| \( s \) | -0.16521 | -0.00022 | 0.02579 | 0.09088 | -0.09536 |
| \( p \) | 0.38802 | 0.00060 | 0.00566 | 0.01918 | 0.40383 |

**Hopping Terms:** \( H_{\ell\ell'}(R) = (a_{\ell\ell'} + b_{\ell\ell'}R + c_{\ell\ell'}R^2)^2 \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( a \) | \( b \) | \( c \) | \( \alpha \) | \( \beta \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|--------|-----------------|
| \( H(ssr) \) | -7.31550 | 2.09241 | -0.23379 | 0.85573 | -0.25908 |
| \( H(spr) \) | -146.6733 | 64.75572 | -8.57386 | 1.21983 | -0.18743 |
| \( H(ppr) \) | -256.2214 | 128.0942 | -10.42990 | 1.17220 | 0.14703 |
| \( H(ppp) \) | 167.1287 | -739.8181 | 70.26517 | 1.13170 | 0.14959 |

**Overlap Terms:** \( S_{\ell\ell'}(R) = (\delta_{\ell\ell'} + t_{\ell\ell'}R + q_{\ell\ell'}R^2 + r_{\ell\ell'}R^3)^2 \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( t \) | \( q \) | \( r \) | \( \alpha \) | \( \beta \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|--------|-----------------|
| \( S(ssr) \) | 0.09874 | -0.05865 | 0.00446 | 0.60130 | 0.24535 |
| \( S(spr) \) | 14.02839 | -2.43203 | 0.33914 | 1.27302 | 0.14823 |
| \( S(ppp) \) | -60.70629 | -0.47990 | 3.29498 | 1.32165 | -0.25833 |
| \( S(ppr) \) | 18.98764 | 6.13369 | -3.44742 | 1.41880 | 0.00689 |

### Mg-B Interactions

**Hopping Terms:** \( H_{\ell\ell'}(R) = (a_{\ell\ell'} + b_{\ell\ell'}R + c_{\ell\ell'}R^2)^4 \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( a \) | \( b \) | \( c \) | \( \alpha \) | \( \beta \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|--------|-----------------|
| \( H(ssr) \) | -15.40626 | 8.92332 | -2.25890 | 1.06263 | -0.11887 |
| \( H(spr) \) | -22.65145 | 5.35089 | -0.60679 | 1.03205 | -0.07642 |
| \( H(ppp) \) | 98.38228 | -45.01479 | 6.05711 | 1.20823 | 0.02245 |
| \( H(ppr) \) | -94.47230 | 33.60639 | -4.25418 | 1.21106 | -0.03269 |
| \( H(psr) \) | 7.80580 | 1.71300 | -0.22442 | 1.03201 | 0.07662 |

**Overlap Terms:** \( S_{\ell\ell'}(R) = (t_{\ell\ell'} + q_{\ell\ell'}R + r_{\ell\ell'}R^2)^4 \exp(-\alpha_{\ell\ell'}R)F(R) \)

| \( \ell \) | \( t \) | \( q \) | \( r \) | \( \alpha \) | \( \beta \) | LDA Equilibrium Values |
|---------|--------|--------|--------|--------|--------|-----------------|
| \( S(ssr) \) | 1.74820 | 0.13546 | 0.07434 | 0.82425 | 0.16873 |
| \( S(spr) \) | 15.27243 | 3.72217 | 0.27051 | 1.09173 | 0.14959 |
| \( S(ppp) \) | -4.51769 | -4.96427 | 0.71842 | 0.95339 | -0.17503 |
| \( S(ppr) \) | 846.58108 | 265.43883 | -10.03535 | 1.30600 | 0.06108 |
| \( S(psr) \) | -0.07337 | 0.00000 | 0.00000 | 0.00000 | 0.00168 |