Electronic structure of an electron on the gyroid surface: A helical labyrinth

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Previously reported formulation for electrons on curved periodic surfaces is used to analyze the band structure of an electron bound on the gyroid surface (the only triply-periodic minimal surface that has screw axes). We find that an effect of the helical structure appears as the bands multiply sticking together on the Brillouin zone boundaries. We elaborate how the band sticking is lifted when the helical and inversion symmetries of the structure are degraded. We find from this that the symmetries give rise to prominent peaks in the density of states.

While the physics of electron systems in crystals has been firmly established, it should be interesting to consider electrons bound on infinite, periodic curved surfaces, which may envisage as crystals composed of surfaces. We have previously calculated the band structure of an electron confined on triply periodic (i.e., periodic along x, y, z) minimal surfaces (called P- and D-surfaces) and found that bands and the Bloch wavefunctions are essentially determined by the way in which the “tubes” are connected into a network.\[1,2\]

One asset of the crystal of surfaces is that we can deform them. We have indeed found that the P- and D surfaces, which are mutually Bonnet(conformal)-transformed, have related electronic structures. We can even twist the tubes, for which there is a special interest: Schoen pointed out in the late 1960’s the following. P-surface (a cubic network of tubes) and D-surface (a diamond network) are typical triply periodic minimal surfaces, where minimal surfaces are defined as negatively-curved surfaces that have minimized areas with the mean curvature \((\frac{1}{2}(\kappa_1+\kappa_2))\) with \(\kappa_1, \kappa_2\) being the principal curvatures) vanishing everywhere on the surface. In addition, however, we have found that P-surface and D-surface are related via the Bonnet transformation, where the Bonnet angle (a parameter in the transformation) \(\beta = 38.015^\circ\) for G-surface, [7] and \(L\) the linear dimension of the unit cell. As stressed in [1,2], Weierstrass-Enneper representation that completely defines the surface is specified solely by its poles, which, in real space, correspond to ‘nervals’ (umbilical points) in differential-geometrical language, at which \(\kappa_1 = \kappa_2 = 0\). So a periodic minimal surface has negative curvatures everywhere except at the nervals.

Figure \[8\] shows a primitive patch of G-surface, which corresponds to eqn. \(1\) with \(0 < \theta < \pi, -\pi/4 < \phi < \pi/4\) when we stereographically map \((u, v)\) to a unit sphere \((\theta, \phi)\) with \(w = u + iv \equiv \cot(\theta/2)e^{i\phi}\). The full surface is depicted in Fig. 3 for its cubic unit cell (containing two bcc cells). The surface has 90° helical symmetry axes along x, y, and z directions, respectively, while the chirality (right- or left-handedness) is opposite across neighboring helices. This is how the surface is a network of helical tubes along x, y, z connected into a single labyrinth.

While the helical structure is unique to the G-surface, it shares with P- and D-surfaces the property called the balance surface (or the in-out symmetry), which is defined as the curved surface that divides the three-dimensional
space into two, congruent labyrinths. For the G-surface the divided spaces are mirror inversions of each other. The surface itself is not chiral, being symmetric with respect to flat points (the center of the primitive patch in Fig. 1), which corresponds to the navels. It has been shown that a balance surface is characterized by a pair of space groups \((G, H)\), where \(G\) maps one side of the surface to itself or the other side (and one labyrinth to itself or the other labyrinth), while \(H\), a subgroup of \(G\), maps each side to itself (and each labyrinth to itself). For G-surface, \((G, H) = (I\bar{a}3d, I\bar{A}32)\).

