PHYSICAL REVIEW B **75**, 121402(R) (2007)

First-principles calculation of the spin-orbit splitting in graphene

J. C. Boettger
Group X-1, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

S. B. Trickey
Quantum Theory Project, Departments of Physics and Chemistry, P.O. Box 118435, University of Florida,
Gainesville, Florida 32611-8435, USA

(Received 25 January 2007; published 9 March 2007)

Recent success in making macroscopic graphene samples has stimulated interest in possible unusual electron physics near the Brillouin zone (BZ) vertex K, notably the prediction of a spin quantum Hall effect. Observability depends critically on the size of the spin-orbit gap Δ_{SO} at K. Prior approximate calculations give results from 1.2 K (≈0.1 meV) down to 10 mK (≈0.00086 meV). We report fully first-principles all-electron calculations of this splitting using large Gaussian basis sets and the Douglas-Kroll-Hess methodology in the density functional theory fitting function code GTOFF. Our result $\Delta_{SO} \approx 0.6$ K or 0.05 meV is robust against the choice of the approximate exchange-correlation functional and against variations of the lattice constant, density of the BZ scan, basis set enrichment, and key numerical convergence parameters.

DOI: 10.1103/PhysRevB.75.121402 PACS number(s): 73.20.−r, 71.20.−b, 71.70.Ej

Success in the preparation of macroscopic graphene samples[1] has caused there to be much attention given to the novel physics offered by the electronic energy levels in the vicinity of the Brillouin zone vertex K. One category is the role of spin-orbit (SO) interactions. Suppressed in crystalline graphite by the relative strength of the interplanar bonding, SO interactions could alter the linear dependence of the electron energy upon crystal momentum (Dirac fermion behavior) in critically important ways. Specifically Kane and Mele[2] recently gave model calculations and arguments for the existence of a low-temperature spin quantum Hall effect (SQHE) enabled by the SO gap Δ_{SO} which they estimated as about 1.2 K (≈0.1 meV). Three subsequent studies gave much smaller values, all in the range from 0.01 K (Refs. 3 and 4) to 0.0093 K (Ref. 5) (≈0.00086 meV). Those values would put the Kane-Mele SQHE at infeasibly low temperatures.

None of those three studies used a fully first-principles, all-electron methodology. Reference 3 used a tight-binding model with parameters from literature values. Both Refs. 4 and 5 used pseudopotential density functional theory (DFT) methods, the former with smoothed projector-augmented-wave pseudo-wave-functions, the latter with noncollinear magnetism and fully relativistic pseudopotentials.

A direct, all-electron (no pseudopotential) DFT calculation of Δ_{SO} is possible in the Gaussian-type orbital fitting function methodology.[6–8] A so-called incomplete Douglas-Kroll-Hess (DKH) transformation yields a computationally well-behaved, highly accurate two-component theory in which the SO contribution can be identified unambiguously. A systematic, well-validated SO approximation is available:[8] the screened nuclear spin orbit (SNSO) approximation. Reliability of the SNSO procedure has been tested primarily on light actinides (Th–Pu). For them, calculated atomic volumes from SNSO agree well with fully relativistic full-potential linearized augmented plane-wave (APW) calculations as do atomic spin-orbit splittings.[8] The basic methods and algorithms in the code used here, GTOFF, and original references are reviewed in Ref. 9. Observe that GTOFF handles both freestanding systems of two-dimensional periodicity without supercells (the option used here) as well as ordinary three-dimensional crystals.

In calculating a small quantity such as Δ_{SO}, one must assure that the value is not strongly dependent on system strain and assure stability against matters of choice. Those include both the DFT exchange-correlation (XC) model and technical parameters—e.g., basis set size, Brillouin zone (BZ) scan density, convergence tolerances, etc. Regarding basis sets (the fitting function methodology uses three), our earlier work[10–12] focused particularly on two delicate energies: interplanar binding and relative stability in the aggregation sequence from fullerenes to the graphite crystal. From those studies there emerged carefully tested, rather rich basis sets (tabulated in Ref. 11) which we used here. To assess stability with respect to the DFT XC model, we used both a venerable form of the local density approximation (LDA) [Hedin-Lundqvist[13] (HL)] and a much-used modern first-principles-based generalized gradient approximation [Perdew-Burke-Ernzerhof[14] (PBE)].

Regarding BZ scans, we primarily used a scan with both the threefold axis (around z normal to the graphene) and three mirror planes for symmetry, which reduces a regular 18×18 grid to 37 points in the irreducible wedge of the BZ (IBZ). For stability testing we used a 12×12 grid with either all the symmetries (19 points in the IBZ) or only the threefold (26 points in the IBZ).

Since the equilibrium lattice parameter of free graphene seems not to be known experimentally, we used the calculated value for the HL XC model from Ref. 11, $a=\sqrt{3}a_{NN}=4.621$ a.u. To test for lattice strain effects, we also did calculations at 5% expansion, $a_P=4.852\,05$ a.u. and 5% contraction $a_M=4.389\,95$ a.u. Table I displays the results. Based on those values and stability tests discussed below, we predict Δ_{SO} for graphene at the BZ K point to be 0.05 ± 0.01 meV—i.e., 0.6 ± 0.1 K. Unlike Ref. 5, we find Δ_{SO} to be somewhat more sensitive to a given compression than to the corresponding percentage expansion.

TABLE I. Graphene SO splittings at the BZ point *K* for the HL LDA and PBE XC models at three lattice parameters.

Lattice parameter (a.u.)	HL-LDA (meV)	PBE LDA (meV)
4.621	0.0504	0.0505
4.85205	0.0408	0.0408
4.38995	0.0646	0.0648

Observe, from Table I, that the choice of XC model is irrelevant, an outcome consistent with a simple argument. Irrespective of the XC model, symmetry dictates the band connectivity at *K* without SO splitting. Second, the XC potential does not enter in the incomplete DKH transform used but this does not matter. Were it to be included, a simple argument shows that for a nearly spherical potential V, the SO operator scales as $(1/r)\nabla V$. Because V_{XC} is very smooth, its effect upon the SO splitting of a valence state would be negligible compared to the nuclear or electron-electron interactions. Test calculations of the XC splitting in atoms are consistent with this argument.[8] The only remaining difference between XC models is in the density and orbitals used to form the approximate diagonal representation of p^2 for the DKH transform. Those differences are known to be quite small; hence, any reasonable XC model (i.e., one that gives a reasonable equilibrium lattice constant) should give virtually the same Δ_{SO}. Note that this argument would seem to be inapplicable to relativistic pseudopotential procedures, which must incorporate XC model differences explicitly. As to the applicability of the bare Kohn-Sham energy bands from DFT, we remark that, whatever their deficiencies (e.g., the underestimate of band gaps), at least in this problem one begins with bands which have the correct crossing and density of states at the *K* point; see Fig. 1, Ref. 10, for example.

Thus, the rest of our stability testing is summarized only for the HL LDA. A change in total energy convergence criteria (absolute value of the iteration-to-iteration difference in hartree a.u.) from 1.0×10^{-6} hartree to 1.0×10^{-7} hartree made no difference. The 26-point IBZ scan gives the identical result as the 37-point scan, Δ_{SO}=0.0504 meV, even though the enforced symmetry for 26 points is lower. Forcing the Kohn-Sham (KS) band states to have integer occupancy and using histogram BZ integration (rather than linear analytical triangular, both on the 37 point scan) changes nothing. Purely to illustrate the insignificant difference, the two values are 0.050 396 meV for linear analytical triangular and 0.050 391 meV for histogram. Reduction of the BZ scan density to 19 points in the IBZ gives an equally insignificant shift, to 0.050 37 meV.

Because SO splitting depends on the shape of the KS orbitals near the nuclei, we also probed the effects of basis set enrichment. In particular, the *p*-type manifold of the basis from Ref. 11 is contracted (set in fixed linear combinations) from six p_x and p_y functions and seven p_z to three and four, respectively. Decontraction (i.e., allowing full variational freedom for all the functions) substantially enriches the KS basis *p* manifold in the vicinity of the nuclei therefore. Even so, at a=4.621 a.u., after decontraction the HL value for Δ_{SO}=0.050 91 meV, not a significant shift.

TABLE II. Graphene cohesive energies (in eV/atom) for the relativistic and nonrelativistic HL LDA and PBE XC models at three lattice parameters (a.u.). See text for atomic reference total energies.