Schrödinger’s equation on a curved surface takes different forms between the following two cases; one is to consider electrons bound to a thin, curved slab of thickness \(d\), where the limit \(d \to 0\) is taken, while the other is to ignore the perpendicular degree of freedom from the outset. We adopt the former as a physical approach, for which the equation reads

\[
\left(\frac{\hbar^2}{2m} \frac{1}{\sqrt{\gamma}} \frac{\partial}{\partial q^i} \sqrt{\gamma} g^{ij} \frac{\partial}{\partial q^j} - \frac{\hbar^2}{8m} (\kappa_1 - \kappa_2)^2\right) \psi(q^1, q^2) = E \psi(q^1, q^2),
\]

where \((q^1, q^2) = (u, v)\), \(g_{ij}\) the metric tensor with summations over repeated indices assumed, and \(\kappa_1, \kappa_2\) the local principal curvatures (with \(\kappa_1 + \kappa_2 = 0\) everywhere for a minimal surface by definition). An effect of the curvature of the surface appears as a curvature potential,

\[-\left(\frac{\hbar^2}{8m}\right) (\kappa_1 - \kappa_2)^2\],

which has its minima at navels.

As shown in Ref. [1], the Weierstrass-Enneper representation transforms Schrödinger’s equation into a neat form of

\[
-\left(\frac{1 - \cos \theta}{|F|^2}\right)^4 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + 1\right) \psi = \varepsilon \psi.
\]

Since the Bonnet transformation preserves the metric tensor as well as the Gaussian curvature, the surfaces connected by a Bonnet transformation obey the identical Schrödinger’s equation, as seen in eqn. [3] where \(F\) only enters as \(|F|\). However, this only applies to a unit patch, so that the band structures are different between P,D, and G, since the way in which unit patches are connected is different. [4]

So we have solved the equation for the appropriate connection between the patches to obtain the band structure for G-surface as shown in Fig. 3. We can immediately notice that the bands are multiply degenerate at some symmetric points on the Brillouin zone boundary: six-fold degenerate at H-point, four-fold at P, etc, which is a phenomenon not seen in P and D-surfaces. The wave functions for six-fold states at H are displayed in Fig. 4. The space group for the G-surface \((I\bar{a}3d)\) is non-symmorphic, i.e., has the screw axes or glide planes, and this should cause the degeneracy at the zone boundary, generally known as ‘the band sticking together’ [10] in e.g. crystals of Se and Te with helical atomic arrangements. We shall elaborate this point below.

We can note in passing the following: We have pointed out in the previous work [1] that Bonnet-connected P- and D-surfaces, despite the different band structures, have a common set of band energies at special \(k\)-points (Brillouin zone corners, edges, or face-centers). This occurs when a wave function on a unit patch can be continued as a “tiling” of patches on both surfaces, where the simplest case is the ground state at \(\Gamma\) point. In G-surface, this occurs at \((and only at; a peculiarity of the spiral structure) \(\Gamma\) at which the band energies accommodate those of P-surface at \(\Gamma\) and H points and D-surface at \(\Gamma\) and R as displayed in Fig. 5.

A question from the materials science point of view is: can we realize the G-surface in some materials? As mentioned above, there are a few classes of materials that possess the same space group as the G-surface. One is a class of clathrate compounds of group-IV elements (e.g., Ge), where Ge\(_{20}\) clusters that include another element (e.g., Ba) are stacked in a triply-helical fashion. A conceptually simpler system would be a three-dimensional labyrinth of graphite sheets that forms a triply periodic surface. Fujita and coworkers have considered such systems, and called them “graphitic sponges” [11].

![Fig. 1: A primitive patch for G-surface. Its center corresponds to the navel (see text), around which the surface is point-symmetric.](image1)

![Fig. 2: A cubic unit cell of G-surface in birds-eye(a) and top(b) views.](image2)
FIG. 3: Band structure of the G-surface displayed on the Brillouin zone for the bcc unit cell. The numbers in the parentheses represent the degeneracy of the band sticking.

FIG. 4: The wave functions in the unit cell of G-surface for the six-fold states at the lowest level in H-point (in Fig. 3), with positive (negative) amplitudes color coded in red (blue).

FIG. 5: Coincidence of the band energies among G-, P- and D-surfaces.