Lattice parameter	Rel. HL	Nonrel. HL	Rel. PBE	Nonrel. PBE
4.621	−8.35	−8.80	−7.61	−8.08
4.85205	−8.20	−8.65	−7.50	−7.97
4.38995	−8.15	−8.60	−7.36	−7.83

Since relativistic effects in low-*Z* systems usually are small, direct validity checks also are important. Again, all are for the HL XC model. We can compare the BZ center (Γ) value of Δ_{SO} from SNSO either to an isolated atom SNSO calculation or to an isolated atom direct DKH calculation without SNSO. All the atomic calculations were done with an enriched basis (one additional function, exponent 0.04 a.u.$^{-2}$ in each the *s* and *p* manifolds) without contractions. We find $\Delta_{SO,\Gamma}$=7.45 meV versus $\Delta_{SNSO,atom}$=7.48 meV and $\Delta_{SO,atom}$=8.16 meV. Given the differences in methodology, our Γ-point σ-orbital splitting also compares respectably with the LDA result reported in Ref. 5, 9.0 meV.

Though the relativistic effects are small, for completeness we report the calculated cohesive energies in Table II. The relativistic reference atomic energies (E_{HLLDA} $=-75.022\,269\,8$, $E_{PBE}=-75.495\,417\,7$ Ry a.u.) were obtained from spin-polarized, scalar relativistic values, corrected by SNSO shifts from the non-spin-polarized atom (spin-polarized SNSO calculations are not supported in our current codes), all with the enriched atomic basis. The nonrelativistic reference energies are −74.960 621 (HL) and −75.586 385 8 (PBE) Ry a.u. Essentially there is a 0.45 eV/atom relativistic increase in binding irrespective of the XC model or lattice parameter.

In sum, high-precision, first-principles, all-electron DFT calculations predict Δ_{SO} for graphene at the BZ *K* point to be 0.05±0.01 meV or 0.6±0.1 K. The value is substantially larger than relativistic pseudopotential results, enough so that the Kane-Mele SQHE may be observable. Though the SNSO approximation has not been used on such a low-*Z* system up to now, we find no evidence of difficulty with it in this calculation. We speculate that the difference in calculated values of Δ_{SO} might occur because the smooth pseudo-orbitals generated by pseudopotential methods may not satisfy the required limiting behavior near the origin of the $J=1/2$ KS states. If so, such a difference might also be related to the agreement with Ref. 5 for the splitting in the σ manifold at Γ but disagreement in the π manifold at *K*.

J.C.B. was supported by the U.S. Department of Energy under Contract No. DE-AC52-06NA25396. S.B.T. was supported in part by the National Science Foundation under ITR Award No. DMR-0218957.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Nature (London) **306**, 666 (2004).

[2] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **95**, 226801 (2005).

[3] D. Huertas-Hernando, F. Guinea, and A. Brataas, Phys. Rev. B **74**, 155426 (2006).

[4] H. Min, J. E. Hill, N. A. Sinitsyn, B. R. Sahu, L. Kleinman, and A. H. MacDonald, Phys. Rev. B **74**, 165310 (2006).

[5] Y. Yao, F. Ye, X-L. Qi, S-C. Zhang, and Z. Fang, Phys. Rev. B **75**, 041401(R) (2007).

[6] J. C. Boettger, Phys. Rev. B **57**, 8743 (1998).

[7] J. C. Boettger and S. B. Trickey, J. Mol. Struct.: THEOCHEM **501-502**, 285 (2000).

[8] J. C. Boettger, Phys. Rev. B **62**, 7809 (2000).

[9] S. B. Trickey, J. A. Alford, and J. C. Boettger, in *Computational Materials Science*, Vol. 15 of *Theoretical and Computational Chemistry*, edited by J. Leszczynski (Elsevier, Amsterdam, 2004), pp. 171–228.

[10] S. B. Trickey, F. Müller-Plathe, G. H. F. Diercksen, and J. C. Boettger, Phys. Rev. B **45**, 4460 (1992).

[11] B. I. Dunlap and J. C. Boettger, J. Phys. B **29**, 4907 (1996).

[12] J. C. Boettger, Phys. Rev. B **55**, 11202 (1997).

[13] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971); V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, NY, 1978).

[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).