FIG. 6: (a) Low-energy band structure for the graphitic G-sponge, to be compared with Fig. 3, constructed from a graphite fragment shown at the top. We take here the hopping parameter $t$ as the unit of energy and the tight-binding band center as the origin. (b) The band structure when we introduce a potential that breaks the helical symmetry, or (c) the inversion symmetry. Extra potential introduced to degrade the symmetry is shown at the top, where an open circle represents the potential for every other patch, while filled one for all the patches. The panels (d) and (e) show the density of states for the systems (a) and (b), respectively, in units of $1/(Vt)$ ($V$: unit cell volume).
negative-curvature fullerene (or C_{60} zeolite) \cite{12} is indeed a realization of the P-surface if we smear out atoms into a surface. \cite{13} The band structure of atomic networks such as the C_{60}-zeolite is expected to basically reflect the properties of an electron on the curved surface, as far as the effective-mass formalism is applicable and effects of the odd-membered atomic rings are neglected. This has in fact been shown for P- and D-surfaces\cite{2}. Fabrication of graphitic sponges has been experimentally attempted with a zeolite as a template\cite{14}, so we should end up with a G-surface sponge if we use a G-structured zeolite (MCM) as the template.

The electronic structures of the negative curvature carbon networks, including G-surface-like structures, were investigated with a first principles method in Ref\cite{15}. However, some of the G-surface-like models (E and O in that paper) contain seven-membered rings, which degrade the symmetry below that of the G-surface, and the band degeneracy was not discussed, either. Here we examine the band structure of the graphite sponge that shares the global topology and the symmetry with the G-surface to investigate how the degeneracy would be lifted when the symmetry is degraded. We constructed the network by arraying the unit patches displayed in Fig. 6(a) (corresponding to Fig. 1), where the resultant structure contains no odd-membered rings, and the band structure is calculated in the one-band, tight-binding model with the hopping parameter $t$.

The result in Fig. 6(b) shows that the bands in the low-energy region have a one-to-one correspondence with those for the G-surface, as expected, so the electronic structure there is basically determined by the structure of the surface on which the atoms reside. Then we have degraded each of the two symmetries (helical and inversion), by introducing an extra potential. We first destroy the helical symmetry in Fig. 6(b), with the space group $Ia3d$ reducing to $Ia3$, with the extra potential introduced on every other patch. We next destroy the inversion in Fig. 6(c) (with the space group reducing to $I4_132$) with the extra potential on triangular sites around the center of every patch. The amplitude of the extra potential energy is taken to be $0.3t$ or $0.5t$ in (b), (c), respectively, which are small enough for the correspondence among the bands to be retained. The band structures show that the multifold stickings split into lower degeneracies, although some degeneracies in (c) (with the inversion symmetry broken) are lifted only slightly. This endorses that both the helical and inversion symmetries are essential for the band sticking. The panels (d) and (e) display the density of states (DOS) before(d) and after(e) the helical symmetry is broken. We recognize that the first and second prominent peaks (labeled as A and B, corresponding respectively to six-fold and two-fold stickings in (a)) split with significantly reduced peak heights after the symmetry is degraded. The effect is more noticeable for the peak B, which is due to the splitting of nearly flat bands. The density of states for the broken inversion symmetry (not shown) exhibits a similar behavior. So the band sticking due to the G-surface space group can generally give rise to prominent peaks in the density of states. The third peak (C) is also suppressed, but this is caused by a change in the band curvature.

Let us finally mention a possible relevance to real materials. A recent band calculation for the clathrate Ba_{6}Ge_{25}, which shares the space group with G-surface, shows that the DOS peak at the Fermi level becomes split when the structural symmetry is reduced, which they suggest causes a band Jahn-Teller instability, and should be responsible for an experimentally observed phase transition\cite{16}. Our result suggests that materials with the G-surface symmetry generally have a potential for such instabilities and corresponding phase transitions.

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